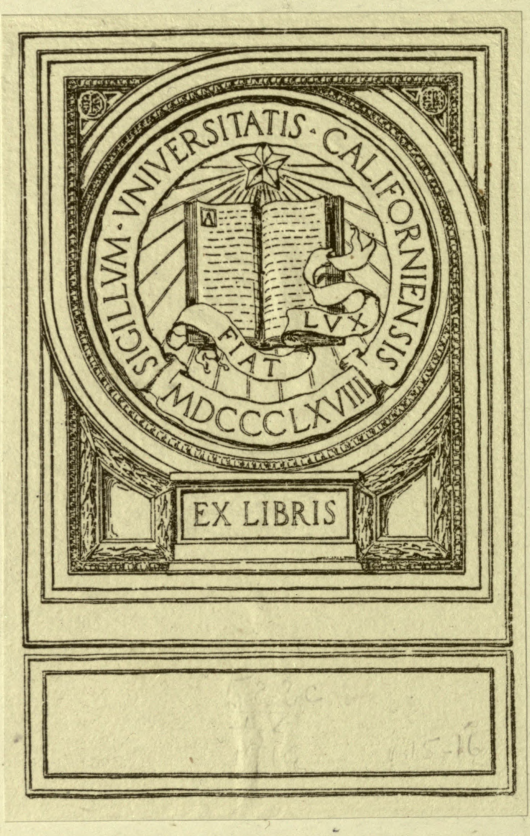


ORIGINAL COMMUNICATIONS

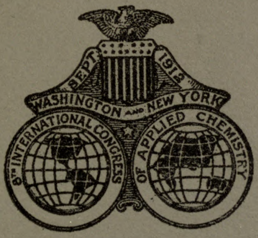
EIGHTH INTERNATIONAL

CONGRESS OF APPLIED CHEMISTRY

Washington and New York

September 4 to 13, 1912

SECTION VII: AGRICULTURAL CHEMISTRY



VOL. XV

ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS
OF APPLIED CHEMISTRY

Washington and New York
September 4 to 13, 1912

SECTION VII: AGRICULTURAL CHEMISTRY

VOL. XV

The matter contained in this volume is printed in exact accordance with the manuscript submitted, as provided for in the rules governing papers and publications.

La matière de ce volume a êté imprimêe strictement d'accord avec le manuscrit fourni et les règles gouvernant tous les documents et publications.

Die in diesem Heft enthaltenen Beiträge sind genau in Übereinstimmung mit den uns unterbreiteten Manuskripten gedruckt, in Gemässheit der für Beiträge und Verlagsartikel geltenden Bestimmungen.

La materia di questo volume e stampata in accordo al manoscritto presentato ed in base alle regole que governano i documenti e le publicazioni.

THE RUMFORD PRESS
CONCORD·N·H·U·S·A·

ORIGINAL COMMUNICATIONS

TO THE

EIGHTH INTERNATIONAL CONGRESS

OF

APPLIED CHEMISTRY

APPROVED

BY THE

COMMITTEE ON PAPERS AND PUBLICATIONS

IRVING W. FAY, CHAIRMAN

T. LYNTON BRIGGS	JOHN C. OLSEN
F. W. FRERICHS	JOSEPH W. RICHARDS
A. C. LANGMUIR	E. F. ROEBER

A. F. SEEKER

SECTION VII. AGRICULTURAL CHEMISTRY.

Executive Committee.

President: Frank K. Cameron, Ph.D.
Vice-President: H. J. Wheeler, Ph.D.
Secretary: J. A. Le Clerc, Ph.D.
L. L. Van Slyke, Ph.D.
H. P. Armsby, Ph.D., LL.D.

Sectional Committee.

G. S. Fraps, Ph.D.
Wm. F. Hand, Ph.D.
E. W. Hilgard, Ph.D., LL.D.
Cyril G. Hopkins, Ph.D.
J. B. Lindsey, Ph.D.
J. G. Lipman, Ph.D.
Andrew J. Patten, B.S.
H. J. Patterson, B.S.
C. L. Penny
M. A. Scovell, Ph.D.
B. B. Ross, M.Sc.
Henry C. Sherman, Ph.D.
F. H. Storer, A.M.
John Phillips Street, B.S.
R. W. Thatcher, M.A.
P. F. Trowbridge, Ph.D.
Harvey W. Wiley, M.D., Ph.D., LL.D.
J. T. Willard, D.Sc.
W. A. Withers, A.M.
Chas. D. Woods, Sc.D.

and the Sectional Executive Committee.

VOLUME XV.

SECTION VII; AGRICULTURAL CHEMISTRY.

CONTENTS.

EMPLOI DU BORE COMME ENGRAIS CATALYTIQUE

PAR M. HENRI AGULHON

Paris, France

Au Congrès de 1909, j'ai exposé mes premiers essais sur l'emploi du bore sous forme d'acide borique comme engrais catalytique. L'ensemble des recherches faites jusqu'en 1909 a été publié dans ma thèse de Doctorat. De nouvelles expériences entreprises en 1910 et 1911 confirment les premiers résultats. Des essais de laboratoire en milieu synthétique avec le radis, en pots de terre avec le pois, le haricot, la betterave, le radis, ont donné des augmentations de récolte pouvant aller jusqu'à 34%. A la Station Agronomique de Meudon, des séries d'expériences ont été entreprises dans des bacs de sable et en pleine terre avec le blé, l'avoine, le maïs, la luzerne, le pois, le colza, le lupin: en 1910 les doses d'acide borique variant de 20 à 50 kgr. à l'hectare se sont montrées trop fortes, et l'augmentation souvent obtenue en poids frais n'apparaissait plus en poids sec, phénomène dû à l'accumulation d'eau dans la plante que j'ai déjà noté comme une réaction aux doses déjà toxiques. Avec 10 kgr. on a obtenu dans plusieurs cas des augmentations sensibles. Une seconde année de culture sur les mêmes terrains sans nouvelle addition d'engrais catalytiques a donné presque partout des résultats favorables. En 1911, les doses de 20 à 40 kgr. essayées à Marchais se sont montrées aussi trop fortes pour l'avoine. En revanche, N. Delaunay qui a près de Gien essayé la dose faible de 1 kgr. 5 à l'hectare a obtenu avec cette même plante un accroissement de récolte de 54%.

L'ensemble de ces différents résultats montre qu'en ce qui concerne l'acide borique il faut s'en tenir à de très faibles doses; pour les Graminées, très sensibles, à part le maïs, les doses inférieures à 3 kgr. à l'hectare semblent devoir donner d'importants résultats en grande culture.

THE COMPOSITION OF THE LOESS SOILS OF THE TRANSITION REGION

Frederick J. Alway

University of Nebraska, Lincoln, Neb.

Loess[1] forms the chief surface deposit of more than half of Nebraska, occurring over the whole eastern end and extending westward for more than 300 miles. Along the different river courses and in the southeastern counties it has been extensively eroded. In many places in the latter it remains only as small, isolated plains. It is generally conceded that the loess of Nebraska consists largely of glacial mud laid down near the close of the glacial epoch, covering hills and valleys alike to a depth of from 20 to 100 feet, being much thicker than this in some places and thinner in others. It has many of the characteristics of an aeolian deposit but there is a lack of agreement as to the part which the wind may have played in its deposition.

Throughout the first hundred miles westward from the Missouri River it is underlaid by Kansas till, while throughout the remaining two hundred miles it overlies Cretaceous and Tertiary formations. It consists chiefly of silt, together with smaller amounts of very fine sand and clay, the proportion of clay being highest in the eastern part and that of sand in the western. Uniformity in physical properties has been recognized as characteristic of the Nebraska loess, but little attention has been paid to its chemical composition and no complete analyses have previously been reported.[2]

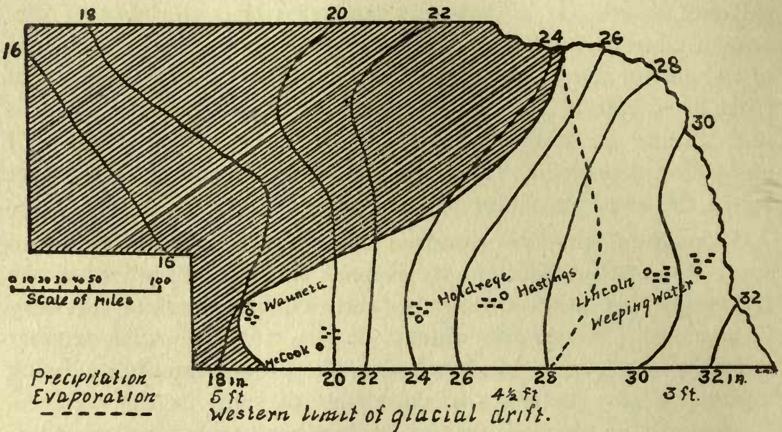
The different parts of this loess formation have been exposed to comparatively uniform temperature conditions but to great

---

[1] Barbour, E. H., Nebraska Geological Survey, Vol. 1, 169, (1903).

[2] Various articles have been published by Alway et al. on the organic and the acid-soluble constituents of the loess soils of Nebraska, Neb. Exp. Sta., Bull. 111, (1909). Twenty-fifth Annual Report, Neb. Exp. Sta. (1912). Jour. Ind. and Eng. Chem. **1**, 771, (1909).

differences in precipitation; if we assume that since the close of the glacial epoch there has been but little change in the climate of what is now Nebraska. In the extreme eastern part the normal precipitation is over 30 inches, while in the southwestern corner it is less than 20, there being a gradual decrease from east to west, as shown on the accompanying map. While the precipitation decreases from east to west there is a rapid rise in the rate of evaporation, which, from a free water surface, amounts to about three feet per annum in the eastern part and to about five feet in the western. As the precipitation falls chiefly during the growing season there is but little seepage from the level prairies in the eastern portion, and practically none from those in the western.



A map of Nebraska showing the loess region (unshaded), the precipitation, the evaporation, the western limit of the glacial drift and the location of the fields sampled.

The normal annual precipitation at the towns near which the samples were taken, as well as their approximate longitude and elevation above sea level are given in Table 1.

In an investigation of this kind the method of taking the samples for analysis is an extremely important consideration. My original intention was to select in each locality five level fields located to one another as are the four corners and the centre of a square, with sides two miles in length, but on account of the very

TABLE I. Longitude, elevation and normal precipitation at towns near which the soil samples were collected.

Stations of the U. S. Weather Bureau	Approximate longitude	Elevation, feet	Normal annual precipitation, inches	Length of record, years
Weeping Water	96° 10′	1,080	30.30	34
Lincoln	96° 40′	1,189	28.65	31
Hastings	98° 20′	1,932	27.27	21
Holdrege	99° 20′	2,324	25.18	19
McCook	100° 40′	2,506	19.44	17
Wauneta	101° 30′	2,934	18.82	11

small area of prairie remaining, my original plan could not be adhered to closely. Five prairie fields were selected in each of six rainfall belts, no field being farther than ten miles from one of the above mentioned stations of the U. S. Weather Bureau. Ten borings were made to a depth of six feet in each field and samples taken from each foot section. Great care was exercised to prevent the samples from below the surface foot becoming mixed with any of the overlying soil. Accordingly, in each of the six areas indicated there are five fields from each of which were collected composites of ten individual samples of the first, second, third, fourth, fifth and sixth feet. The "area samples," the analyses of which are reported in the accompanying tables (Tables 2 to 9), were prepared by mixing equal weights of the corresponding "field samples," each thus being a composite of 50 individual borings.

The complete analysis given in the first part of each table was made by the methods in use in the laboratory of the U. S. Geological Survey.[1] The manganese, however, was determined by another method,[2] that described by Hillebrand being found unreliable for such small quantities as occur in the loess. The

---

[1] Hillebrand, W. F., U. S. Geol. Survey, Bull. 422 (1910).

[2] Gortner, R. A. and Rost, C. O., Twenty-fifth Annual Report, Nebr. Exp. Station, (1912).

organic carbon was determined by combustion with copper oxide after previous treatment with phosphoric acid to decompose carbonates. For nitrogen the Kjeldahl method was used. The "water of constitution" has been found by subtracting from the volatile matter the organic matter as calculated by multiplying the organic carbon by 1.724. The hygroscopic coefficient was determined by the Hilgard method[1]—the exposure of a thin layer of soil to a saturated atmosphere, temperature fluctuations being avoided.

TABLE II. Soils from near Weeping Water. Normal annual precipitation 30.30 inches.

	First foot	Second foot	Third foot	Fourth foot	Fifth foot	Sixth foot
SiO_2	69.65	68.10	68.95	70.38	70.28	70.61
Al_2O_3	11.57	12.81	12.91	13.20	13.00	12.76
Fe_2O_3	4.24	5.10	5.25	5.03	4.77	4.93
MnO	.11	.12	.12	.12	.12	.15
MgO	.88	1.27	1.57	1.35	1.28	1.33
CaO	.89	.95	1.37	1.08	1.08	1.18
Na_2O	1.13	1.06	1.12	1.36	1.34	1.44
K_2O	2.38	2.31	2.34	2.30	2.38	2.35
TiO_2	1.25	1.25	1.25	1.30	1.30	1.30
P_2O_5	.13	.12	.13	.16	.18	.17
CO_2	.01	.01	.05	.00	.02	.01
BaO	.06	.06	.09	.06	.09	.08
SO_3	.12	.10	.10	.06	.07	.05
Volatile matter	8.43	7.17	5.24	4.46	4.27	3.99
Total	100.85	100.43	100.49	100.86	100.18	100.35
Nitrogen	.236	.153	.083	.059	.043	.038
Organic C	2.94	1.62	.82	.48	.30	.22
C/N Ratio	12.4	11.4	10.1	7.3	7.0	5.3
Organic matter	5.07	2.79	1.41	.83	.52	.38
Water of const.	3.36	4.38	3.83	3.63	3.75	3.61
Hyg. coeff.	12.1	13.7	13.9	13.0	12.6	12.5

---

[1] Hilgard, E. W., Soils, p. 106, (1906).

TABLE III. Soils from near Lincoln. Normal annual precipitation 28.65 inches.

	First foot	Second foot	Third foot	Fourth foot	Fifth foot	Sixth foot
SiO_2	69.81	67.78	69.46	70.49	70.53	70.71
Al_2O_3	11.43	14.04	13.42	13.00	13.26	12.94
Fe_2O_3	3.71	4.52	5.00	5.03	4.81	4.81
MnO	.10	.10	.11	.12	.12	.12
MgO	1.02	1.21	1.18	1.33	1.21	1.32
CaO	1.24	1.00	1.21	1.21	1.39	1.31
Na_2O	1.04	1.02	1.13	1.22	1.28	1.25
K_2O	2.38	2.39	2.44	2.46	2.45	2.46
TiO_2	1.25	1.25	1.25	1.25	1.14	1.16
P_2O_5	.12	.11	.16	.17	.19	.17
CO_2	.01	.02	.02	.06	.12	.08
Volatile matter	8.60	7.16	5.25	4.22	4.07	3.90
Total	100.71	100.33	100.63	100.56	100.57	100.23
Nitrogen	.240	.129	.069	.060	.042	.043
Organic C	2.95	1.31	.68	.44	.33	.32
C/N Ratio	12.3	10.2	9.9	7.0	7.1	7.5
Organic matter	5.08	2.26	1.17	.76	.57	.55
Water of const.	3.52	4.90	4.08	3.46	3.50	3.35
Hyg. coeff.	12.0	14.4	13.6	13.0	12.8	12.7

TABLE IV. Soils from near Hastings. Normal annual precipitation 27.27 inches.

	First foot	Second foot	Third foot	Fourth foot	Fifth foot	Sixth foot
SiO_2	72.58	70.39	70.72	70.27	71.15	71.15
Al_2O_3	11.05	12.52	13.31	12.18	12.45	12.80
Fe_2O_3	2.91	4.07	4.14	4.03	4.00	3.85
MnO	.07	.07	.07	.07	.07	.07
MgO	.88	1.07	1.23	1.32	1.34	1.39
CaO	1.13	1.16	1.45	1.75	1.80	1.72
Na_2O	1.56	1.44	1.43	1.67	1.54	1.61
K_2O	2.41	2.37	2.44	2.48	2.60	2.58
TiO_2	1.03	1.03	1.03	1.03	1.03	1.03
P_2O_5	.11	.11	.12	.11	.13	.15
CO_2	.01	.02	.10	.36	.38	.41
Volatile matter	6.25	5.45	4.63	4.00	3.83	3.71
Total	99.99	99.70	100.67	99.27	100.32	100.47
Nitrogen	.175	.098	.057	.041	.033	.029
Organic C	2.15	1.01	.53	.34	.31	.26
C/N Ratio	12.3	10.3	9.3	8.3	9.4	8.9
Organic matter	3.71	1.74	.91	.59	.53	.45
Water of const.	2.54	3.71	3.72	3.41	3.30	3.26
Hyg. coeff.	9.6	11.6	12.4	11.1	10.7	10.7

Table V. Soils from near Holdrege. Normal annual precipitation 25.18 inches.

	First foot	Second foot	Third foot	Fourth foot	Fifth foot	Sixth foot
SiO_2	71.88	70.75	70.68	70.21	70.68	70.77
Al_2O_3	10.88	12.75	12.08	11.54	11.26	12.76
Fe_2O_3	3.13	3.70	4.00	3.86	3.83	3.52
MnO	.06	.06	.06	.06	.06	.07
MgO	.90	1.16	1.22	1.53	1.43	1.48
CaO	1.18	1.33	1.60	2.15	2.30	2.19
Na_2O	1.57	1.46	1.47	1.52	1.65	1.57
K_2O	2.32	2.39	2.49	2.59	2.56	2.58
TiO_2	.98	.98	.98	.98	.98	.98
P_2O_5	.11	.11	.13	.15	.13	.11
CO_2	.01	.03	.13	.75	1.00	1.05
Volatile matter	7.10	5.10	4.48	3.98	3.34	3.10
Total	100.12	99.82	99.32	99.32	99.22	100.18
Nitrogen	.181	.101	.065	.045	.033	.034
Organic C	2.26	1.08	.69	.41	.30	.28
C/N Ratio	12.5	10.7	10.6	9.1	9.0	8.2
Organic matter	3.90	1.86	1.19	.71	.52	.48
Water of const.	3.20	3.24	3.29	3.24	2.82	2.62
Hyg. coeff.	10.1	11.2	11.3	10.2	9.6	9.4

TABLE VI. Soils from near McCook. Normal annual precipitation 19.44 inches.

	First foot	Second foot	Third foot	Fourth foot	Fifth foot	Sixth foot
SiO_2	72.10	70.88	68.35	68.22	68.82	69.47
Al_2O_3	11.33	11.73	11.66	11.43	11.76	11.86
Fe_2O_3	3.55	4.00	3.71	3.75	3.55	3.48
MnO	.06	.06	.06	.06	.06	.06
MgO	1.15	1.34	1.58	1.59	1.45	1.50
CaO	1.40	1.80	3.59	3.91	3.54	3.44
Na_2O	1.58	1.56	1.48	1.43	1.58	1.58
K_2O	2.43	2.42	2.42	2.48	2.56	2.52
TiO_2	.98	.98	.98	.98	.98	.98
P_2O_5	.13	.12	.11	.12	.13	.13
CO_2	.02	.40	2.02	2.34	2.11	2.08
Volatile matter	5.70	4.52	3.74	3.44	3.28	3.00
Total	100.43	99.81	99.70	99.75	99.82	100.10
Nitrogen	.139	.084	.054	.038	.032	.030
Organic C	1.73	.86	.62	.50	.34	.34
C/N Ratio	12.3	10.1	11.2	12.8	10.6	11.3
Organic matter	2.98	1.48	1.07	.86	.58	.59
Water of const.	2.72	3.04	2.67	2.58	2.70	2.41
Hyg. coeff.	10.0	10.9	10.7	9.7	9.1	9.1

TABLE VII. Soils from near Wauneta. Normal annual precipitation 18.82 inches.

	First foot	Second foot	Third foot	Fourth foot	Fifth foot	Sixth foot
SiO_2	72.98	72.70	71.24	69.28	70.98	70.57
Al_2O_3	11.32	11.80	11.87	11.91	11.01	11.17
Fe_2O_3	3.07	3.39	3.46	3.36	3.24	3.17
MnO	.05	.05	.05	.05	.05	.05
MgO	1.05	1.30	1.46	1.49	1.36	1.51
CaO	1.67	1.69	2.72	3.93	3.91	3.94
Na_2O	1.49	1.51	1.42	1.49	1.53	1.55
K_2O	2.55	2.60	2.62	2.58	2.59	2.68
TiO_2	.98	.98	.98	.98	.98	.98
P_2O_5	.12	.13	.12	.15	.15	.14
CO_2	.09	.07	.60	1.72	1.84	1.72
BaO	.06	.08	.06	.06	.06	.04
SO_3	.11	.09	.06	.07	.09	.07
Volatile matter	5.05	4.03	4.08	3.47	2.75	2.97
Total	100.69	100.54	100.86	100.66	100.66	100.68
Nitrogen	.136	.082	.065	.046	.038	.030
Organic C	1.49	.83	.64	.49	.42	.34
C/N Ratio	11.0	10.1	10.0	11.4	10.8	11.3
Organic matter	2.57	1.43	1.10	.85	.72	.59
Water of const.	2.48	2.60	2.98	2.62	2.03	2.38
Hyg. coeff.	9.1	9.6	9.7	9.9	9.0	8.3

TABLE VIII. Average composition of the soils from the different areas.

	Weeping Water	Lincoln	Hastings	Holdrege	McCook	Wauneta	Average
SiO_2	69.66	69.79	71.04	70.82	69.64	71.29	70.37
Al_2O_3	12.71	13.01	12.39	11.88	11.63	11.51	12.19
Fe_2O_3	4.88	4.67	3.83	3.67	3.67	3.28	3.98
MnO	.12	.11	.07	.07	.07	.06	.08
MgO	1.28	1.21	1.20	1.28	1.43	1.36	1.29
CaO	1.09	1.23	1.50	1.79	2.94	2.97	1.91
Na_2O	1.24	1.16	1.54	1.54	1.53	1.50	1.40
K_2O	2.34	2.43	2.48	2.49	2.47	2.60	2.47
TiO_2	1.27	1.21	1.03	.98	.98	.98	1.07
P_2O_5	.15	.15	.12	.12	.12	.13	.13
CO_2	.02	.05	.21	.49	1.49	1.00	.54
BaO	.07	*	*	*	*	.06	.07
SO_3	.08	*	*	*	*	.07	.08
Volatile matter	5.59	5.53	4.64	4.51	3.95	3.72	4.65
Total	100.50	100.55	100.05	99.64	99.92	100.53	100.23

*Not determined.

TABLE IX. Average composition of each foot section.

	First foot	Second foot	Third foot	Fourth foot	Fifth foot	Sixth foot	Average
SiO_2	71.50	70.10	69.90	69.80	70.40	70.54	70.37
Al_2O_3	11.27	12.60	12.53	12.22	12.10	12.41	12.19
Fe_2O_3	3.43	4.13	4.26	4.17	4.03	3.96	3.98
MnO	.08	.08	.08	.08	.08	.09	.08
MgO	.97	1.22	1.37	1.43	1.34	1.42	1.29
CaO	1.25	1.32	1.97	2.33	2.33	2.30	1.91
Na_2O	1.39	1.34	1.34	1.45	1.49	1.50	1.40
K_2O	2.41	2.41	2.46	2.48	2.52	2.53	2.47
TiO_2	1.06	1.08	1.08	1.08	1.07	1.07	1.07
P_2O_5	.12	.12	.13	.14	.15	.14	.13
CO_2	.02	.09	.48	.87	.91	.89	.54
BaO*	.06	.07	.07	.06	.07	.07	.07
SO_3*	.11	.09	.08	.07	.08	.06	.08
Volatile matter	6.85	5.57	4.57	3.92	3.59	3.44	4.65
Total	100.52	100.22	100.32	100.10	100.16	100.41	100.23

*Incomplete.

From the tables it will be seen that in general the mineral constituents are very uniformly distributed from east to west and from the first to the sixth foot. The chief exception to this is calsium in the form of carbonate, which rises rapidly from east to west and is low in the first two feet of all the areas, even in those where it is very high in the other four feet.

Alumina, ferric oxide and magnesia are somewhat lower in the surface foot than in any of the other five feet, except in a few samples of subsoil in which the calcium carbonate is very abundant. Silica, on the other hand, is highest in the first foot. The other constituents show no regularity in their vertical distribution, when all the areas are taken into consideration.

Comparing the different areas with one another it will be seen that in regard to the distribution of the various mineral constituents they fall into two divisions, the one including the eastern two areas where the climate is the most humid and where the loess is immediately underlaid by till, and the other including the western four areas which have a drier climate and are far to the west of the glacial drift. The former are lower in sodium and potassium but higher in iron, titanium, manganese and phosphorous.

The nitrogen and the organic carbon in the surface foot of the virgin fields show a dependence upon the aridity of the area, both decreasing from east to west. The C/N ratio of the surface soils is constant but that for the subsoils rises from east to west.

The increase of calcium carbonate from east to west is due to the decrease in the amount of seepage accompanying the increasing aridity. The decrease of both nitrogen and organic carbon results from equilibrium between the production and the decay of organic matter being attained with a lower proportion the more arid the climate is, other conditions being uniform. The differences between the eastern and the western areas in iron, titanium and manganese are to be attributed to a difference in the original deposit, rather than to any influence of climate.

(Investigations at the Institute of Animal Nutrition of The Pennsylvania State College in co-operation with the Bureau of Animal Industry of the United States Department of Agriculture.)

THE INFLUENCE OF STANDING OR LYING UPON THE METABOLISM OF CATTLE

By Henry Prentiss Armsby and J. August Fries

State College, Pa.

In a number of previous publications,[1] we have called attention to the very marked increase in the total metabolism of cattle in the standing as compared with the lying position which has been uniformly observed in our experiments. In thirty-seven published experiments, this increase varied from a minimum of 28.3 per cent. to a maximum of 64.5 per cent., averaging 41.4 per cent. and a considerable number of unpublished experiments have given entirely similar results. The foregoing figures refer primarily to that portion of the total heat which was given off by radiation and conduction and do not include that eliminated by means of the evaporation of water. On various grounds, however,[2] it was assumed in discussing the experimental results that the proportion of the total heat produced which was carried off as latent heat of water vapor was essentially the same in the standing and lying positions, and the results of the experiments were computed upon the basis of this assumption.

Such an increase in metabolism as a result of standing is quite in accord with the results of numerous previous investigations, especially upon man. Thus Katzenstein[3] in experiments upon himself observed an increase in the oxygen consumption varying from a maximum of 32 per cent. to practically zero when standing

---

[1] U. S. Dept. Agr., Bureau of Animal Industry, Bulletins No. 51 (1903), p. 35; No. 74 (1905), p. 21; No. 101 (1908), p. 20; No. 128 (1911), p. 42.

[2] Compare especially U. S. Dept. Agr., Bureau of Animal Industry, Bulletin No. 128, pp. 122-124.

[3] Arch. Physiol. (Pflüger), **49** (1891), 361-362.

with the least possible muscular exertion. Zuntz[1] in experiments on a dog observed an increase of 40.9 per cent. in the oxygen consumption and one of 36.5 per cent. in the carbon dioxid excretion in the standing as compared with the lying position. Bornstein and Ott[2] in experiments on themselves found an increase of 6.6 Cals. and 11.8 Cals. per hour, respectively, in the computed heat production when standing over that when lying. Widlund,[3] on the other hand, obtained but a slight increase in the carbon dioxid excretion in standing as compared with lying. Benedict and Carpenter,[4] as the average of a number of experiments comparing sitting with standing, find an increase in the latter of 12 per cent. for carbon dioxid, 16 per cent. for oxygen and 17 per cent. for heat production.

Quite recently, however, Zuntz[5] has called attention to the apparently small influence of standing and lying upon the metabolism of the sheep, as computed from experiments by Hagemann[6] in which the difference in the heat production as computed from the respiratory exchange was only 8 per cent. Dahm,[7] working in Zuntz's laboratory and by his methods, likewise found an increase of only 8 per cent. in the respiratory excretion of carbon dioxid by a young bull when standing as compared with that when lying. Zuntz points out that even with a uniform rate of heat production the heat emission would tend to be less in the lying posture, since less of the animal's surface is exposed for radiation and evaporation, and is inclined to attribute the discrepancy between our results and those of Hagemann and of Dahm to this effect. In other words, Zuntz believes that the differences in the heat emission observed in our experiments are much exaggerated by a storing up of heat, during the intervals of lying, in the platform upon which the animal rests or in the body of the animal itself, this heat being given off again in the succeeding intervals of standing.

---

[1] Arch. Physiol. (Pflüger), **68** (1897), 194-5.

[2] Arch. Physiol. (Pflüger), **109** (1905), 621.

[3] Skand. Arch. Physiol., **17** (1905), 290.

[4] Carnegie Institution of Washington, Publication 126 (1910), pp. 243-253.

[5] Medizinische Klinik, 1910.

[6] Arch. (Anat. u.) Physiol., 1899, Suppl. p. 111.

[7] Biochem. Ztschr., 28, 494.

That there must be a tendency in this direction is undeniable, but we have not believed the effect to be of sufficient magnitude to seriously affect our comparisons of the metabolism in the two positions. There must necessarily be a limit to the amount of heat which can be stored up in the platform in this way and it is easy to find in our experiments comparatively long intervals of lying in which, if Zuntz's explanation of the results be accepted, there must have been a storage in the platform of two or three times as much heat as it can be computed to have retained even upon the most extreme assumptions. Morever, such an accumulation of heat in the platform would necessarily tend to increase radiation from the latter so that the heat emission during lying should tend to increase until it reached the level of the actual production by the animal. As a matter of fact, we have failed to find any distinct tendency of this sort in our experiments. Indeed, the heat emission during the periods of lying tends to be very uniform—more so, in fact, than during the periods of standing.

Obviously, however, arguments like the foregoing cannot be conclusive and it still appeared that in comparisons between shorter intervals of standing and lying the difference in the heat emission as measured might be considerably greater than that indicated by a comparison of the gaseous exchange. In order to test this, appliances have been devised which permit the separate determination of the carbon dioxid and water vapor excreted in the intervals of standing and lying, respectively, and the present paper is a preliminary report upon the results obtained.

The experiments were made with the respiration calorimeter of the Institute which is a modification of the original Atwater-Rosa apparatus for experiments on man.[1] The apparatus is essentially a respiration apparatus of the Pettenkofer type with the addition of appliances for the determination of the heat emitted by the animal under experiment. A general description of the apparatus has been more than once given,[2] and a recent

---

[1] U. S. Dept. Agr., Office of Experiment Stations, Bulletin No. 63 (1899).

[2] U. S. Dept. Agr., Bureau of Animal Industry, Bulletin No. 51 (1903); Experiment Station Record, 15 (1903-4), 1037; Bureau of Animal Industry, Twenty-third Annual Report (1906).

publication[1] describes in considerable detail the experimental methods pursued in these investigations. Repeated check tests in which pure alcohol was burned in the apparatus have shown that the results obtained may be regarded as accurate within the following percentages of the total amounts determined.

Carbon dioxid, 0.5 per cent.
Water vapor, 6.0 per cent.
Heat, 1.0 per cent.

For the special determinations of carbon dioxid and water vapor here reported, samples of both the ingoing and outcoming air are taken by means of rotary blowers. Each sample passes through an absorption train in which the carbon dioxid and water are absorbed and weighed, then through the blower, which is immersed in an oil bath, and finally through a calibrated meter (made by the Daansk Maalerfabrik, Copenhagen) which records the volume of the sample. By means of a series of valves coupled together the two currents of air may, at the instant when the animal stands up, be shunted from one absorption train and meter to another, while when he lies down again the current may be shunted back to the first series. In this way the aggregate excretion of carbon dioxid and water vapor for the experimental period in the two positions is determined. At each change of position, samples of the air in the chamber of the apparatus are also taken for determination of the residual carbon dioxid and water vapor.

The three experiments upon a steer here reported form part of a series upon alfalfa hay and the so-called " alfalfa meal " (finely ground alfalfa hay). Each experiment extended over 48 consecutive hours (exclusive of 5 or 6 preliminary hours), covering the eighteenth and nineteenth days of a twenty-one day feeding period, and was divided into four subperiods of 12 hours each, the results for which are given separately. The rations consumed were:

Period II, 7.5 Kgs. alfalfa meal.
Period III, 6.0 Kgs. alfalfa hay.
Period V, 3.5 Kgs. alfalfa hay.

---

[1] U. S. Dept. Agr., Bureau of Animal Industry, Bulletin No. 128 (1911), pp. 200-222.

TABLE I. Total excretion of water vapor and carbon dioxid.

	Subperiod 1		Subperiod 2		Subperiod 3		Subperiod 4	
	H_2O Grams	CO_2 Grams	H_2O Grams	CO_2 Grams	H_2O Grams	CO_2 Grams	H_2O Grams	CO_2 Grams
Period II								
Sampled by pump	2251.04	2239.75	2062.28	2267.46	2373.64	2315.53	2355.03	2294.06
Sampled by aspirator	2271.92	2285.94	2078.37	2307.36	2389.89	2337.46	2358.88	2309.87
Sum of standing and lying	2295.61	2274.27	2061.56	2271.19	2410.29	2333.28	2374.22	2323.73
Total	6818.57	6799.96	6202.21	6846.01	7173.82	6986.27	7088.13	6927.66
Average	2272.86	2266.65	2067.40	2282.00	2391.27	2328.76	2362.71	2309.22
Period III								
Sampled by pump	1921.56	1999.09	1786.38	2003.38	1944.90	2005.47	1792.07	2015.43
Sampled by aspirator	1882.01	1997.01	1787.33	2053.65	2022.55	2061.69	1816.74	2026.87
Sum of standing and lying	1885.66	2014.93	1786.65	2062.29	2023.48	2069.51	1791.51	2009.42
Total	5689.23	6011.03	5360.36	6124.32	5990.93	6136.67	5400.32	6051.72
Average	1896.41	2003.68	1786.79	2041.44	1996.98	2045.56	1800.11	2017.24
Period V								
Sampled by pump	1291.47	1429.42	1301.31	1420.96	1299.48	1419.60	1151.66	1374.69
Sampled by aspirator	1269.37	1410.98	1264.89	1424.91	1219.29	1458.28	1206.29	1412.11
Sum of standing and lying	1296.25	1395.68	1280.22	1427.63	1220.51	1456.87	1227.34	1443.20
Total	3857.09	4236.08	3846.42	4273.50	3739.28	4334.75	3585.29	4230.00
Average	1285.70	1412.03	1282.14	1424.50	1246.43	1444.92	1195.10	1410.00

TABLE II. Metabolism of a Steer, Standing and Lying.

	Subperiod 1		Subperiod 2		Subperiod 3		Subperiod 4		Totals	
	Standing	Lying	Standing	Lying	Standing	Lying	Standing	Lying	Standing	Lying
Period II										
Minutes	302.0	418.0	271.0	449.0	301.0	419.0	265.2	454.8	1139.2	1740.8
Water vapor										
Total, grams	1119.21	1176.40	902.30	1159.26	1134.54	1275.75	1062.97	1311.25	4219.02	4922.66
Per minute, grams	3.7060	2.8144	3.3295	2.5819	3.7692	3.0447	4.0082	2.8831	3.7035	2.8278
Carbon dioxid										
Total, grams	1113.45	1160.82	1001.78	1269.41	1087.81	1245.47	995.86	1327.87	4198.90	5003.57
Per minute, grams	3.6869	2.7771	3.6966	2.8272	3.6140	2.9725	3.7551	2.9197	3.6858	2.8743
Heat										
Total										
Radiated, cals.	2024.39	2132.02	1740.82	2277.93	2129.12	2191.63	1817.28	2152.16	7711.61	8753.74
Latent in H_2O, cals.	656.98	690.55	529.65	680.49	665.97	748.87	623.96	769.70	2476.56	2889.61
Sum, cals.	2681.37	2822.57	2270.47	2958.42	2795.09	2940.50	2441.24	2921.86	10188.17	11643.35
Per minute										
Radiated, cals.	6.7033	5.1005	6.4237	5.0733	7.0735	5.2306	6.8525	4.7321	6.7693	5.0286
Latent in H_2O, cals.	2.1754	1.6521	1.9544	1.5158	2.2125	1.7872	2.3528	1.6924	2.1739	1.6599
Sum, cals.	8.8787	6.7516	8.3781	6.5891	9.2860	7.0178	9.2053	6.4245	8.9433	6.6885
Period III										
Minutes	204.5	515.5	183.5	536.5	194.3	525.7	263.5	456.5	845.8	2034.2
Water vapor										
Total, grams	651.74	1230.27	565.61	1221.72	669.57	1352.98	807.10	1009.64	2694.02	4814.61
Per minute, grams	3.1870	2.3866	3.0823	2.2772	3.4461	2.5737	3.0630	2.2117	3.1852	2.3668
Carbon dioxid										
Total, grams	696.79	1300.22	642.38	1411.27	702.50	1359.19	886.04	1140.83	2927.71	5211.51
Per minute, grams	3.4073	2 5223	3.5007	2.6305	3.6155	2 5855	3.3626	2.4991	3.4615	2.5619

Heat										
Total										
Radiated, cals.	1282.51	2379.26	1142.31	2473.44	1329.16	2577.04	1698.49	2105.60	5452.47	9535.34
Latent in H_2O, cals.	382.57	722.17	332.01	717.15	393.04	794.20	473.77	592.66	1581.39	2826.18
Sum, cals.	1665.08	3101.43	1474.32	3190.59	1722.20	3371.24	2172.26	2698.26	7033.86	12361.52
Per minute										
Radiated, cals.	6.2714	4.6154	6.2251	4.6103	6.8408	4.9021	6.4459	4.6125	6.4465	4.6875
Latent in H_2O, cals.	1.8708	1.4009	1.8093	1.3367	2.0229	1.5108	1.7980	1.2983	1.8697	1.3893
Sum, cals.	8.1422	6.0163	8.0344	5.9470	8.8637	6.4129	8.2439	5.9108	8.3162	6.0769
Period V										
Minutes	215.5	504.5	206.6	513.4	308.8	411.2	259.8	460.2	990.7	1889.3
Water vapor										
Total, grams	449.93	846.32	477.04	803.18	599.43	621.08	544.13	683.21	2070.53	2953.79
Per minute, grams	2.0878	1.6775	2.3090	1.5644	1.9412	1.5104	2.0944	1.4846	2.0900	1.5634
Carbon dioxide										
Total, grams	504.94	890.74	494.55	933.08	717.07	739.80	610.32	832.88	2326.88	3396.50
Per minute, grams	2.3431	1.7656	2.3938	1.8175	2.3221	1.7991	2.3492	1.8098	2.3487	1.7978
Heat										
Total										
Radiated, cals.	1061.80	1830.30	1058.34	1838.40	1530.07	1443.58	1280.08	1634.00	4930.29	6746.28
Latent in H_2O, cals.	264.11	496.79	280.02	471.47	351.87	364.57	319.40	401.04	1215.40	1733.87
Sum, cals.	1325.91	2327.09	1338.36	2309.87	1881.94	1808.15	1599.48	2035.04	6145.69	8480.15
Per minute										
Radiated, cals.	4.9271	3.6279	5.1227	3.5808	4.9549	3.5107	4.9272	3.5506	4.9766	3.5708
Latent in H_2O, cals.	1.2256	0.9847	1.3554	0.9183	1.1395	0.8866	1.2294	0.8714	1.2268	0.9177
Sum, cals.	6.1527	4.6127	6.4780	4.4992	6.0944	4.3973	6.1566	4.4221	6.2034	4.4885

The ration of Period III was estimated to be approximately a maintenance ration. The subject was a pure-bred shorthorn steer about twenty months old, in moderate condition, and weighing about 360 Kgs.

The total excretion of carbon dioxid and water vapor during each subperiod of 12 hours was determined in duplicate, viz., in a sample taken automatically by the meter pump (intermittent sampling) and in a continuous sample taken by a large aspirator having a capacity of about 800 liters. In Table I the results obtained on these two samples are compared with the totals obtained by adding the results for the intervals of standing and lying. The close agreement of the three attests the general accuracy of the work.

The partition of water vapor, carbon dioxid and heat eliminated between the intervals of standing and of lying during each subperiod and for the entire forty-eight hours was as shown in Table II. In Period II there were seventeen intervals each of standing and lying, the length of the standing intervals varying from 2 to 147 minutes and that of the lying intervals from 20 to 145 minutes. In Period III there were twenty-one intervals of standing, varying from 4 to 111 minutes each and twenty intervals of lying varying from 9 to 142 minutes each. In Period V there were 16 intervals of standing, varying from 11 minutes to 186 minutes each and fifteen intervals of lying, ranging from 72 minutes to 177 minutes each. Few of the intervals of either standing or lying, however, were less than 10 minutes, the exception being, 2 in Period II, standing, 4 in Period III, standing, and 1 in Period III, lying. The average length of the standing and lying intervals was

	Period II	Period III	Period V
Standing	67 minutes	40 minutes	62 minutes
Lying	102 "	102 "	126 "

These rather frequent changes of posture on the part of the animal would tend to emphasize any effect of a storing up of heat in the platform upon the partition of the heat emission between the standing and lying intervals.

From the data contained in Table II, the percentage increase observed in the standing over the lying periods may be computed with the results shown in Table III.

TABLE III.—Percentage Increase in Standing over Lying.

	Subperiod 1	Subperiod 2	Subperiod 3	Subperiod 4	Whole period
Period II					
Carbon dioxid	32.8	30.7	21.6	28.6	28.2
Water vapor	31.7	28.9	23.8	39.0	31.0
Total heat	31.5	27.2	32.3	43.3	33.7
Radiated heat	31.4	26.6	35.2	44.3	34.6
Period III					
Carbon dioxid	35.1	33.1	39.8	34.6	35.1
Water vapor	33.5	35.4	33.9	38.5	34.6
Total heat	35.3	35.1	38.2	39.5	36.8
Radiated heat	35.9	35.0	39.5	39.7	37.5
Period V					
Carbon dioxid	32.7	31.7	29.1	29.8	30.6
Water vapor	24.5	47.6	28.5	41.1	33.7
Total heat	33.4	44.0	38.6	39.2	38.2
Radiated heat	35.8	43.0	41.1	38.8	39.4

It is clear that the increase emission of heat in the intervals of standing was accompanied by a correspondingly increased elimination of both carbon dioxid and water vapor, the parallelism being quite close although with a tendency to a greater increase in the heat than in the carbon dioxid which in a few instances is somewhat marked. The same thing is shown in a different way by computing the heat emission per gram of carbon dioxid excreted as in Table IV. We conclude, therefore, that the increased heat emission by cattle during standing, which has been invariably observed in our experiments, represents substantially the increase in heat production during the same time.

It will be noted that the influence of standing and lying upon the excretion of carbon dioxid was very much greater in these experiments than was observed by Hagemann or by Dahm. We are unable at present, however, to suggest any explanation of this difference.

That the calorific equivalent of carbon dioxid is in most cases materially lower than that corresponding to either protein, fats, or carbohydrates is doubtless to be ascribed to the very low thermal equivalent of the considerable amount of carbon dioxid produced in the methan fermentation, estimated by Zuntz[1] at 0.5 Cal. per liter, equal to 0.253 Cal. per gram.

TABLE IV—Total Heat per Gram Carbon Dioxid.

	Subperiod 1	Subperiod 2	Subperiod 3	Subperiod 4	Whole period
Period II					
Standing	2.408	2.266	2.569	2.451	2.426
Lying	2.431	2.330	2.361	2.200	2.327
Period III					
Standing	2.390	2.295	2.451	2.451	2.402
Lying	2.385	2.261	2.480	2.365	2.372
Period V					
Standing	2.626	2.706	2.625	2.621	2.641
Lying	2.613	2.476	2.444	2.444	2.497

Finally, the computation, in Table V, of the percentage of the total heat which was given off as latent heat of water vapor shows that this relation also was remarkably uniform and fully justifies the assumption previously mentioned upon which we have based the computation of our earlier results.

---

[1] Jahrbuch des Vereins der Spiritusfabrikanten in Deutschland, 12, (1912) 328.

TABLE V—Percentage of Heat Given off in Water Vapor.

	Subperiod 1	Subperiod 2	Subperiod 3	Subperiod 4	Whole period
Period II					
Standing	24.50	23.33	23.83	25.56	24.31
Lying	24.47	23.01	25.47	26.34	24.82
Period III					
Standing	22.98	22.52	22.82	21.81	22.48
Lying	23.29	22.48	23.56	21.96	22.86
Period V					
Standing	19.93	20.92	18.70	19.97	19.78
Lying	21.35	20.41	20.16	19.71	20.45

(*Résumé*)

SUR LA PRÉSENCE NORMALE DU MANGANÈSE CHEZ LES ANIMAUX

PAR MM. GABRIEL BERTRAND ET F. MEDIGRECEANU

Paris, France

A l'aide d'une méthode dont la sensibilité et la précision ont été éprouvées (Bulletin de la Société Chimique de France, année 1912), nous avons recherché et dosé le manganèse dans le sang, les organes ou le corps entier d'un grand nombre d'animaux appartenant aux différents groupes de l'échelle zoologique.

Nous avons fait prés de 250 déterminations quantitatives du métal et examiné environ une soixantaine d'espèces: nous avons, sauf dans le blanc de l'oeuf des oiseaux, toujours trouvé des traces appréciables de manganèse, en général quelques centièmes ou dixièmes de milligramme pour cent grammes de substance fraîche. Les oeufs des oiseaux ne sont pas exempts de manganèse, mais c'est dans le jaune que la provision du métal nécessaire aux premiers stades de développement du jeune animal est accumulée.

La généralité des physiologistes ont admis et tendent encore à admettre que les traces de manganèse signalées çà et là dans l'organisme animal par certains observateurs sont purement accidentelles et sans conséquence physiologique. Il semble, au contraire, à la suite des résultats que nous avons obtenus, que l'existence constante et la répartition remarquable du manganèse dans les organes soient plutôt de nature à faire attribuer à ce métal une place importante à côté des autres éléments catalytiques de la matière vivante.

(*Résumé*)

EMPLOI DU SULFATE DE L'ALUMINIUM COMME ENGRAIS CATALYTIQUE

PAR MM. GABRIEL BERTRAND ET HENRI AGULHON

Paris, France

Stoklasa a publié en 1911 des résultats intéressants obtenus en pleine terre avec le sulfate d'aluminium employé comme engrais catalytique. Nous avons entrepris à cet égard quelques expériences de laboratoire avec l'orge et le radis cultivés en pots de terre. Les résultats obtenus confirment ceux de Stoklasa. Avec la faible dose de 2 milligrammes d'aluminium élément, mis sous forme de sulfate, par kilog. de terre, nous avons observé avec l'orge une augmentation de récolte de 18% en poids frais et de 17% en poids sec; avec le radis, 10% en poids frais et 6% en poids sec. La dose de 4 mgr. a été presque indifférente pour le poids sec bien qu'elle ait marqué encore nettement pour le poids frais; on retrouve à propos de cet élément le phénomène d'accumulation d'eau dans la plante aux doses élevées d'engrais catalytique. Avec 10 mgr. par kilog. de terre, la dose a été trop forte; l'orge a cependant encore marqué une augmentation de poids frais.

L'aluminium semble bien être un élément susceptible de présenter un intérêt agricole. Comme pour les autres engrais catalytiques, il serait désirable de voir se multiplier à son égard les expériences de grande culture.

(*Résumé*)

EMPLOI DU MANGANÈSE COMME ENGRAIS CATALYTIQUE

M. Gabriel Bertrand

Paris, France

En outre des recherches théoriques dont les résultats sont présentés à la section de Chimie physiologique, j'ai effectué, depuis le dernier Congrès, de nouvelles expériences sur la valeur du manganèse comme engrais catalytique.

Des expériences de laboratoire sur le pois, l'orge, le radis, cultivés en pots de terre, ont présenté des augmentations de récolte de 10 à 20% pour les pots additionnés de manganèse à l'état de sulfate.

En 1911, à la station agronomique de Meudon, le blé a donné des résultats analogues dans des expériences en bacs de sable. En pleine terre, j'ai obtenu les augmentations de récolte suivantes: pour 60 kilog. de sulfate de manganèse desséché à l'hectare, 9,5% avec l'avoine; pour 30 kilog. de sulfate, 20% avec le pois; pour 40 kilog. de sulfate, 18% avec le colza et 15% avec le lupin; pour deux parcelles de 25 et de 50 kilog. de sulfate, une moyenne de 33% d'augmentation avec la luzerne.

A Marchais, dans la propriété de S. A. S. le Prince de Monaco, où j'ai essayé des doses fortes, 40 kilog. de sulfate de manganèse à l'hectare ont donné une récolte d'avoine supérieure aux témoins de 17% en grains et de 12% en paille; les doses plus fortes, jusqu'à 100 kilog., ont donné des résultats moins favorables; mais il faut remarquer que la terre était sablonneuse et la saison très sèche.

Tous ces résultats confirment la valeur déjà éprouvée du manganèse comme engrais catalytique; les doses les plus favorables en pleine terre ne semblent pas devoir dépasser, en général, 30 à 50 kilog. de sulfate desséché à l'hectare.

THE CONSERVATION OF PHOSPHATES IN THE URINE

By Philip E. Browning

New Haven, Conn.

The utilization of waste products for their possible fertilizing value has been the subject of much study and it is not the object of this paper either to review the work done or to add any very important contribution to it. Some interest however may be attached to the result of certain experimental observations recently made.

When urine is brought in contact with calcium hydroxide the phosphates present unite readily with it to form the calcium salt. This is easily brought about either by placing the urine with lime in a bottle and agitating from time to time, or by pouring it through a filter upon which a layer of lime has been placed. The action is rapid, for even when the latter process is employed the urine is found, after passing through the filter to contain no phosphate.

About 10 grams of dry calcium hydroxide were placed in a bottle and urine added from time to time, amounting in all to about two liters, until the supernatant liquid gave the test for phosphates when a portion of it was tested with the molybdic acid solution. It is perhaps of interest to note in this connection that although this operation continued over several days no disagreeable odors and no ammonia were noticed until the reaction with the lime was complete and the filtrate from the calcium salt gave tests for phosphates. The lime product was then filtered off, washed and dried and was found to contain 24.18% total phosphoric acid (P_2O_5) or to be a fair grade "phosphate rock."

Should the time arrive when the mineral supply of phosphatic material threatens to be exhausted possibly the public urinals of our larger cities might utilize this reaction to keep up the supply. A fair average amount of P_2O_5 eliminated by one person in twenty-four hours is 2.5 grams.

CONCENTRATION OF THE SOIL SOLUTION

Frank K. Cameron

Washington, D. C.

The composition of the Soil Solution is generally recognized to be of fundamental importance to the relation between a soil and its crop producing powers. A considerable body of investigation and literature has been accumulated, but it is evident that a lack of knowledge or appreciation of the fundamental principles governing solubilities permeates the work of investigators in this field.

The composition of the aqueous solution in the soil is determined by the nature of the solids and the gas with which it is in contact and by the temperature. Living organisms within the soil aid in continually modifying or changing the composition. Normally, when the soil is in good condition for plant growth, the soil moisture is all in the form of film moisture.[1] It has been established that under such conditions, most important " surface effects " may supervene, profoundly modifying the character of the solution, not only quantitatively but qualitatively. Unfortunately but little is known of these effects although it offers a most interesting and profitable field for investigation. It is complicated in the case of the soil solution by the fact that the film is continually changing and moving. As has been emphasized elsewhere, all soil phenomena are dynamic rather than static,[2] a fact too often overlooked or ignored in soil studies.

The soil atmosphere is continually changing. Its most prominent feature is the relatively large content of carbon dioxide. With the change of partial pressure due to carbon dioxide in the atmosphere, there is a corresponding change of dissolved carbon dioxide. The distribution ratio of carbon dioxide between soil

---

[1] Cameron and Gallagher, Bull. No. 50, Bureau of Soils, United States Department of Agriculture (1908).

[2] Journ. Ind. and Eng. Chem., **1**, 806 (1909).

atmosphere and film moisture is not necessarily a linear function. In fact it is practically certain that it is quite a complicated function. And it is equally certain that the dissolved carbon dioxide is very potent in modifying the solvent action of the soil water on some of the solid components of the soil. As the concentration of the soil water with respect to carbon dioxide is continually changing, the concentration of constituents thus affected is also changing in ways which may sometimes be recognized qualitatively if not quantitatively.

The solid components of the soil whether mineral or organic can be classified as:

(1) Definite compounds, or chemical individuals, such as a fragment of orthoclase, a crystal of gypsum, etc.

(2) Indefinite complexes, but homogeneous, such as the solid solutions formed by phosphoric acid with lime or iron.

(3) Indefinite complexes, but not homogeneous, such as the absorbed potash on the surface of clay particles, or ammonium salts condensed on the surface of organic remains, etc.

A definite compound has a definite solubility (for any given temperature) which is altogether independent of the relative masses of the solid and the liquid. This solubility may be affected by the presence of a third substance, especially if the two solutes are electrolytes. In soil solutions the concentrations are usually so small that mutually solubility effects can be considered negligible excepting only those due to dissolved carbon dioxide. Two other modifying influences however may be commonly effective in the case of soil minerals. It has been shown by Ostwald[1] and by Hulett[2] that a very finely comminuted substance may have quite a different solubility than the same substance in coarser particles. Thus very finely powdered gypsum has been shown to be a fifth more soluble than coarse particles. The extremely fine mineral particles in the " clay " (mechanical separates) of a soil may well therefore have different solubilities than those same particles in the fine sands, and intermediate solubilities may pertain to the finer silt particles. Again, many if not most

---

[1] Zeit. phys. Chem., **34**, 496 (1900).

[2] Zeit. phys. Chem., **37**, 385 (1901).

soil minerals, since they are salts of strong bases with weak acids, on dissolving are more or less completely hydrolized, one of the products of hydrolosis (the acid usually) being but very slightly soluble and tending toward a negligible active mass. A simple application of the mass law[1] in its usual form will show therefore that the concentration of the more soluble product may become relatively very large before equilibrium is reached. It is quite improbable, in fact, that equilibrium is ever actually attained in soils in humid areas. It is equally improbable that any of the ordinary rock forming minerals can be synthetized at the concentrations and temperatures ordinarily realized in soils.[2]

From the foregoing it appears that the major part of the definite compounds which dissolve in the soil solution under

---

[1] Consider:

$$\underset{m}{\text{Mineral}} + \underset{w}{\text{water}} = \underset{s}{\text{unhydrolized salt}} + \underset{b}{\text{base}} + \underset{a}{\text{acid}}$$

then $k.\ mw = sba$

$\therefore\ b = k.\ \frac{mw}{sa}$

S is always small, relatively, and *a* usually approaches zero. Consequently, *b*, as the concentration of the hydrolized base must be relatively large to attain equilibrium or to effect the synthesis of a silicate mineral, conclusions sustained by the literature of laboratory experiments in this field.

[2] The burden of proof is distinctly on those who claim that " zeolitic " minerals are being formed in the soils. It is in the last degree improbable that they would be formed by " building up " processes. On the other hand, there is geological evidence that zeolites are sometimes alteration (or " building down ") products of feldspar, so that their existence in soils may be possible though yet unproved.

That concentrations sufficient to cause the " building up " of minerals may be attained in the absorption film to be discussed presently seems quite possible and there is a large amount of cumulative evidence in this direction in the geological literature. See for examples, Sorby, Quart. Jour. Geol. Soc., London, **36,** 62 (1880); Van Hise, A Treatise on Metamorphism, Minograph 47, U. S. Geol. Survey, p. 75 et seq. Also Bonney, Quart. Jour. Geol. Soc., London, 39, 19 (1883); Becke, Tschermak Min. Mitth., 5, 147 (1883); Wadsworth, Proc. Boston Soc. Nat. Hist., 22, 201, (1883); Young Am. Jour. Sci., (3) **23,** 257 (1882); 24, 47 (1882); Irving, Am. Jour. Sci., (3) **25,** 401 (1883); Cameron, The Soil Solution, Chemical Publishing Company, Easton, Pa., 1911. Obviously, however, plant roots do not come into contact with solutions of such concentrations.

humid conditions are hydrolized and the soil solution never reaches the concentration of the more soluble constituents required by definite equilibrium or "saturation." Practically, therefore, the concentration of the soil solution is not independent of the ratio of the mass of solid to the mass of liquid, although theoretically such a condition should be obtained, if the time element, surface effects, and like disturbing factors did not enter.

Quite different is the case of an aqueous solution in contact with a solid solution containing a common component. In this case the concentration of the common component in both liquid and solid phase is dependent upon the relative masses of the two. Increasing the concentration in one increases (or sometimes decreases) the concentration in the other. In other words there is a distribution of the common component between the solid and the liquid solution which may be expressed by the equation $C = k.C_2$ or $C = k.C_2^n$ or often by some more complicated form. The exponent n is usually positive, but that it may have negative value is indicated by the case of the addition of lime to lime phosphate in contact with water.

As a practical example of a solid solution in the soil it has been shown that phosphoric acid when added to a soil is more or less promptly taken up by the ferric hydrate to form a basic (?) phosphate, i.e., a solid solution;[1] and it would require the addition of enormous and impracticable amounts of the phosphate to so increase the concentration of the ferro-phosphoric acid solid solution to the point where there would be any appreciable increase in the concentration in the liquid solution.

The third form of mineral complex in which a more soluble substance is condensed or absorbed on the surface of a much less soluble substance (absorbent) also presents a case of distribution. Consequently the concentration of the liquid solution is here also dependent upon the relative masses of the solid or liquid; or, more correctly, upon the relative volume of the solution and the absorbing surface of the solid. Much of the soluble potash in solids is probably distributed between the soil solution and the surface of the solid particles, mainly the clay. Attempts to study

---

[1] Cameron and Bell, Bull. 41, Bureau of Soils, U. S. Dept. Agric., 1907.

the distribution of a solute between a soil and free water in contact with it have shown the equation describing the distribution to be generally of a complex form, owing largely no doubt to changing aggregation (flocculation or deflocculation) of the soil particles.[1]

The equation for the distribution of such a solute as potassium between the film water and the soil particle is quite probably much simpler, possibly a linear function. But whatever the form of the equation it is beyond doubt that the concentration in the soil solution changes coincidentally with and in the same direction as the concentration on the absorbent. That is, the exponent *n* in the distribution equation, has always a positive value. As the effective surface of the soil is continually changing it is necessary to conclude that the concentration of the soil solution is continually changing or tending to change. But with such dilute aqueous solution as are soil solutions, it requires a considerable increase in the absorbed constituent to produce a noticeable increase in the liquid phase. This has been repeatedly shown experimentally in the case of soils and other absorbents, both by shaking the absorbent with aqueous solutions of the solute and by percolation experiments.

It is clear therefore that the concentration of the soil solution resulting from contact with definite compounds, solid solutions and absorption films, *is* determined by the relative masses of the liquid phase and of the solid phases, in so far as the masses of the solid phases determine their effective surfaces to solvent action. As the moisture content of a soil is continually changing and as the effective surface of the soil particles is always changing, the concentration of the soil solution is always changing. But as the foregoing analysis of the mechanism of the formation of the soil solution developes, but very small changes in concentration occur in the liquid phase with relatively large changes in the amount of the common constituents in the solid phases, at least with respect to those mineral constituents of recognized importance for plant growth and fertilizer practice. Consequently under any given climatic conditions, the concen-

---

[1] Cameron and Patten, Jour. Phys. Chem., **11**, 851 (1907).

tration of the soil solution with respect to those constituents derived from the soil minerals varies within narrow limits, no matter what may be the relative masses of these minerals in the soil. That differences in climate may make marked difference is indicated by the results of Mooney[1] who showed for instance that the concentration of potassium in the soil solution in Bahaman soils varies quite widely but was of the order of 175 parts per million while in the soils of the eastern United States it normally is in the neighborhood of 30-35 parts per million. Not only the actual amount, but the variation in the amount from soil to soil was much greater in the Bahaman soils.

Obviously, other constituents of the soil solution organic or inorganic may vary quite widely in concentration. But in all cases the principles of solubility pointed out above apply. It is essential to a clear understanding of the phenomena of plant production and soil management that these principles be recognized. The readjustment and modification of theories which have long held sway is now actively in progress, and the tendency to ignore the fundamental principles involved is the justification for restating them in the form here given, in the hope that they prove useful to colleagues less accustomed to the point of view they represent.

---

[1] The Bahama Islands, The Geog. Soc. Balto., Johns-Hopkins Press, 1905.

THE ROLE OF THE LYSIMETER IN SOIL SOLUTION STUDIES

By Frank K. Cameron

Department of Agriculture, Washington, D. C.

The employment of lysimeters in soil investigations appears to be on the increase, a highly desirable fact, for their employment intelligently will doubtless add much valuable data. It appears to be a common assumption, however, that the composition of the water collected in the lysimeter is the same as the soil solution (film water). This assumption is quite incorrect, but is so generally made as to warrant particular notice.

As has been pointed out elsewhere[1] the water entering the soil or the " cut off " divides into two portions which may be conveniently designated the *capillary water* and the *seepage.* Under conditions of average humidity, the capillary water, or that returning to the surface as films over the soil particles, is far larger than the seepage, and in fact may be two thirds or more of the rainfall. It moves slowly (relatively), is long in intimate contact with the soil particles, and encounters in its path a large number of different minerals. In arid regions the evaporation of the capillary water at or near the surface may result in the accumulation of soluble salts (alkali), but in humid regions no such accumulation can occur for the simple reason that the next rain would wash them down into the soil to recommence their rise in the capillary waters. Excepting possibly the case of excessive rainfall or an excessively open soil, the general tendency is toward the rise of dissolved mineral matter from the subsoil towards the surface. The composition of the film water, or the soil solution is of fundamental importance, but can only be approximated by indirect methods, since no method has yet been

---

[1] The Soil Solution, The Chemical Publishing Company, Easton, Pa., 1911 p.   et seq.

devised for separating it mechanically from the solid soil to which it adheres.

The water collected in a lysimeter is in fact, seepage water, free water of the interstitial spaces of the soil, or that water in excess of what is required for the condition that all the water in the soil shall be film water. It may pass through or drain from the soil at widely differing rates, depending upon the character of the soil, the length of path, moisture content of the soil and possibly other factors, and its composition may vary widely with the same soil as well as with different soils. Springs and wells are, in effect, lysimeter waters and their composition is notoriously variable. Generally the water is not long in contact with any particular soil particle and diffusion of dissolved mineral salts, at best very slow, is probably extremely slow between the film water and the free water of the soil interstices.

It would seem, therefore, that while the composition of a lysimeter water may approach that of the film water as a limiting case, it can never be identical with it and generally will be quite different. Great as may be the value of data on the composition of lysimeter waters, they are, in the nature of the case, quite incompetent to give any direct quantitative information on the concentration of the soil solution with respect to its several constituents.

A STUDY OF SOIL POTASSIUM

By B. E. Curry and T. O. Smith

Durham, N. H.

Until recent years the theory of soil fertilization has rested almost entirely upon the practice of adding plant food or amendments to the soil in the form of fertilizers and manures for the purpose of increasing production. In practice the ultimate aim is to obtain an increased production at a profit. With our present knowledge of soil management, tillage, and fertilization it is a simple proposition to increase yields but it is not a simple proposition to secure profitable increased yields. It is doubtful from a practical point of view whether the maximum yield is the most profitable.

The practice of applying fertilizers is followed because the amount of plant food in the soil is considered insufficient or unavailable for the needs of the crop. For special cases as in market gardening and greenhouse culture where high-priced crops are grown the relatively small cost of fertilizers becomes almost negligible. In other crops such as the average farmer grows the difference of a few dollars makes the difference between profit and loss in an operation on an acre. The aggregate of values of farm crops is largely derived from the ordinary crops grown under ordinary conditions.

In New Hampshire one of the large cash crops is hay. The farms have generally been allowed to run down and become unproductive. The soil is apparently as good as it ever was but through neglect production has decreased. A larger acreage is devoted to grass than to any other crop. This condition has become established through the natural adaptibility of the soil to grass culture and through certain economic factors due to location and labor problems. The heavy horse and ox power once so common on New Hampshire farms is now a condition of the past. Partly because of this the land does not get the cultivation it once had.

Commercial fertilizers have in part been substituted for tillage in order to maintain production under conditions of lessened tillage.

A good many general observations lead one to believe that the present method of using commercial fertilizers in the production of hay is often unprofitable. There seems to be very little doubt that in the common use of fertilizers a very large proportion of the plant food added is never converted into profitable plant production. It is doubtful if the use of commercial fertilizers can long be substituted for tillage. There are other important soil and plant growth factors which enter into profitable production and which cannot be eliminated by the use of fertilizers alone.

The soils of New Hampshire are extremely varied in character and are for the most part of granitic origin. Almost any type may be found between the limits of sand and pure boulder clay. However, the sands in many instances seem to be rich in feldspathic and other minerals. Many of the types have been considerably washed while others seem to have been formed in place. Areas of limestone soil are very limited and are found in only a few sections.

In connection with the use of commerical fertilizers in the production of grass some very interesting facts have been found. Many of the grass fertilizers carry a large amount of potassium. Also the tillable soils are on the average very rich in potassium. Those soils which are relatively poor in potassium contain large amounts in the aggregate. Some of the boulder clay soils contain as high as $3\frac{1}{2}\%$ K_2O. Assuming that an acre foot of soil weighs three million pounds, such a soil would contain fifty-two and one-half tons of K_2O per acre. Some of the medium clay soils carry about 2% K_2O. while the light soils carry still less. Some very sandy soils have been found which contain as much as 1% K_2O. Such soils carry a considerable amount of mineral in connection with the sand.

With these large quantities of potassium present in the soil there came the question of the use of potassium in commercial fertilizers. Is it not reasonable to think that the soil under proper tillage conditions could supply enough potassium for the needs of the crop without the addition of potassium from artificial sources? It is a remarkable fact that where potassium is added in comparatively large quantities as a fertilizer constituent that that amount is very insignificant when compared with the amount of potassium present in the soil under natural conditions. To illustrate: sixty pounds of K_2O is higher than the average application per acre. In a soil which carries 2% K_2O the amount per acre foot aggregates thirty tons. In comparison with sixty thousand pounds, sixty becomes a very small quantity: under such conditions one pound is added to one thousand pounds already present.

In this connection it is interesting to note that the soil very rapidly renders the applied potassium insoluble. For instance, when dilute solutions containing potassium salts are percolated through columns of soils the potassium is removed from solution and changed into a comparatively insoluble form. If the salt is the nitrate, chloride, or sulphate the acid radical remains in solution as the acid radical of some new salt. When potassium is percolated through as a phosphate both the base and acid radicals are removed from solution and no new salt appears in the percolate as in the first instances.

The same conditions hold when potassium salts come in contact with the soil in other ways. In order to show these reactions five soils fairly representative of the different types found in New Hampshire were selected. An analysis of these soils follows:

TABLE I

Soil No.	1	2	3	4	5
Loss on Ignition	2.660	5.33^{3}	5.830	4.905	7.260
Moisture	.770	1.419	0.516	.908	1.681
SiO_2	81.050	74.090	72.020	71.850	62.340
P_2O_5	.070	.084	.073	.085	.089
Fe_2O_3	1.448	2.856	2.896	2.688	3.428
Al_2O_3	9.017	12.195	13.446	14.702	18.638
CaO	.756	.722	.764	.806	.956
K_2O	1.630	1.730	1.910	2.470	2.990
N	.081	.186	.290	.148	.257
Total	97.482	98.615	98.745	98.462	97.609
Na, Mg, etc., not determined.	2.518	1.385	1.255	1.538	2.391

Sample No. 1 is a light sandy soil, No. 2, a light clay loam, No. 3 a sandy loam, No. 4, a heavy clay loam, and No. 5 a heavy boulder clay.

Known amounts of potassium chloride in solution were added to these soils and the moisture content brought up to twenty per cent. by the addition of water. The samples were thoroughly mixed, placed in sealed jars, and allowed to stand for several weeks. They were then shaken with water and the amount of soluble potassium determined by the chloroplatinate method.

The results follow:

TABLE II

No. of Soil	Grams K_2O as K Cl per Kg. soil	Total grams K_2O recovered	Total grams K_20 retained in the soil
1	.9354	.7012	.2342
	.6236	.4471	.1765
	.3118	.2024	.1094
	.1559	.0072	.0587
2	.9354	.6173	.3181
	.6236	.3872	.2364
	.3118	.1871	.1237
	.1559	.0841	.0718
3	.9354	.5517	.3837
	.6236	.3460	.2776
	.3118	.1724	.1394
	.1559	.0709	.0850
4	.9354	.4400	.4954
	.6236	.3101	.3135
	.3118	.1240	.1878
	.1559	.0561	.0998
5	.9354	.3243	.6111
	.6236	.2712	.3524
	.3118	.0779	.2339
	.1559	.0437	.1122

The table shows that large amounts of potassium are taken up and held by the soils. Also, that the amount of potassium so held increases with increase in the clay content of the soil.

If di-potassium phosphate is substituted for potassium chloride under the above conditions the same results are observed as is shown in the following table:

TABLE III

No. of Soil	Grams K_2O as K_2HPO_4 per Kg. of soil	Total grams K_2O recovered	Total grams K_2O retained in the soil
1	3.1840	1.6238	1.5602
2	3.1840	.7378	2.4462
3	3.1840	.4458	2.7382
4	3.1840	.7472	2.4368
5	3.1840	.5520	2.6320

A further examination of the water extract of the soil treated with potassium chloride shows that the solubility of the acid radical is not affected by the soil. All the chloride appears in the solution as potassium chloride and as the acid radical of a new salt. The new salt or salts are chiefly chlorides of calcium and magnesium. If the acid radical is the sulphate or nitrate the same conditions of solubility occur. A possible exception is the case where more calcium sulphate is formed than can dissolve in the given volume of water.

Salts of iron and aluminum must in some cases be formed in the process of these reactions. Their rare appearance in the solution is probably due to alkalinity of the water extract which in many instances is sufficient to cause these salts to hydrolyze and the bases to reprecipitate.

Different conditions of solubility are observed in the case of the phosphates. The extent to which they are taken from solution and retained by the soil is shown in the following table:

TABLE IV

No. of Soil	Grams P_2O_5 as K_2HPO_4 per Kg. of soil	Total grams P_2O_5 recovered	Total grams P_2O_5 retained in the soil
1	2.4000	1.1985	1.2015
2	2.4000	.4806	1.9194
3	2.4000	.0846	2.3154
4	2.4000	.8355	1.5645
5	2.4000	.5553	1.8447

When soils react with potassium chloride, nitrate, etc., the reaction must be chemical because the amounts of new salts which appear in the water extract are equivalent to the amount of potassium removed. When soils react with potassium phosphate both the base and acid radical are removed from solution. No new salts appear in solution and the water extract gives no evidence of the nature of the reaction. By analogy, however, the reaction must be chemical. When potassium exchanges places with calcium and magnesium these in turn form phosphates which have a very low solubility and do not appear in the solution. This is further substantiated by the fact that where large amounts of calcium sulphate are formed not all of the acid radical appears in solution.

At present there are no data at hand which show the relation between bacterial activities in the soil in New England and in other sections. The probabilities are that such action is comparatively small and that the rate of activity of bacterial action increases with increase of temperature. Plant growth is greatly affected by change in temperature. Bacterial activities undoubtedly are affected by temperature changes in much the same way. This may account in part for the slow nitrification of the organic matter in the soil and afford an explanation why active nitrogenous fertilizers are so uniformly effective. The organic matter in the soils of old grass fields nitrifies slowly also because of lack of tillage and consequent poor aeration. The field of soil bacteriology is still almost untouched and affords some very interesting sources for speculation in the problems of soil fertility under these conditions.

In order to secure as much information as possible about the potassium in these soils both laboratory and field observations, have been made. It has been shown in a preceeding table how the soil behaves toward potassium salts when applied as soluble fertilizer constituents. The amount of water-soluble potassium in many different samples of soil has been determined to show if possible whether there is any definite relation between the total potassium content of the soil and the amount of water-soluble potassium in the same soil. Such a relation cannot be established with any satisfactory assurance because it has not been possible to secure soils which differ only as regards the total amount of potassium.

The total amount of potassium is usually in proportion to the amount of clay in the soil. The amount of clay has considerable effect on the nature of the organic matter. The amount and nature of organic matter apparently affects the solubility of potassium and other mineral constituents; also, some soils carry a large portion of their potassium in the form of minerals. This is particularly true of the sandy soils. The solubility of potassium in mineral form must be different from that in the form of clay. This must be true because of the influence of the clay itself. Also the past treatment of the soil may influence the solubility of potassium depending upon cultivation and whether or not commercial fertilizers have been used.

The solubility of potassium in pure ground feldspar for instance is very different depending on whether the solvent consists of pure water, water carrying calcium hydroxide, or such salts as sodium nitrate, calcium sulphate, etc., and whether the mineral is pure or mixed with clay. These facts are shown by data in the following tables:

TABLE V

Reagent added	Amt. of reagent added in grams	cc water	Amount of K_2O liberated in grms.	Average	Amount of K_2O liberated by action of reagent
O	0	180	.0064	.0067	0
O	0	"	.0069		
O	0	"	.0070		
CaO	1	"	.0122	.0149	.0082
CaO	2	"	.0156		
CaO	2	"	.0168		
$CaSO_4$	1	"	.0076	.0091	.0024
$CaSO_4$	2	"	.0080		
$CaSO_4$	3	"	.0118		
$NaNO_3$	1	"	.0120	.0120	.0053
$NaNO_3$	2	"	.0121		
$(NH_4)_2SO_4$	1	"	.0120	.0126	.0059
$(NH_4)_2SO_4$	2	"	.0132		
Na_2CO_3	1	"	.0096	.0103	.0036
Na_2CO_3	2	"	.0109		
Na_2HPO_4	1	"	.0109	.0107	.0040
Na_2HPO_4	2	"	.0087		

Table V shows the amount of potassium going into solution in a given volume of water upon stirring the feldspar with some of the more common fertilizer constituents. Figures showing the solubility of potassium when feldspar is stirred with clay and calcium oxide follow:

TABLE VI

Bottle	Grams Feldspar	Grams Clay	Grams CaO.	cc water	Soluble K_2O in grams
1	0	25	0.0	180	.0014
2	0	25	2.	180	.0011
3	30	25	1.	180	.0072
4	30	25	2.	180	.0062
5	30	0	0.	180	.0067
6	30	0	0.	180	.0072
7	30	0	1.	180	.0151
8	30	0	2.	180	.0158

The data in Table V and Table VI were obtained by placing the different combinations in a thermostat at room temperature and stirring until there was no further action.

These data show conditions which may be met with in soil studies and why it is difficult to eliminate them when making comparisons. The mineral feldspar has a certain solubility as regards the potassium when the solvent is pure water. The addition of calcium oxide, sodium nitrate and other salts increases the solubility very greatly. The presence of clay decreases this effect. All soils except the sands contain some clay, therefore the solubility of the minerals in the soil is affected by the clay and is different from what would be expected from the pure mineral. At present, it has not been determined whether the clay reduces the effect of the solvent or whether the effect is on the potassium after it is acted upon by the solvent.

The preliminary part of this work was begun by looking into the field conditions to determine if possible whether anything could be found from this point of attack. A series of plots were fertilized with fairly heavy amounts of nitrogen in nitrate of soda, phosphoric acid in acid phosphate, and potassium in the form of sulphate and chloride. These plots have been under observation for the past five years. To date, but little information has been obtained from these plots excepting that the fertilizers disappear very rapidly after they are applied. It is an easy matter to find the nitrate and ammonium salts for sometime after they are applied but for all practical purposes it is safe to say that the potassium and phosphoric acid disappear from soluble forms after the first good rainfall and in an ordinary application they cannot be found by chemical methods now in use. This is in harmony with the results obtained in the experiments which have already been discussed and which show the chemical reaction which takes place between soils and potassium salts. Like the sulfate and chloride the nitrate radical remains soluble until it finally disappears through decomposition or some other destructive process. Because of the chemical change which takes place in the case of potassium fertilizers this plan of attack could not give any very definite observations. Also, the relative amounts of soil and fertilizing elements were so different that no very satisfactory results could be had in this way to determine the effect of the fertilizers on the soil constituents. On this account the effects of different salts were studied under conditions which were subject to closer control.

In order to meet these conditions, solutions of various salts of known strengths, were percolated through columns of soils, the rate of percolation being controlled by means of capillary tubes and the height of the water level in the containing vessel. The flow was adjusted at the rate of about 90 c.c. per 24 hours and maintained at that rate throughout the period of observation. The strength of the solutions was made uniform on the basis of the potassium equivalent. The changes effected in the passage through the soil were determined by studying the percolate. In this way it was possible to determine what had been taken from and what added to the original solution.

Preliminary observations showed that all the chloride, nitrate and sulfate radicals were left in solution; for that reason these radicals were not considered further in this discussion. Excepting phosphates all the solutions were destructive in respect to the soil itself; but, in the process of destruction new bases were substituted for the ones removed.

The results when potassium chloride solution, 0.35 grams per liter, is percolated through 500 gms. of soil are shown in the following table:

TABLE VII

No. of Soil	Grams K_2O removed from first 300 cc.	Grams K_2O removed from third 300 cc.	Grams K_2O removed from fifth 300 cc.	Grams K_2O removed from seventh 300 cc.	Grams K_2O removed from ninth 300 cc.	Grams K_2O removed from eleventh 300 cc.	Grams removed from first 3600 cc. (Approx.)
1	.0152	.0078	.0050	.0030	.0020	.0018	.0609
2	.0193	.0096	.0068	.0064	.0040	.0024	.0861
3	.0205	.0089	.0074	.0061	.0058	.0032	.0928
4	.0250	.0104	.0080	.0078	.0058	.0028	.1057
5	.0280	.0139	.0090	.0080	.0067	.0043	.1305

While lime and small amounts of iron and aluminum became soluble a certain amount of potassium was removed from solution and retained in the soil. The data show that some of the soils remove a large part of the potassium from the first portions of the percolate. As more solution is percolated through the soils smaller quantities of potassium are retained. While these soils contain naturally large amounts of potassium they remove additional amounts from solution. The soils richer in clay and also in potassium retain larger amounts than the lighter soils which are relatively poorer in clay and potassium.

It has been shown in Table VII that when potassium chloride is percolated through columns of soil potassium is removed from solution and retained in the soil. The solubility of the soil potassium is therefore not increased by such a solution. A number of solutions of different salts were percolated through the soils to determine what effect they might have on the solubility of the soil potassium. For these experiments solutions were made of sodium nitrate, sodium chloride, sodium carbonate and acid phosphate. The strength of these solutions was the same as that of the potassium chloride used in Table VII on the basis of the potassium equivalent. The amount of soil was also five hundred grams. In order to determine the effect of calcium carbonate and calcium sulphate these salts were mixed dry with the soil at the rate of 1 gram per 100 grams of soil. Distilled water was percolated through these and the percolate examined for potassium. The results follow:

TABLE VIII

No. of Soil	Parts per million of potassium in first 300 cc. of percolate of distilled water through 500 grams soil	Parts per million of potassium in first 300 cc. of percolate of distilled water through 500 gms. soil plus 1% calcium carbonate	Parts per million of potassium in first 300 cc. of percolate of distilled water through 500 grams. soil plus 1% calcium sulfate
1	75	92	224
2	287	323	442
3	179	68	383
4	58	72	140
5	136	50	172

The data in Table VII as well as other observations made in this laboratory show that calcium oxide and calcium carbonate do not liberate potassium from these soils. Some observations have indicated a decreased solubility. A limited number of observations with calcium sulfate indicate that small amounts of potassium are made soluble. These determinations have been made colorimetrically and the evidence is not as positive as that obtained in the following tables by the gravimetric method.

TABLE IX. SODIUM NITRATE SOLUTION

No. of Soil	Grams K_2O in first 300 cc. of percolate	Grams K_2O in third 300 cc. of percolate	Grams K_2O in fifth 300 cc. of percolate	Grams K_2O in seventh 300 cc. of percolate	Grams K_2O in ninth 300 cc. of percolate	Grams K_2O in eleventh 300 cc. of percolate	Grams K_2O in first 3600 cc. of percolate (Approx.)
1	.0029	.0036	.0015	.0007	.0005	.0003	.0190
2	.0027	.0036	.0013	.0006	.0007	.0002	.0182
3	.0032	.0023	.0020	.0011	.0006	.0004	.0192
4	.0039	.0037	.0025	.0016	.0014	.0007	.0276
5	.0051	.0046	.0024	.0018	.0012	.0006	.0314

TABLE X. SODIUM CHLORIDE SOLUTION

No. of Soil	Grams K_2O in first 300 cc. of percolate	Grams K_2O in third 300 cc. of percolate	Grams K_2O in fifth 300 cc. of percolate	Grams K_2O in seventh 300 cc. of percolate	Grams K_2O in ninth 300 cc. of percolate	Grams K_2O in eleventh 300 cc. percolate	Grams K_2O in first 3600 cc. of percolate (Approx.)
1	.0021	.0017	.0010	.0004	.0005	.0003	.0120
2	.0017	.0022	.0010	.0005	.0003	.0004	.0122
3	.0024	.0024	.0009	.0008	.0002	.0004	.0142
4	.0025	.0026	.0018	.0006	.0008	.0006	.0178
5	.0042	.0037	.0015	.0017	.0008	.0010	.0258

TABLE XI. SODIUM CARBONATE SOLUTION

No. of Soil	Grams K_2O in first 300 cc. of percolate	Grams K_2O in third 300 cc. of percolate	Grams K_2O in fifth 300 cc. of percolate	Grams K_2O in seventh 300 cc. of percolate	Grams K_2O in ninth 300 cc. of percolate	Grams K_2O in eleventh 300 cc. of percolate	Grams K_2O in first 3600 cc. of percolate (Approx.)
1	.0019	.0015	.0011	.0005	.0004	.0003	.0114
2	.0021	.0013	.0008	.0009	.0003	.0004	.0116
3	.0025	.0020	.0010	.0010	.0004	.0004	.0146
4	.0022	.0019	.0014	.0007	.0005	.0007	.0148
5	.0025	.0024	.0022	.0018v	.0008	.0006	.0206

TABLE XII. ACID PHOSPHATE SOLUTION

No. of Soil	Grams K_2O in first 300 cc. of percolate	Grams K_2O in third 300 cc. of percolate	Grams K_2O in fifth 300 cc. of percolate	Grams K_2O in seventh 300 cc. of percolate	Grams K_2O in ninth 300 cc. of percolate	Grams K_2O in eleventh 300 cc. of percolate	Grams K_2O in first 3600 cc. of percolate (Approx.)
1	.0020	.0026	.0017	.0002	.0004	.0003	.0144
2	.0014	.0026	.0019	.0003	.0008	.0005	.0150
3	.0025	.0027	.0021	.0005	.0006	.0004	.0176
4	.0024	.0041	.0015	.0003	.0010	.0007	.0200
5	.0043	.0042	.0018	.0005	.0010	.0009	.0254

Tables IX, X, XI and XII show that dilute solutions of sodium nitrate, sodium chloride, sodium carbonate and acid phosphate in contact with these soils liberate potassium in considerable amounts. The data in Table XII was secured to determine the effect of commercial acid phosphate in liberating potassium. A sample was found which contained no potassium and the soluble phosphate extracted with water. The free acid was neutralized with lime, the solution filtered and standardized.

As already stated these observations could not be obtained from field work because of the relatively small amounts of fertilizers generally used. There is, however, no reason to believe that these same reactions do not take place under field conditions. The solutions used in these experiments while dilute are much more concentrated than soil solutions excepting under special conditions. Nitrate of soda and acid phosphate solutions are very active in their effect on potassium. This has a very practical bearing in relation to crops grown in connection with nitrate and acid phosphate fertilizers.

In the field observations have been made to determine the relation between potassium fertilizers and the yield of the crop. Potassium salts have been used alone and also in connection with nitrogenous and phosphate constituents. For this work soils of uniform character have been selected and plots laid out and treated in various ways to show the specific effect of the potassium salts. The plots have been placed on different types of soil to afford an opportunity to show how different soils respond to the same treatment. The fertilizers have consisted of nitrate of soda, acid phosphate, potassium sulphate and potassium chloride and have been applied singly and in combinations as a top dressing on grass fields. One or more check plots have received no fertilizers. This provided a means for observing the value of potassium under all ordinary conditions. In general the effect of a combination of fertilizers has not been additive. To show the results on different types of soils the yields on a number of series follow. The results show average yields for a period of two or more years on the same field: The following five tables show the influence of the various fertilizing constituents when applied as a top dressing under ordinary field conditions to soils representing the five types already discussed. Whenever used the fertilizers were applied at the rate of 120 lbs. K_2O, 40 lbs. N, and 50 lbs. P_2O_5 per acre.

The plots to which these fertilizers were applied had received no fertilizers for more than a year and were covered with a good timothy sod from which, in most cases, at least one crop of grass had been removed.

TABLE XIII. YIELD ON A SANDY SOIL

Check	Muriate of Potash	Nitrate of Soda and Acid Phosphate	Nitrate of Soda and Muriate of Potash	Muriate of Potash and Acid Phosphate	Nitrate of Soda, Acid Phosphate and Muriate of Potash
1.155	1.155	1.575	1.330	1.120	2.170

TABLE XIV. YIELD ON A LIGHT SANDY LOAM

.945	.875	1.715	1.890	1.085	2.625

TABLE XV. YIELD ON A LIGHT CLAY LOAM

.931	.805	2.660	2.415	.945	2.975

TABLE XVI. YIELD ON A HEAVY CLAY LOAM

1.505	1.330	2.537	3.110	1.910	2.905

TABLE XVII. YIELD ON A HEAVY BOULDER CLAY

1.702	1.616	2.079	2.089	1.819	.2140

In general the yields from the different plots on the various types of soils were uniform in a number of respects. There is considerable variation in the yields which come from the plots on the different types of soils but these may be due more to seasonal differences than to productiveness of the soil itself or influence of the fertilizers.

The effect of muriate of potash when used alone or in connection with acid phosphate produced no increased yield of hay. A considerable increase in yield was produced when muriate of potash was used with nitrate of soda. This increase, however, is due to the effect of the nitrate of soda. Some increase in production is obtained when muriate of potash is used in connection with nitrate of soda and acid phosphate. This increase is greatest on the lighter soils. On heavier soils the potassium has very little effect under any conditions.

The following data show the average yield obtained by the use of chloride and sulphate of potassium on a series of plots over a period of five years.

TABLE XVIII. COMPARATIVE YIELDS FOR THE CHLORIDE AND SULPHATE OF POTASSIUM

Check	Sulphate of Potassium	Chloride of Potassium
1.565	1.595	1.485

Potassium was applied at the rate of 90 lbs. K_2O per acre. The check plot as shown in Table XVIII has produced more hay than the plot fertilized with potassium chloride. The difference is small but is not an unusual observation. The sulphate of potassium has produced practically no increased yield during this period.

A large number of analyses have been made to determine whether the yield affects the composition of the crop. Crops producing both small and large yields were studied to determine whether the amount of potassium removed was directly proportional to the weight of the crop. With the almost unlimited and inexhaustible amount of potassium existing in the soil this becomes a very important consideration. Samples of hay have been analyzed from the plots already discussed located on the different types of soils and the amount of K_2O removed per acre calculated. These data follow:

TABLE XIX

No.	Yield per acre	Per cent. K_2O	Lbs. K_2O
1	945	1.80	17
2	1875	1.77	32
3	2344	1.67	39
4	2818	1.87	52
5	3088	1.54	48
6	3268	1.85	60
7	3616	1.61	58
8	4504	1.51	68
9	5174	1.86	96
10	5412	1.73	94
11	6010	1.62	97
12	6374	1.81	115

It is evident from Table XIX that the percentage of potassium is practically the same for all samples of hay from the unfertilized plots regardless of the yield. While slight variations were found the general tendency has been for the potassium to vary directly with the amount of hay. These results are shown graphically in Fig. 1.

In the figure the amount of potassium is shown along the line AB and the yield of hay along the line AC. The line AD represents the relation between the yield of hay and quantity of K_2O contained. The range represented in this figure is wide and in the case of the heavier crops the yield is near a maximum. The analysis of samples of hay grown on plots which have received potassium fertilizers does not show that they contain a higher per cent. of potassium than hay grown on unfertilized plots. In cases where the yield has been increased by the addition of nitrate of soda and acid phosphate the composition is again fairly constant showing that the soils must have supplied relative amounts of potassium.

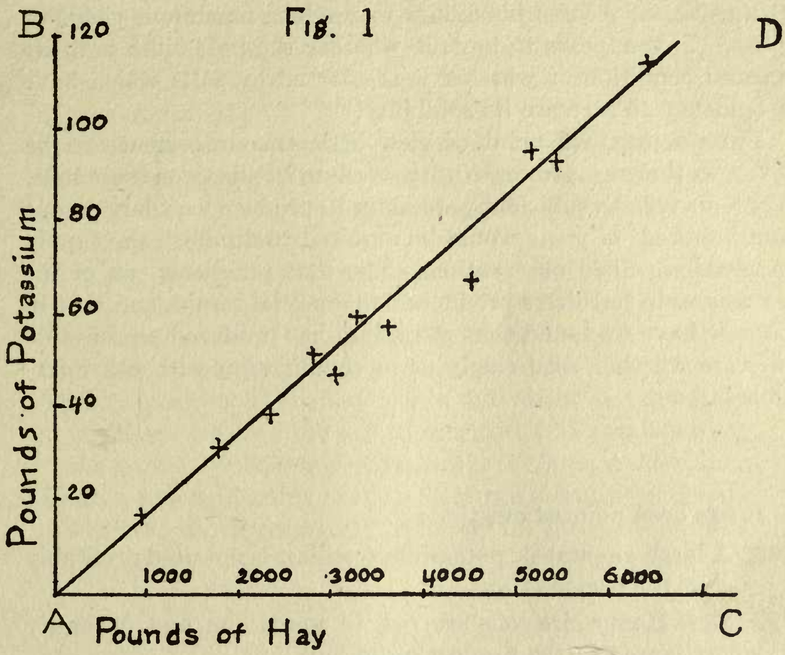


Figure 1

In the light of the information received from the percolation experiments and from the observations made in field work it appears to be logical for the yield of the nitrate of soda plots to be equal to those which have been treated with nitrate of soda in connection with potassium salts. From the percolation experiments it is evident that where nitrate of soda is used, the results are produced by the action of the nitrate of soda itself and also by the action of the nitrate of soda on the potassium in the soil. The effects of nitrate of soda, as observed should therefore be much the same as would be obtained by the use of both nitrate of soda and potassium salts. In this connection the percolation experiments indicate that common salt might in some ways replace potassium salts in fertilizers for some soils. The same might be said of acid phosphate.

Field observations show that a large number of our soils contain sufficient soluble potassium to produce maximum yields of grass. This appears to be true whether the potassium is in its natural condition or whether it is affected by salts which have a tendency to increase its solubility.

From a practical point of view little encouragement can be given to the grass grower to use potassium fertilizers on these soils. The soils furnish sufficient potassium to produce very large crops and hundreds of years would be required to diminish the supply materially. Field observations show that practically all of the potassium in fertilizers produces no beneficial results and that in no case have we found that potassium has produced a profitable increase whether used singly or in combination with other fertilizers.

SUMMARY

It has been pointed out that:

1. A large amount of potassium fertilizer is not used profitably at the present time.
2. New Hampshire soils are rich in potassium and naturally adapted to the production of hay.
3. The soil potassium is present in clay and in mineral form.
4. The soils remove large quantities of potassium from solution under both laboratory and field conditions.
5. When potassium phosphate reacts with the soils no new soluble salts appear in solution.
6. When other potassium salts react with the soil new bases do appear in solution.
7. Excepting phosphoric, the solubility of the common acid radicals is not affected by the action of the soil.
8. The effect of such salts as sodium chloride, sodium nitrate, sodium carbonate and acid phosphate is to greatly increase the solubility of the soil potassium.
9. The reaction between these salts and the soil is chemical.

10. Calcium carbonate, calcium sulphate and calcium oxide have practically no effect on the solubility of soil potassium.
11. The feldspar minerals have a definite solubility in water. This solubility is affected by lime and the common salts found in fertilizers. The effect of these is modified by the presence of clay.
12. Field observations show that potassium fertilizers do not produce increased yields of grass, particularly on clay soils. In some combinations they are more effective on the sandy soils, but not profitably so.
13. In many cases nitrate of soda alone produces yields as good as are obtained with a combination of nitrate of soda and potassium salts. This may be due to the effect of the nitrate of soda on the soil potassium.
14. The composition of the hay shows that when no potassium fertilizers are used the soil affords plenty of potassium for the growth of the crop. This is true for large yields.
15. From a practical point of view little profit can be expected from the use of potassium fertilizers for the production of hay.

COMPARISON OF ROCK GRINDING WITH BALLS AND CYLINDERS

By R. O. E. Davis

Bureau of Soils, Washington, D. C.

The use in grinding mills of cylindrical iron pieces instead of balls was found in certain industries and explained on the basis of efficiency. The fact that the cylinders were small and of soft iron made the proposition doubtful. An explanation given was that in grinding phosphate rock, for instance, the balls became coated with the ground rock and the mill had to be stopped while the balls were cleaned by hand, but that this coating did not form on the cylindrical pieces.

In performing some experiments in the laboratory, an ordinary stoneware laboratory mill was used and grinding performed by cylinders of wrought iron and steel, balls of steel one inch in diameter and half an inch in diameter. In the first experiments the same total grinding surface of balls and cylinders was used. The cylinders were approximately $\frac{5}{8}$ x $\frac{3}{8}''$, and the balls one inch. In grinding feldspar after five hours, the percentage passing 130 mesh sieve was 45.5 for the balls, 17.3 for the steel cylinders and 5.8 for the wrought iron cylinders. The amounts adhering to the surface were less than 0.05% for the balls, 0.3% for steel cylinders and 3.4% for the wrought iron. Other experiments were made using the same weights of balls and cylinders. A typical result gave adhering to the surface for the balls 0.1%, for the steel cylinders 0.26% and for the wrought iron 2.6%. Passing 130 mesh sieve, with balls 48%, steel cylinders 35.2%, wrought cylinders, 33.6%.

Experiments performed using phosphate rock (hard Tennessee) gave similar results to those with feldspar, but the amounts of material adhering to the surface of the balls and the cylinders were increased. Amounts on the surface were with balls 2.4%, with steel cylinders 3.0%, with wrought iron 3.0%. On screening

63.2% of that ground by balls passed 130 mesh, 38.4% by steel cylinders and 24% by wrought iron. In the last experiments balls one inch, and one-half inch in diameter were used, and the wrought iron cylinders. With phosphate rock the small balls had 0.8% adhering to the surface, the large 1.2%, and the cylinders 3.4%. Amounts passing 130 mesh sieve were for the small balls 61.6%, for large balls 87.2% and for wrought iron cylinders 45.6%.

The results show that the grinding is best done by the large steel balls. No reason for the use of wrought iron cylinders exists, as the largest amount of material adheres to their surface, the grinding is not so rapid and from the nature of the material, their wear is greatest.

(*Abstract*)

THE MOVEMENT OF SOIL MOISTURE

By R. O. E. Davis

U. S. Dept. Agriculture, Washington, D. C.

Moisture on the soil is the controlling factor in plant growth and its movement in the soil is of great importance. Capillary and hygroscopic forces are the same, the difference in action depending on the thickness of the film. The chief movement is produced by gravity and molecular forces. When the soil interspaces are filled, gravity causes a downward movement; as water evaporates from the surface, molecular forces produce an upward and to some extent a lateral movement. Changes in moisture relations within the soil produced by changes in temperature, humidity, and pressure are generally of minor importance.

SPONGE SPICULES IN CERTAIN SOILS

R. O. E. Davis

Bureau of Soils, U. S. Dept. of Agric., Washington, D. C.

Recently the Department of Agriculture has received a number of inquiries concerning the peculiar effect produced by certain soils in Georgia and Florida. The cause of complaint is that in working the soils of certain areas during dry weather, the workmen suffer with terrible itching of the feet, and the feet of horses or mules used in plowing become sore and inflamed. The land on which the trouble occurs is in all cases some that has been drained. In a moist condition the effects are not so bad, although still noticeable.

One of the places in Georgia where the trouble has long been noticed is an old cypress pond of 8 to 10 acres. This has been drained 30 years. The soil is fertile and from 1 to 8 feet deep. The soil can be cultivated only when wet. Shoes are ruined in a day and mules' feet are made raw in the same length of time. Most land in the neighborhood is affected in the same way, and this fact deters people from undertaking work in drainage.

Various suggestions as to the cause of this peculiar action of the soil, such as the presence of hook-worms, pollen, alkali and sulphuric acid proved improbable. Chemical examination failed to reveal any peculiar conditions. The soil was then examined to determine, if possible, whether the phenomenon was physical. The suggestion that the drying effect produced on the skin by an intimate mixture of finely divided organic matter and mineral clay particles caused the burning sensation, was not entirely satisfactory.

The microscopic examination[1] revealed what is believed to be the cause of the trouble described. There were present in the soil immense numbers of sharply pointed crescent-shaped bodies

---

[1] Mr. W. J. McCaughey made the microscopic examination which located the trouble.

of silicious material. These have been identified[1] as the silicious residues (spicules) of fresh water sponges. They are somewhat crescent-shaped, about 0.2 mm. long and 0.02 mm. in diameter, and are readily distinguished from the silicious residues of certain elongated diatoms by the lack of elaborate sculpturing generally present in the latter. These are the remains of fresh water sponges and may vary in size and shape. The most common in the Georgia soil is the Mayenia Millsii, which is crescent-shaped with tiny spines projecting from the body of the spicules. The presence of large quantities of these spicules in soils is believed to have caused the irritation described.

Edward Potts[2] described the Mayenia Millsii as found in Sherwood Lake, near De Land, Florida. All forms of fresh water sponges as yet discovered are silicious. The skeleton or framework (corresponding to the elastic fiber of which commercial sponges are composed) upon which slime-like sponge flesh, known as "sarcode," is supported, is composed of silicious spicules, slightly bound together by an almost invisible quantity of firm sarcode, or perhaps of colloidal silica. In the different species these skeleton spicules vary in size, in the shape of their termination and in their more or less spinous character.

The soils of the region referred to carry as high as 25 per cent. of these spicules. Of course, their presence in such quantities is unusual and presents a problem to the soil technologist. Importance attaches to its solution because any land that has remained as a swamp for a long time may become infested with these spicules. Their presence has been frequently noted in regular mineralogical examinations of soils and are quite widely distributed.

Examination made of nearly 200 samples of soil selected from different parts of the United States from the residues of lakes and swamp bottoms, revealed the presence of spicules in nearly all, but generally in small amounts. Those in soils from other localities than Georgia varied somewhat in character. The muck soils of Florida showed them in largest quantity with exception

---

[1] The identification was made by Dr. Albert Mann, Bureau of Plant Industry, who also kindly examined several samples of soil.

[2] Synopsis of forms of fresh water sponges. Philadelphia Acad. of Nat. Sci., **39**, 225 (1887).

of Georgia locality mentioned, but the spines were missing from those also. In none of the forty soils collected from cypress swamps and bayous of Louisiana and the Gulf States were the spicules found in any quantity.

Samples of soil taken from the soil in Georgia at different depths showed that the quantity was largest near the surface and below ten inches was negligible.

The treatment of soils thus affected must be regarded as a physical problem as the spicules are silicious in character and no hope could be entertained of their removal by chemical means. The presence of the spicules in the soil up to 4 or 5 per cent. does not produce any noticeably bad results, but with larger amounts the difficulties ensue. The microscopic spicules are like finely divided glass and cut into the flesh of both man and beast; upon the amount depends the severity of the result. It has been observed in the infested district when sand has washed down on the soil, the unpleasant results are not encountered.

It appears then that the best way to treat the difficulty is to mix other soil with the infested portion. The most convenient and practical way to do this is by deep plowing or by subsoiling; and since in the worst infested areas the spicules are confined to the first 6 inches of soil, it is also a comparatively easy method.

It is likely that no land submerged in fresh water can exist for a very long time without a growth of fresh water sponges, and the consequent deposition of the sponge spicules. It is their presence in large quantities that presents a subject of interest. The suggestion is offered that in areas where drainage is contemplated, the lake or swamp bottoms be examined microscopically for these remains. If present to any degree, the depth of the deposit and the possibility of admixing extraneous material to ameliorate the condition should be determined. It appears that subsoiling would in most cases answer the purpose.

THE DISTRIBUTION OF SILT AND CLAY PARTICLES IN SOILS[1]

R. O. E. Davis and C. C. Fletcher

Bureau of Soils, U. S. Dept. of Agric., Washington, D. C.

The natural soil contains mineral particles of various sizes. In the classification adopted by the Bureau of Soils, the sizes range from 2 mm. in diameter to particles not distinguishable under a powerful microscope. The different proportion of the various sized material present in the soil gives rise to a difference in classification, associated with which are certain physical characteristics of the soil. The smaller particles are probably the most important constituent from the standpoint of agricultural usefulness. It is of interest, then, to understand the agencies producing changes in the distribution of these smallest particles in the various soils.

With this object in mind the results of analyses made by the Bureau of over 20,000 samples of soil from every portion of the United States has been tabulated. The soils of the United States are divided into thirteen provinces,[2] the distinction between them being based on the material from which the soils are derived and upon the different agencies which led to the formation of the soil. The two great divisions of the country are the humid and the arid and semi-arid regions. There are seven provinces in the humid and six in the arid and semi-arid regions. A brief outline of the provinces is as described below.

In the humid region the Coastal Plains extend from the New England States southward to Florida Peninsula and then westward to the Mexican boundary. The River Flood plains are usually known as bottom lands, found in the flood plains of various rivers. The largest areas occur along the Mississippi River.

---

[1] Published by permission of the Secretary of Agriculture.

[2] Soils of the United States. Milton Whitney. Bul. 55, Bu. Soils, U. S. Dept. Agr. (1909).

The Piedmont Plateau lies between the Appalachian Mountains and the Atlantic Coastal Plain, extending from the Hudson River to East-central Alabama. The Appalachian Mountains and Plateau is the area occupied by the mountain ranges extending from New York to Alabama and by the plateau to the west of the mountain. The Limestone uplands are mainly in central Tennessee and Kentucky, northern Alabama and Georgia and in Missouri. The valley soils are found principally in Pennsylvania, Maryland, and Virginia and in the mountain section of Eastern Tennessee and Kentucky and Northern Alabama and Georgia. The Glacial and Loessial touches the coast about New York City, passes through Northern New Jersey, Southern New York, Northern Pennsylvania, through Ohio to Cincinnati, across to St. Louis, follows the south side of the Missouri River into Montana and courses the Canadian boundary. Then it dips into Idaho and crosses northwestern part of Washington. The Glacial Lake province lies in the region once covered by glacials and are the beds of lakes and streams left at the close of the glacial epoch.

The arid and semi-arid regions occupy the western part of the country. The Western Prairie extends from the Missouri River southward through Texas to the Rio Grande and merges into the Plateau region on the west. The Gulf Coastal Plain is its eastern boundary. The Great Basin lies principally in Nevada, but extends into Wyoming, Utah and other adjacent states. The Northwestern Intermountain Province occurs on mountain foot slopes, lower foothills, etc., and consists of colluvial mountain waste mixed with stream delta-cone deposits. Rocky Mountain Valleys and Plains describes its location by its name. The Arid Southwest lies partly in Arizona, California and the extreme southern part of Nevada. The Pacific Coast Province includes a strip bordering the Pacific Ocean and foothills and valleys of interior mountain ranges.

A summary of the analyses is given in Table I. The figures show the per cent. of types in a given province with subsoil containing a larger amount of silt and clay than the soil, and also the per cent. of types with greater amount of clay alone in the subsoil. Each of the types includes a number of samples, in some cases running into the hundreds. The analyses for each type were averaged and then the per cent. of the type with heavier subsoils on the basis mentioned, was determined.

Of the coastal soils examined 85 per cent. of the types had more silt and clay in the subsoil than in the soil, and 91 per cent. more clay alone in the subsoil. The soils of this region have been washed from the Piedmont Plateau and have been submerged several times below sea level. Wave action and running water have had a distributing effect upon the soil material. The action of water has caused a collection of the fine particles in the subsoil. The Appalachian Province shows a very large per cent. with heavier subsoils; in the Piedmont Plateau, where erosion effects are not so great, the per cent. with heavier subsoils is somewhat smaller. The Limestone and River Flood Plains, show heavier subsoils. The Western Prairies also show heavier subsoils, due first probably to the fact that these are residual soils and the finer particles have been removed from the surface soil.

Those provinces having most of their soils heavier than the subsoils, or very close to an even distribution of the smaller particles between the soil and subsoil, are provinces of the arid and semi-arid regions and are not subjected to humid conditions or to any large amount of water erosion.

Without going into a detailed discussion of the results, it seems that water is the main agency in causing a difference in distribution of the finer soil particles between soils and subsoils. The slight rainfall of the arid and semi-arid regions is not sufficient to cause the finer particles to be carried into the subsoil or to be carried off by erosion. Wind erosion is greater in the arid regions, and, of course, it is the finer soil material that is transported. That the surface soil does not show a lowering in content of the smaller particles is probably due to the variable direction of the wind. While large quantities of material are transported, there is more or less an exchange of position. The sudden changes in temperature in arid regions may cause a splitting up of the particles in the surface soil, and as these changes are not marked at greater depths, the collection of finer particles in the surface soils is accentuated. The absence of water in the soil permits of this condition, and also causes a difference in bacterial action.

The fact that in general soils of the humid regions have larger amounts of clay and silt particles in the subsoils than in the soils and that those of arid and semi-arid regions have nearly an equal distribution of these particles between the soils and subsoils, or slightly more in the soils, is explained by the difference in climatic conditions and by the movement of the finer material under the influence of water in the humid region.

TABLE I. Distribution of Silt and Clay in Soil and Subsoils According to Soil Provinces

Provinces	Number of types	Per cent. of types with subsoil heavier than soil, considering silt and clay	Per cent. of types with subsoil heavier than soil, considering clay alone
Coastal Plain	124	85	91
Glacial and Loessial	60	40	70
Limestone	34	81	97
Glacial Lake	85	41	54
River Flood Plains	115	62	81
Appalachian	53	81	96
Piedmont	31	77	87
Great Basin	23	52	43
N. W. Intermountain Region	22	36	59
Rocky Mountain Valley and Plains	40	57	57
Arid South West	13	46	53
Pacific Coast Soil	146	47	53
Western Prairie Region	29	72	89

THE FERTILIZING EFFECT OF PALMAERPHOSPHATE ON PEAT SOILS

By Hjalmar von Feilitzen, Ph.D.

Director of the Experiment Station of the Swedish Peat Society

Jönköping, Sweden

Many attempts have been made to obtain available phosphoric acid fertilizers from phosphates, which contain too little phosphoric acid, and are too impure, to use for the production of superphosphate.

In the north of Sweden the vast amounts of iron-ores at Gellivara and Kiruna contain a fair percentage of apatite, remaining behind after the magnetic separation of the ores; and if it were possible, in an economical way, to convert that impure apatite into a soluble phosphoric acid fertilizer, it would be of great importance for Swedish agriculture, as at present we have to import from other countries all raw phosphates employed for the production of superphosphate, and also about three-fourths of the yearly consumption of basic slag.

About twenty years ago the late Professor *J. P. Wiborgh* of the Polytechnic Institute in Stockholm invented a process for converting the triphosphate of lime into an available form by heating apatitepowder with carbonate of soda to a temperature of 900-1000 centigrade. The product, which is called Wiborghsphosphate, contained 21-27% citrate-soluble phosphoric acid, and its fertilizing effect was, according to experiments, made on different soils and with different plants at the Experiment Station of the royal Swedish Academy of Agriculture at Stockholm by Professor *L. F. Nilsson* and at our station in Jonkoping, shown to be equal to that of the soluble phosphoric acid in superphosphate and basic slag.

A large factory for the production of Wiborghsphosphate was erected at Lulea and ran for some years (1899-1905), but unfortunately the prime costs were too high, and the fertilizer could not therefore compete with the older ones.

Professor *W. Palmaer* at the same Stockholm Institute, then tried to solve the problem in another way, and in the first years of the twentieth century he invented an electrolytic process for producing bicalcic phosphate from the same raw material.

In the section X A for Electrochemistry of this congress Professor *Palmaer* has read a paper on this process, and it is therefore not necessary for me to give you the details of the invention. A solution of sodium chlorate or perchlorate is electrolyzed, and the acid anode solution then allowed to act on the raw phosphate, which it dissolves. In this solution a part of the alkaline cathode solution is introduced, when bicalcic phosphate is precipitated as a fine crystalline powder. To the filtrate from it, the remainder of the cathode solution is added, precipitating the greater part of the lime in the solution as hydrate (the rest is precipitated by the introduction of carbonic acid as carbonate). The original electrolyte is regenerated by the process and again enters into the electrolyzing apparatus.

With the phosphoric acid fertilizer thus obtained, which is called Palmaerphosphate from its inventor, and contains most of its phosphoric acid as dicalcium phosphate with a percentage of 36-38% phosphoric acid, of which 95 per cent. is soluble in ammonium citrate solution, many fertilizing experiments have been made in Sweden during the last few years both at the chemical division of the Central Agricultural Experiment Station at Stockholm (pot cultures) in sandy soils, by Professor *H. G. Soderbaum,* and at the Experiment Station of the Swedish Peat Society in Jönköping in peat soils.

As it may be of some interest for the members of this section, I will, with regard to the paper of Professor *Palmaer,* give you a brief account of the results, obtained at the Jönköping station.

I have already published papers on the results of the years 1908 to 1910 in the German Journal,[1] but as we now have results showing the residuary effect from the year 1911 and have completed the experiments with the new phosphate, I will herewith give you a few notes about it.

---

[1] Journal für Landwirtschaft 1910, page 33 and 1911, page 371.

The experiments were carried out both in our experimental garden in bottomless wooden boxes, having a surface of 0.36 square meter and a depth of 60 centimeters, filled with a peat soil very poor in phosphoric acid and potash, but rich in nitrogen, and with a sufficient amount of lime, and also as field experiments on a peat bog, directly cultivated for that purpose.

The phosphate was compared with superphosphate and basic slag in two different quantities, 50 and 100 kg. P_2O_5 per hectare, and was tested for different plants such as potatoes and peas in the year 1908, blue lupins, potatoes, cabbage and oats in 1909, potatoes and lupins in 1910 and oats and ryegrass in 1911.

In each case the same amount of ammonium citrate-soluble phosphoric acid was given in the form of bicalcic or Palmaer-phosphate, citric-acid soluble P_2O_5 in basic slag, and water-and citrate-soluble P_2O_5 in superphosphate.

The effect of the direct fertilizing with the Palmaerphosphate in the years 1908 and 1909 was with all plants practically the same as that of the two other phosphates, as is shown by the following figures, when the increase in yield is taken as per cent. of those of the superphosphate.

	50 Kg. P_2O_5 on 1 hectar in			100 Kg. P_2O_5 on 1 hectar in		
	Super-phosphate	Basic Slag	Palmaer-phosphate	Super-phosphate	Basic Slag	Palmaer-phosphate
1908						
Potatoes	100	174	100	100	88	83
Peas	100	102	141			
1909						
Blue lupins	100	95	127	100	66	91
Potatoes	100	101	100	100	96	93
Cabbage	100	98	118	100	111	104
Oats	100		96			

In two series the residuary effect of the fertilizing was tried for two years (1910 and 1911) with the following results:

Increase in yield from the phosphoric acid fertilizing, given in the year 1909.

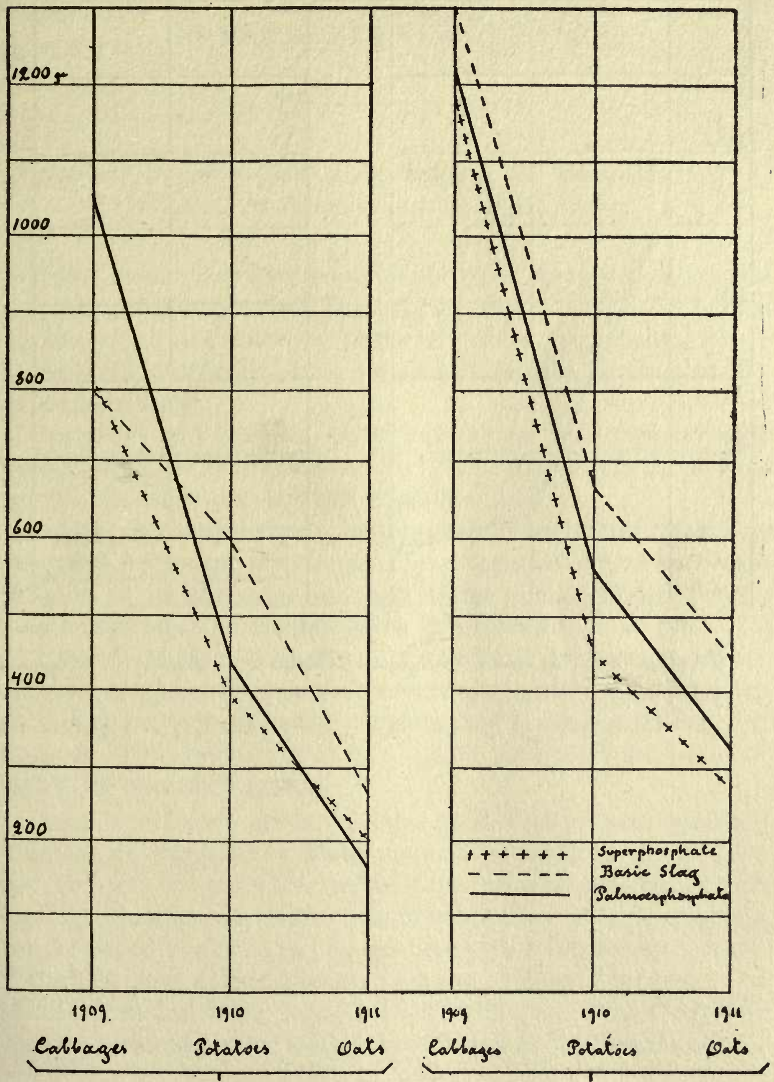
	Serie A.					Serie B.				
	1909 Cabbage gram	1910 Potatoes gram	1911 Oats gram	Total increase gram	Relative value	1909 Potatoes gram	1910 Lupins gram	1911 Rye-grass gram	Total increase gram	Relative value
50 kg. P_2O_5 on 1 hektar in Superphosphate	808	390	200	1398	**100**	526	113	71	710	**100**
Basic slag	795	597	258	1650	**118**	532	153	118	803	**113**
Palmaerphosphate	953	433	162	1548	**111**	527	115	66	708	**100**
100 *kg.* P_2O_5 *on* 1 *hectar in* Superphosphate	1177	445	273	1895	**100**	730	159	145	1043	**100**
Basic slag	1302	667	443	2412	**127**	703	171	181	1055	**102**
Palmaerphosphate	1218	557	322	2095	**111**	681	197	161	1039	**100**

The following diagrams illustrate the direct and residuary fertilizing effect of the three phosphates, and confirm the results, obtained by Professor *Soderbaum* on sandy soils, that the electrolytic precipitated bicalcic phosphate from the *Palmaer* process has at least the same direct and residuary fertilizer value as super-phosphate.

Basic slag has in the above experiments on peat soil proved to possess a slightly better residuary effect than the two other phosphates.

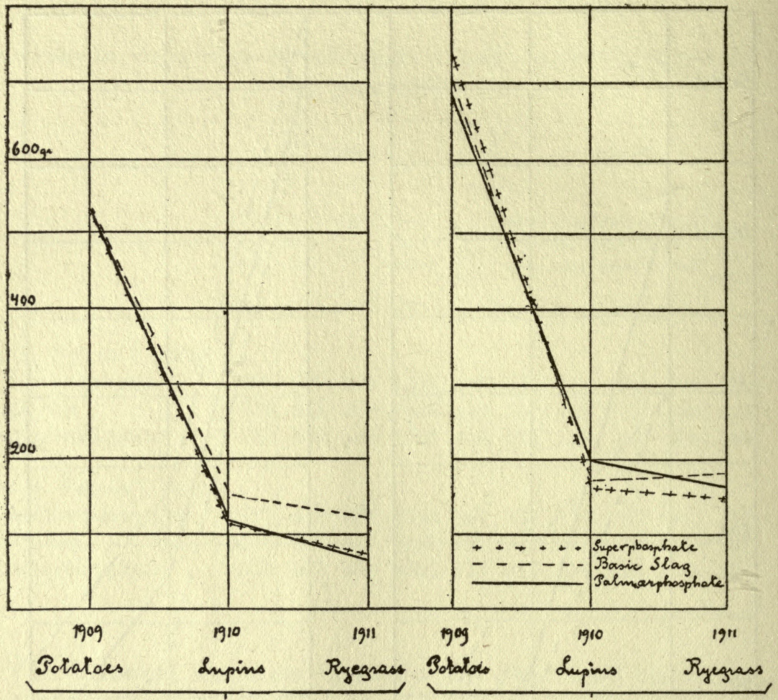
At the Trollhatta-falls in Sweden, an experimental plant was erected last year in order to obtain greater practical experience on the technical and economical details of this process, and the results thus obtained are so favorable, that it is to be hoped, that the apatite of the above mentioned iron-ores will in this way be rendered available for Swedish agriculture.

Series I



50 kilo P_2O_5 on 1 Hectare 1909 100 kilo P_2O_5 on 1 Hectare, 1909

Series II



50 kilo P_2O_5 on 1 Hectare 1909

100 kilo P_2O_5 on 1 Hectare 1909

COMPOSITION ET EXIGENCES DES BULBES FLEURS EN ÉLÉMENTS FERTILISANTS

PAR M. M. LOUIS FONDARD

Professeur Départemental d'Agriculture des Basses-Alpe et F. Gauthié, Ingénieur chimiste, Digne, France

Nous avons précédemment établi,[1] la composition, et les exigences, en éléments fertilisants, d'un certain nombre de plantes florales, dont la culture est particulièrement importante, sur le littoral méditerranéen, dans les départementes du Var et des Alpes Maritimes.

Ces travaux d'analyses, nous ont permis de constater que, pour ces plantes, exploitées en vue de la production de la fleur coupée, les exigences sont très considérables.

Parmi elles, un certain nombre sont bulbeuses: Narcisse, Jacinthe, Anémone, Renoncule. La détermination de leur composition et de leur poids fut faite sur la plante entière, fleurie, au moment où la hampe florale va être récoltée.

Après la récolte de la fleur, et, après ce forçage les bulbes étant en général portés au compost, ou au fumier, il y a donc lieu de déterminer les éléments exportés par la plante entière. Il faut, en effet, prévoir pour le sol, une restitution des ces éléments, en quantités égales.

Dans la présente étude, et bien qu'il s'agisse pour quelques plantes, de végétaux utilisés pour la production de la fleur coupée notre but a été trés différent, car nous n'avons eu, en vue, que la production des bulbes secs destinés à la vente et qui ne sont pas forcés, en vue de la récolte des fleurs, au cours de leur culture.

Parfois, pour quelques-unes, Jacinthe et Narcisse, surtout, on récolte bien les fleurs, mais cette récolte peut être considérée comme accidentelle ou secondaire; l'horticulteur cherche à pro-

---

[1] Composition et exigences des Plantes Florales en éléments fertilisants, par L. Fondard et F. Gauthié.

duire des bulbes aussi gros que possible. Il n'a donc pas intérêt à les épuiser, par une abondante floraison.

Pour les petits bulbes, et pour beaucoup d'espèces, on ne récolte même pas les fleurs, qui se déssèchent, se dècomposent et s'incorporent au sol, de même que les feuilles.

Dans la culture nettement spécialisée des Bulbes-fleurs, on n'exporte donc, d'une façon générale que les bulbes mûrs, dont l'arrachage se fait quand les feuilles se sont déssèchées, et la plante revenue au complet repos de végétation.

C'est à cette culture spéciale, pour la production des bulbes destinés au commerce que se rapportent nos analyses et nos déterminations.

Pour plus de précision, nous allons donner la composition des bulbes, par rapport à la matière sèche à 100, puis par rapport à la matière verte.

Composition (Pour 100) de la Matière Sèche.

Désignation des Bulbes	Cendres	Azote	Acide Phosphorique	Potasse	Chaux
Jacinthe	9,04	2,998	1.680	2,664	1,717
Glaïeul	5,66	1,691	1.120	1.296	1.153
Narcisse	3,42	1,222	0,640	0,480	0,691
Anémone	6,36	1,792	0,880	0,840	1.140
Renoncule	5,98	3,165	1.000	0,816	0,717
Tulipe	2,98	0,771	0,580	0,768	traces
Freesia	3,76	3,048	1,400	1,392	0,384
Cyclamen	8,04	1,691	0,920	1,344	1,306
Amaryllis	5,08	0,720	1,320	1,104	1,153
Lilium	8,06	2,700	1,080	3,024	traces
Jonquille	3,82	2,376	0,560	1,248	0,565

Malgré quelques chiffres voisins, il est assez difficile de faire un rapprochement sérieux, au point de vue de la composition de la matière sèche, entre les différents bulbes. Même entre des bulbes de la même famille botanique, on trouve des différences considérables.

Examinons maintenant, la composition des bulbes à l'état frais, tels qu'ils sont au moment de la plantation, au mois d'Août.

Composition (Pour 1000, des Bulbes Frais)
1000 kilogs de bulbes frais renferment:

Désignation des Bulbes	Eau Kg.	Cendres Kg.	Azote Kg.	Acide Phosphorique Kg.	Potasse Kg.	Chaux Kg.
Jacinthe	858,1	12,827	4,254	2,383	3,780	2,436
Glaieul	730,7	15,242	4,553	3,016	3,490	3,105
Narcisse	825,1	5,981	2,137	1,119	0,839	1,208
Anémone	132	55,200	15,554	7,638	7,291	9,895
Renoncule	127,6	52,169	27,611	8,724	7,118	6,255
Tulipe	428,6	17,027	4,405	3,314	4,388	traces
Freesia	551,8	16,852	13,661	6,274	6,238	1,721
Cyclamen	734,9	20,590	4,330	2,356	3,441	3,344
Amaryllis	750	12,700	1,800	3,300	2,760	2,882
Lilium	779,5	17,772	5,953	2,381	6,667	traces
Jonquille	700,4	11,444	7,118	1,677	3,739	1,692

Comme on pouvait s'y attendre, de la part d'organes de réserves, les bulbes se montrent très riches comme composition. A remarquer, particulièrement, la teneur en azote du Freesia, et surtout de l'Anémone et de la Renoncule. Ce riche dosage s'explique par la faible teneur en eau de ces bulbes. Du moment de l'arrachage, en fin Mai, environ, au moment de la plantation, en Août, les bulbes perdent beaucoup d'eau en se desséchant.

Par kilogr. de bulbes, nous avons pu constater une perte d'eau de 75 grammes pour les Narcisses; de 100 grammes pour l'Iris; de 185 grammes pour les Jacinthes; de 240 grammes pour les Freesias. Elle est encore bien plus considérable pour l'Anémone et la Renoncule.

Comme composition, on peut comparer les Bulbes, aux graines, en général.

On parle souvent de l'exigence des plantes bulbeuses, en général, pour la potasse. Cette exigence particulière, ne s'affirme pas, au contraire, pour les Bulbes-fleurs; elle est plus comparable à celle en acide phosphorique, et bien inférieure aux exigences en azote.

La sensibilité d'une plante, au point de vue végétation, par rapport à un élément fertilisant, ne se mesure pas toujours, d'ailleurs à ses exigences. Il convient, en outre, de faire intervenir l'influence qu'on peut appeler qualitative, de chaque élément. A cet égard, la potasse exerce, assurément, une influence très nette; elle permet, par exemple, d'obtenir une proportion plus forte de gros bulbes qui sont également de meilleure conservation.

On peut faire la même remarque, en ce qui concerne l'acide phosphorique, de plus en plus employé, par les cultivateurs de bulbes, qui, autrefois, s'en tenaient presque exclusivement au fumier et aux tourteaux. Ils les complétent, aujourd'hui, par du superphosphate.

EXPORTATIONS

Les exigences se mesurent exactement par les exportations en éléments fertilisants et, celles-ci, se déterminent par le poids des récoltes. Nous devons dire, à cet égard, que nous avons éprouvé de grandes difficultés, pour nous procurer, pour les différentes catégories de bulbes, des chiffres précis sur les poids des bulbes récoltés à l'are.

Nous devons, ceux que nous fournissons ici, à l'obligeance de M. Philippe de Vilmorin, et au Syndicat agricole et horticole d'Ollioules, auxquels nous adressons nos bien vifs remerciements.

Si l'on fait exception, pour le Lis, les chiffres des exportations ou des exigences sont très comparables entre eux.

Ces exigences sont, d'ailleurs, peu considérables, et même, pour l'acide phosphorique, et souvent pour la potasse, très faibles.

Les exigences des Bulbes-fleurs sont, dans tous les cas, bien plus faibles que celles des plantes cultivées pour la production de la fleur coupée, sauf, cependant, pour l'Anémone et la Renoncule.

Aussi apporte-t-on, pour la production des bulbes, des quantités d'engrais beaucoup moins considérables que pour les fleurs.

EXPORTATIONS EN ÉLÉMENTS FERTILISANTS, PAR *are*:

Désignation des Récoltes	Poids de la récolte à l'are Kg.	Azote Kg.	Acide phosphorique Kg.	Potasse Kg.	Chaux Kg.
Jacinthe	200	0,850	0,476	0,756	0,486
Glaieul	150	0,682	0,452	0,523	0,465
Narcisse	200	0,427	0,223	0,167	0,241
Anémone	50	0,777	0,381	0,364	0,494
Renoncule	25	0,690	0,218	0,177	0,156
Tulipe	150	0,660	0,497	0,658	0,156
Freesia	50	0,683	0,313	0,312	0,086
Cyclamen	150	0,649	0,353	0,516	0,501
Amaryllis	150	0,270	0,495	0,414	0,432
Lilium	250	1,488	0,595	1,666	0,432
Jonquille	75	0,534	0,125	0,280	0,126

Les engrais employés, dans la culture des bulbes sont surtout, et souvent exclusivement, les engrais organiques, principalement les fumiers de cheval, de mouton et de vache. Ce dernier est le meilleur, apporté en quantités plus considérables que celui de mouton, parce que moins riche, il constitue une réserve d'humus, dans le sol, et il n'est pas si échauffant pour les terres, que le fumier de cheval.

Un certain nombre d'horticulteurs ajoutent au fumier, des engrais chimiques complémentaires: superphosphate et sulfate de potasse. Ils obtiennent de bien meilleurs résultats, et sur la quantité des bulbes, et sur le pourcentage des gros bulbes, qui sont vendus plus chers.

Beaucoup, enfin, se servent de tourteaux, soit seuls, soit concurement avec le fumier ou les engrais chimiques. L'advantage des tourteaux, outre leur richesse, leur rapidité de décomposition et leur facilité d'emploi, c'est, surtout pour les tourteaux sulfurés, de ne pas apporter, ni de ne pas favoriser le développement des germes de maladies, ce qu'on reproche souvent, dans la culture des bulbes, au fumier, et surtout, au fumier frais.

Aussi, ce qui convient particulièrement aux bulbes, c'est le reliquat d'une très forte fumure organique, faite à une précédente culture comme l'Oeillet. Souvent, d'ailleurs, les cultures d'oignons à fleurs succèdent aux cultures d'Oeillets et, dans ce cas, la quantité d'humus en terre, en reliquat, est suffisante. On se contente d'apporter un peu de tourteaux, avec des engrais chimiques.

Voici, à titre documentaire, le bilan d'une culture de jacinthes, rapporté à un are.

Il faut, dans cette production, cultiver, en même temps, des *mères* destinées à produire les *cailleux*;

des *cailleux* récoltés l'année précédente, et qui vont grossir pour fournir les recettes de l'année suivante;

enfin des *recettes*, bulbes qui, à la récolte seront bons pour la vente.

On pourrait décompter ainsi les quantités de chaque catégorie, et la surface qui leur est consacrée, sur un are de culture totale: Pour les *mères*: 30 mètres carrés, à 60 par m. carré soit 1800 bulbes: Pour les *cayeux*: 20 mètres carrés: Soit 4000 à 6000 cayeux Pour les recettes: 50 mètres carrés, à 60 bulbes par m. carré soit 3000, sur lesquels, à la récolte, on en aura 2000 de 12cm et au dessus à 70 francs le 1000, et 1000 de 12cm et au dessous, à 35 francs le 1000.

Ceci posé, on peut établir les recettes et les dépenses, de la façon suivante, par are:

1° DÉPENSES:

Préparation du sol	4 frs.
Engrais	7 frs.
Location de la terre	15 frs.
Plantation	5 frs.
Travaux d'entretien	18 frs.
Arrosage	40 frs.
Arrachage et triage	15 frs.
Magasinage	15 frs.
Total	119 frs.

2° RECETTES:

2000 bulbes à 70 frs. le 1000	140 frs.
1000 bulbes à 35 frs. le 1000	35 frs.
Rendement en fleurs	8 frs.
Total	183 frs.

Soit un bénéfice net de 64 frs. par are.

RELATION OF ACTIVE PHOSPHORIC ACID AND POTASH OF THE SOIL TO POT AND FIELD EXPERIMENTS

By F. S. Fraps

College Station, Texas

For several years, work has been carried out at the Texas Experiment Station, to determine the relation between the active phosphoric acid, active potash, and total nitrogen of the soil, and the results of pot and field experiments. The terms active phosphoric acid or active potash, are used to designate such which is soluble in N/5 nitric acid.

Active Phosphoric Acid

In Bulletin 126 of the Texas Experiment Station is presented the results of a study of the active phosphoric acid of the soil. It was found that the results of the pot experiments are related to the active phosphoric acid. Expressing the average quantity of phosphoric acid removed from the soil by the plants, from the different groups of soils, in terms of bushels of corn which would require this quantity of phosphoric acid for leaves, stalk and grain, we secured the following results:—

Parts per Million Active Phosphoric Acid in Soils	Average Corn Possibility in Bushels Per Acre
0. –10	4.5
10.1–20	12.5
20.1–40	20.0
40.1–100	24.3
100.1–190	52.5
310.–420	60.7

Active Potash

In Bulletin No. 145 of this Experiment Station, we have published the results of a study of the active potash of the soil.

Stated in a way similar to that above, the results of the pot experiments are as follows:—

Parts per Million Active Potash in Soil	Average Corn Possibility, Bushels per Acre
0- 50	58.6
50-100	74.4
100-150	102.0
150-200	161.8
200-300	240.2
300-400	313.8
400-600	238.8
600-800	413.8

TOTAL NITROGEN

A similar study of the relation of the total nitrogen of the soil to pot experiments has been made, but is not published at the date of this paper. The results are as follows:—

Percentage of Nitrogen in Soil	Average Corn Possibility, Bushels per Acre
0. -.02	8
.021-.04	12
.041-.06	18
.061-.16	30
.161-.18	56

These averages in all cases are probably low, rather than high. The maximum corn possibility is much greater than the average, with all three forms of plant food.

These figures enable us to compare the results of chemical analyses with pot experiments, and judge as to the relative deficiency of the soil in pot experiments. The figures must not, and cannot, be considered to represent the field production. The relation between the field production and the pot experiments must be traced out. Very probably the relation will vary with moisture, temperature, and other climatic conditions. Certainly the depth of the soil and its physical character will have something to do with it, and also the quantity of carbonate of lime and humus in the soil.

Relation to Field Production

In the following table, we make a comparison between the chemical analysis of a number of soils, transferred to terms of corn possibility per acre, and compared with the actual crop of corn said to be produced on the land by those who are farming it. In considering this table, we must remember that the field production of corn depends upon seed, season, cultivation, and other factors than the chemical composition of the soil.

The lower corn possibility is supposed to be the controlling element. We find that phosphoric acid and nitrogen are controlling plant foods of these soils. Potash, apparently might be left out of consideration.

The corn actually produced in the field is greater than the average corn possibility. As an average of nine soils where nitrogen apparently controls, the average possibility is 14, the field production is 18. As an average of 5 soils where phosphoric acid controls, the average possibility is 12 and the actual 15. Thus, in these cases, the corn possibility estimated on the basis of the chemical analysis comes very near to the actual field production, and is on an average, 0.8 of the field production.

We believe that the method here outlined affords a basis for correlating chemical analyses with field work, particularly when moisture, depth of soil, and other limiting conditions, are taken into consideration.

RELATION OF ANALYSIS OF SOIL TO ESTIMATED YIELD IN FIELD

Laboratory Number	Total Nitrogen	Active Phosphoric Acid	Active Potash	Average Corn Possibility:			Crop Produced, Bushels per acre
				For Nitrogen	For Phosphoric Acid	For Potash	
3124	.086	8	105	30	4.5	102	7-8
3367	.047	188	155	18	52.5	162	15
3357	.041	12	123	18	12.5	102	15
3250	.034	34	—	12	20.	—	15
3256	.075	9	54	30	4.5	74	15
3377	.035	14	216	12	12.5	240	20
3373	.023	21	89	12	20.	74	15
3379	.031	16	127	12	12.5	102	20
3411	.053	27	104	18	20.	102	20
3254	.031	13	54	12	12.5	74	10
3252	.064	17	62	18	12.5	74	20
3381	.043	18	21	12	12.5	59	10-15
3362	.057	38	106	18	20.	102	25-30
3385	.055	18	179	18	12.5	162	15-20
Average (9)				14			18
Average (5)					12.		15

SUMMARY AND CONCLUSION

(1) The content of active phosphoric acid, of active potash, and of total nitrogen, in a soil, is related to its behavior towards fertilizer in pot experiments.

(2) The relative deficiency of a soil in these three plant foods may be judged from the chemical analysis.

(3) The average estimated production of corn in the field was related to the corn possibility based upon the chemical analysis.

COMPOSITION AND DIGESTIBILITY OF THE CHLOROFORM EXTRACT OF PLANTS

By G. S. Fraps and J. B. Rather

College Station, Texas

(*Contribution from the Texas Experiment Station*)

In the course of an investigation of the alcohol-soluble constituents of hays and fodders, it was found that, although previously extracted with ether, the alcohol extract contained a quantity of ether-soluble material. As the substance was easily soluble in chloroform, this led to a study of the chloroform extract of plants.

METHOD OF WORK

The material was first extracted for sixteen hours with ether, in a Soxhlet apparatus, and the residue then extracted in the same way with chloroform. The chloroform extract was saponified, and the unsaponified material extracted with hot petroleum ether and ethyl ether. The extract was then acidified with acetic acid, and the fatty acids extracted with petroleum ether. The residue was acidified with hydrochloric acid and extracted with ethyl ether. This extract contained the chlorophyll, and was highly colored, but it evidently contained other substances in addition to chlorophyll.

RESULTS OF THE WORK

TOTAL EXTRACT:—The following table shows the average results from eleven hays and fodders, and the excrements therefrom in digestion experiments:—

	Ether Extract	Chloroform Extract
11 hays, per cent.	1.42	0.79
11 excrement,	1.79	1.04

The chloroform extract is about two-thirds of the ether extract, on an average.

COMPOSITION OF EXTRACT:—The chloroform extract consists largely of chlorophyll and other weak acids which accompany it. For example, the extract from Johnson grass hay had the following composition:—

Total chloroform extract	0.91
Unsaponified	0.23
Saponified	0.11
Chlorophyll and weak acids	0.41
Loss	0.16

DIGESTIBILITY:—The digestibility of the chloroform extract as compared with the ether extract in four experiments is as follows:—

	Ether Extract	Chloroform Extract
Alfalfa	4.9	63.0
Buffalo grass	35.5	47.1
Johnson grass	53.2	47.5
Rice straw	36.4	47.7

DIGESTIBILITY OF CONSTITUENTS:—The digestibility of the constituents of the chloroform experiment as found in an experiment with alfalfa hay is as follows:—

	Per cent.
Total Extract	63.0
Unsaponified	29.8
Saponified	55.7
Chlorophyll and weak acids	42.8
Loss	85.6

SUMMARY AND CONCLUSIONS

(1) The chloroform extract of hays and fodders is about sixty per cent. as much as the ether extract previously made on the same samples.

(2) The chloroform extract consists largely of chlorophyll and other weak acids, though it contains fatty acids and wax alchohols also.

(3) The chloroform extract has a higher digestibility than the ether extract.

(*Contribution from the Texas Agricultural Experiment Station*)

COMPOSITION AND DIGESTIBILITY OF ETHER EXTRACT OF HAYS AND FODDERS

By G. S. Fraps and J. B. Rather

College Station, Texas

A few experimental articles (notably Stellwaag, Landw. Versuchsstat, 37,148) have shown that the ether extract of hays and fodders may contain quantities of non-fats, but no extensive investigation of the subject has yet been made, and no determinations of the digestibility of the ether extract.

Methods

The ether extract was prepared both from large samples of 100 grams, for the purpose of further study of the constituents thereof, and from 5 or 10 gram samples, for the purpose of determining the quantitative relations of the unsaponifiable matter and the saponifiable. It was found that ordinary methods of shaking out the unsaponifiable with cold ether after saponification do not apply to ether extracts such as we secured on account of the unsaponifiable matter being difficultly soluble in cold ether. A method was devised, which without going into details, involves heating the mixture of soap and unsaponifiable matter, first with petroleum ether, and then with ethyl ether. This rather vigorous treatment carries with it the danger of extracting some of the fatty acids, which was obviated by washing the ethereal solution, and by correction for the quantity of fatty acids present in the unsaponifiable, in care of the quantitative separation on the small samples. The unsaponifiable material appears to be soluble in the soap solution, and difficult of removal from it.

The digestion experiments were carried out as usual, on sheep, with a preliminary period of ten days and a collection period of eight days.

COMPOSITION OF THE ETHER EXTRACT

The table contains a summary of the results of the examination of 18 samples of 16 hays and fodders, including alfalfa, Bermuda hay, Johnson grass, burr clover, rice straw, and others.

Composition of Ether Extract

	Unsaponifiable	Saponifiable	Nitrogen	Phosphoric Acid
Average	58	36	0.30	0.11
Maximum	71	61	0.44	0.25
Minimum	36	25	0.07	0.02

The unsaponifiable consists chiefly of wax alcohols, probably including alcohols approximating the formula of myricil alcohol, $C_{30}H_{62}O$, together with other wax alcohols possibly as low as $C_{18}H_{38}O$. An alcohol having approximately the formula and acetyl number of myricil alcohol, was separated by recrystallization from some of the products, and similar crystals were separated from almost all of the materials. Several mother liquors had acetyl numbers varying from 151 to 190.

The saponifiable consists of fatty acids, chlorophyll products, and other bodies. If it were all fatty acids, the average molecular weight would be 203, or between that of palmitic and stearic acids.

DIGESTIBILITY OF THE CONSTITUENTS OF THE ETHER EXTRACT

The table below contains a summary of the coefficients of digestibility, 18 experiments being made.

COEFFICIENTS OF DIGESTIBILITY OF THE ETHER EXTRACT OF HAYS AND FODDERS

	Total	Unsaponifiable	Saponifiable	Nitrogen	Phosphoric Acid
Average	41.9	29.1	66.4	52.5	48.6
Maximum	90.0	86.6	92.3	75.8	78.6
Minimum	0.0	0.0	8.6	0.0	9.9

The unsaponifiable has a much lower digestibility than the total ether extract, and the saponifiable a much higher digestibility. In other words, the low digestibility of the ether extract of hays and fodders is due to the presence of quantities of wax alcohols or non-fats, of low digestibility.

SUMMARY AND CONCLUSIONS

The ether extract of hays and fodders contains on an average 58 per cent. unsaponifiable material, chiefly wax alcohols.

The unsaponifiable material is digested to a much less extent than the saponifiable matter, which includes chlorophyll and fatty acids.

The low digestibility of the ether extract of hays and fodders is due largely to the presence of large proportions of non-fats, which are not as easily digested as the fats.

THE COMBUSTIBLE GASES EXCRETED BY CATTLE

By J. August Fries

State College, Pa.

Several years ago the writer[1] called attention to the composition and quantity of the combustible gases excreted by cattle as affected by variations in the quantity of timothy hay consumed. During four experimental periods the daily ratio of hydrogen to carbon in the combustible gases ranged from 1:2.899 to 1:3.096 with an average of 1:2.967, which is practically identical with the ratio of carbon to hydrogen in methan. Since that time many nutrition experiments upon steers have been carried on by the aid of the respiration calorimeter under the direction of Dr. H. P. Armsby at the Institute of Animal Nutrition of The Pennsylvania State College, in all of which the carbon and hydrogen of the combustible gases excreted by the animals have been determined.

Apparatus and Methods

As related to the experiments here reported, the respiration calorimeter is substantially a Pettenkofer respiration apparatus, the ventilation being maintained and measured by means of a pump which also takes automatically duplicate analysis samples of 1/200 of the total ventilation. One of these samples, after passing through an absorbent train which takes up the H_2O and CO_2, passes over platinized kaolin at a dull red heat, the H_2O and CO_2 formed being absorbed in a second train of U tubes. The sampling by the meter pump is intermittent but for the twelve-hour subperiods of these experiments it has been shown to be accurate.

During Periods IV and V with Steer D and Periods III, IV and V with Steer G, Experiment No. 211, an electric furnace[2]

---

[1] Proceedings of the Twenty-third Annual Meeting of the Society for the Promotion of Agricultural Science (1902), p. 110.

[2] Jour. Amer. Chem. Soc., Vol. XXXII, No. 8 (1910).

was used, but previous to that the combustion tube was heated by gas. The combustion tube is a long copper tube 2.5 c.m. inside diameter filled with lumps of platinized kaolin and heated to dull redness, about 700° C., over a length of 2.1 meters. The combustion furnaces and tubes were tested by burning known quantities of ethyl alcohol vapor and determining the H_2O and CO_2 produced. The following tests, Table I, show that the oxidation of the vapor was complete. The CO_2 found agrees closely with the theoretical, but the water was probably not driven completely from the connections where it had condensed.

TABLE I

Date		C_2H_6O Gms.	Hours	H_2O Gms.	CO_2 Gms.	
Oct. 4, 1906	Gas furnace	4.0566	4	5.1955	7.7570	Found
				5.2429	7.7521	Theoretical
Mar. 3, 1910	Electric furnace	4.8192	3	6.1812	9.2150	Found
				6.2497	9.2093	Theoretical

CHECK TESTS

Blank tests:—It was not possible to make parallel determinations of the combustible gases in the ingoing air and hence blank tests were made from time to time in order to obtain corrections for the apparatus and the outside air. These blank determinations were not made at, or necessarily near, the time of the individual respiration experiments. They represent rather the average condition of the ingoing air and the combustion furnace, and since the analytical error is relatively large, on account of the large apparatus used and the small total quantity of hydrogen and carbon found, the average result of all the tests is used.

Table II gives the average of 22 blank tests which represent many different climatic conditions during a number of years.

Between the individual blank determinations there is considerable variation, yet the total correction is not very large. The ratio of hydrogen to carbon is 1:0.682, so that when the carbon is computed to methan, there is an excess of free hydrogen equivalent to 0.001475 gram or 16.38 c.c. in 1000 liters air at 0° and 760 m.m.

TABLE II—Blank Tests of Outside Air

Combustible hydrogen and carbon weighed as water and carbon dioxid

Year	Number of single determinations	Average results		
		Air sample at 0° & 760 m.m. Liters	In 1000 liters air	
			H_2O Gram	CO_2 Gram
1903	5	1078.18	.021754	.005937
1904	3	940.67	.017142	.008206*
1905	6	1349.97	.017924	.004510
1906	3	1899.60	.011989	.003202
1907	3	1558.37	.013689	.004618*
1910	2	1800.00	.017143	.001911
	Average of all determinations	1376.66	.017230	.004790

*Average of two determinations only.

Alcohol check tests:—These alcohol check tests, by which the efficiency and reliability of the respiration calorimeter as a whole is tested, also serve as a check on the combustible hydrogen obtained in the blank tests. With the exception of probably less than 1 per cent. of the total ventilation which comes in close contact with the flame, in an alcohol check test all gases from without must pass through the chamber unchanged. Hence the combustible hydrogen obtained during such a test is a maximum above which the blank tests should not go. In Table III is given the average result as regards combustible gases of 20 alcohol check tests; and, leaving out one of the water determinations in 1902 which gave a high result in water without a corresponding increase in carbon dioxid, the average of the 19 determinations would be .017800 gram water in 1000 liters, a close agreement with the average of the blank tests.

TABLE III—Combustible Gases Found in Alcohol Check Tests

Hydrogen and carbon weighed as water and carbon dioxid

		Average Results			
Year	Number of single determinations	Air sample at 0° & 760 m.m. Liters	Pure ethyl alcohol burned Grams	In 1000 liters air	
				H_2O Gram	CO_2 Gram
1902	3	1432.65	641.62	.020999	.030718
1903	3	1035.82	467.92	.023583	.021791
1904	3	1074.15	459.54	.020609	.023660
1905	1	1977.74	843.73	.017393	.014562
1906	2	1601.56	649.64	.012411	.018419
1907	4	1567.46	641.52	.015935	.015768
1908	2	1551.47	603.14	.018259	.012453
1909	2	1521.95	588.38	.017758	.012225
	Average of all determinations	1411.27	589.97	.018678	.019582

RECORD OF EXPERIMENTS

In Table IV are given the results obtained in 57 respiration calorimeter experiments with various steers and feeds, carried on between the years 1903 and 1911, showing the average combustible hydrogen and carbon excreted per day in each period, corrected for blank, and the ration of hydrogen to carbon. Further, there is given the combustible carbon per kilogram dry matter eaten and the combustible carbon in per cent. of the total gaseous carbon excreted as carbon dioxid. The experiments with the same kind of feed are grouped together and the periods for each animal arranged in order of the amount of feed eaten so as to facilitate the study of the results.

TABLE IV. Excretion of Combustible Gases by Steers Weighed as Water and Carbon Dioxid

Steer	Average live weight	Experiment number	Period	Dry matter eaten	Total combustible		Ratio	Carbon per Kg. dry matter eaten	Carbon in p. c. of total gaseous carbon as carbon dioxid
					Hydrogen	Carbon	H : C		
	Kgs.			Grams	Grams	Grams		Grams	
					CLOVER HAY				
R	520	179	II	3143.0	17.751	57.485	1:3.238	18.290	5.726
	544	179	I	4459.0	24.895	77.506	1:3.113	17.382	6.532
	561	186	I	2933.3	15.691	50.473	1:3.217	17.207	4.649
	566	186	III	4139.1	18.900	59.731	1:3.160	14.430	4.774
	572	186	II	5025.3	19.537	61.652	1:3.155	12.267	5.395
							1:3.176		
				CLOVER HAY AND MAIZE MEAL					
R	514	179	III	3162.8 734.7	25.236	77.951	1:3.089	20.000	7.061
	531	179	IV	3186.4 3450.8	44.858	137.212	1:3.059	20.672	10.771
							1:3.075		
					TIMOTHY HAY				
A	269	190	III	2001.0	10.953	35.127	1:3.207	17.512	5.788
	277	190	IV	3493.0	20.062	59.728	1:2.982	17.100	7.535
	507	207	III	2974.0	19.337	61.092	1:3.159	20.542	7.238
	514	207	IV	4892.0	31.317	97.597	1:3.116	19.950	8.826
							1:3.116		
B	194	190	III	1774.0	10.651	34.489	1:3.238	19.440	6.639
	190	190	IV	2610.0	14.563	44.855	1:3.080	17.185	7.500
	374	207	III	2798.0	18.696	58.915	1:3.151	21.055	7.036
	385	207	IV	4030.0	29.581	91.734	1:3.101	22.762	8.551
							1:3.142		

Steer	Average live weight	Experiment number	Period	Dry matter eaten	Total combustible		Ratio	Carbon per Kg. dry matter eaten	Carbon in p. c. of total gaseous carbon as carbon dioxid
	Kgs.			Grams	Hydrogen Grams	Carbon Grams	H : C	Grams	
				TIMOTHY HAY AND WHEAT BRAN					
A	271	190	I	1977.8 1370.2	20.464	62.474	1:3.053	18.660	7.158
	279	190	II	1995.8 2583.2	25.480	79.715	1:3.128	17.407	7.856
							1:3.090		
B	199	190	I	1770.5 1032.5	16.069	49.759	1:3.096	17.752	7.046
	197	190	II	1779.4 1802.6	22.050	66.601	1:3.020	18.592	8.447
							1:3.058		
				TIMOTHY HAY AND MIXT GRAIN*					
A	499	207	I	2934.8 1996.2	33.222	103.320	1:3.110	20.952	8.702
	519	207	II	2949.0 4759.0	49.152	150.697	1:3.066	19.550	8.817
							1:3.088		
B	373	207	I	2759.2 1397.8	28.978	89.988	1:3.105	21.647	5.142
	386	207	II	2774.1 2676.9	38.183	117.327	1:3.073	21.522	8.782
							1:3.089		
				ALFALFA HAY					
D	162	208	II	1299.7	5.445	19.477	1:3.577	14.985	4.876
	171	208	I	2154.9	9.254	31.440	1:3.397	14.587	5.941
							1:3.487		
C	285	208	V	3098.5	14.332	46.472	1:3.243	14.997	6.238
	287	208	IV	4743.9	17.777	56.542	1:3.181	11.917	5.803
							1:3.212		
E	197	208	VI	1412.9	6.415	21.904	1:3.414	15.502	4.830
	214	208	V	2408.0	11.456	36.935	1:3.224	15.337	6.184
	223	208	IV	4170.2	17.662	55.970	1:3.169	13.420	6.676

Steer	Average live weight Kgs.	Experiment number	Period	Dry matter eaten Grams	Total combustible		Ratio H : C	Carbon per Kg. dry matter eaten Grams	Carbon in p. c. of total gaseous carbon as carbon dioxid
					Hydrogen Grams	Carbon Grams			
				ALFALFA HAY					
							1:3.269		
F	291	209	VI	2226.4	10.660	34.707	1:3.256	15.587	5.141
	310	209	V	3562.2	16.488	52.266	1:3.170	14.672	6.577
	321	209	IV	6173.7	27.555	85.542	1:3.104	13.855	7.120
							1:3.177		
				ALFALFA HAY AND MIXT GRAIN†					
C	260	208	III	520.7 1018.3	10.243	34.674	1:3.385	25.030	5.718
	271	208	II	730.6 1453.3	14.666	47.502	1:3.239	21.750	6.490
							1:3.312		
E	197	208	III	386.8 763.8	5.445	20.050	1:3.682	17.425	4.121
	205	208	II	590.1 1162.7	11.138	36.948	1:3.317	21.077	6.363
	209	208	I	1086.3 2221.9	17.830	56.681	1:3.180	17.132	7.099
							1:3.393		
F	283	209	III	536.1 1112.0	9.111	30.817	1:3.382	18.697	4.879
	293	209	II	893.5 1862.0	14.733	46.659	1:3.167	16.932	5.893
	301	209	I	1461.5 3040.6	22.272	68.946	1:3.095	15.312	6.583
							1:3.215		
				CORN STOVER					
D	325	210	III	2562.8	15.937	50.496	1:3.168	19.702	6.818
	340	210	II	3547.4	21.005	66.354	1:3.159	18.705	7.518
	354	210	I	4335.3	25.811	81.140	1:3.144	18.715	7.805
							1:3.157		

Steer	Average live weight Kgs.	Experiment number	Period	Dry matter eaten Grams	Total combustible		Ratio H : C	Carbon per Kg. dry matter eaten Grams	Carbon in p. c. of total gaseous carbon as carbon dioxid
					Hydrogen Grams	Carbon Grams			
			MIXT HAY (CLOVER AND TIMOTHY)						
D	439	211	V	1786.4	10.878	34.487	1:3.170	19.305	4.519
	463	211	IV	3498.3	21.580	64.880	1:3.006	18.546	6.705
	469	211	I	6204.2	32.119	99.148	1:3.087	15.980	7.567
G	375	211	V	1607.8	10.459	32.111	1:3.070	19.970	4.848
	395	211	IV	3148.4	18.716	56.254	1:3.006	17.867	6.172
	397	211	I	6092.0	33.309	102.191	1:3.068	16.775	7.776
							1:3.068		
		MIXT HAY (CLOVER AND TIMOTHY) AND HOMINY CHOP							
D	441	211	II	1747.3 1763.7	25.510	79.179	1:3.104	22.550	7.493
	503	211	III	3910.5 3948.8	49.240	149.725	1:3.041	19.057	8.866
							1:3.072		
		MIXT HAY (CLOVER AND TIMOTHY) AND CORNMEAL							
G	367	211	II	790.3 1541.9	18.257	57.861	1:3.169	24.810	6.644
	405	211	III	2383.2 4643.7	47.422	138.604	1:2.923	19.725	8.594
							1:3.046		

*Wheat bran, 1 part; cornmeal, 3 parts; linseed meal, 3 parts.
†Cracked corn, 6 parts; oats (whole), 3 parts; linseed meal, 1 part.

This record shows a great variation in the daily quantities of hydrogen and carbon given off in the form of combustible gases, ranging from 5.445 grams hydrogen and 19.477 grams carbon with Steer D in Period II of Experiment No. 208, to 49.152 grams hydrogen and 150.697 grams carbon with Steer A in Period II of Experiment No. 207. A variation in the ratio of Hydrogen to carbon also appears, the average of all being 1: 3.167. Several other things are brought out in this table to which attention may be called:

1. The amount of combustible gases increases with increase in quantity of feed eaten.
2. The production of combustible carbon is relatively greater with the smaller rations.
3. In per cent. of the total carbon given off in carbon dioxid, the combustible carbon increases with the increase in the rations.
4. The individuality of the animals does not seem to have any marked influence upon the production of combustible gases.
5. A tendency for higher percentage of carbon to hydrogen is noticed with the smaller rations, but this is especially marked in the rations containing alfalfa hay.

Point 1 is clearly illustrated in Table V, which gives the results obtained with two steers on varying amounts of the same kind of feeds.

TABLE V—Daily Combustible Hydrogen and Carbon from two Steers Fed Increasing Quantities of the Same Kind of Feed

Steer	Experiment No.	Alfalfa hay			Hay and grain		
		Dry matter fed	Combustible		Dry matter fed	Combustible	
		Grams	Hydrogen Grams	Carbon Grams	Grams	Hydrogen Grams	Carbon Grams
E	208	1412.9	6.415	21.904	1150.6	5.445	20.050
"	208	2408.0	11.456	36.935	1752.8	11.138	36.948
"	208	4170.2	17.662	55.970	2183.9	14.666	47.502
F	209	2226.4	10.660	34.707	1648.1	9.111	30.817
"	209	3562.2	16.488	52.266	2755.5	14.733	46.659
"	209	6173.7	27.555	85.542	4502.1	22.272	68.946

Computed per 1000 grams dry matter eaten, the following amounts of combustible carbon were excreted:

Average for the 23 smallest rations = 19,201 grams carbon
" " " 23 heaviest " = 17.505 " "

Although there is more combustible gaseous carbon produced per unit of dry matter eaten with the smaller rations, the combustible carbon in per cent. of total carbon excreted as carbon dioxid is, as stated in point 3, greater with the larger rations. This is shown if we average the percentages of the smallest and heaviest rations as follows:

	Total carbon given off as carbon dioxid	Combustible gaseous carbon
23 smallest rations	100.00	6.013
23 heaviest "	100.00	7.623

In regard to Point 5, we find that the average ratio of hydrogen to carbon is:

For the 23 lightest rations, 1: 3,230
" " 23 heaviest " 1: 3.110

but with the rations containing alfalfa hay, the average ratio of hydrogen to carbon is

for the 7 lightest rations, 1: 3.411
" " 7 heaviest " 1: 3.195

This represents such an unusual condition of things that it requires more than a passing notice. The regularity with which these variations in the ratio of hydrogen to carbon occur and the magnitude of them exclude, I think, the possibility of ascribing them to analytical error or to errors in the blank. The greatest difference is found in the case of Experiment No. 208, Steer E, the ration being alfalfa hay and mixed grain. Here the ratio of hydrogen to carbon varies from 1: 3.180 with the highest to 1: 3.862 with the lightest ration.

To explain these variations by errors in the average for the blank tests would require, either a reduction of the hydrogen of the blank by 73 per cent. or an increase of its carbon by 416 per cent. Errors of this magnitude in the blanks seem beyond the range of possibility. Neither is it possible to ascribe these variations in the ratios to diffusion of gases through the rubber diafram and connections. While it is not easy to explain the excess of carbon over hydrogen found in these experiments, it would seem that, at least for the present we must tentatively accept the results as found. These results indicate that the bulk of feed, and length of time which it remains in the animal's body, especially in the case of rations containing alfalfa hay, influence the composition of the combustible gases produced.

Earlier investigators arrived at the conclusion that the combustible portion of the fermentation products in cattle was almost exclusively methan. Markoff,[1] however, finds that the composition of the gases contained in the paunch of ruminants varies greatly both as regards carbon dioxid and free hydrogen. Thus 21 gas samples taken directly from the paunch of a goat showed a variation as follows:

CO_2	14.95% to 54.32%
CH_4	19.88% to 42.55%
H_2	0.05% to 4.07%

These samples, each about 15 c. c. were taken once or sometimes twice a day, some in the morning and others in the afternoon. It is, therefore, not admissible to compare the results based on these samples with those of our own experiments which represent the whole day and the total output of gases from paunch and intestines combined. How closely the results obtained with goats are applicable to cattle is still undetermined.

In Markoff's valuable work, it is noteworthy that an addition of sugar to the paunch content either through the feed or directly through the fistula, caused no marked change in the amount of free hydrogen found. Neither was there any marked change in the composition of the gases when large quantities of protein material were added to the feed.

On the other hand, in the case of the fermentation trials with the paunch contents outside the body it was found possible to change almost at will the composition of the gases by the addition of varying quantities of sugar, etc. Thus in 10 samples:

CO_2	ranged	from	17.08% to 87.49%
CH_4	"	"	0.12% to 22.80%
H_2	"	"	0.03% to 20.04%

showing that outside of the animal body the fermentation processes may be reversed so that instead of methan, only hydrogen and carbon dioxid are produced.

---

[1] Biochem. Ztschr., **34** (1911), 211.

SOME FACTORS INFLUENCING THE QUANTITATIVE DETERMINATION OF ARSENIC IN SOILS

By J. E. Greaves

Utah Experiment Station, Logan, Utah

Since it has been announced that arsenic occurs in many virgin soils[1] and that it may, on account of its extensive use as an insecticide, accumulate in soils to such an extent as to become injurious to vegetation,[2] the principles involved in its accurate determination is of considerable practical importance at the present time. Many methods, both qualitative and quantitative, have been proposed for its determination in soil, but even the most modern[3] do not make allowance for the influence of the iron in the soil upon the quantitative determination of arsenic.

That arsenic is retained by iron when the Marsh method is used for its determination was first shown by Parson and Stewart[4] and later corroborated by the work of Harkins.[5] These investigators found that the arsenic retained by the iron increased as the iron introduced with the arsenic increased. They made tests in which considerable iron was used (6 grams) and found that in some cases only 32 per cent. of the arsenic was evolved when introduced into the Marsh apparatus. In their reported work, the smallest amount of iron used was 60 mg. and even with this amount only 69 per cent. of the total arsenic was recovered.

In order to determine the influence of traces of iron upon the quantity of arsenic evolved, as with some methods, it is recommended that traces of iron be introduced to accelerate the action of the acid upon the zinc, and to check with the above reported

---

[1] Headden, Proc. Colo. Scientific Soc. 9 (1910), 349.

[2] Headden, Colo. Exp. Sta. Bull. 131 and 157.

[3] Mai. Phar. Centr. 50, 169-200, Headden, Colo. Scientific Soc. 9 (1910), 348; Haywood, U. S. Dept. of Agr., Bureau of Chem. Bul. 113 (Revised) (1910) 58.

[4] Parson and Stewart, Jour. Amer. Chem. Soc. 24 (1902) 1005.

[5] Harkins, Jour. Amer. Chem. Soc. 32 (1910) 518.

results, tests were made, using varying amounts of iron with constant amounts of arsenic. This was done by introducing a solution of sulphuric acid containing the iron and arsenic into the Marsh apparatus and determining by weighing on fine assay balances the amount of arsenic deposited. The tube was heated by means of an electric combustion furnace, the temperature of which was maintained just below the melting point of hard glass by means of a rheostat. The constriction in the glass tube where the arsenic was to be deposited was wrapped with a wick dipping into a beaker of cold water. A sketch of the apparatus is shown in Fig. 1.

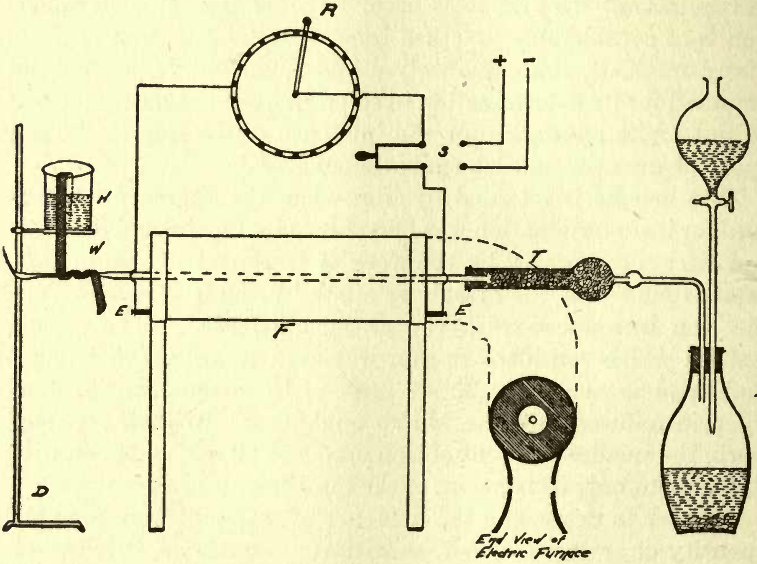


Figure 1.

Twenty-five grams of arsenic and iron free zinc were placed in the generator and the acid solution from the soil was added drop by drop. The sulphuric acid used was the No. 2 (260cc pure con. H_2SO_4 + 100 cc of H_2O) and No. 3 (425 cc pure conc. H_2SO_4 + 1000 cc of H_2O) recommended by Chittenden and Donaldson.[1] Acid No. 2 was used first and No. 3 later.

---

[1] Fresenius, Cohn, Quantitative Chemical Anaylsis. Vol. II (1906), 694.

All chemicals before using were tested and found to be free from arsenic. The calcium chloride used in the drying tubes was carefully reprecipitated, as recommended by Bishop.[1]

The apparatus was allowed to run two hours in each determination. The tube containing the arsenic was carefully wiped with a moist cloth, dried over calcium chloride, a rough weighing made and then allowed to remain in the balance case ten minutes, after which it was carefully weighed, the arsenic was dissolved out by dilute nitric acid (1 to 3), the tube washed in water, alcohol and ether, dried and weighed as before. The tube was handled throughout by means of platinum tipped tweezers, and all possible precautions taken to insure accuracy. All determinations are the average of two or more closely agreeing determinations.

In Table 1 is given the amount of arsenic obtained with varying amounts of iron.

TABLE I. EFFECT OF IRON ON ARSENIC OBTAINED BY MARSH GENERATOR

Treatment	Arsenic added mg.	Arsenic found mg.
Arsenic, no Iron,	1.00	0.98
" 1 mg. iron	1.00	0.78
" 5 mg. iron	1.00	0.61
" 10 mg. iron	1.00	0.58
" 50 mg. iron	1.00	0.66
" 100 mg. iron	1.00	0.65
" 500 mg. iron	1.00	0.33
" 1000 mg. iron	1.00	0.38

From the above results, it may be seen that the arsenic recovered decreases very rapidly as the iron added increases. In fact, the amount retained is almost directly proportional to the amount of iron introduced. Even as small amount as 1 mg. of iron in these tests was sufficient to retain one-fourth of the arsenic, so that even traces of iron must be considered in determining arsenic by the Marsh method.

---

[1] Bishop, Jour. Amer. Chem. Soc. 28 (1906), 182.

Harkins suggested that this retaining influence of iron be overcome by the use of stannous chloride and he found that two grams of stannous chloride was sufficient to overcome the retaining effect of three-tenths gram of iron. Inasmuch as there would be more than this amount in some soil solutions, it was thought advisable to check on this with varying amounts of iron and stannous chloride. The results are given in Table II.

TABLE II. SHOWING THE LIBERATION OF ARSENIC FROM IRON BY MEANS OF STANNOUS CHLORIDE

Treatment	Mg. Arsenic added	Mg. Arsenic found
1 mg.Fe 5 Mg. $SnCl_2$	1.00	0.89
1 " " 10 " " "	1.00	0.83
1 " " 20 " " "	1.00	0.83
1 " " 50 " " "	1.00	0.81
1 " " 100 " " "	1.00	0.86
1 " " 200 " " "	1.00	1.04
1 " " 500 " " "	1.00	1.02
5 " " 1000 " " "	1.00	0.90
5 " " 1000 " " "	1.00	0.97
10 " " 1000 " " "	1.00	0.99
50 " " 1000 " " "	1.00	1.00
100 " " 1000 " " "	1.00	0.99
500 " " 1000 " " "	1.00	0.985
1000 " " 1000 " " "	1.00	0.65
1000 " " 1250 " " "	1.00	0.70
1000 " " 1500 " " "	1.00	0.985

From these results it may be seen that the retaining action of one mg. of iron upon the arsenic was offset by 200 mg. of stannous chloride, and that one-half gram of iron was offset by one gram of the stannous chloride. One and one-half grams of stannous chloride completely neutralize the retaining influence of one gram of iron upon arsenic.

These facts have been applied to the determination of arsenic in soil. A soil 40 per cent. of which was soluble in hydrochloric acid, (sp. gr. 1.115) and containing 2 per cent. of iron was analysed and found to be free from arsenic. To 10 grams of this soil was added one mg. of arsenic and 25 cc. of concentrated nitric acid. The mixture was heated for 30 minutes in a casserol on an electric hot plate and while still moderately hot 10 cc. of concentrated sulphuric acid was added drop by drop. When considerable organic matter is present, this caused a violent reaction but no arsenic was lost. This was heated for 30 minutes, taken up with distilled water, filtered and washed with hot water until free from sulphates. The filtrate was evaporated nearly to dryness or until free from nitrates, the solution being kept strongly acid with sulphuric acid. The residue was taken up with arsenic free dilute hydrochloric acid and the arsenic determined in the following ways. In one set the solution was introduced directly into the Marsh generator without further treatment, in another with varying amounts of stannous chloride. Still other determinations were made in which the arsenic was precipitated as the ferroarsenate by the addition of an excess of ammonium hydroxide as suggested by Headden,[1] and later by Mai.[2] This precipitate was dissolved in hydrochloric acid and one set introduced directly into the generator without further treatment, while other samples were added in connection with varying amounts of stannous chloride. The results are given in Table III.

The 25 cc of concentrated sulphuric acid referred to in some of the determinations was introduced at the end of the process, that is after the main part of the arsenic had been evolved, but there remained considerable undecomposed zinc in the generator. The introduction of the sulphuric acid at this point in the reaction tends, by increasing the temperature of the solution in the generator, and the rapid evolution of hydrogen, to liberate the arsenic which is retained by the iron. An examination of the above results shows that the addition of the concentrated sulphuric acid at the end of the process gave an increase in the arsenic recovered, except in the cases where the stannous chloride had

---

[1] Headden. Proc. Colo. Scientific Soc. 9 (1910) p. 348.

[2] Mai. Phar. Centr. 50 p. 169-200.

TABLE III. GIVING AMOUNT OF ARSENIC OBTAINED FROM SOIL CONTAINING 1 MG. AS. WITH VARIOUS METHODS, BOTH WITH AND WITHOUT THE ADDITION OF STANNOUS CHLORIDE

Treatment	Stannous chloride added	Mg. arsenic added	Mg. arsenic found
Whole of acid extract	0	1.00	.705
Whole of acid extract + 25 c.c. con. H_2SO_4	0	1.00	.82
Whole of acid extract + 25 c.c. con. H_2SO_4	1.5	1.00	.95
Whole of acid extract + 25 c.c. con. H_2SO_4	2.0	1.00	.96
Excess of NH_4OH added to soil extract, filtered, residue dissolved in acid	0	1.00	.62
Excess of NH_4OH added to soil extract, filtered, and dissolved in acid + 25 c.c. con. H_2SO_4	0	1.00	.71
Excess of NH_4OH added to soil extract, filtered, residue dissolved in acid + 25 c.c. con. H_2SO_4	1.5	1.00	.87
Excess of NH_4OH added to soil extract, filtered, residue dissolved in acid +25 c.c. con. H_2SO_4	2.0	1.00	.90
Excess of NH_4OH added to soil extract, filtered, residue dissolved in acid + 25 c.c. con. H_2SO_4	3.0	1.00	.88

been used. In these cases there was no increase probably because all of the arsenic had been liberated by the stannous chloride. The addition of 1.5 grams of stannous chloride together with the concentrated sulphuric acid was sufficient to liberate the greater part of the arsenic, as no more arsenic was recovered when the amount of stannous chloride was increased to three grams. Where the arsenic was precipitated with ammonia a smaller proportion of the total arsenic was recovered than when the entire acid solution was introduced into the generator. Even when three grams of stannous chloride was added, it was impossible to recover all of the arsenic added. This is probably due to the slight solubility of the ferro-arsenate.

EFFECT OF SODIUM CHLORIDE

The soil used in the above tests contained only .0002 per cent. of sodium chloride. Inasmuch as the tri-chloride of arsenic is formed under certain conditions when an arsenic solution is treated with hydrochloric acid and as arsenic tri-chloride is volatile at a comparatively low temperature, tests have been made with a soil containing varying amounts of sodium chloride. Varying quantities of sodium chloride were added to ten grams of soil containing one mg. of arsenic, to which was added 25 cc of concentrated nitric acid, the mixture was heated thirty minutes and then 10 cc of concentrated sulphuric acid added and heated thirty minutes longer, filtered, washed and the arsenic determined as in the preceding work, using 2 grams of stannous chloride. The results are given in tabular form below.

Per Cent. of NaCl in soil	Mg. Arsenic Added	Mg. Arsenic Found
.0002	1.00	.955
.0052	1.00	1.04
.0102	1.00	.92
.0502	1.00	.96
.1002	1.00	.95
.5002	1.00	.91
1.0002	1.00	1.01
1.5002	1.00	.93
2.0002	1.00	.96
2.5002	1.00	.97
3.0002	1.00	.94

From the above results it may be seen that no appreciable quantity of arsenic is lost by this method even when the percentage of sodium chloride in the soil reaches 3 per cent. The results of Chittenden and Donaldson[1] on the other hand show that there would be no loss even when large amounts of organic matter are present.

---

[1] Chittenden and Donaldson, Amer. Chem. Jour. II. 235.

SUMMARY

An electric combustion apparatus can be used in connection with the Marsh apparatus for the determination of small amounts of arsenic with excellent results as it gives a steady uniform temperature readily controlled. The presence of even small quantities of iron retard very materially the evolution of arsenic in the Marsh generator. This may, however, be overcome by the use of stannous chloride as suggested by Harkins, and the amount of stannous chloride required depends upon the quantity of iron present. The introduction of concentrated sulphuric acid into the hydrogen generator at the end of the operation tends to liberate the last traces of arsenic by increasing the temperature of the solution in the generator and by a rapid evolution of hydrogen. More accurate results are obtained in the determination of arsenic in soils when the nitric acid extract is introduced into the generator than when the arsenic is precipitated by means of ammonia and the residue dissolved in acid and introduced as suggested by Headden and later by Mai. Soils can be digested with first nitric acid then sulphuric acid for the extraction of arsenic even when they contain large amounts of sodium chloride without danger of loss of arsenic due to volatilization. The method, therefore, which has given the best results in the preceding work is briefly summarized as follows: Ten grams of soil (where the amount of arsenic present in the soil is small larger samples should be used) was weighed into a casserol to which was added 25 cc of concentrated arsenic, free nitric acid and the mixture heated on a hot plate for 30 minutes. While still moderately hot there was added to this 10 cc of concentrated sulphuric acid and the whole heated for 30 minutes longer. The soil was taken up and thoroughly washed with hot distilled water, the filtrate evaporated to dryness, and heated until free from nitrates. The residue was treated with dilute arsenic free sulphuric acid to which was added 20 cc of stannous chloride solution 1cc of which contained one tenth of a gram of stannous chloride. This solution was slowly introduced into a Marsh apparatus, the glass tube through which the hydrogen was conducted being heated by means of an electric combustion furnace. The deposit of arsenic was carefully weighed on fine analytical balances. By this method very small quantities of arsenic can be accurately determined as is shown by the reported results.

THE EFFECT OF SODIUM MANURES ON THE PERCENTAGE OF SUGAR IN CERTAIN PLANTS

BURT L. HARTWELL AND P. H. WESSELS

Rhode Island State College, Kingston, R. I.

A field experiment was begun in 1894 at the Agricultural Experiment Station of the Rhode Island State College, with forty-eight sixtieth-acre plats, to determine the effect on plant growth of different relative applications of sodium and potassium when added in chlorids and carbonates to plats which were limed at two different rates. In no case had the soil been made permanently alkaline. Certain plats received so-called full rations of either sodium or potassium, or of both; others, one or more quarter rations of either sodium or potassium, in connection with the full ration of the other element; while still others received one or more quarter rations of each. In all cases these rations were accompanied by liberal applications of other manures, for the purpose of supplying optimum amounts of the nutrients which were not being specifically studied.

During each of the years 1902, 1903 and 1904, when the plats were in grass, the only top-dressing was 1200 pounds of tankage per acre. During the eight years prior to this period the usual average annual application of manures per acre was about as follows:

	Lbs.
Dried blood	980
Acid phosphate, or dissolved boneblack,	700
Undissolved rock phosphate,	400
Magnesium sulfate,	380
Sodium chlorid (if full ration),	250
Sodium carbonate (if full ration),	220
Potassium chlorid (if full ration),	420
Potassium carbonate (if full ration),	330

During the years 1907 to 1910, in which was undertaken the analytical work forming the basis for this paper, the average annual applications constituting the full rations of sodium and potassium salts per acre were less, namely:

	Lbs.
Sodium chlorid,	78
Sodium carbonate,	74
Potassium chlorid,	102
Potassium carbonate,	99

In case of equal rations, the potassium chlorid and carbonate supplied the same amount of potassium; and the sodium carbonate furnished the same neutralizing power as the latter, together with an amount of sodium equal to that in the sodium chlorid.

The field results, part of which have been recorded in the bulletins and annual reports of the Rhode Island Station have shown that, with certain crops, sodium salts increased the yield, especially when the potassium was somewhat deficient. The growth of cereals in solutions, under conditions where no potassium could be liberated, proved that sodium was directly beneficial when potassium was somewhat deficient.[1]

The effect upon the ash constituents and nitrogen having been determined already,[2] it seemed important to ascertain whether the advantage from the sodium was accompanied by undesirable changes in the sugar of the plants. The effect was studied principally in connection with globe mangel-wurzel beets, partly because they contain some reducing sugar. In 1908, onions were also analyzed for the same reason.

It was recognized at the outset that the amounts of certain constituents were subject to quite rapid variation, and precautions were therefore taken to analyze, under identical conditions, the samples which were used for special comparison. Generally the changes were limited to those which occurred during growth, but the analyses of the onions were made after the crop had been stored for a few months under like conditions. Considering collectively the four series of plats (chlorids and carbonates, limed once and three times), the addition of a full ration of sodium

---

[1] See especially Ann. Rpt. **21**, 243-285.

[2] Ann. Rpt. **19**, 186-316.

to a full ration of potassium did not affect in a uniform direction, either the size of this crop, or its composition, so far as the total and reducing sugars were concerned.

Analyses of mangel-wurzels from some of the plats were made each year from 1907 to 1910, inclusive, but only those of 1908 and 1909 will be considered now. The yields of this crop showed as a rule that even with a full ration of sodium, the quarter ration of potassium was not sufficient for maximum growth, and that in many cases the same was true of even a half ration of potassium. Likewise, taking into account the results of all the years, the yields of mangels were usually larger with a full ration of sodium than with a quarter ration, when these applications accompanied a quarter ration of potassium; which latter, as has been stated, was below optimum requirements. It is of interest to notice whether this extra amount of sodium had caused the increase in yield without depressing the percentage of sugar in the dry matter of the beets. In each year, 1908 and 1909, analyses were made from which five comparisons were possible with reference to these two applications of sodium. Seven of these ten comparisons showed that the percentage of total sugar was less where the additional sodium was applied, the entire average per cent. of total sugar, as invert, being 54.4; whereas, when only a quarter ration of sodium was used, it was 58.8.

Also in 1908 and 1909 a number of analyses of mangels were made, from which it was possible to observe the effect of adding a full sodium ration to a full potassium ration. Out of sixteen available comparisons, nine showed that the per cent. of total sugar was less when sodium was present, the entire average per cent. of sugar being 62.6 with the full rations of both sodium and potassium, and 65.2 with the full ration of potassium. Although the average was slightly less when the sodium was present, but very little significance should be attached to the fact, owing to the large minority of individual cases in which there was not a depression. It is of interest to note in this connection that in both years with all four series (chlorids and carbonates, limed once and three times), the addition of the full ration of sodium resulted in an increase of crop.

Comparisons of the percentages of reducing sugar in the mangels failed to show any differences of interest which could be correlated with the addition of the sodium salts.

The principal object in preparing this paper was to show, especially in the case of beets, whether the increase in yields which has resulted from applications of sodium salts was accompanied by a serious depression in the sugar content of the plant. In order to present in condensed form such results as bear particularly upon this question, Table I has been compiled to illustrate the larger yields which resulted from increasing the sodium in the manures, and Tables II and III to show the increase (+) or decrease (—) in the accompanying percentages of total and reducing sugar. In certain instances the percentage recorded for the beets of a given plat is the average of the determinations made on different dates, or in beets of different sizes.

TABLE I. Yields of beets showing the effect of an increase in sodium manures.
(The areas were not always the same in different years).

	Ration		Once-limed chlorids	Thrice-limed chlorids	Once-limed carbonates	Thrice-limed carbonates	Total percentage increase
	Sodium	Potassium					
Mangels, 1908	¼	¼	34	96	94	124	32.5
	1	¼	94	122	70	175	
Mangels, 1909	¼	¼	80	156	107	129	22.2
	1	¼	126	133	155	163	
Sugar Beets, 1907	½	½	42	63	40	64	6.7
	1	½	37	69	46	71	
Mangels, 1908	0	1	89	123	108	186	34.6
	1	1	121	168	180	212	
Mangels, 1909	0	1	147	187	201	222	26.4
	1	1	182	250	264	261	
Total percentage increase			42.9	18.7	30.0	21.7	

It may be seen by reference to Tables II and III that the *average* differences, with the different rations and series, indicate a tendency toward a depression in the percentage of both the total and reducing sugar, as a result of the addition of sodium. These differences, however, are usually within the limit of error, and furthermore are the resultants, in many cases, of *individual* increases, as well as decreases, in the content of sugar.

TABLE II. Compilation of percentages in dry matter of *total* sugar as invert, showing the effect of an addition of sodium manures.

	Ration		Once-limed chlorids	Thrice-limed chlorids	Once-limed carbonates	Thrice-limed carbonates	Average difference
	Sodium	Potassium					
Mangels, 1908	¼	¼	55.8	61.6	58.7	62.9	
	1	¼	61.5	64.7	48.7	49.7	
			+ 5.7	+ 3.1	— 10.0	— 13.2	— 3.6
Mangels, 1909	¼	¼		61.9	60.1	53.1	
	1	¼		51.7	58.9	54.5	
				— 10.2	— 1.2	+ 1.4	— 3.3
Sugar Beets, 1907	½	½	79.5	75.0	62.6	58.5	
	1	½	65.8	70.1	72.0	75.6	
			— 13.7	— 4.9	+ 9.4	+ 17.1	+ 2.0
Mangels, 1908	0	1	60.5	65.9	67.8	63.6	
	1	1	66.2	61.7	64.3	65.1	
			+ 5.7	— 4.2	— 3.5	+ 1.5	— 0.5
Mangels, 1909	0	1		70.7	63.8	61.1	
	1	1		61.0	62.8	56.8	
				— 9.7	— 1.0	— 4.3	— 5.0
Average difference			— 0.8	— 5.2	— 1.3	+ 0.5	

TABLE III. Compilation of percentages of *reducing* sugar in dry matter, showing effect of an addition of sodium manures.

	Ration		Once-limed chlorids	Thrice-limed chlorids	Once-limed carbonates	Thrice-limed carbonates	Average difference
	Sodium	Potassium					
Mangels, 1908,	¼	¼	17.9	11.1	9.9	6.7	
	1	¼	19.4	9.1	10.4	10.4	
			+1.5	— 2.0	+ 0.5	+ 3.7	+ 0.9
Mangels, 1909,	¼	¼		4.2	4.8	5.2	
	1	¼		3.7	4.9	4.7	
				— 0.5	+ 0.1	— 0.5	— 0.3
Mangels, 1908,	0	1	10.7	7.9	13.6	10.0	
	1	1	7.4	7.9	12.8	9.6	
			— 3.3	.0	— 0.8	— 0.4	— 1.1
Mangels, 1909,	0	1		4.6	6.0	6.1	
	1	1		3.0	5.2	3.9	
				— 1.6	— 0.8	— 2.2	— 1. 5
Average difference			— 0.9	— 1.0	— 0.3	+ 0.2	

A twenty-five per cent. increase in yield of beets has not been an unusual result of adding sodium manures; consequently, even if the *percentage* of sugar were slightly depressed, the *amount* produced would be much increased.

In field experiments it is of course impossible to know how much of the influence of sodium manuring upon the percentage of sugar is due to a direct, and how much to an indirect, effect. Furthermore, if plants contain a constant amount of sugar, an increase in the amount of other constituents will of course lower the *percentage* of the sugar. For example, an addition of sodium in the manures usually increased the ash-content in the plant, due in part at least to an increase in the amount of sodium and phosphorus. A possible decrease in the percentage of sugar may not mean, therefore, that the metabolism of sugar has been interfered with, but simply that there has been an increase in the relative amount of other constituents.

A detailed study was made of the relative effects of the chlorid and carbonate of sodium, as well as of the different amounts of lime, on the content of sugar; but, on the whole, the differences do not warrant a discussion at this time.

Abstract

CALCIUM ARSENITE AS AN INSECTICIDE

By E. B. Holland and J. C. Reed

Amherst, Mass.

The preparation, composition, physical characteristics and chemical behavior of this arsenical are considered from the standpoint of its possible use as an insecticide.

FIELD TESTS WITH FERTILIZERS

H. A. Huston, A.M., A.C.

New York City

Our Agricultural Experiment Stations and other authorities are constantly called upon for advice in regard to the matter of increasing the productiveness of our soils. Such requests often call for a soil analysis as a basis for any suggestion regarding the use of additional plant food. The careful official suggests that better information may be derived from field tests with the plant food and often outlines such tests. In other cases, a certain fertilizer formula is recommended which itself may be the result of field tests already conducted. While no one doubts the sincerity of the officials offering the suggestions it often happens that the advice given merely affords temporary relief rather than a permanent solution of the difficulty. One reason for this is that we often overlook the fact that in the matter of increasing the productiveness of land there are two distinct stages—one, the correction of a single conspicuous physical or chemical difficulty, the other, the maintenance of normal conditions after they have been once established.

Most of the field experiments with fertilizers in this country have been made and interpreted with reference to the first stage, that is, finding out the present difficulty or deficiency and suggesting a remedy for the most conspicuous fault. This tendency is increased by the fact that most of the fertilizer field tests are so conducted that they are almost certain to be misinterpreted or not to admit of proper interpretation. Many of the common fertilizer formulas are based upon field experiments conducted under these faulty conditions.

In conducting fertilizer experiments it is customary to apply the three plant foods to one plat and omit one from each plat in turn and thus determine, or seek to determine, the effect of the element omitted. Two systems are commonly used—in one a certain yield per acre is assumed and enough of each plant food is added to supply the requirements of this yield. In the second, a certain amount of an arbitrary formula is used as a starting point. Experiments of this class are sometimes more extended, including different amounts per acre and also supplementing the formula by doubling each element in turn.

Some experiments started under the first system a quarter of a century ago are in progress but in most cases it has been necessary to reduce the amount of nitrogen. The present tendency is to follow the second system.

Whatever system is used precautions should be taken to so arrange details that the results may be as free as possible from error and may permit of prompt and correct interpretation.

For this reason it is necessary to select materials that contain but a single plant food and that are as free as possible from other substances which may exert any indirect fertilizer effect. This point has been very commonly overlooked. One tendency has been to select materials commonly used and readily obtainable rather than those that would yield accurate results.

In these experiments the nitrogen is usually derived from nitrate of soda, the phosphoric acid from acid phosphate and the potash from muriate or sulfate. Both nitrate of soda and ordinary acid phosphate contain substances which by reacting with the zeolites and other compounds of the soil, produce such pronounced indirect effects as to render them quite unsuitable for such experiments, notwithstanding their high value for general fertilizer purposes. The soda in 100 pounds of nitrate of soda is capable of releasing 55 pounds of potash from zeolites and the gypsum in 100 pounds of an ordinary acid phosphate is capable of releasing 18 pounds of potash.

With these facts before us let us see what will happen in an experiment to determine the most profitable fertilizer for cotton, the crop to which most of the fertilizer used in the United States is applied.

If the experiment is planned for 1500 pounds per acre of seed cotton and the older plan of supplying all of the plant food is adopted, we should require 38 pounds phosphoric acid, 61 pounds potash and 97 pounds nitrogen. Using the customary ingredients the complete fertilizer plot would receive per acre,

300 lbs. Acid phosphate
120 lbs. Sulfate of Potash
600 lbs. Nitrate of Soda

The gypsum in 300 pounds of acid phosphate is capable of releasing 54 pounds of actual potash and the soda in 600 pounds of nitrate is capable of releasing 330 pounds of actual potash. Expressed in terms of Sulfate of Potash this is equivalent to the application of 768 pounds Sulfate per acre while the assumed crop only requires 120 pounds. It is not surprising that where these materials are used in experimenting there should be very frequent instances where the plot with nitrogen and phosphoric acid should give quite as good yields as that receiving all three elements, for the plot without potash has received material capable of releasing more than six times as much potash as the assumed crop requires.

If we take a case where the other system is used the effect is the same in kind, although somewhat different in degree. Suppose the experiment is started on the basis of 500 pounds per acre of the so-called " basal " fertilizer of the Cotton States, containing phosphoric acid 10 per cent., ammonia 2 per cent., potash 2 per cent. The complete fertilizer plot would require per acre,

350 lbs. Acid Phosphate
20 lbs. Sulfate of Potash
55 lbs. Nitrate of Soda

The combined potash releasing power of the phosphate and nitrate would be 93 pounds per acre or 1½ times as much as the crop requirements. In this case we can express the matter in a somewhat different way. If the potash capable of being released by the phosphate and the nitrate be included in the fertilizer formula we have on the K. P. N. plot the equivalent of 500 pounds of fertilizer containing

Phosphoric acid	10 per cent.
Ammonia	2 per cent.
Potash	20.6 per cent.

and on the P. N. plot the equivalent of 500 pounds of a fertilizer containing

Phosphoric Acid	10 per cent.
Ammonia	2 per cent.
Potash	18.6 per cent.

As both formulas provide much more potash than the assumed crop requires it is not strange that in many cases little or no difference is found between the yield of the two plots and that the experimenter concludes that potash is not necessary.

Such results are likely to be secured on any soil with a relatively high fixing power such as that of clay and clay loam unless care is taken to use proper materials in experimenting. On sandy soil and on clay and loam where much acid phosphate has been used there is less to be feared from this source of error since sand has a low fixing power and little zeolithic potash and in the course of five or 10 years heavy applications of acid phosphate with the accompanying gypsum will remove from most soils much of the zeolithic potash. When this happens, the evidence of potash starvation such as weak straw, lack of resistance to fungous diseases as well as reduced sugar and starch formation appear but their cause is not recognized because the high total potash on such soils is too frequently considered as being available while, in fact, the evidence indicates that when the zeolithic potash is removed the feldspathic potash, even under the better systems of soil tillage becomes available too slowly to provide for the potash requirements of paying crops. Moreover, when the zeolithic potash has been removed the evidence seems to indicate that no inconsiderable amount of it must be replaced before the crop can utilize the soluble potash salts which may be applied. In this contest between the fixing power of the soil and the feeding power of the plant, such a soil seems to fix small quantities of potash so firmly that it becomes unavailable to the plant. This may explain why small applications of potash to soils long treated with acid phosphate sometimes give no returns, while large applications are very profitable. Such cases are common in sections where the principal fertilization of sugar beets has consisted of acid phosphate and nitrate of soda.

So far as the making of field experiments or plat experiments is concerned, it is not difficult to use materials that are practically free from products giving indirect effects. As a source of phosphoric acid precipitated calcium phosphate can be used taking care to wash out the free lime which it sometimes contains and as a source of nitrogen blood can be used. Both materials can easily be obtained at a cost per unit not materially different from the materials ordinarily used.

The selection of suitable materials would greatly increase the accuracy of field and plat experiments as well as permit reliable conclusions to be made more promptly. For example—on the Rothamsted wheat plots the mixed minerals and nitrate of soda had a potash releasing capacity of 400 pounds of actual potash per acre annually, while the crop required about 40 pounds. One record shows that the gypsum continued to release potash about 10 years while sulfate of magnesia and the sulfate and nitrate of soda continued to release potash for about 30 years. This soil however, is much superior to the average since it has produced for over 65 consecutive years without any fertilizer or manure, yields of wheat in excess of the American average yield including all rotations, fertilizing and manuring.

In planning field and plat tests on certain types of soil, the experimenter might gain much valuable preliminary information if he would test the soil which he intends to investigate and determine how much potash is capable of being replaced by gypsum and how much by nitrate or sulfate of soda as well as how much lime can be displaced by muriate of potash. The determination of the fixing power of the soil for phosphoric acid would also be most useful in indicating whether a large initial application of phosphate should be made or whether only the actual requirements of the assumed crop should be supplied. Had our experimenters a quarter of a century ago observed some of the simple precautions suggested above, our soil fertility would have been conserved, our fertilizer practice would have been more rational and more profitable to the farmer and the advice and suggestions of our educational authorities would be more in harmony with what is found to be profitable in practical agriculture.

So far as applied chemistry is concerned it must be quite evident that had proper methods and materials been used in experimental work the fertilizer industry would have far surpassed its present volume, its products would have been used to better advantage by the farmer, and it could have extended to sections of the country where at present the agricultural authorities are too apt to answer inquiries by saying that " expensive " fertilizers are unnecessary.

If our soil fertility is to be conserved our soil tests should be so conducted as to give reliable results and to enable us to plan a system of maintaining productivity in addition to merely correcting the greatest present deficiency.

SUR L'EMPLOI DU ZINC COMME ENGRAIS CATALYTIQUE

PAR M. M. JAVILLIER

Paris, France

Les premières expériences que j'ai effectuées sur l'emploi du zinc comme engrais catalytique, expériences exposées au Congrès de Londres en 1909, avaient été exécutées dans des conditions très éloignées de celles de la grande culture; elles n'autorisaient pas à préjuger des résultats que l'on pourrait obtenir dans la pratique agricole. Les essais tentés en 1910 et 1911 se rapprochent plus des conditions pratiques; certains même ont été exécutés dans de grandes exploitations agricoles.

Les expériences ont porté sur le blé, le maïs, l'avoine, le lupin et le pois. Les doses d'engrais catalytique employées ont varié de 1 à 10 kilog. de sulfate de zinc cristallisé à l'hectare. Les sols recevaient simultanément les engrais généraux appropriés. Des résultats unanimement favorables ont été obtenus avec le maïs, puisque les récoltes de la plante, faites avant fructification, ont toujours accusé des accroissements de poids sec atteignant 18 et 25% dans les meilleurs cas, et encore 5% dans les moins bons. Avec les autres plantes les résultats ont été très irréguliers: des doses de 1 Kgr. de sulfate de zinc à l'hectare pour le blé; de 2 et 5 kilog. pour le lupin ont exercé une action favorable sur les rendements en poids sec, mais ces améliorations n'ont pas été assez constantes pour qu'il nous soit permis d'énoncer à ce sujet des conclusions définitives. Avec l'avoine, dans le terrain sablonneux de la Beauce et pendant la saison de 1911 où la température élevée et la sécheresse ont été vraiment exceptionnelles, le résultats n'ont pas été favorables.

Les observations des deux dernières années témoignent de l'importance qu'il y a, en ce qui concerne le zinc, à se limiter à des doses extrêmenent petites de cet élément; elles montrent aussi qu'il importe de l'expérimenter sur chacune des espèces individuellement et de ne pas formuler de conclusion générale, l'espèce végétale, la composition du sol arable, la dose de l'élément catalytique, la nature des engrais associés à celui-ci, exerçant une influence sur l'orientation des résultats.

Ces études pratiques n'ont pas empêché la question de se développer par des études de laboratoire. C'est ainsi que nous avons, avec le Professeur Gabriel Bertrand, développé la notion de l'action cumulative des éléments catalytiques. C'est ainsi que, personnellement, nous avons cherché à élucider le mode d'intervention du zinc dans la végétation par de nouvelles recherches sur l'*Aspergillus niger*, recherches qui ont mis en évidence l'influence de cet élément sur les sécrétions diastasiques de la plante, sur la consommation par celle-çi de ses aliments hydro-carbonés, azotés, et minéraux,[1] et sur sa composition élémentaire. Nous avons pu enfin manifester l'action du zinc à des dilutions supérieures à celles que nous avions jusqu'içi expérimentées (le cinq cent millionnième et même le milliardième), et élever le coefficient d'utilité du zinc jusqu'au chiffre de 500.000.

Ces expériences confirment l'intérêt de l'étude théorique du zinc comme élément catalytique et l'importance des recherches relatives à son emploi comme engrais complémentaire.

---

[1] Voir le mémoire présenté dans la Section VIII D.

NORMAL AND ABNORMAL CONSTITUENTS OF SOIL ORGANIC MATTER[1]

BY ELBERT C. LATHROP

(Contribution from Laboratory of Soil Fertility Investigations.)

With the increasing number of definite organic compounds isolated from soils,[2] and the knowledge of their chemical properties and their various effects on plant life, several questions naturally arise. Are these compounds peculiar to the soils from which they are first isolated, or, are they constituents common to most soils? Do they appear in the same soil under all conditions, or, are they the result of special treatment of crop practices? Are they common constituents of fertile soils, or, are they found mainly or entirely in infertile soils? It is at once obvious that the solution of such questions is not only of scientific but also of practical importance. In a word such investigations lead to an understanding of the normal and the abnormal of soil organic matter.

The compounds already isolated from soil organic matter cover fairly well the principal classes of compounds encountered in other lines of biochemistry, and the knowledge of their chemical properties, their relationships, origin, and processes of change, acquired in such other lines can be applied directly to an understanding of the biochemistry of soils and the constitution of soil organic matter. In regard to the effects of these compounds on plant growth they fall into three classes: (1) Those which on account of their insolubility or for other reasons are without action of any sort, (2) those which are either slightly or decidedly detrimental to plant growth, of which dihydroxystearic acid has

---

[1] Published by permission of the Secretary of Agriculture.

[2] In this connection see: "The Isolation of harmful organic substances from soils" by Oswald Schreiner and Edmund C. Shorey, Bul. 53, Bureau of Soils, U. S. Dept. of Agric. (1909); "Some effects of a harmful organic soil constituent," by Oswald Schreiner and J. J. Skinner, Bul. 70, ibid.

been most fully studied, and (3) those which are more or less beneficial to plant growth. This class comprises a large number and among them are found the purine bases, creatinine, etc.

With a view to determining the normal and abnormal constituents of soil organic matter a rather large number of samples of soils from various parts of the United States has been examined for known organic constituents and the results are summarized in this paper.

Pentosans have been isolated and identified from all the soils examined, and it seems that they are a constant constituent of the soil organic matter of all soils. The exact nature of these pentosans has not been established, with the exception of two cases, when by hydrolysis the pentose sugar xylose was isolated, showing the pentosan, xylan, to be present. It does not necessarily follow, however, that all the pentosan in even those two soils is xylan.

Pentose sugars were found in all the soils examined for them; the examination was made by suitable qualitive methods and the sugars as such were not identified. Pentose sugars or pentose containing complexes, not pentosans seem to be a normal constituent of all soils and probably arise either from the hydrolysis of pentosans, or the decomposition of nucleo-proteids.

Histidine is a primary decomposition product of protein material. It has been isolated from 19 of the 26 soils examined for it, and the indications are strong that this hexone base is a common and normal constituent of soils, and also that the protein cleavage in the soil is similar to that brought about in the laboratory by chemical and other means. That this compound remains in the soil during and after the decomposition of plant residues, etc., may be attributed to the fact that it is more resistant to change than other compounds of similar nature and origin.

(1910); "Chemical nature of soil organic matter," by Oswald Schreiner and Edmund C. Shorey, Bul. 74, ibid. (1910); "Examination of soils for organic constituents, Especially Dihydroxystearic Acid," by Oswald Schreiner and Elbert C. Lathrop, Bul. 80, ibid. (1911); "A beneficial constituent of soils; Creatinine," by Oswald Schreiner, Edmund C. Shorey, M. X. Sullivan, and J. J. Skinner, Bul. 83, ibid. (1911); "Organic Soil Constituents" by Edmund C. Shorey, Bul. 88, ibid. (1912).

Arginine, another hexone base, closely allied to histidine, and also a common primary cleavage product of protein material, has been found in but two soils. This would point to the fact that it is rather an unusual constituent, probably being formed in the soil, but not persisting for any time, being changed rapidly into other compounds, or entering into other combinations.

Cytosine, a nitrogenous compound derived from the breaking down of nucleo-proteids, and from nucleic acids existing in plant cells, has been found in 10 of the 23 soils examined for it, and it can therefore be considered to be a fairly normal soil constituent. The fact of its occurrence in so many soils proves conclusively that the breaking down of such constant complex plant constituents as nucleic acid takes the same course in the soil, as is attained by the direct action of chemical agents outside of the soil.

Creatinine is of special interest, because it is a nitrogenous compound which is decidedly beneficial to plant growth. Its occurrence in various farm crops has been demonstrated and reported. While only a small number of samples of soils have been examined for this compound, still it has been found in considerably over half of the soils examined for it, and it appears to be a frequently occurring compound. The question of its wide occurrence and its relation especially with fertile soils has not been as yet determined, but should be of extreme interest.

Xanthine and hypoxanthine, both more or less beneficial compounds, exist in many plants as such, and like cytosine arise from the decomposition of nucleo-proteids, and also from two closely allied purine bases, guanine and adenine. Five of twenty-four soils contained xanthine and ten out of twenty-five soils contained hypoxanthine. Some of the soils contained xanthine only and some hypoxanthine only, and four of the soils contained both. It is thus shown that these purine bases are normal soil constituents and are likely to be encountered in any soil. The fact that hypoxanthine is more resistant to bacterial action may account for its more frequent occurrence in the soils examined.

Adenine, another purine base, has been found in but two soils and like arginine, it may be considered to be an abnormal soil constituent because of its infrequent occurrence. It seems likely that it is formed in the same manner as the other purine bases, but is quickly changed, by bacterial and other action perhaps into hypoxanthine.

Dihydroxystearic acid is of special importance because of its known harmful action on growing plants. A very large number of soils have been examined for this constituent. It was found without exception in all the soils which have a known record for infertility; in soils which were classed as poor soils, without any definite record for infertility, but which were not as good as soils in adjoining fields, it was found in 33 per cent. of the samples; and in good soils it was found but twice, one of these soils was classed as good, but neither a better nor poorer sample of the same soil type was at hand, so that no means of determining the relative fertility of this particular sample was available. In the other case a poor sample from an adjoining field was examined. This soil gave a large yield of the compound, while the good soil showed but traces. The good soil had been so treated that the dihydroxystearic acid present should have been destroyed, which almost seems to have been accomplished. This compound on account of its detrimental influence on crop growth, and its close association with infertile soils must be classed as abnormal.

Picoline carboxylic acid, a nitrogenous compound with a pyridine grouping, has been found but seldom, but it is also detrimental to plant growth and may be classed as abnormal for this reason.

Although agroceric acid, lignoceric acid, paraffinic acid and α mono-hydroxystearic acid, as well as agrosterol, phytosterol and hentriacontane have been found only once or twice, no general statement covering their frequency or infrequency of occurrence is warranted. This is due to the fact that the amount of material in the course of procedure of examination was generally too small for a satisfactory examination for them. It may be stated that these compounds are probably inert as regards plant growth.

The results may be summed up as follows:—pentosans, pentose sugars, histidine, xanthine, hypoxanthine, cytosine and possibly creatinine may be considered to be normal soil constituents.

Arginine and adenine on account of their infrequent occurrence and their rapid disappearance, and dihydroxystearic acid and picoline carboxylic acid on account of their detrimental action on plant growth, and the striking relation of the former to infertility, must be classed as abnormal soil constituents.

Regarding agroceric acid, lignoceric acid, paraffinic acid, and ∝ mono-hydroxystearic acid, agrosterol, phytosterol and hentriacontane no statement is warranted.

THE RELATIVE EFFECTS ON PLANT GROWTH OF (A) SODIUM CARBONATE AND (B) IMPERVIOUSNESS IN SOILS

By Dr. J. Walter Leather, Ph.D., F. I. C.

Pusa, Bengal, India

During the examination recently of some sterile alkali land in the United Provinces of Agra and Oudh, India, the question was raised in how far the infertility was due to the impervious character of the land apart from the Sodium carbonate. The soil contained .063% Na_2CO_3, apart from $NaHCO_3$, which amount is probably always sufficient to render land practically sterile. But in addition, supposing no normal carbonate had been present, the rate at which water can move through such soils is so low, that it is legitimate to ask whether plants could mature properly, for it is to be recollected that all water assimilated by the plant has to move *some* distance through the soil to the root.

The above question was put to the following tests by means of pot cultures.

(a) In one series of cultivation jars the alkali soil was treated with amounts of gypsum, sufficient to neutralise the following proportions of the Sodium carbonate, namely one-half, three-fourths and five-sixths. The Na_2CO_3 was thus reduced from .06% to .03%, .015% and .01%. Such partial treatment with gypsum does not materially alter the physical state of the soil, and hence in this series the plants were exposed to the influence of the imperfect physical state plus a small amount of alkali; experience has generally shown that .01% of Na_2CO_3 is not sufficient by itself to render soils entirely sterile though it would usually affect growth.

(b) In a second series of jars, the soil was rendered permeable to water by the addition of sodium chloride in quantities .25%, .1%, .05% and .025%. Thus in this series the alkali would remain unchanged, whilst the clay was in the first two coagulated and the soil would be freely permeable to water.

(c) In a third series the effect of sodium chloride on plants was determined by adding the salt in the above-mentioned proportions to a good soil. Considering the last series first, it was found that the highest proportion of salt, namely .25% was too high and most plants could not develop in it; but the lesser proportions, including .1%, were not seriously prejudicial, and the lowest proportion, namely .025% was generally beneficial.

A large number of plants were sown in the soils, namely: Sorghum vulg., Pennisetum typhoid., Phas. mungo, P. aconit., Paspalum scrobiculatum, Cyamopsis psoral., Dolichos lab., Oriza sat., Triticum sat., Hordeum vulg., Avena sat., Lens esculanta, Lathyrus sat., Cicer arietinum, Pisum avense, Glycine hispida, Braccica camp., Linum usitatissimum, Carthamus tinct. The result of the tests may be thus stated:—

(a) Where the sodium carbonate was partially neutralised with gypsum, 33% of the seeds germinated and 16% matured, of which, varieties of rice were the most successful and some wheats did fairly well.

(b) Where the soil was rendered permeable to water by the addition of sodium chloride 12% of the seeds germinated but none matured.

The experiment thus showed that the Sodium carbonate has a considerably greater effect on plants than the defective physical state of black alkali soil, but that the latter feature exerts a material effect apart from the carbonate.

THE DETERMINATION OF THE PERMEABILITY OF SOILS TO WATER

By J. Walter Leather, Ph.D., F. I. C.,

Pusa, Bengal, India

By permeability of soils to water is meant the rate at which water can flow through a short column of soil when a constant supply is maintained on the surface.

Some of the alkali lands in India are highly impervious to water and in order to measure this property in comparison with ordinary soils, a special machine has been designed to fill soils uniformly into metal cylinders; measuring 3″ high by 2″ diameter, and provided with a false bottom of brass wire gauze. Water is then poured on the surface and, after it has commenced to flow from the lower surface, a measurement of the rate of percolation is made; the hydrostatic " head " being at the same time maintained within certain limits.

A description of the machine is given in following pages.

The method has been found extremely useful as is illustrated by the following data:

Depth	Good soil No. 60 cm. per hour	No. 62 cm. per hour	No. 66 cm. per hour	Black alkali No. 27 cm. per hour
0″-6″	.16	.12	.12	.034
6″-1′0″	.49	.16	.20	.004
1′0″-1′6″	.35	.06	.01	.034
1′6″-2′0″	.20	.08	.01	.006
2′0″-2′6″	.25	.14	.02	.006
2′6″-3′0″	.69	.28	.05	.002
3′0″-3′6″	.89	.34	.03	.014
3′6″-4′0″	.54	.45	.16	.004

No. 60 is permeable to water throughout.

No. 27 is impervious to water throughout.

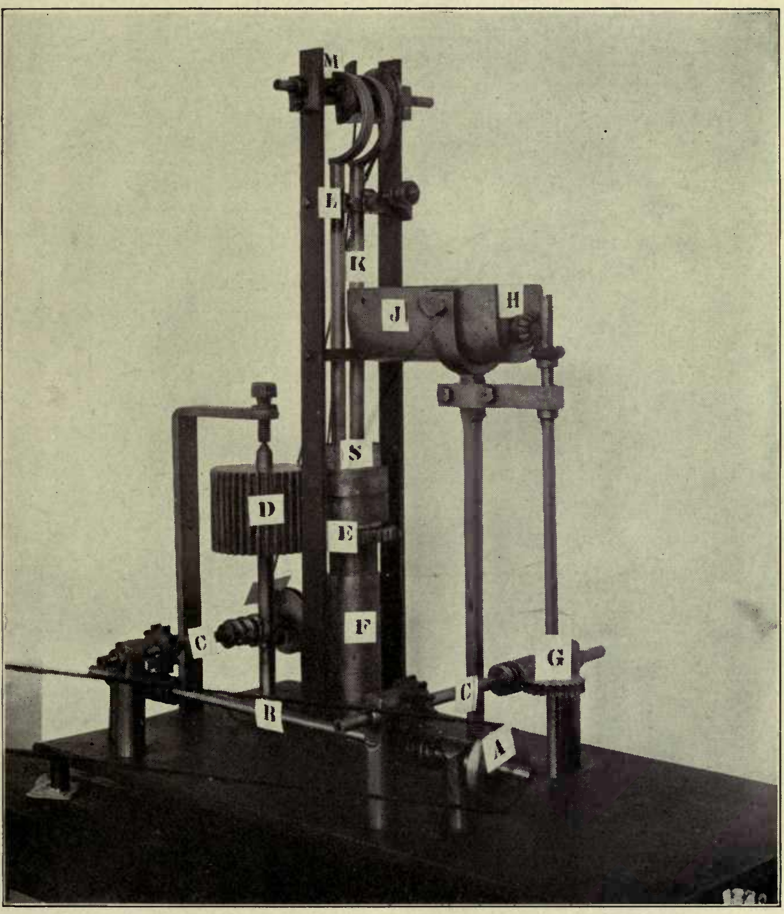
No. 62 is somewhat impervious in the 2nd foot.

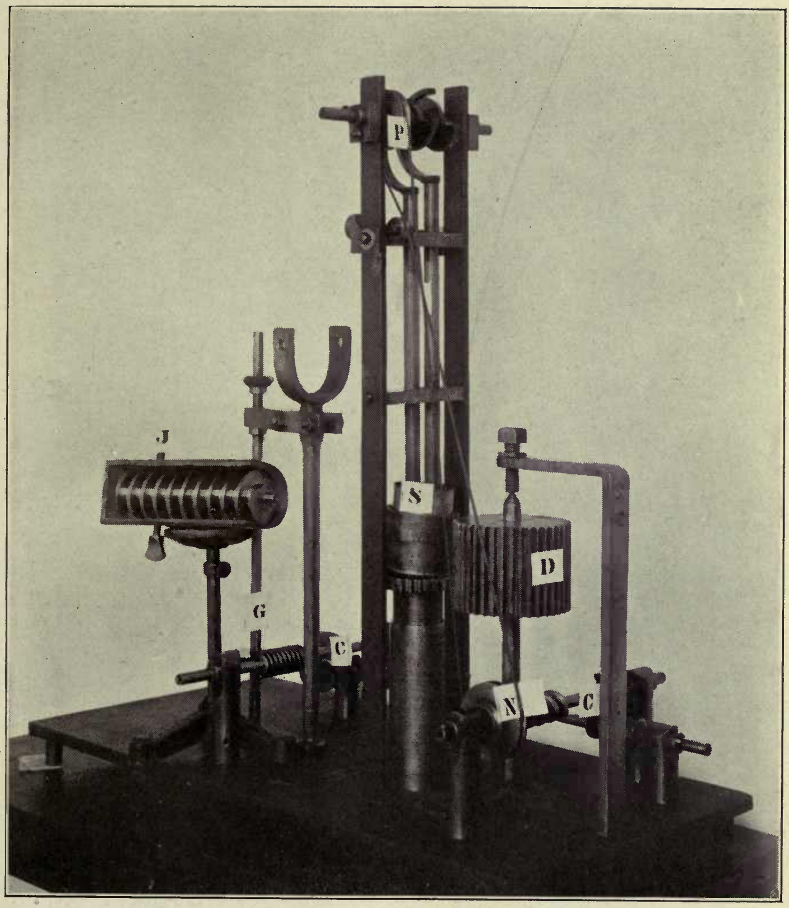
No. 66 is good at the surface, but is impervious below this down to 3′6″.

The soil packing machine is illustrated by the accompanying two photographs, taken from opposite sides of it. It will be seen that there are two rods marked K each of which is surmounted by a semicircular hook. The rods are raised by the " cut-away " cams M, and each falls by its own weight when the "releasing point " of the cam passes the end of the hook. These rods have flat faces and fall on the soil which is in the metal cylinder marked S. Motion is given to the cams through the pulleys P and N which are actuated by the pulley and gearing marked A, B, C. The beating rods, hereafter styled the " beaters," act only in one fixed plane and in order that all portions of the soil in the cylinder S may be uniformly beaten, the cylinder is attached (four miniature legs fit into holes in the bed E) to a bed E which is caused to revolve by the toothed gearing E, D, which is actuated from pulley A through B, C. As the portion of soil which is first placed in the cylinder becomes compressed, provision must be made for space for further additions. This space is secured by the vertical motion of the bed E, which, as it revolves screws downwards into the column F. The other parts of the machine marked G. H. J. in the photograph were fitted to provide for automatic filling, but have not proved altogether successful.

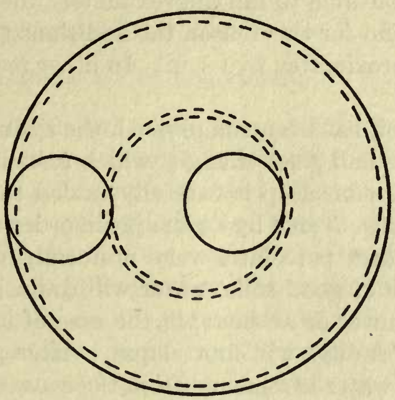
The machine thus provides three motions; (1) the revolution of the soil surface under the beaters, (2) the alternate rise and fall of the beaters, and (3) the descent of the cylinder to make room for additions of soil under the beaters.

The beaters work concentrically; one beats over a ring the outer edge of which is approximately one m.m. from the side of the metal cylinder; the other beats over a ring which includes the centre of the earth surface in its inner edge; the inner edge of the outer ring and the outer edge of the inner ring overlap by about one m.m. These two rings are indicated by dotted circles, and the position of the two beaters and the metal cylinder by the


M
L
K
J
H
D
S
E
F
C
G
C
B
A


P
J
S
D
G
C
N
C

closed circles in the marginal drawing. Thus every portion of the soil surface is uniformly beaten. Since the mean length of the track followed by the outer beater is approximately twice



that of the inner beater, the former is actuated by a double cam, and it hence falls twice as frequently as the inner beater. The gearing is so arranged that the mean distance travelled by the soil surface between each stroke of the beaters, is approximately one-half the diameter of a beater, and hence every part of the soil surface receives an average of two strokes of each beater during each revolution of the soil cylinder.

The following is the mode of using the apparatus. To 100 grms. of the air-dry soil which has been passed through a sieve of one m.m. mesh is added a sufficient quantity of water to render it very slightly moist. This water is worked into the soil carefully by hand, all lumps being rubbed down.

The machine will have been already prepared in the following manner. The tin cylinder with its wire gauze bottom is placed on the bed E together with the rather heavy iron ring (see photograph, employed to make the cylinder more rigid) and the bed E screwed upwards until the beaters have been raised to 1 c.m. below the " cut-away " of the cam. About 10 grms. of the soil is transferred to the cylinder and the machine set in motion by the engine (this is not shown; small hot air engine of $\frac{1}{20}$ H.P. is sufficient to work it). So soon as the first portion of soil has been compressed and the beaters fall 1 c.m. about 3 or 4 grms. more soil is added, and such small additions of the soil are made until the whole has been introduced. It is important that the beaters should continue to fall approximately the same distance on to the earth and for this reason the additions are made whenever the fall approximates to 1 c.m. In other respects the process is automatic.

After all the soil has been compressed, the cylinder is removed and placed on a small glass triangle, which rests in a flat saucer. Water equal to 2 c.m. deep is carefully added to the upper surface, and the whole covered by a glass jar in order to reduce evaporation. The water percolates very uniformly throughout the soil. In the case of good soils, water will drain into the saucer within a few minutes or an hour; in the case of impervious *usar* soil one or several days will first elapse. After percolation has commenced, the water is removed from the saucer, and sufficient fresh water is added to the surface to make it 2 c.m. deep. The time is noted and after about one-half of the water has disappeared from the surface the time is again noted and the volume which has percolated is recorded. This is then calculated to c.m. deep in respect of the soil surface or cross section of the cylinder, and this divided by the time, gives the rate in c.m. per unit time. The unit time adopted has been one hour. The percolating water is always slightly muddy at first because it washes out a part of the soil which was beaten into the gauze bottom of the cylinder. But thereafter the water percolates quite clear, excepting in the case of some fine sandy soils, through which the rate of percolation is very high and this would not occur if the wire gauze were sufficiently fine.

EXPERIMENTS WITH REINOCULATION OF STEAMED SOILS

T. Lyttleton Lyon and James A. Bizzell

Cornell University, Ithaca, N. Y.

The writers contributed to the Seventh International Congress of Applied Chemistry a paper on the composition of the water soluble extract of soils steamed under pressure.[1] In this article some reference was made to steamed soils that had been inoculated with untreated soil. One result of this treatment was found to be a marked change in plant growth on the inoculated soil as compared with that on the uninoculated soil. Plants on the inoculated soil made a more rapid growth at first, but were gradually overtaken and exceeded by plants on the uninoculated soil, so that at the time of complete maturity, which in this case was about seven months after planting, the production of dry matter on the uninoculated soil was larger. Similar results have been obtained by other investigators working with partially sterilized soils, and as other experiments with sterilized soils have a direct bearing on these results a brief résumé of the work in this field since our last paper was written will not be out of place.

Pfeiffer, Frank, Friedlander and Ehrenberg[2] showed that the effect of steam sterilization is to increase nitrogen fixation.

Lemmermann and Fischer[3] reinoculated sterilized soil with fresh soil of the same kind. They found that the processes of neither ammonification nor nitrification went on so rapidly in sterilized soil reinoculated as in fresh soil.

---

[1] Lyon, T. Lyttleton and Bizzell, James A. Changes produced in soils by subjecting them to steam under pressure. Seventh International Congress of Applied Chemistry, Section VII, pp. 19-31.

[2] Pfeiffer, Frank, Friedlander and Ehrenberg. Stickstoff Haushalt des Ackerbondens. Mitt. d. Landw. Inst. d. Koniglichen Universitat Breslau, Bd. 4 (1909), S. 773-779.

[3] Lemmermann and Fischer, Bacteriologish-chemishe Untersuchungen, Landw. Jahr. 6. Bd. 38 (1909) S. 319.

Pickering[1] heated soils to temperatures below 100° C. and also above 100° C. He concludes that toxins are formed at temperatures over 100° C. but not at lower temperatures and that the subsequent increase in solids is not accompanied by the formation of toxins. " This increase in soluble matter, due to the formation of a non-toxic substance, is preceded by a preliminary diminution of soluble matter, similar to the diminution of toxic matter occurring continuously in the more highly heated soils; such toxic matter, therefore, appears to be present in all soils, whether heated or not, though in the latter case it is present in such small quantities that it soon becomes completely oxidized."

Pickering[2] also grew plants of different kinds on heated soil. He concludes that different species of plants vary greatly in their susceptibility to toxins and suggests that this may throw light on the poor growth which trees sometimes make when grass grows under them.

Russell and Hutchinson[3] heated soils to 98° C. and also treated them with toluene. They found that following these treatments ammonification was increased and ammonia accumulated in the soil. Inoculation of partially sterilized soil with fresh soil caused a decreased plant growth as compared with the uninoculated heated soil. They conclude that the organisms concerned with ammonification are not injured by heating to 98° C., or by toluene, but that such treatment destroys organisms which are inimical to the development of the ammonifying bacteria.

Pfeiffer, Guttmann and Thiel[4] confirmed the previous conclusions of Pfeiffer and others that soils steamed for two hours at three atmospheres pressure fixed an appreciable quantity of nitrogen during one summer. Their figures indicate that an

---

[1] Pickering, S. U. Changes occurring in heated soils. Jour. Agr. Sci., Vol. 3 (1910), pp. 258-276.

[2] Pickering, S. U. Plant growth in heated soils. Jour. Agr. Sci., Vol. 3, pp. 277-284.

[3] Russell, E. J. and Hutchinson, H. B. The effect of partial sterilization of soil on the production of plant food. Jour. Agi. Sci., Vol. 3 (1909), pp. 111-144.

[4] Pfeiffer, Guttmann and Thiel. Der Stickstoffhaushalt des Ackerbodens. Mitt. d. Landw. Institute d. Kg. Universitat, Breslau, Bd. 5, S. 657.

amount of nitrogen corresponding to one-tenth of the quantity in the soil was fixed during this period.

Laidlaw and Price[1] give no detailed results or description of their experiments, but say that (1) the new bacterial flora in partially sterilized soils, being more active decomposing agents than the original ones, cause an increased production of ammonia; (2) the large organisms being killed off by the treatment serve as food for the new bacterial flora.

Fred[2] in a study of the effect of an inoculation of cultures of *Bacillus denitrificans* on soils with and without addition of sodium nitrate, found that in every case in which carbon bisulfide was used the growth and yield of crop were much superior to those in the corresponding pots not treated. He considers that there was no lack of available plant food and other favorable conditions for growth and hence that the better growth on the soil treated with carbon bisulfide was due to the direct stimulating action of that substance on the plant, and not through soil improvement.

Greig-Smith[3] states that when disinfectants such as carbon bisulfide, chloroform, ether, and the like are applied to soils they not only kill the less resistant bacteria but also dissolve a substance (" agricere ") and carry it to the surface of the soil, thereby removing the waterproofing from the soil particles and thus enabling the surviving bacteria to obtain a greater food supply. He holds that heat destroys the toxins and the less resistant bacteria, thus permitting the more resistant forms to multiply very rapidly, due to the absence of the bacteriotoxins.

Fletcher[4] grew plants in a nutrient solution until he considered it to have been made toxic by plant excreta. He then steamed it at a pressure of 150 pounds for two hours. There were thrown

---

[1] Laidlaw and Price. Sterilization of soils. Jour. Dept. Agr. Victoria, Vol. 8, Part 6, pp. 365-368.

[2] Fred, E. B. Effect of fresh and well-rotted manure on plant growth. Va. Agr. Expr. Sta. Ann. Rept. 1909-10, pp. 142-159.

[3] Greig-Smith. The bacteriotoxins and the " agricere " of soils. Centbl. Bakt. II Abt., Bd. 30 (1911), S. 154.

[4] Fletcher, F. Effect of previous heating of the soil on the growth of plants and the germination of seeds. Cairo Scientific Journal, Vol. 4, No. 43, pp. 81-86.

down plates of an organic substance which did not dissolve on removal of pressure. This substance he considers the toxic excreta. He contends that heating soils does not produce toxins which delay germination of seeds, but that this delay is caused by decreased imbibition of water from the strong solution in heated soils. He immersed seeds in heated and unheated soils and in extracts of the same soils and found that at the expiration of eleven hours and forty-seven hours respectively the seeds in the unheated media had absorbed a greater quantity of water.

THE PROBLEM STUDIED IN THIS INVESTIGATION

That the formation of toxic material during the process of steaming is a factor in the retarded early growth of plants on steamed soils is evidenced by numerous investigations. That this injurious action may be, at least partially, overcome by oxidation has likewise been demonstrated. To what extent bacterial action may aid in this removal or may retard it, and how the toxic matter may be affected by modifications in the bacterial flora of the original soil were studied in a preliminary way in the experiments here described.

THE SOILS USED

Soil No. 1 is a heavy clay loam known as Dunkirk clay loam. It contains a rather small quantity of organic matter with about 0.10 per cent. of nitrogen calculated to the dry soil. It produces good crops of small grain and of timothy. Soil No. 2 is a loam classified as Volusia silt loam. It is very unproductive, but contains a fair quantity of organic matter and about the same percentage of nitrogen as does Soil 1. Soil No. 3 is composed of Soil 1 to which a quantity of organic matter has been added by piling up grass sod and allowing it to decompose for two or three years.

EXPERIMENT NO. 1

The object of this experiment was to ascertain the effect on certain constituents of adding to the soil, rendered completely sterile by steam, a quantity of the original soil untreated in any way, and to another portion of the sterilized soil a similar quantity of the original soil heated in the autoclav to 100° C. for one half hour. For this purpose a number of glass fruit jars were each filled with 500 grams of soil and steamed. Analyses were made of the soil in two of the jars as soon as they were cool. Other jars were inoculated with 50 grams of the fresh soil and still others with 50 grams of the heated soil, and these, with additional jars, that were steamed but not inoculated were allowed to stand loosely covered in a greenhouse for different periods of time. The moisture content was maintained in each jar at 25 per cent. of the dry weight of the soil, which is about the optimum mositure content for these soils. At the end of certain periods analyses were made of the soils treated in each of the three ways. Duplicate jars were used for analysis in each case.

TABLE I.—Soil No. 1, Effect on Certain Soil Constituents of Inoculation of Steamed Soil with Fresh and with Heated Soil.

Jar No.	Treatment	Parts per million dry soil			Oxygen consumption	Ratio of oxygen consumption to total solids	N. in nitrates and ammonia
		Total solids	Nitrates	Ammonia nitrogen			
15, 16	Freshly steamed	3334	64.9	33.0	910	3.6	47.7
	Five weeks after Steaming						
17, 18	Steamed	2161	61.9	41.5	377	5.7	55.5
19, 20	Steamed, fresh soil added	1505	57.6	45.5	241	6.2	58.5
21, 22	Steamed, heated soil added	1846	57.5	41.5	302	6.1	54.5
	Fourteen weeks after Steaming						
23, 24	Steamed	1740	69.0	51.0	243	7.1	66.6
25, 26	Steamed, fresh soil added	1068	63.5	60.0	115	9.3	74.4
27, 28	Steamed, heated soil added	1592	60.5	50.0	212	7.5	63.7

A study of Table I shows, as have previous experiments, a gradual decrease in the water soluble material as the period after sterilization increased. Comparing the inoculated soil with that inoculated with fresh soil, it will be seen that the water soluble matter in the latter decreased much more rapidly than in the uninoculated soil. This would indicate that the bacteria, or possibly the enzymes, of the fresh soil were concerned in the process by which the soluble matter disappears.

Inoculation with heated soil resulted in a more rapid decrease of soluble matter than did no inoculation, but less rapid than inoculation with unheated soil. Apparently the heating process destroyed, or in some way rendered less active, the agents concerned in reducing the quantity of soluble matter. If the quantity of soluble matter is a measure of the toxic matter, then inoculation with heated soil is less effective in the removal of toxic matter than is inoculation with fresh soil.

Nitrates are present in the inoculated and uninoculated soils in about the same quantities, and there had been no marked change in the amounts present immediately after sterilizing and fourteen weeks after. The nitrifying process is quite evidently inhibited for several weeks and possibly months, even when the steamed soil has been inoculated with soil containing bacteria.

The formation of ammonia has apparently progressed in all soils, as there is a larger quantity of it present five weeks after steaming than immediately after and still more fourteen weeks after than five weeks after. Furthermore, there is slightly more ammonia in the soil inoculated with fresh soil than in either of the others, but whether this is enough to be significant is doubtful.

Oxygen consumption decreases on standing and is markedly less for the steamed soil inoculated with fresh soil. The ratio of oxygen consumption to total solids increases on standing which indicates that the soluble organic matter is disappearing more rapidly than is the soluble inorganic material. This is particularly noticeable in the steamed soil to which fresh soil has been added.

The results of analyses of soils 2 and 3 immediately after steaming and at intervals of several weeks are stated in Tables II and III respectively.

An examination of Tables II and III confirms the conclusion previously reached regarding the rapid disappearance of the soluble matter in the soil to which fresh soil was added, its less rapid disappearance in that inoculated with heated soil, and the

Table II.—Soil No. 2, Effect on Certain Soil Constituents of Inoculation of Steamed Soil with Fresh and with Heated Soil.

Jar No.	Treatment	Parts per million dry soil: Total solids	Nitrates	Ammonia nitrogen	Oxygen consumption	Ratio of oxygen consumption to total solids	N. in nitrates and ammonia
1, 2	Freshly steamed	3020	175.1	33.5	812	3.7	73.1
	Five weeks after Steaming						
3, 4	Steamed	2098	178.2	36.5	290	7.2	76.8
5, 6	Steamed, fresh soil added	1501	130.8	39.5	202	7.4	69.1
7, 8	Steamed, heated soil added	1733	150.0	35.5	276	6.2	69.4
	Fourteen weeks after Steaming						
9,10	Steamed	1801	191.5	45.0	272	6.6	88.3
11,12	Steamed, fresh soil added	1145	176.0	47.5	113	10.1	87.3
13,14	Steamed, heated soil added	1538	172.5	47.5	200	7.7	86.5

relative slow elimination of this matter from solution in the uninoculated soil.

Nitrates in Soil 2 when inoculated, apparently decreased in amount on standing during the first period. There was a slight tendency in this direction in Soil 1. In Soil 3, on the other hand nitrates did not show this tendency. The tendency to nitrate reduction, when the soil is inoculated, is in the inverse order of the productivity of the soils, and in the inverse order of the quantity of nitrate formation when the fresh soils are subjected to similar conditions, as, for instance, standing in the incubator at 30° C., for two weeks with a moisture content of 25 per cent. of the dry weight of the soil. This suggests that the rate of nitrate formation in these soils is influenced by the presence of nitrate reducing organisms as well as by the activity of nitrate formers.

Ammonia formation has evidently gone on in soils 2 and 3 on standing just as it did in soil 1. Since even the uninoculated soil was not guarded against infection from the atmosphere, it is altogether likely that ammonifying bacteria infected the soil very soon after sterilizing, and the formation of ammonia has been

TABLE III.—Soil No. 3, Effect on Certain Soil Constituents of Inoculation of Steamed Soil with Fresh and with Heated Soil.

Jar No.	Treatment	Parts per million dry soil			Oxygen consumption	Ratio of oxygen consumption to total solids	N. in nitrates and ammonia
		Total solids	Nitrates	Ammonia nitrogen			
29, 30	Freshly steamed	7194	234.0	84.1	1737	4.1	136.9
	Seven weeks after steaming						
31, 32	Steamed	3288	306.0	79.5	638	5.1	148.7
33, 34	Steamed, fresh soil added	2467	306.0	72.0	406	6.1	141.2
35, 36	Steamed, heated soil added	2732	222.5	78.5	515	5.3	128.8
	Ten weeks after Steaming						
37, 38	Steamed	2719	282.5	96.0	425	6.4	159.8
39, 40	Steamed, fresh soil added	1748	302.5	93.5	254	6.9	161.9
41, 42	Steamed, heated soil added	1950	246.5	86.0	282	6.9	141.7
	Nineteen weeks after Steaming						
43, 44	Steamed	2173	160.0	111.0	323	6.4	147.2
45, 46	Steamed, fresh soil added	1575	266.2	92.0	175	9.0	152.2
47, 48	Steamed, heated soil added	1749	149.0	110.0	336	5.2	143.7

comparatively rapid. In soils 1 and 2 there was a slight tendency for the ammonia production to be somewhat increased in the soil inoculated with fresh soil, but in Soil 3 there is less ammonia in the soil to which fresh soil was added. In the soil last mentioned the ammonia nitrogen has evidently been transformed into nitrate nitrogen, as the column showing the nitrogen in ammonia and nitrates plainly indicates; so that the total quantity of nitrogen transformed from organic matter into ammonia was slightly greater in almost every case in which fresh soil was used for inoculation. Our results, therefore, oppose the assumption that natural soil contains organisms inimical to ammonification, which organisms are destroyed by complete or partial sterilization unless the organisms in question do not thrive in a medium like steamed soil.

The oxygen consumption decreased rapidly in all soils, especially in the period between steaming and the first analysis. In only one case was the oxygen consumption greater than when a previous analysis was made. This was in the soil to which heated soil had been added and was nineteen weeks after analysis.

If the oxygen consumption is a measure of the organic matter in solution the soluble organic matter has decreased more rapidly than has the soluble inorganic material, as shown by the ratio of oxygen consumption to total solids. This disappearance of soluble organic substance is more rapid in the soil to which fresh soil has been added than in the soil inoculated with heated soil, and least rapid in the uninoculated soil. The organisms introduced by the fresh soil have aided the natural oxidation, precipitation and other agencies in the elimination of organic matter from solution.

EXPERIMENT 2

This experiment was somewhat similar to Experiment 1 in that the soil was steamed for two hours at two atmospheres, and the inoculated soil was allowed to stand for some time; it differed however in that an infusion of the fresh soil, and not the soil itself, was added to certain vessels, and that to other vessels a heated infusion was added instead of the heated soil. The infusion was made by shaking 100 grams of fresh soil with 250 c.c., of sterile water, after which it was allowed to stand twenty minutes, and the supernatant infusion (about 200 c.c.), containing some soil in suspension, was added to the steamed soil. When the heated infusion was used for inoculation the infusion as described was heated for thirty minutes in the autoclav at 100° C. It is quite probable that the organisms transferred to the soil were similar to those carried by the fresh and the heated soils respectively. The steamed soil was allowed to stand in three gallon glazed earthenware pots for six and one half months, when it was analyzed. Only one soil was used, the one previously designated as Soil 1. The main difference between Experiment 1 and Experiment 2 was in the length of time that elapsed between steaming and analysing.

TABLE IV.—Soil No. 1, Effect on Certain Soil Constituents of Inoculation of Steamed Soil with Fresh and with Heated Infusions of the Same Soil. Six and one half months after steaming.

Pot No.	Treatment	Parts per million dry soil						
		Water soluble material					Ammonia nitrogen	Nitrogen in ammonia and nitrates
		Total solids	Inorganic solids	Nitrates	Nitrites	Soluble organic nitrogen		
77, 78	Untreated	607	215	183	0.30	2.8	0	41.4
79, 80	Steamed	806	192	35	0.33	47.0	74.5	82.4
81, 82	Steamed, infusion of fresh soil added	1136	315	235	0.37	16.9	14.5	67.6
83, 84	Steamed, heated infusion added	677	185	56	0.50	45.0	80.5	93.2

Standing for six months after steaming is shown in Table IV to bring about somewhat different relationships in the various constituents in the steamed and inoculated soils from those found to obtain after standing for shorter periods. A very striking difference is in the total soluble matter. In the analyses previously stated inoculation with fresh soil had always resulted in a lower content of soluble matter than when the soil was uninoculated or when heated soil was added. In Table IV this is not the case, but quite unexpectedly the total solids and inorganic solids are highest in the soil inoculated with the infusion of fresh soil.

Referring to Table III it may be noticed that in the last period the decrease in solids is much less in the soil inoculated with fresh soil than in either of the other soils. In other words, it is evident that although the first effect of inoculation is to rapidly decrease the soluble matter, this action becomes less on standing for several months, until it is finally weaker than in the uninoculated soil.

Nitrification has been resumed in the soil treated with an infusion of fresh soil, but if any nitrification has taken place in the soil to which a heated infusion was added such action has been very weak. This experiment and the previous one indicate that heating to 100° C. destroys the nitrifying bacteria, or at least weakens their vitality to such an extent that they do not resume growth for several months after heating.

The difference in the quantities of ammonia present in the steamed soil treated in different ways is very striking. Infusion with fresh soil has undoubtedly resulted in a pronounced decrease in ammonia present, while the soil treated with a heated infusion contains slightly more than does the steamed soil untreated. Moreover, if the nitrogen present in the form of nitrates plus the nitrogen in ammonia be taken as a measure of the quantity that has passed through the ammonification process the three treatments rank in the same order, although not in the same proportions as when ammonia nitrogen alone is considered. This makes it appear as if inoculation with infusion of fresh soil had resulted in decreasing ammonification. If, however, we look at the column stating the quantity of nitrogen in the form of easily soluble organic nitrogen, it will be seen that this material is present in much smaller amount in the soil inoculated with infusion of fresh soil than it is in either of the other steamed soils. Assuming that this form of organic nitrogen furnishes the immediate supply for ammonia formation, the logical conclusion is that the soil containing the smallest quantity of soluble organic nitrogen is the one in which the largest quantity of nitrogen has been converted from that form into ammonia. It may be seen in Table IV that the soil treated with an infusion of fresh soil contains about 30 parts per million less nitrogen in the easily soluble organic matter than do the other steamed soils, and that it contains 15 to 26 parts per million less nitrogen in the form of ammonia and nitrates. If, therefore, we are to consider that the decrease in easily soluble nitrogen is a measure of the activity of the ammonifying process, we are forced to the conclusion that ammonification has proceeded more rapidly in the soil treated with fresh infusion than in either of the other steamed soils.

The acceptance of either one of these conclusions will necessitate the assumption that nitrogen has been lost from the soil or has become insoluble at some stage in the process. If ammonification has gone on more rapidly in the soil treated with fresh infusion, then nitrogen has been lost or has become insoluble after ammonification has taken place. As no drainage water was allowed to come from the soil, loss by drainage is precluded. Denitrification, either with formation of free nitrogen or with production of insoluble organic compounds, is a possibility.

If, on the other hand, ammonification has proceeded more rapidly in the uninoculated soil or in the soil inoculated with heated infusion than in the soil treated with fresh infusion, then nitrogen must have been lost or rendered insoluble before ammonification took place. There is some indication that denitrifiers were introduced by both inoculations, as has already been remarked in discussing Experiment 1.

It would appear reasonable to believe that all of the nitrogen transformations had gone on more rapidly in the soil treated with the infusion of fresh soil, and that consequently there is less nitrogen present in the intermediate steps which are represented by the soluble nitrogenous organic substances and by ammonia and that when the final product is reached denitrification sets in.

As the analyses stated in Table I indicate plainly that ammonification is proceeding more rapidly in the soil inoculated with fresh soil than in either of the others, this hypothesis is strongly confirmed.

EXPERIMENT 3

When soils 1, 2, and 3 were steamed and inoculated for Experiment 1, other portions of the same soils were steamed and inoculated in a similar manner and placed in glazed earthenware pots; these were kept in the greenhouse at a moisture content of 25 per cent. of the dry weight of the soil, and plants were grown in them. The plants were wheat followed by millet, except in Pots 95 to 100 in which the order of cropping was reversed. With each of the three soils two pots were filled with steamed soil; two pots with the same quantity of steamed soil to which was added fresh soil that had not been allowed to dry after being

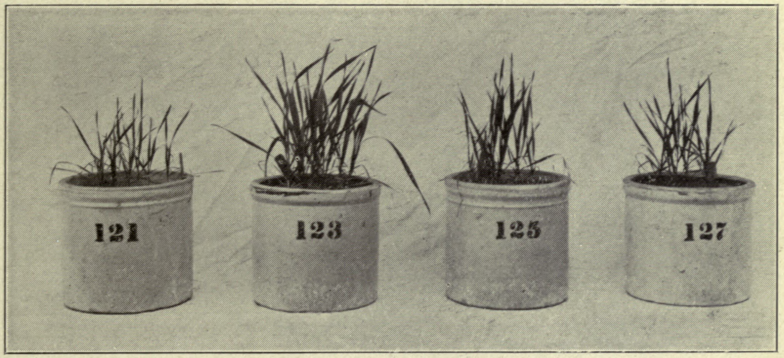


Fig. 1. Wheat plants three months after planting in Soil No. 2.
Pot 121 Soil steamed.
Pot 123 “ “ and inoclulated with fresh soil.
Pot 125 “ “ “ “ “ heated soil.
Pot 127 “ “ “ treated with sodium nitrate.

taken from the field; two pots of steamed soil to which was added the same soil heated to 100° C. for one half hour, and two pots of steamed soil with sodium nitrate added after steaming. The object in using the nitrate was to insure an abundant supply of available nitrogen.

Pots 95-100 and 121-128 contained 4 kg. of soil each, and the inoculated pots each received 50 grams of soil. Pots 337-344 and 345-350 each contained 10 kg. of soil and the inoculated pots received 100 grams of soil. Nitrate of soda fertilizer was added to pots 127, 128, 343 and 344 at the rate of 1000 pounds to 4,000,000 pounds of soil. The other pots received no fertilizer.

The increased growth on soil inoculated with fresh soil is brought out strikingly in Table V. Not only is the yield of dry matter large, but the absorption of nitrogen is enormous. That this is not due merely to an abundant supply of available nitrogen is evident from the comparison with plants on the soil containing the nitrate fertilizer, which was applied at the rate of 1000 pounds per acre foot and was consequently ample. Evidently inoculation with fresh soil, and to a less extent with heated soil, has done something more important than increasing the supply of available nitrogen.

In Table VI is given a statement of the yields of plants harvested at maturity on soils 1, 2 and 3. Pots 95-100 had been prepared and planted in the spring of 1910, while the others were not steamed and planted until the autumn of 1910, consequently the pots in the former lot had one more crop grown in them. The reason that the yields of wheat are expressed in terms of green weight and the yields of millet in dry weight is because some of the samples of the former were injured before their dry weight was determined.

In all three soils inoculation with fresh soil caused the early growth to be more rapid. It also affected the germination, although that was not so marked as was the growth.

In Fig. 1 and 2, which are reproductions of photographs of plants on soils 1 and 2, taken three months after planting, is shown the better growth on the soil inoculated with fresh soil, although the beneficial effect of this inoculation was beginning to disappear on Soil 1, at the time the photograph was taken.

The first crop of wheat on pots 121-128 was harvested fourteen weeks after planting, which is the same length of time that jars 9-14 with the same soil, stood after steaming. These pots were

TABLE V.—Yield and Nitrogen Content of Wheat Grown on Soil No. 2 and Harvested Fourteen weeks after Planting.

Pot No.	Treatment	Dry matter in plants (grams)	Nitrogen in dry matter of plants (%)	Nitrogen in plants (grams)
121, 122	Steamed	1.72	2.80	.0241
123, 124	Steamed plus fresh soil	4.13	5.57	.1150
125, 126	Steamed plus heated soil	2.57	4.40	.0564
127, 128	Steamed plus nitrate fertilizer	2.09	3.72	.0386

TABLE VI. Yields of Plants on Soils Nos. 1, 2 and 3, when Steamed and when Steamed and Inoculated with Fresh Soil and with Heated Soil.

Treatment	Soil No. 2				Soil No. 2			Soil No. 1			Soil No. 3		
	Pot No.	Green weight of 1st crop millet, grams	Green weight of 2d crop wheat, grams	Dry weight of 3d crop millet, grams	Pot No.	Green weight of 1st crop wheat, grams	Dry weight of 2d crop millet, grams	Pot No.	Green weight of 1st crop wheat, grams	Dry weight of 2d crop millet, grams	Pot No.	Green weight of 1st crop wheat, grams	Dry weight of 2d crop millett, grams
Steamed	95, 66	13	23	1.46	121, 122	26	2.34	337, 338	170	5.45	345, 346	113	15.98
Steamed plus fresh soil	97, 98	96	28	2.23	123, 124	29	2.87	339, 340	154	10.28	347, 348	104	33.49
Steamed plus heated soil	99, 100	55	26	3.08	125, 126	25		341, 342	186	8.82	349, 350	103	27.74
Steamed plus nitrate fertilizer					127, 128	27	1.96	343, 344	185	7.41			

	Soil No. 5			
	Pot No.	Dry Matter in Crops		
		Wheat	Millet	Wheat
Steamed	33, 34	12.1	7.9	4.6
Steamed plus fresh soil	53, 54	11.3	0.9	14.5

again planted. The yields of the first crop are given in Table V and of the second crop in Table VI.

It is quite apparent from the figures given in Table VI that the effect of inoculation with fresh soil has been entirely different in soil 2 from what it was in soils 1 and 3. Such inoculation has increased the first crop on Soil 2 while it has decreased the yield on Soils Nos. 1 and 3. In all soils, except No. 5 the second crop was increased by this kind of inoculation. The behavior of the second crop on soil 5 we shall not attempt to account for. It seems safe to say that the nitrogen supply is not an important factor in the yield of plants on either the inoculated or uninoculated soils. Certainly for the first crop there was an abundant supply of nitrogen in the form of nitrate and ammonia to say nothing of the probably available supply in the form of soluble nitrogenous organic compounds. In soils 1 and 3 the pots inoculated with fresh soil produced less plant substance in the first crop, in spite of the fact that the soil contained a larger quantity of nitrogen in the form of nitrates and ammonia than did the uninoculated soil when judged by the analyses reported in Tables I and III. Taking Table IV as an indicator of the nitrogen supply for the second crop it is evident that the supply of nitrate nitrogen was considerably higher in the soil inoculated with infusion of fresh soil, but the total supply of nitrate and ammonia nitrogen was somewhat less in this soil, although it is quite likely that the quantity of nitrogen passing through these forms was not materially different in any of the inoculated and uninoculated soils.

It is evident that inoculation has produced some important changes in these soils, among which are transformations in the nitrogen, but that these are not of a nature to account for the difference in yield in soils 1 and 3 in the uninoculated pots and the pots inoculated with fresh soil.

EFFECT OF STEAM STERILIZATION ON THE GROWTH OF PLANTS ON SOILS 1 AND 2

The extent to which steaming affects the productiveness of these two soils is very marked. Soil No. 1 responds with a crop three or four times the normal immediately following the treatment, and does not fall below the normal until two or three crops have been removed. Soil 2 does not produce a crop much larger than the normal immediately after steaming, and the succeeding crops are uniformly smaller. This is shown in Table VII.

TABLE VII.—Effect of Steam Sterilization on the Growth of Plants on Soils 1 and 2 When Aerated.

Pot No.	Soil and treatment	1908-9 Wheat dry matter (grams)	1909 Millet dry matter (grams)	1909-10 Wheat dry matter (grams)	1910 Millet dry matter (grams)	1910-11 Wheat dry matter (grams)	1911 Millet dry matter (grams)	Total weight of all Crops (grams)
15, 16	Soil No. 1, unsteamed	19.7	22.6	11.5	16.2			70.0
55, 56	Soil No. 1, steamed	84.3	25.0	25.5	15.5			150.3
31, 32	Soil No. 2, unsteamed	8.8	12.7	6.2	7.3	2.9	1.8	39.7
35, 36	Soil No. 2, steamed	12.1	7.9	4.6	1.9	2.0	1.2	29.7

Reference to the analyses of the same two soils when steamed demonstrates the fact that a difference in the quantity of water soluble matter in the steamed soils will not account for this difference in productiveness. Evidently the supply of readily available nutrient material is not the controlling factor in the unfavorable effect of steam sterilization on Soil 2.

It should be explained that the soils referred to in Table VII were aerated before they were steamed and that the unsteamed soils were likewise aerated. The effect of resteaming without aerating after the soil has been in pots for two or three years, is to decrease its productivity.

In order to test the effect of a second steam sterilization on soil standing in pots until it had become compact, pots 55 and 56 were resteamed in the autumn of 1910. The yields on soils 1 and 2 when treated in this way are shown in Table VIII. In both of these cases the untreated soil had stood in pots for two to three years without stirring and without fertilization and had become very unproductive. The previous steaming had been done two or three years previously.

TABLE VIII.—Effect of Steam Sterilization on the Growth of Plants on Soils Nos. 1 and 2 when Not Aerated.

Pot No.	Soil and treatment	1910 Millet dry matter (grams)	1910-11 Wheat dry matter (grams)	1911 Millet dry matter (grams)
15, 16	Soil No. 1, unsteamed		8.6	7.9
55, 56	Soil No. 1, steamed		0.0	6.3
31, 32	Soil No. 2, unsteamed	7.3	2.9	1.8
53, 54	Soil No. 2, steamed	0.0	7.7	5.8

The immediate effect of steaming both soils was to decrease their productivity. Pots 55 and 56 produced no crop whatever in 1910-11. Only eight seeds germinated in one pot and three in the other, and these soon died. A similar condition obtained in pots 53 and 54 in 1910 after steaming, but the soil recovered somewhat afterwards. However, the yields on the unsteamed soil had by that time become very light. The injurious effect of steaming was apparently due to the lack of aeration.

EFFECT OF AERATION AFTER STEAMING ON THE GROWTH OF PLANTS IN THE AQUEOUS EXTRACT

In order to ascertain the effect of aeration of soil after steaming Soil 1 was allowed to stand for three months after treatment. A part of the soil had been spread out and worked over after steaming in the pots. The soil in pots 85 and 86 was not disturbed after steaming, but was allowed to stand in the greenhouse without being planted. The surface was covered with crushed quartz and the moisture was maintained at 25 per cent. of the dry soil. The soil in pots 87 and 88 was removed after steaming and was well aerated. It was then replaced and allowed to stand under the same conditions as was the other soil. The soil in pots 89 and 90 was planted to wheat after steaming. At the end of the three months all of the pots were extracted with distilled water, using one part of water to one part of soil. Wheat seedlings were grown in the extract thus obtained, and in the same extract diluted by adding three parts of water to one part of the strong extract. Some fresh soil was steamed at the same time and extracted in the same way. In table IX appears a statement of the total solid matter and inorganic (by ignition) in the extracts and of the transpiration and dry matter in the tops and roots of plants grown in the extracts:

TABLE IX. Effect of Aeration after Steaming on the Growth of Plants in Aqueous Extracts.

Pot No.	Treatment	Extract	Parts per million Solids in Extract		Plant Growth			
					Transpiration grams	Dry Matter		
			Total	Inorganic		Tops grams	Roots grams	Entire Plant
85, 86	Steamed, stood 3 months	Strong	590	126	145	.4742	.3261	.8003
		Dilute	147	31	93	.2533	.4297	.6830
87, 88	Steamed, aerated, stood 3 months	Strong	434	120	170	.5142	.2980	.8122
		Dilute	108	30	131	.2866	.3125	.5991
89, 90	Steamed, plants grown 3 months	Strong	488	134	139	.3019	.3354	.6373
		Dilute	122	33	95	.2356	.2810	.5166
	Steamed and extracted immediately	Strong	1010	246	101	.3298	.3074	.6372
		Dilute	252	61	140	.3820	.3550	.7370

As in experiments previously described, the soluble matter decreased on standing. The decrease was greatest in the aerated soil, and next in the planted soil, but the inorganic matter was greater in the soil on which plants were grown than in the unaerated soil. Apparently the plants had a solvent action on the inorganic matter.

Plant growth was better in the strong extracts of the soil that stood after steaming than in the extract of the freshly steamed soil. As a concentration of 1000 parts per million is not sufficient to injure wheat seedlings, the better growth was due presumably to toxic matter produced by the steaming process. This conclusion is substantiated by the better growth in the extract of the aerated soil than in the unaerated.

The diluted extract of the soil steamed just before extraction produced a better growth than did the strong extract, while the reverse was the case with the extracts of the soil that stood for three months. This is another indication of the removal of toxic matter on standing.

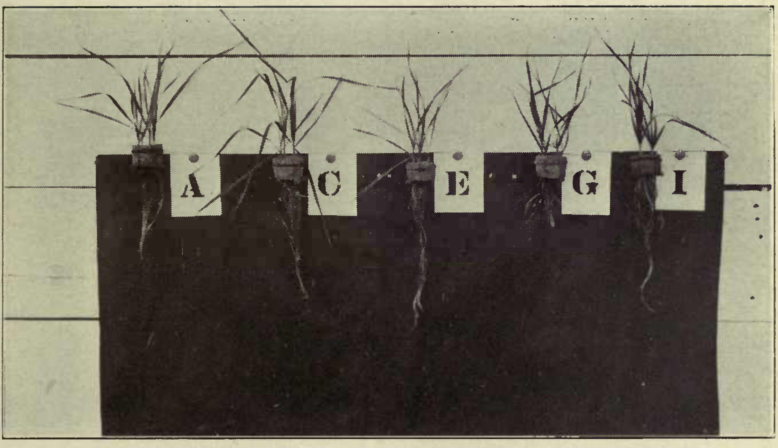


Fig. 3. Plants grown in strong extracts of soil that had been steamed, a portion inoculated with fresh soil, a portion inoculated with heated soil and a portion of which was uninoculated. The soil after treatment was allowed to stand for three months before extraction. Also plants grown in strong extract of freshly steamed soil.

A Plants from extract of uninoculated soil.
C “ “ “ soil inoculated with fresh soil.
E “ “ “ “ “ “ heated soil.
G “ “ “ freshly steamed soil.

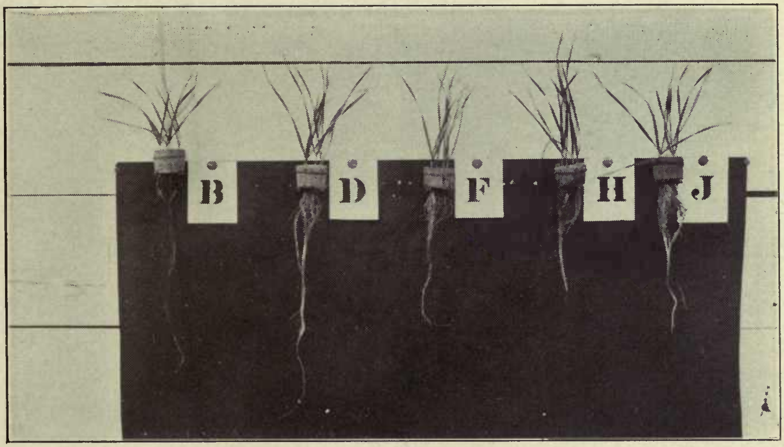


Fig. 4. Plants grown in dilute extracts of soil that had been steamed, a portion inoculated with fresh soil, a portion inoculated with heated soil and a portion of which was uninoculated. The soil after treatment was allowed to stand for three months months before extraction. Also plants grown in dilute extract of freshly steamed soil.

B Plants from extract of uninoculated soil.
D " " " soil inoculated with fresh soil.
F " " " " " " heated soil.
H " " " freshly steamed soil.

In Fig. 3 is reproduced a photograph of some of the plants grown in the strong extracts and Fig. 4 a photograph of the plants in the dilute extracts. So far as the root development is concerned, these photographs bring out differences not represented by the figures in Table IX. This is in the length of the roots which is not a function of the weight of root, a short root often weighing more than a long one, as for instance, the roots from the extract of pots 85 and 86 which is represented by A in Fig. 3, are shorter than the roots from pots 87 and 88, represented by B in the same figure, although it is shown in Table IX that the former roots weigh more than the latter.

The shortened root has been used by some investigators to indicate the presence of toxic matter. According to this criterion the unaerated extract contains more toxic matter than does the extract of the soil aerated after steaming, and the extract of the planted soil least of all, while the extract of the freshly steamed soil contains the most. These conclusions are in line with those previously reached.

SUMMARY

Steamed soils inoculated with fresh soil and with heated soil, and uninoculated were allowed to stand for different periods and then analysed. There was a gradual decrease in water soluble matter on standing, and this was more rapid in the soil inoculated with fresh soil for several weeks; but after six months the soluble matter was higher in the soil thus inoculated. There was an indication that nitrate-reducing organisms were an important factor in determining the quantites of nitrates formed in the soils worked with. There was no indication that inoculation with fresh soil introduced organisms which lessened ammonia formation, but it is possible, of course, that such organisms, if introduced, would not thrive in soil previously steamed.

Plants grown on steamed soils that were inoculated as described above and on those that were uninoculated made a much better growth at first on the soil inoculated with fresh soil, but did not continue at the same rate throughout the growing period; the result being that on one soil the yield of the first crop grown after inoculation was less at harvest than was that of the crop on the uninoculated soil, while on the other soil the ratio of increase diminished greatly during the latter period of growth. The luxuriance of growth in this particular soil is apparently a function of the rate of disappearance of the soluble matter in that soil. The soluble matter at first, disappeared more rapidly in the soil inoculated with fresh soil than in the others but gradually diminished its rate of disappearance until at the end of six months and a half there was more soluble matter in the soil inoculated with fresh soil than in either the uninoculated soil, or in that inoculated with heated soil.

On one of these soils plant growth was better, for at least three crops, on the steamed soil than on the unsteamed and was very much more luxuriant for the first crop. On the other soil the first crop on the steamed soil was only moderately larger than on the unsteamed and thereafter it was uniformly less. This difference in productiveness is not a matter of available nutrients in the steamed soil, for the analyses of both soils show little difference in that respect. Since the evidence points strongly to toxic matter as being the controlling factor in the productivity of steamed soils, its seems that there must be a fundamental difference in these soils in respect to the nature of the toxic matter formed when steamed, and in its elimination afterwards.

The condition of the organic matter before steaming apparently influences the toxicity of the steamed soil. Thus, Stone found that a steamed subsoil was more toxic than the top soil when steamed. The quantity of water soluble material was not a measure of the relative toxicity of two different soils. Soluble matter disappears as rapidly from Soil 2 as from Soil 1 and yet the former always showed much greater toxicity. The rapidity of oxidation in the soil, as measured by the oxygen requirement, does not always indicate the rate at which toxicity disappears, although aeration of the steamed soil and the growth of plants in steamed soil both caused a decrease in toxicity.

Soil 2 is under field conditions, a very poor soil, in spite of the fact that it contains as much organic matter and nutrient materials as does Soil 1. The inability of the former soil to rid itself of toxic material formed by steaming indicates that a similar condition causes its sterility in the field.

ERROR IN THE BABCOCK BUTTER-FAT TEST OF FRESH MILK CAUSED BY IMPROPER DIAMETER OF TEST BOTTLE NECKS

T. C. Manchester

Berlin, Wisconsin

The majority of the 10 per cent. Babcock milk test bottles at present on the market give erroneous fat tests because the diameter of the necks of same are too great.

It is commonly understood and is recommended by authorities[1] that the upper reading of the fat column should be taken at the top of the upper meniscus. In practice, it is soon discovered by most operators, who use the ordinary 10 per cent. fresh milk test bottles, that if the readings are taken at the very top of the upper meniscus, the readings obtained are on an average higher than can be obtained by gravimetric analysis and further if the milk is paid for according to the Babcock test, he is unable to account for all the fat in the manufactured product—even after making a very liberal allowance for losses. He, therefore, concludes that it is erroneous to take the readings as recommended. For this reason, nearly every operator has his own method for arriving at what he considers an impartial reading.

Probably the majority of persons take this reading at the point intermediate between the bottom of the meniscus and the top of same. This would seem to be as fair a rule as could be universally adopted provided the bottles were manufactured with the same average diameter of neck as at present. However, it is often very difficult to determine the correct lower reading of the meniscus and consequently the intermediate point. And since it is true that some of the bottles have a diameter of

---

[1] Van Slyke, Modern Methods of Testing Milk and Milk Products, 1909, p. 63.

Ferrington and Woll, Testing Milk and its Products, 19th Rev. Edit., p. 35.

neck which will give a true reading if the upper limit of the fat column is taken as the reading point, it is evident that in case of these bottles, an intermediate reading would be below the true amount. Although most authorities agree that the reading should be taken at the top of the meniscus, there are some who believe this to be erroneous, and therefore make allowance for the meniscus. For great accuracy Leffman and Beam[1] recommend that a correction for each bottle should be determined by comparison with figures obtained by the Adams or other standard process. While true results could be obtained by this method, it would not be practicable except in a regular chemical laboratory, and ever there the time necessary to do this work would be almost prohibitive if a large number of test bottles were used. While extreme accuracy may not always be essential, yet a constant error—such as now often exists—of from .05 to 0.2 per cent., and in extreme cases perhaps 0.3 per cent., should not be tolerated.

It has already been shown by Webster and Gray,[2] and by Hunziker,[3] that in the testing of cream where cream bottles with wide necks are used, a considerable error is introduced into the analysis if the upper limit of the fat column is taken as the reading point, this error in some instances amounting to over 1.0 per cent. Both of above authorities attribute this error to the fact that in the wide necked bottles, the meniscus covers a very wide range in per cent. and they conclude that it is not allowable in case of these cream bottles to take the reading to the top of the meniscus. The average error introduced, as shown by them, is approximately 0.6 per cent.

The data included in this paper will show that the average 10 per cent. milk test bottle will introduce an error of approximately 0.1 per cent. because of the fact that their diameter of neck is also too great. When it is considered that the average fresh milk test is approximately 4.0 per cent., while the average

---

[1] Leffman and Beam Select Methods of Food Analysis, 2d Edition, p. 35.

[2] The Fat Testing of Cream by the Babcock Method. U. S. Dept. of Agr. Bureau of An. Ind. Bul. No. 58.

[3] Testing Cream for Butter Fat. Purdue Univ. Bul. 145, Vol. XV.

cream test is approximately 25.0 per cent., it will be seen that the actual difference in pounds of butter fat between that found in any given lot of milk by the Babcock method and that actually present will be just as great as the difference would be in case the cream from the same lot of milk were tested in the ordinary cream test bottle. As by far the greater part of the milk produced is sold as such and not as cream, it is seen that the magnitude of this error present in the testing of fresh milk is far greater than that present in the testing of cream.

In the data and discussion which follows, have used the total length of graduation (0 to 10 per cent.) as a method of making comparisons instead of the diameter of bore, both because of the greater dispatch obtained in taking the measurements and because most small laboratories where the results of this investigation might want to be made use of have no suitable apparatus for measuring the exact diameters of the bottle necks. For the purpose of making accurate comparisons, two independent sets of bottles with varying length of graduation were chosen, care being taken to have the average length of graduation of each lot to be as near as possible to that of an ordinary equipment of 10 per cent. test bottles. Each bottle was carefully tested for accuracy of calibration by the mercury method. A sample of milk was then taken and a test of same made in each bottle of the 1st series: all of the tests being run at the same time. The tests were then repeated with the same set of bottles to obtain duplicate readings, the average reading being given in the data as here presented. These average readings are compared against the average of duplicate determinations made by the R. Göttlieb method. As the tests made with the second series of bottles were made at a later date, in order to obtain a check against the 1st series, a different sample of milk was used, details of manipulation being carried out in just the same manner. The results of this series, as presented, are the average of triplicate determinations in all cases and are compared with the average of triplicate determinations by the R. Göttlieb method.

DATA

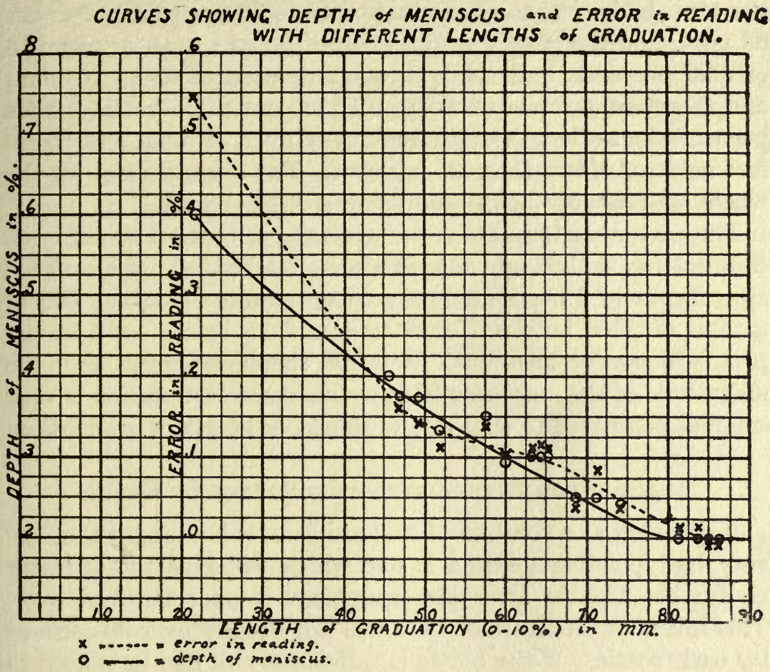
SERIES I. Per cent. fat R. Göttlieb method. 3.865.

Bottle No.	Depth Men. in %	Length Grad. in mm. (0 - 10%)	Av. Read.	Error in Read.
*C	.60	22.0	4.40	+ .535
1	.375	46.75	4.025	+ .160
15	.35	57.5	4.00	+ .135
X	.30	63.75	3.975	+ .110
XI	.30	64.4	4.00	+ .135
2	.30	65.25	3.975	+ .110
XII	.25	71.25	3.95	+ .085
A	.20	81.25	3.875	+ .010
D	.20	83.75	3.875	+ .010

SERIES II. Per cent. fat R. Göttlieb method. 4.15.

A1	.40	45.6	4.34	+ .19
A2	.375	49.4	4.29	+ .14
A3	.333	51.9	4.258	+ .108
A4	.292	60.0	4.25	+ .10
A5	.250	68.75	4.19	+ .04
A6	.242	74.4	4.19	+ .04
A7	.20	86.25	4.133	— .017
A8	.20	85.0	4.133	— .017

*This was a 30 per cent. cream bottle used to give a better idea of what error might be expected if a bottle with a larger bore than any of the others used were to be employed.



Conclusions

From the above data and curves, it is seen that the error introduced when the length of graduation (0 to 10 per cent.) is 60 to 65 mm., is approximately 0.1 per cent.; when the length of graduation is 45 to 50 mm., the error is approximately 0.2 per cent.; when the length of graduation is 22 mm., the resulting error is approximately 0.55 per cent. Bottles with a length of graduation (0 to 10 per cent.) of 80 mm., are seen to be practically free from error.

It is seen that the general tendency is for the curve representing the error to increase somewhat more rapidly, as the length of graduation decreased, than does the curve representing the depth of meniscus, but that both follow the same general course. A regular creamery equipment of 10 per cent. bottles was checked over and it was found that out of a total of 37 bottles, 19 or 51.3

per cent. had a length of graduation (0 to 10 per cent.) of under 63 mm., and therefore gave an error of 0.1 per cent. or over; 16 or 43.3 per cent. had a length of graduation of 63 to 70 mm., and therefore an error of .05 to 0.1 per cent.; two bottles or 5.4 per cent. had a length of graduation of over 74 mm., and therefore an error of less than .05 per cent. The average error for the whole lot probably being slightly over 0.1 per cent.

The writer has found that the average per cent. of 10 per cent. test bottles, which are not accurately calibrated, will average approximately 2 per cent. in the better grade of bottles. Out of a total of 2243 bottles Hunziker[1] found 25 bottles or 1.11 per cent. which were incorrect. It would therefore appear as if the magnitude of the inaccuracy due to inaccurate calibration is very small as compared to that due to improper length of graduation.

METHOD FOR ELIMINATING THIS SOURCE OF ERROR

In arriving at a solution of this problem, it is thought that the very best possible solution is one which will give the operator no further trouble after his equipment is once checked over. This initial expenditure of time will not occupy over 30 seconds for each bottle. If the bottle is satisfactory, it can be placed in the equipment, and if not, it can be excluded. It has been seen from the data given above that a bottle with a total length of graduation (0 to 10 per cent.) of 80 mm. gives a true reading. Since a length of graduation of 80 mm. requires the total length of neck to be longer than convenient or satisfactory, it is recommended that 8 per cent. bottles with a corresponding minimum length of graduation (0 to 8 per cent.) of 64 mm. be adopted. It is also thought best to place a maximum upon the length of graduation (0 to 8 per cent.) of 72 mm. since the more slender the fat column, the more readily it will be influenced by changes of temperature which might introduce an appreciable error if any greater length of graduation is allowed. As it is very seldom that a sample of milk is found which will test over 6 or 7 per cent., it is believed that the 8 per cent. bottles graduated to 0.1 per cent. would give entire satisfaction, and if only such bottles are

---

[1] Purdue Univ. Bulletin 145 Vol. XV p. 537.

used as come within the above specified limitations, the error due to improper length of graduation will be eliminated.

The milk test bottles at present specified by the Official Agricultural Chemists[1] are " Babcock milk test bottles graduated to 10 per cent." no restriction being made as to the length of graduation. States have passed laws requiring the bottles used in making the Babcock test to be accurately calibrated, and it is to be hoped that some steps will be taken to universally limit the length of graduation (diameter of bottle neck) of milk test bottles, so that this greater source of error will be eliminated.

---

[1] U. S. Dept. Agr. Bureau of Chemistry Bul. 107 (rev.) p. 120.

THE RADIO-ACTIVITY OF SOME TYPICAL SOILS OF THE UNITED STATES

RICHARD B. MOORE

Bureau of Soils, Department of Agriculture, Washington, D. C.

Strutt[1] first called attention to the radioactivity of igneous and sedimentary rocks. The average of his results on igneous rocks showed a radium content of 3.3×10^{-12} grams of radium per gram of rock. The radium content of the sedimentaries was somewhat less. Joly[2] has examined a large number of rocks for radium and thorium. His radium values are somewhat larger than those of Strutt and other workers. The average of a number of his thorium determinations indicates the presence of 1.58×10^{-5} grams of thorium per gram of rock. Fletcher,[3] working primarily with secondary rocks, has confirmed Joly's results and at the same time pointed out that, with the exception of the calcareous rocks, those of the same type have always very nearly the same radium content.

Although a considerable amount of work has been done on the radio-activity of rocks and minerals very little has been attempted along this line with soils. A knowledge that the atmosphere was radio-active was naturally followed by an investigation of the activity of the underground air. Elster and Geitel, Brunstead, Blanc, Dadourian, Wilson, Ebert, Eve, Sanderson and others have contributed to our knowledge of this subject. Whereas a study of the underground air indicates very plainly that the soil is radio-active, it does not give any absolute values for the activity of the soil itself, as the activity of the underground air depends as much upon the emanating power of the radio-active

---

[1] Roy. Soc. Proc. A 77, 472 (1906).
[2] Phil. Mag., 17, 760, (1909).
Phil. Mag., 18, 140, (1909).
Phil. Mag., 23, 201, (1912).
[3] Phil. Mag., 23, 279, (1912).

matter in the soil as it does upon the amount of that material actually present. Some rough minimum determinations have been attempted. Wilson states that there is probably seven times as much thorium as uranium in the surface soils at Manchester. Blanc on the other hand estimates that from 5 per cent. to 70 per cent. of the activity of the Roman soil is due to thorium; whilst Sanderson's[1] work indicates that 1 cubic centimeter of soil at New Haven produces radium emanation in equilibrium with 8.9×10^{-14} gram of radium, and thorium emanation in equilibrium with 1.35×10^{-6} gram of thorium. Fletcher[2] gives the radium content of two Dublin soils passing a 50 mesh sieve as 5.2×10^{-12} gram and 2.8×10^{-12} gram.

Apparently no systematic attempt has yet been made to correlate the radio-activity of soils with their other properties. Recently an elaborate study of the chemical composition of a number of typical soils of the United States has been undertaken by W. O. Robinson and G. H. Failyer of the U. S. Bureau of Soils. A mineralogical examination has been made of the same soils by Prof. W. J. McCaughey. The author has these unpublished results at his disposal and has examined the soils for their radium content. The present paper constitutes a preliminary report on the results obtained.

Strutt's[3] method of getting the material in solution was used. The soil was fused with four times its weight of mixed alkali carbonates, treated with water, filtered, the residue washed with sodium carbonate solution to prevent hydrolysis, and then dissolved in hydrochloric acid. After standing a month the combined emanation from the alkaline and acid solutions was introduced into the electroscope. Joly[4] has criticised this method on the basis that it is almost impossible to get the solutions perfectly limpid and the precipitated silica carries down with it some of the radium. This is probably true to some extent but in the case of rocks and minerals fairly concordant results can be ob-

---

[1] Am. Jour. Sc. 32, 169, (1911).

[2] Phil. Mag. 23, 279 (1912).

[3] Phil. Mag. 22, 134 (1911).

[4] Phil. Mag. 22, 134 (1911).

tained by its use. Much more difficulty is experienced with soils than with rocks. Hydrolysis nearly always takes place and the filtering process is long and tedious. On standing a short time silica invariably separated from the solutions. This was filtered off and refused with alkali carbonates and the process repeated until clear solutions were obtained. Even with the greatest care some of the solutions became turbid before the emanation was boiled off. In order to lessen the difficulty with the silica some of the soils were first treated with hydrofluoric acid and a little sulphuric. After evaporation and ignition they were fused with fusion mixture in the ordinary way. The addition of the sulphuric acid at first sight would seem to be inadvisable but as the solutions obtained by this method remained more limpid and as practically all soils contain both sulphates and barium the advantages would seem to outweigh the disadvantages.

The results are expressed in terms of the uranium standard first suggested by Boltwood and used by Strutt, Joly, Schlundt and Moore and others. The results obtained are as follows:

	Depth	Radium (gram x 10^{-12} per gram of soil)
(1) Volusa Silt Loam, Naples, N. Y.,	0″- 8″	3.76
(2) Volusa Silt Loam, Naples, N. Y.,	8″-36″	1.10
(3) Cecil Clay, Charlotte, N. C.,	0″- 6″	0.54
(4) Cecil Clay, Charlotte, N. C.,	6″-36″	0.78
(5) Cecil Sandy Loam, Charlotte, N. C.,	0″- 8″	0.28
(6) Cecil Sandy Loam, Charlotte, N. C.,	8″-36″	1.33
(7) Durham Sandy Loam, Ancher, N. C.,	0″-10″	0.45
(8) Durham Sandy Loam, Ancher, N. C.,	10″-36″	1.66
(9) Norfolk Sandy Loam, Laurinburg, N. C.,	0″-14″	2.56
(10) Norfolk Sandy Loam, Laurinburg, N. C.,	14″-36″	2.80
(11) Decatur Clay Loam, Hollywood, Ala.,	0″- 4″	2.78
(12) Decatur Clay Loam, Hollywood, Ala.,	4″-36″	1.27

In four cases the subsoils are more active than the soils, the ratios of the activities of the two in the Durham Sandy Loam and the Cecil Sandy Loam being very similar.

There seems to be no relation between the activities of the soils and their chemical composition, except in respect to silica. In the four cases where the subsoils are more active than the soils the amount of silica present in the soils is much larger than in the subsoils. In the two cases where the soils are the more active (1 and 11) the amount of silica in the subsoil about equals that in the soil. The connection is easily understood as the more metallic elements present, the greater the chance for the occurrence of uranium.

The amount of rare earths present in the soils was so small that the analytical results were not reliable. No connection could therefore be drawn with them.

Since the activity of at least secondary rocks of the same type is fairly constant it would seem that there ought to be some connection between the mineralogical composition of a soil and its activity. Unfortunately the mineralogical data at my disposal are not sufficiently complete to draw any such connection. Only the potash feldspars and micas were determined quantitatively—the others qualitatively, and as most rock forming minerals occur in all soils the qualitative results showed no significance. Monozite occurs in some soils but was not specially looked for in the twelve samples examined and was not listed among the minerals in any of them.

SOME EFFECTS OF FERTILIZERS ON THE GROWTH AND COMPOSITION OF ASPARAGUS ROOTS.[1]

By Fred W. Morse

Massachusetts Agr. Expt. Station, Amherst, Mass.

Asparagus is an important truck crop in eastern Massachusetts and for several years the Association of Asparagus Growers has co-operated with the Massachusetts Agricultural Experiment Station in investigations of its culture, which have included an extensive series of fertilizer experiments.

A successful method of manuring asparagus pursued by some of the growers, is the use of a large amount of stable manure and some supplemental fertilizers like bone and potash salts, at the time of setting the young plants, followed annually by liberal top-dressings with nitrate of soda, superphosphates and potash salts. Vegetable matter is maintained in the soil by working into it all of the matured tops and any weeds which may develop after the tops are too large to permit tillage operations.

A series of fertilizer experiments was planned, in 1906, by Dr. William P. Brooks, director of the experiment station, to ascertain the efficiency of different methods of top-dressing the crop. The field for the purpose was donated by Mr. C. W. Prescott, a member of the Association of Asparagus Growers, and is located on his farm in the town of Concord. The soil is like that of most asparagus fields, a sandy loam of little natural fertility.

In January, 1910, the writer was assigned the task of ascertaining the specific effects of the principal chemical fertilizers—nitrate of soda, superphosphate, and potash salts—on the composition of the crop, as probable factors in determining the relative efficiency of these fertilizers. This paper will deal only with the effects of these fertilizers on the roots of the asparagus plant, since there has been but little work reported on that subject.

---

[1] Published by permission of the Director of the Massachusetts Agricultural Experiment Station.

Rousseaux and Brioux made a partial analysis of the roots as a minor part of an elaborate research on the asparagus crop published in 1906.[1]

Tauret has made an extended study of the properties of the carbohydrates contained in the roots.[2]

Wichers and Tollens have reported very complete analyses of roots collected before and after the cropping season.[3]

The material studied by the writer consisted of the entire underground portion of the asparagus plant, except the fine, fibrous feeding-rootlets which were removed as it was impossible to collect any reasonable proportion of them.

No effort was made to separate the crown or center of the plant from the fleshy roots. The plants were selected by the size of their tops and the effort was made to get average plants for each type of fertilization. The plants were carefully excavated and as nearly as possible, all the fleshy roots were collected. In some instances growth had been so extensive that adjacent roots were much interlaced and it was impossible to secure one plant without destroying all others around it. Therefore, our largest heaviest roots were more or less incomplete.

On the day following the collection of the specimens, the roots were shipped from Concord to the Experiment Station where they were placed in a cool cellar. The process of washing free from soil, weighing when free from surface moisture, drying and grinding, was very laborious and required several weeks owing to the weight and bulk of the material. There is always danger of respiratory changes during the period of preparation, between collecting and drying; but it is believed that they were reduced to a minimum by keeping the roots in a cool place at about 10° C. Washing was performed within a few days after digging and the weights of the fresh roots were obtained before there could have been any respiratory losses.

The material was prepared for drying by passing the crown and roots through a hand-lever fodder-cutter by which they were

---

[1] Annales de la Science Agronomique, 3rd Series, I, pp. 189-326 (1906).

[2] Bulletin de Soc. Chim. (4) V., pp. 889-893 (190); Compt. Rend. 149, p. 48 (1909).

[3] Jour. fur Landwirthschaft 58, pp. 101-112 (1910).

cut into pieces about 2 centimeters in length. Drying was done in a large oven at a temperature between 50° and 60° C., and the material was dried until sufficiently brittle to be easily ground. The weight of the specimen was taken at this stage, and then the entire lot was coarsely ground in a drug-mill after which it was sampled by quartering and the sample reduced to a powder which would pass through a 1 m.m. mesh sieve. Moisture determinations were then made in the powdered samples, from which were calculated the weights of absolutely dry matter contained in the specimen roots.

Three different series of samples have been studied during this investigation.

The first series consisted of forty-four roots, or four specimens from each of eleven plots, used for testing different quantities and different seasons of application of nitrate of soda. They were collected in November, 1908, two years after the field had been set with plants, by Mr. E. F. Gaskill of the Agricultural Department of the Experiment Station, and were prepared for analysis in part by the Fertilizer Section and in part by the Feed and Dairy Section of the Department of Chemistry.

The second series consisted of seventy-six roots, or four from each of eleven nitrogen plots before mentioned together with four plots used for a test of different quantities of superphosphate and four plots for different quantities of muriate of potash. These samples were secured by Mr. Gaskill and the writer in November, 1910, and were prepared for analysis under the supervision of the latter.

The third series consisted of sixteen roots, or four from each of four of the nitrogen plot, and were gathered under the supervision of Mr. C. W. Prescott on June 23, 1911, and were prepared for analysis by the writer.

All the analytical work has been based on the methods of the Association of Official Agricultural Chemists[1] except where departures are mentioned as necessary owing to the character of the material.

---

[1] Bul. 107 Revised, Bur. of Chem., U. S. Dept. of Agr.

AMOUNT OF FERTILIZERS APPLIED

Each plot in these tests contained one-twentieth acre and was 129 feet long by 16 feet 10½ inches wide. At the time of setting the plants, the entire area received a uniform dressing of the following chemical fertilizers:

Lime,	2000 lbs. per acre.
Fine ground bone,	1000 " " "
Nitrate of soda,	150 " " "
Acid phosphate	600 " " "
Muriate of potash,	350 " " "

No check plots without fertilizer were included in the plan.

The annual top-dressing was applied to the different plots in the following quantities per acre:

	Plot Number	Nitrate Soda	Acid Phosphate	Muriate Potash
No Nitrate	1 and 40	0 lbs.	200.1 lbs.	260.0 lbs.
Low Nitrate	31, 32, 33	311.2 "	200.1 "	260.0 "
Medium Nitrate	34, 35, 36	466.6 "	200.1 "	260.0 "
High Nitrate	37, 38, 39	622.4 "	200.1 "	260.0 "
No Phosphate	5	466.6 "	0 "	260.0 "
Low Phosphate	6	466.6 "	133.4 "	260.0 "
Medium Phosphate	7	466.6 "	200.1 "	260.0 "
High Phosphate	8	466.6 "	266.8 "	260.0 "
No Potash	9	466.6 "	200.1 "	0 "
Low Potash	10	466.6 "	200.1 "	173.4 "
Medium Potash	11	466.6 "	200.1 "	260.0 "
High Potash	12	466.6 "	200.1 "	346.8 "

The nitrate of soda was applied to plots 31, 34 and 37 in the spring before growth began; to plots 32, 35 and 38 in the summer after cutting had ceased; and to plots 33, 36 and 39 one-half in spring and one-half in summer. All phosphate and potash salts were applied in the spring.

EFFECT OF FERTILIZERS ON THE WEIGHT OF ROOTS

Since the marketable crop from the asparagus plant must be grown almost entirely at the expense of the reserve plant food stored in the crown and roots, the size of the roots at the beginning of the growing season would seem to be an important factor in the yield of sprouts. While their relationship has not yet been determined, it has been noted that the different top-dressings influenced the size of the roots to a marked extent.

The effects of nitrate of soda have been observed in all three series of samples, but only one series has afforded an opportunity to study the effects of phosphates and of potash salts. Nevertheless, the series gathered in 1910 was at the end of the fourth season of growth and hence should have the cumulative effect of three annual dressings.

EFFECT OF DIFFERENT AMOUNTS OF NITRATE OF SODA

Season of 1908. Average Roots end of 2nd season

	Plot Number	Fresh Weight
No Nitrogen	1 and 40	1027 gms.
Low Nitrogen	31, 32, 33	947 "
Medium Nitrogen	34, 35, 36	1248 "
High Nitrogen	37, 38, 39	1127 "

Season of 1910. Average Roots end 4th

	Plot Number	Fresh Weight
No Nitrogen	1 and 40	2128 gms.
Low Nitrogen	31, 32, 33	2362 "
Medium Nitrogen	34, 35, 36	2703 "
High Nitrogen	37, 38, 39	2464 "

Season of 1911. Average Roots end 5th

	Plot Number	Fresh Weight
Low Nitrogen	31 and 32	2259 gms.
Medium Nitrogen	34 and 35	2555 "

It is noted that the medium application of nitrate of soda has produced the heaviest average roots in each season.

EFFECT OF PHOSPHATE AND POTASH SALTS

Season of 1910. Average Roots

	Plot Number	Fresh Weight
No Phosphate	5	1783 gms.
Low Phosphate	6	2853 "
Medium Phosphate	7	2735 "
High Phosphate	8	2246 "
No Potash	9	1674 "
Low Potash	10	2395 "
Medium Potash	11	2893 "
High Potash	12	2709 "

In spite of the large application of bone, acid phosphate and muriate of potash at the time of setting the plants, the absence of either in the top-dressing produces a notably lower average weight of roots. The medium applications of phosphate and of potash salts produce the highest average weights of roots.

Rousseaux and Brioux[1] found the heaviest roots where manure and chemicals were combined and it is of interest that the fresh weight was 2600 grams, which is practically the same as the weight of our roots from the plots receiving top-dressings of medium amounts of fertilizers.

EFFECT OF SEASON OF APPLICATION OF NITRATE OF SODA ON WEIGHT OF ROOTS

Spring application

	Plot	1908	1910	1911
Low	31	1025 gms.	2545 gms.	1852 gms.
Medium	34	1260 "	2733 "	2776 "
High	37	1336 "	2854 "	
Average		1207 "	2711 "	2314 "

---

[1] Loc. cit. p. 312.

Summer application

	Plot	1908	1910	1911
Low	32	923 gms.	2004 gms.	2666 gms.
Medium	35	1274 "	2289 "	2335 "
High	38	1302 "	2311 "	
Average		1166 "	2201 "	2501 "

Spring and Summer applications

	Plot	1908	1910
Low	33	895 gms.	2538 gms.
Medium	36	1211 "	3089 "
High	39	730 "	2227 "
Average		945	2618

The summer top-dressing with nitrate has produced smaller mature roots than the spring top-dressing, in both years 1908 and 1910. On the other hand, the roots of 1911 taken at the end of the cutting season in the summer show variable results, with the average weight heavier on the summer-dressed plots. The individual roots in this summer collection showed much wider variations than the late fall series, which is attributed to the difficulty of judging average plants by the young shoots, and it is probable that the different plots are not as fairly represented as in the fall collections.

EFFECT OF FERTILIZERS ON THE FERTILIZING CONSTITUENTS OF THE ROOTS

The fertilizing constituents of asparagus roots were found by Rousseaux and Brioux[1] to be as follows:

---

[1] Ibid.

	Manure only %	Manure and Chemicals %
Dry matter	28.26	26.27
Ash	6.90	7.22
Nitrogen	1.20	1.73
Phosphoric acid	0.50	0.48
Potash	1.23	1.57
Lime	0.31	0.41
Magnesia	0.04	0.05
Sulfuric acid	0.33	0.36

Wichers and Tollens[2] reported the following results on the principal fertilizing constituents:

	Roots %	Crown %
Moisture	3.00	3.86
Nitrogen	2.26	1.64
Phosphoric acid (P_2O_5)	0.89	0.54
Potash (K_2O)	1.44	1.60

The general average of fertilizing constituents calculated from the various analyses made at this Experiment Station is as follows:

	Per Cent.
Dry matter	21.68
Ash*	6.56
Nitrogen	1.95
Phosphoric acid (P_2O_5)	0.48
Potash (K_2O)	2.36
Lime (CaO)	0.34
Soda (Na_2O)	0.30
Magnesia (MgO)	0.17
Sulfuric acid (SO_3)	0.56

*Ash determinations and all ash analyses were made in the Fertilizer Section by Mr. H. D. Haskins and Mr. L. S. Walker.

An interesting fact shown by this table is the higher average percentage of sulfuric acid over that of phosphoric acid. The proportions of fertilizing constituents were varied somewhat by

---

[2] Loc. cit. p. 109.

the applications of different quantities of the chemical fertilizers, as is usually observable in similar experiment with crops.

EFFECT OF NITRATE OF SODA ON ASH CONSTITUENTS

Roots of 1908

	No Nitrate Plots 1 and 40	Low Nitrate Plots 31, 32, 33	Medium Nitrate Plots 34, 35, 36	High Nitrate Plots 37, 38, 39
Ash	5.73	6.40	6.69	6.59
Phosphoric acid	0.47	0.53	0.47	0.51
Potash	2.27	2.33	2.46	2.54
Lime	0.30	0.28	0.32	0.34
Soda	0.07	0.20	0.27	0.26
Magnesia	0.13	0.14	0.15	0.15
Sulfuric acid	0.39	0.48	0.52	0.52

EFFECT OF SUPERPHOSPHATE ON ASH CONSTITUENTS

Roots of 1910

	No Phosphate Plot 5	Low Phosphate Plot 6	Medium Phosphate Plot 7	High Phosphate Plot 8
Ash	6.81	7.09	7.54	7.34
Phosphoric acid	0.47	0.46	0.46	0.49
Potash	2.36	2.66	2.73	2.54
Lime	0.41	0.32	0.37	0.38
Soda	0.43	0.35	0.38	0.33
Magnesia	0.18	0.16	0.21	0.19
Sulfuric acid	.069	0.62	0.68	0.63

EFFECT OF MURIATE OF POTASH ON ASH CONSTITUENTS

Roots of 1910

	No Potash Plot 9	Low Potash Plot 10	Medium Potash Plot 11	High Potash Plot 12
Ash	5.94	6.17	6.18	7.10
Phosphoric acid	0.44	0.42	0.46	0.48
Potash	1.44	2.10	2.20	2.53
Lime	0.38	0.33	0.34	0.40
Soda	0.55	0.48	0.33	0.33
Magnesia	0.19	0.18	0.19	0.20
Sulfuric acid	0.66	0.57	0.62	0.62

The presence or absence of phosphoric acid in the top-dressing produces little or no perceptible effect on the ash and ash constituents, even the phosphoric acid percentages being remarkably uniform throughout the whole series of tests. The absence of nitrate of soda and muriate of potash reduces the percentage of ash and in the former case the soda and sulfuric acid are reduced also; while in the latter case it is the potash which is reduced. Lime and magnesia are apparently unaffected by the variations in top-dressings.

EFFECT OF FERTILIZERS ON THE NITROGEN AND NITROGENOUS RESERVE MATERIAL

The nitrogenous matter stored in the roots was definitely affected by the different quantities of nitrate of soda applied, and also by its season of application; but the superphosphate and muriate of potash had no effect on the percentage of this element.

EFFECT OF NITRATE OF SODA ON NITROGEN

	Plots	1908 %	1910 %
No Nitrate	1 and 40	1.28	1.53
Low Nitrate	31, 32, 33	1.69	1.82
Medium Nitrate	34, 35, 36	2.10	1.97
High Nitrate	37, 38, 39	2.10	2.05

EFFECT OF SUPERPHOSPHATES ON NITROGEN

	Plot	1910 %
No Phosphate	5	2.27
Low Phosphate	6	2.05
Medium Phosphate	7	2.18
High Phosphate	8	2.04

EFFECT OF MURIATE OF POTASH ON NITROGEN

	Plot	1910 %
No Potash	9	2.10
Low Potash	10	2.02
Medium Potash	11	2.06
High Potash	12	2.08

EFFECT OF SEASON OF APPLICATION OF NITRATE OF SODA ON THE NITROGEN

SPRING APPLICATION

	Plot	1908 %	1910 %
Low	31	1.57	1.64
Medium	34	2.18	1.97
High	37	1.96	1.96
Average		1.90	1.86

SUMMER APPLICATION.

	Plot	1908 %	1910 %
Low	32	1.78	1.99
Medium	35	2.23	2.01
High	38	2.36	2.22
Average		2.12	2.07

SPRING AND SUMMER APPLICATIONS

	Plot	1908 %	1910 %
Low	33	1.73	1.82
Medium	36	1.92	1.94
High	39	1.98	1.98
Average		1.88	1.91

The higher percentage of nitrogen due to the summer top-dressing with nitrate of soda is very noticeable, as was the smaller average weight of roots, compared with the spring application.

The roots of 1911 gathered in the summer just before the annual summer top-dressing showed the same general differences between the spring top-dressing and summer top-dressing.

SPRING APPLICATION

Plot	Per Cent.
31	1.81
34	2.05
Average	1.93

SUMMER APPLICATION.

Plot	Per Cent.
32	2.06
35	2.15
Average	2.10

Whatever exhaustion of material occurred during the cutting season did not influence the percentages of nitrogen in the roots.

EFFECT OF FERTILIZERS ON THE NON-NITROGENOUS MATERIAL OF ASPARAGUS ROOTS.

Wichers and Tollens[1] have shown the proximate composition of asparagus roots and crowns to be as follows:

	April		July	
	Roots	Crowns	Roots	Crowns
Moisture,	3.00	3.86	3.61	2.93
Ash,	12.20	15.21	11.77	11.67
Crude Protein,	14.13	10.25	16.56	9.90
Crude Fiber,	8.72	15.42	13.54	19.79
Fat,	0.72	1.59	1.10	1.67
Nitrogen-free Extract,	61.23	53.67	53.42	54.04
	100.00	100.00	100.00	100.00
Sugar,	36.80	17.70	23.19	15.32
Pentosans	6.25	9.77	7.73	11.48

The writer has found the composition of the combined crowns and roots in his samples to average as follows:

	Nov., 1908 16 Roots	Nov., 1910 4 Roots	June, 1911 8 Roots
Dry Matter,		22.40	18.34
Ash,	6.24	7.68	8.87
Crude Protein,	11.03	11.02	12.75
Crude Fiber,	15.39	17.89	23.66
Fat,	1.00	1.58	1.63
Nitrogen-free Extract,	66.34	61.83	53.09
	100.00	100.00	100.00
Sugar,	41.43	35.85	20.87
Pentosans,	8.78	10.12	11.66

---

[1] Loc. cit. p. 109.

The sugar which forms such an important percentage of the reserve material has been found to be a soluble carbohydrate readily hydrolyzed to glucose and fructose, having a rotatory power differing widely from cane sugar, but otherwise resembling it in all its chemical properties.[1]

In the series of 1910 and that of 1911, particular attention was paid to the sugar to determine if fertilizers had any effect on its development.

The sugar was extracted by heating 2 gms. of the dry, finely powdered material with 50 cc. water in the boiling water-bath. Basic lead acetate and alumna cream were added after the solution was cool, and the volume made up to 100 cc. When the precipitate had settled, which its usually did in an hour, the solution was filtered through a dry filter. The lead was then removed with sodium carbonate and an aliquot of 50 cc. was inverted by HCl by standing for 24 hours at 20° to 25° C.

About half of the samples showed the presence of reducing sugars before inversion, but seldom more than a trace; the remainder showed no presence of reducing sugars.

The total invert-sugar was determined by use of Fehling's solution in the usual manner, and the copper was determined volumetrically.

In the nitrogen series the sugar was determined in each root and then averaged for the plot as in the nitrogen investigation, but in the superphosphate and potash series only two roots from each plot were used.

EFFECT OF NITRATE OF SODA ON SUGAR

No Nitrate

Plot	1910 %	1911 %
1	29.80	
40	37.41	

---

[1] Tanret, loc. cit.
Wichers and Tollens, loc. cit.
Morse, Jour. Am. Chem. Soc., 33, 211-215.

Low Nitrate

	Plot	1910	1911
Spring	31	35.76	25.76
Summer	32	29.79	13.30
Spring and Summer	33	31.85	

Medium Nitrate

	Plot	1910	1911
Spring	34	34.56	27.84
Summer	35	38.56	25.90
Spring and Summer	36	31.59	

High Nitrate

	Plot	1910 %	1911 %
Spring	37	35.48	
Summer	38	36.04	
Spring and Summer	39	34.43	

Effect of Superphosphate and Muriate of Potash on Sugar

	Plot	1910 %
No Phosphate	5	26.02
Low Phosphate	6	25.89
Medium Phosphate	7	28.05
High Phosphate	8	24.86
No Potash	9	28.72
Low Potash	10	32.56
Medium Potash	11	32.10
High Potash	12	34.79

The percentages of sugar vary independently of the various kinds of top-dressing, since there are wide variations in the results for plots 7, 11 and 34, on which identical amounts of fertilizers had been applied.

The season of application of nitrate of soda apparently did not influence the percentages of sugar in the fall roots, but there is less apparent exhaustion in the 1911 roots where nitrate had been applied in the spring (plots 31 and 34).

Since the variations in sugar showed so little relationship to the scheme of fertilization, it was not deemed worth while to pursue the investigation into the effects upon fiber and pentosans as there are too many factors to be correlated.

Summarizing the results briefly, it has been shown that the medium amounts of chemicals in this series of fertilizer tests produced the most favorable results on size and composition of the asparagus roots.

The absence of any one of the three fertilizers resulted in depression of weight of root, which was accompanied by a depression in nitrogen in the absence of nitrate of soda, and by a depression in the potash and ash in the absence of muriate of potash.

The summer top-dressing with nitrate of soda produced smaller roots than the spring top-dressing, but with notably higher percentages of nitrogen. The exhaustion of the roots by the cropping season was most manifest in the percentages of sugar, in the roots from the summer top-dressed plots.

The thanks of the author are due Messrs. Haskins and Walker for the analytical data on ash and ash constituents, to Dr. W. P. Brooks, Director for the fertilizer data, and to Dr. J. B. Lindsey, Chemist, for many timely suggestions.

CONCLUSION

ETUDE AGROLOGIQUE DU MANGANESE

P. Nottin

Paris, France

Le phénomène d'absorption du manganèse par la terre arable et l'étude des eaux de drainage montrent que les terres ne contiennent que fort peu de manganèse soluble dans l'eau. Au contraire, dans les terres que j'ai pu examiner, j'ai trouvé de notables quantités de manganèse soluble dans l'eau acidulée; ces quantités sont suffisantes pour permettre un dosage facile et exact.

Il serait intéressant de savoir si la teneur d'un solen manganèse soluble dans l'eau acidulée a un rapport avec l'exigence de ce sol en engrais mangané. Pour résoudre cette question, il y aurait lieu, dans tous les essais culturaux qui seront faits sur les engrais manganés, de déterminer la teneur du sol en manganèse soluble dans les réactifs faibles.

Lorsque de nombreuses déterminations auront été faites dans ce sens, on pourra seulement juger de la nécessité des engrais manganés dans un sol déterminé par comparaison avec les résultats pércédemment obtenus.

REMARKS ON THE THEORY CONCERNING THE ACTION OF FERTILIZERS

By Arthur Rindell

Helsingfors, Finland

Liebig's theory for the action of fertilizers was founded on the postulate, that the soil must receive a compensation for the mineral plant food carried away by the crops. On the other hand he demanded no supply of the atmospheric nutrients carbon, hydrogen, nitrogen and oxygen. His well-known failure with the patent-fertilizers taught him very soon, that a certain degree of solubility is necessary for the desired action and the experience of later times has only confirmed this conclusion. We know for instance, that the potash of feldspar and the phosphoric acid of mineral phosphates have a very feeble fertilizing action. On the other hand, we cannot agree with *Liebig's* opinion about the nitrogen compounds in the soil after all the brilliant progresses of our knowledge of their importance and biological transformations.

With these corrections the compensation-theory is still alive and actually in use as a basis for the manuring of cultivated fields. For my part I must confess, that there are still some points to criticise. My first remark is directed not properly against the theory itself, but against the manner to apply it to the calculation of fertilizers needed for the pretended compensation. It is usual to tell the farmers of the amount needed for the compensation and then add a certain supplement to assure the effect. This is more than a compensation. But even if we strictly follow the rule of *Liebig* we compel the people to give a surplus. It is to be remarked, that the spontaneous weathering processes every year yield considerable amounts of plant food not taken into consideration by *Liebig*. The accumulation of these nutrients is possible to a certain extent and must enrich the soil. It is not necessary to dwell upon the different conditions affecting the leaching processes in their contest with the accumulating absorptive power, but I would emphasize, that the chemical investigations of cultivated soils have fully demonstrated cases of such enrichment. The considerable increase of the average yields of the cultivated fields in Germany and other European countries gives the practical demonstration of the high value, which, must be awarded to this manuring system. It is evident, that there must be a limit for the increased fertility, but that is still a question of future experience.

From the above considerations we must conclude, that the action of the fertilizers is not, to give the compensation demanded by *Liebig.* On the other hand their aim can not be to enrich the soil indefinitely. What is then the signification of fertilizers?

To this question I might give an answer with the following considerations. *Liebscher*[1] has clearly demonstrated, that assimilation of plant food and growth vary for every crop at different stages of its development and not in the same manner. The investigations of *Hellriegel* have made it highly probable, that a certain amount of water is needed to produce the unit of dry matter. When at a certain period, nitrogen for instance, is assimilated faster, as the dry matters are formed, it is obvious, that the solution of the required nitrogen compounds must be more concentrated than in periods when the increase of dry matter keeps pace with the nitrogen assimilation. Already *Liebscher* has claimed that the want of fertilizers is connected with a quicker assimilation of plant food.

The condition for a quick assimilation is evidently a sufficient solubility and hence we arrive at the conclusion, that the aim of the fertilizers is to yield a nutrient solution of the concentration demanded at the periods of the most lively assimilation. This is not incompatible with the effects of the absorptive power in the soil. On the contrary, according to the absorption isotherm, we must expect that a concentrated solution gives absorptive compounds of higher solubility, than a weaker one.

When a soil is cultivated without fertilizers the yields are determined by the possibility of getting the right food at the right time and in the right concentration. With regard to the

---

[1] Journal f. Landwirtschaft, 35. 335.

very slight solubility of the mineral constituents this concentration seems to be very weak and scarcely different in different soils. But it is to be observed, that the evaporation of water must tend towards producing a higher concentration of the soil solution and towards creating absorptive compounds corresponding to such concentrations. A large stock of absorbed plant food can thus be accumulated, when the physical and chemical conditions are favorable. It is evident, that the supply of easily soluble substances, must create such favorable accumulation in the most efficient manner, but this accumulation is of importance to the crops only, when the natural supply is too feeble.

Taking in consideration all these circumstances we can easily explain the frequent discrepance of theory and practice in questions of manuring. We can also see, that there must be a possibility to determine the amount of available plant food in the soil, but only by the aid of methods founded on the basis of physical chemistry and not the obsolete proceedings actually in use. In a paper presented to the II international agrogeological conference in Stockholm 1911, I have indicated the leading ideas in this direction and can here only refer to the Reports of this Conference.

It seems to me, that the conception indicated above is very suitable for the removal of all reasonable objections against the approved theory of *Liebig* and also most agreeable to nature, to practical experience and to the present state of knowledge.

(*Abstract*)

THE CHEMICAL COMPOSITION OF IMPORTANT AMERICAN SOILS

By W. O. Robinson

Department of Agriculture, Washington, D. C.

The results obtained by the analysis of 18 soils and subsoils of important types from New York, Pennsylvania, Virginia, North Carolina, South Carolina and Alabama have led to the following conclusions:—

1. Silica is uniformly higher in the surface soil than in the subsoil. Iron, aluminum and titanium are uniformly higher in the subsoil. In all cases but one manganese had concentrated in the surface soil.

2. Of the elements not ordinarily determined, lithium was shown to be present in all cases; caesium and rubidium could not be found. The rare earths were present in all soils; chromium, vanadium, and zirconium were present in all cases and in decided amounts; barium and strontium were present in all cases in determinable amounts; molybbdenum was proved to be present in one soil only.

3. The sulphur content of soils is much lower than expected. The average of 18 determinations gave 0.044 per cent. S. More attention should be given to this element in fertilizer practices.

THE USE OF GROUND ROCKS AND GROUND MINERALS AS FERTILIZERS

W. O. Robinson and W. H. Fry

Department of Agriculture, Washington, D.C.

Since the experiments of Mangus in 1850 it has been known that ground orthoclase could furnish enough potash to grow plants to maturity. Later experiments have shown that a large number of ground minerals could be successfully used for the same purpose, and in recent years some of these have been proposed as commerical fertilizers.

The Germans have been particularly active in the investigation of the value of mineral fertilizers. This seems to be partly due to Julius Hensel and his followers who believed that the filth of manures and commercial fertilizers produced plant growth unfit for human consumption. The strictly inorganic ground minerals, they contended, stimulated a healthy growth.

The monopoly control of the potash supply added zest to the investigation of potash minerals as substitutes for the soluble potash fertilizers, and numerous field and pot experiments carried on in the United States and abroad have definitely proven that ground leucite, phonolite, muscovite and orthoclase can function as potash fertilizers and in the order of merit named.

There is great variation of opinion concerning the economic value of these materials. In the case of phonolite it is agreed that the acid soluble potash must be bought as cheaply as in the Stassfurt salts.

Leucite and phonolite are not of sufficiently wide occurrence in the United States to merit consideration for use here. Orthoclase and muscovite, however, are very widely distributed and are being mined on a large scale for various purposes.

The potash in both these latter minerals is insoluble in the fertilizer sense of the word, and, moreover, they are normal constituents of soils.

The potash in feldspar and mica, ground sufficiently fine to pass a sieve of 100 meshes to the linear inch, can now be obtained for about $75 and $150 per ton respectively. The potash of the Stassfurt salts costs from $90 to $100 per ton. Pound for pound of potash, ground feldspar produces less than one fifth the yield of the Stassfurt salts. This is a liberal estimate based on over 50 pot and field experiments.

There is another point which clearly illustrates the futility of applying ground orthoclase and mica to our soils. American soils contain much more than can be economically added. Nine soils of important types from New York, Pennsylvania, Virginia, North Carolina, South Carolina and Alabama contained, on the average, in the very fine sands and silts, 206 tons of orthoclase and 298 tons of muscovite per acre to a depth of three feet. No soil contained less than 25 tons of potash feldspars, though in two soils muscovite was not present in a quantity sufficient to determine. The data were gotten by microscopical count and represent only the amount of the minerals in question in the very fine sands and silts. The amounts present in the coarser sands and clays could not be readily estimated. These figures therefore represent but a part of the total amount present.

The main points brought out in this paper are:—

1. Numerous field and pot experiments hitherto performed have proven that orthoclase and potash mica are not efficient potash fertilizers.

2. At present prices the insoluble potash of orthoclase and muscovite costs more than the soluble potash of the Stassfurt salts.

3. Orthoclase and muscovite are present in American soils in such amounts that any economic application is, figuratively speaking, only a drop in the bucket, and surely can produce no more than proportionate yields.

THE EXTRACTION OF POTASH FROM SILICATE ROCKS

By William H. Ross

Bureau of Soils, Washington, D. C.

The potash-bearing minerals of the United States may conveniently be divided into three classes, as follows: (1) Alunite and similar minerals; (2) the greensand marls; and (3) the igneous rocks.

Alunite is a hydrated sulphate of aluminum and potassium. It differs from the minerals of the other two groups in that the potassium is readily available by simple ignition of the mineral to a dull red heat.[1] When occurring in sufficient quantity and purity alunite is thus a possible economic source of potash and has long served as a source of potassium alum in Italy and other countries. Its occurrence in this country is limited to comparatively small deposits in Utah, Colorado and Nevada, the largest so far known, near Marysvale, Utah, having been recently described.[2]

Greensand, or glauconite, is essentially a hydrated silicate of iron and potassium, but it is extremely variable in composition and never occurs pure. It is formed through the interaction of various alteration products, and organic matter is believed to play a part in its formation,[3] which would explain its occurrence in the marl deposits of Kentucky, New Jersey, Tennessee and other States. Like the minerals of the third group it is a refractory silicate, and the potash which it contains is not readily available.

The potash-bearing igneous rocks are among the most widely distributed minerals and occur as constituents of nearly all rocks. The principal minerals of this class from the point of view

---

[1] Waggaman, Circular No. 70, Bureau of Soils, U. S. Dept. Agri.

[2] Butler and Gale, Bull. U. S. Geol. Survey, No. 511.

[3] Clarke, Bull. U. S. Geol. Survey, No. 491, p. 492.

of the potash which they contain are orthoclase, or microcline, muscovite, and leucite. Millions of tons of rock containing one or more of these and related minerals with a potash content in the neighborhood of 10 per cent. are to be found widely distributed all over the globe. It is for this reason that the igneous minerals, particularly the potash feldspars, are most often spoken of as a source of potash salts.

In Table 1 is given sample analyses of the most important potash-bearing minerals:

TABLE I.—Analyses of potash-bearing minerals.

	(1)	(2)	(3)	(4)	(5)
SiO_2	0.22	51.56	65.87	44.39	50.23
TiO_2	——	——	——	——	2.27
Al_2O_3	37.18	6.62	19.10	35.70	11.22
Fe_2O_3	Trace	15.16	——	1.09	3.34
FeO	——	8.33	——	1.07	1.84
MgO	——	.95	None	——	7.09
CaO	——	.62	.20	.10	5.99
Na_2O	.33	1.84	2.56	2.41	1.37
K_2O	10.46	4.15	12.24	9.77	9.81
H_2O	12.99	10.32	.64	5.88	2.65
P_2O_5	.58	——	——	——	1.89
SO_3	38.34	——	——	——	.74
Fl	——	——	——	.42	.50
Other constituents	——	——	——	——	1.68
	100.10	99.55	100.61	100.83	100.62

[1] Alunite from Marysvale, Utah. Selected Specimen. Analysis by W. T. Schaller, Bull. U. S. Geol. Survey, No. 511, p. 8.

[2] Glauconite from greensand marl. Hanover Co., Virginia. Analysis by M. B. Corse and C. Baskerville, Am. Chem. Jour., 14,627.

[3] Ground commercial feldspar from quarry of J. B. Richardson & Sons, Bedford, Ont. Analysis by George Steiger, Bull. U. S. Geol. Survey, No. 420, p. 9.

The desirability of finding some economical way of extracting potash from these minerals has long attracted the attention of various investigators and numerous patents have been issued covering processes which are claimed to solve this difficult problem.

The increasing yearly demand for potash salts in connection with artificial fertilizers has of late renewed interest in this direction, and in some cases companies have been organized for the purpose of manufacturing potash by one or other of the various processes which have been proposed, but up to the present no potash prepared in this way has been placed on the market.

Practically all methods yet proposed, in principle at least, have been covered by patents. A comparative study was therefore undertaken of all the processes for which patents have been allowed, with a view to finding what methods, if any, give promise of being practicable commercially. It is thought advisable to publish some of the results thus far obtained.

The most convenient way of determining the alkalies in silicate rocks is the well-known J. Lawrence Smith method. According to the directions usually given for this method, 0.5 gram of the ground material is mixed with an equal weight of pure ammonium chloride and 4 grams of calcium carbonate. On igniting the mixture gently at first, the ammonium chloride is volatilized and part of the calcium carbonate is converted into calcium chloride. These two compounds of calcium when heated at a temperature of about 1,000° C. with feldspar, or other silicate rock, brings about its decomposition, and any potash present is converted quantitatively into potassium chloride. The same result is obtained if the proper amount of calcium chloride is used instead of ammonium chloride in the first place.

Of the many patents which have been issued for extracting potash from silicate rocks, at least four may be considered modifications of the J. Lawrence Smith method, since the essential feature of each consists in heating the potash-bearing material with calcium carbonate and some metallic chloride.

---

[4] Muscovite from Auburn, Maine. Analysis by R. B. Riggs, Bull. U. S. Geol. Survey, No. 419, p. 286.

[5] Leucite-bearing rock, Wyoming. Analysis by W. F. Hillebrand, Bull. U. S. Geol. Survey, No. 512, p. 11.

The first of these, United States patent No. 513001, was issued to H. S. Blackmore in 1894. To produce a soluble potassium salt according to this patent, orthoclase, reduced to a fine powder, is mixed with finely powdered calcium chloride in about equal proportions to the potassium silicate present. To the mixture is then added an excess of calcium oxide and a sufficient quantity of water to render the entire mass moist. This is introduced into a sealed furnace, or retort, and heated to a temperature of about 1,100° C., whereby the water mixed with the mass is converted into superheated steam at a high pressure, which is supposed to assist materially in the transformation of the orthoclase into soluble potassium chloride and insoluble silicates of calcium and aluminum. The heating is continued for about two hours, and, after cooling, the mass is placed in vats and lixiviated.

The part of the process as patented which requires the moist mass to be heated in a sealed furnace to a temperature of 1,100° C. could obviously not be carried out on a large scale, for it would not be feasible to make a furnace which would stand the pressure produced at this temperature.

In 1900 United States patent No. 641406 was granted to G. J. Rhodin for obtaining soluble potassium salts from feldspar. In carrying out the process according to this invention, 1 part of feldspar is mixed with 1 part of lime, and 0.2 part of sodium chloride, all in a finely powdered condition. The mixture is then heated in a closed vessel of iron or other material, or else in an open-hearth or blast furnace, to a bright yellow heat and maintained at that temperature for a considerable time, care being taken not to melt or fuse the mixture. The cooled mass which still remains in a powder may be applied directly as a manure, since the potash present is claimed to be rendered available by the treatment, or it may be separated from the mass by treatment with acids.

In 1907 United States patent No. 869011 was issued to Ralph H. McKee for a process for producing potassium compounds from potash-bearing material containing mica by essentially the same treatment as that covered by Rhodin's patent for the extraction of potash from feldspar.

United States patent No. 987436 was granted to A. S. Cushman in 1911 for a method for obtaining potash from silicate rocks. According to this method the feldspathic rock is reduced to as fine a subdivision as possible and mixed with finely powdered quicklime in the proportion of 100 parts of the rock to 20 parts of lime. The mixture is then spread on a suitable conveyor, as belt or drum, in the form of a bed having a thickness from three-eighths to one-half inch. To the surface of this bed is now applied a solution of calcium chloride in separate drops, and of such a concentration that the amount of calcium chloride added should be sufficient to supply chlorine in quantities at least molecularly equivalent to the total alkali contained in that portion of the feldspar which becomes aggregated into lumps on the addition of the solution. The aggregates, which harden quickly at ordinary temperatures, are separated from the unconverted powder by screening, and are then heated in a rotary kiln at a temperature preferably, but not necessarily, below the point at which a substantial part of the potassium chloride is sublimed. The product is discharged continuously from the furnace in lumps and may be crushed for use directly as a fertilizer; or the potassium chloride may be extracted by means of water and recovered from the solution, or utilized therein in any preferred way.

From a comparative study which was made of these patents it does not appear that the use of sodium chloride has any advantage over calcium chloride. The latter is a by-product obtained in large quantities in the manufacture of sodium carbonate, and is somewhat more effective than the former in bringing about complete decomposition of the feldspar, but when limited amounts of the reagents are used, a somewhat larger amount of the potash is rendered soluble with the use of sodium chloride than with calcium chloride. In Table II is given the percentages of the total potash in the feldspar which have been rendered soluble on heating a given amount of feldspar at 1,000° to 1,050° C. with varying amounts of calcium carbonate and calcium chloride and with calcium carbonate and sodium chloride. The feldspar used in these experiments was ground to pass a 100-mesh sieve and contained 13.72 per cent. of K_2O and 2.18 per cent. of Na_2O.

Table II:—Showing percentages of alkalies rendered soluble when feldspar is ignited with varying amounts of calcium carbonate and calcium chloride, and with calcium carbonate and sodium chloride.

Feldspar	$CaCO_3$	$CaCl_2$	NaCl	Time of ignition	Na_2O obtained in percentage of feldspar	K_2O obtained in percentage of feldspar	Percentage of K_2O in feldspar rendered soluble
Grms.	Grms.	Grams	Grams	Hours			
1	1	0.25		2	1.8	8.2	59.8
1	1	.50		2	1.6	9.4	68.5
1	2	.25		2	1.8	10.7	78.0
1	2	.50		2	2.0	13.0	94.8
1	3	.25		1	1.8	10.8	78.7
1	3	.25		2	1.8	10.9	79.4
1	3	.50		1	2.0	13.0	94.8
1	3	.50		2	2.0	13.2	96.2
1	3	1.00		2	2.2	13.6	99.1
1	1		0.25	2		9.5	69.2
1	1		.50	2		11.2	81.6
1	2		.50	2		11.7	85.3
1	3		.25	2		9.4	68.5

In these experiments the results show that while a considerable portion of the potash was rendered available when using approximately the proportions of the reagents stated in the patents, the total potash in the feldspar was not rendered soluble in this way at the temperature specified. Thus, when 1 part of feldspar is ignited with 1 part of calcium carbonate and 0.25 part of calcium chloride, which is 0.05 part in excess of that equivalent to the alkalies in the feldspar, only about 60 per cent. of the potash in the feldspar is rendered soluble. Increasing the proportions of calcium carbonate and calcium chloride used produces a comparatively small increase in the amount of soluble potash obtained, and complete decomposition of the feldspar only takes place when

1 part is ignited, under the conditions of the experiment, with about 1 part of calcium chloride and about 2 to 3 parts of lime. When this proportion of the reagents is used, considerable variation in the temperature of ignition will give the same results, and almost the entire amount of the potash is rendered soluble at a temperature below the melting point of potassium chloride.

The results obtained on igniting feldspar with lime and sodium chloride are in agreement with those published by Rhodin,[1] the author of the patent covering the process, who only claimed an extraction of about 41 per cent. of the potash in the feldspar when using the proportion of the reagents stated in the patent, viz., 1 part feldspar, 1 part lime, equal to 1.8 part calcium carbonate, and 0.2 part sodium chloride. It was pointed out, however, that a more favorable result was obtained by using a larger amount of salt with a smaller amount of lime. Thus, when 100 parts of feldspar were ignited to 900° C., with 40 parts of lime and 40 parts of salt, about 70 per cent. of the potash in the feldspar became soluble, which agrees with the value given in the table for approximately this proportion of the reagents.

Unless a large excess of calcium chloride is used, when ignited with feldspar and lime, no vitrification takes place on heating to a temperature up to 1,050° C. The ignited mass remains in the form of a powder, and consequently the soluble material present can be readily leached out without the necessity of any previous grinding of the mass. The same statements hold true when sodium chloride is used, but with a more limited variation in the proportions of the reagents which may be taken. Thus, a hardened mass is obtained when 1 part of feldspar is ignited to 1,050° C., and with 1 part of calcium carbonate and 0.25 part of sodium chloride, but if the proportion of calcium carbonate is doubled the mass remains in a powdered form. When calcium chloride is used, the mass does not harden on ignition, even with 1 part of calcium carbonate.

On account of its simplicity, the method of decomposing feldspar by heating with calcium carbonate and with calcium chloride (or sodium chloride) could undoubtedly be carried out on a large

---

[1] J. Soc. Chem. Ind., 20, 439 (1901).

scale without involving any serious mechanical difficulty, and the method would thus be a practical one providing the value of the products obtained would compensate for the expense involved. Although pure feldspar may be obtained which contains upward of 15 per cent. potash, the average grade of feldspar which could be mined on a large scale would undoubtedly contain less than 10 per cent. If potash be quoted at 66 cents a unit,[1] then the potash in a ton of feldspar containing even 10 per cent. of this constituent would be worth only $6.60 when converted into a soluble form. It is thus evident that the value of the potash alone will not compensate for its extraction by this process, or by any modifications of it for which patents have been granted; nor is it at all likely in view of the comparatively low percentage of potash in all silicate rocks that any process can be derived which will prove so simple that the value of the potash alone will pay for its extraction. It seems safe to say, therefore, that any method to be economical must produce at the same time other products of value in addition to the potassium.

One of the first patents on a process for converting the insoluble potash in feldspar into a soluble form was issued in 1856 to Charles Bickell (United States patent No. 16111). The process consists in heating in a reverberatory or other suitable furnace to a light-red heat for about 2 hours 1 part feldspar, 0.5 part phosphate of lime, and 3 or 4 parts of lime, all in a finely divided state. According to the patent the potash becomes available by this treatment, and may be extracted in a caustic state by lixiviating with water, or the mass may be used directly as a manure.

At first sight this process seemed particularly attractive, for if both the potash and phosphoric acid were rendered available by this treatment, as claimed by the patent, the method might be an economical one, since when used as a fertilizer no separation of the constituents would be necessary, and the mixture would be of value for its phosphoric acid as well as its potash content.

It was found, however, that the calcium phosphate has a passive effect in this treatment of the feldspar, and that no greater

---

[1] Estimated from prices quoted by the German Kali Works.

decomposition was produced in this way than when it was heated with calcium carbonate alone.

Thus when 1 gram of feldspar, 0.5 gram of calcium phosphate, and 3 grams of calcium carbonate were mixed and ignited for two hours at 1,000° C., in a J. Lawrence Smith crucible, the amount of potash rendered soluble only amounted to about 2 per cent. of the feldspar. The amount of soluble potash obtained when 1 gram of feldspar and 3 grams of calcium carbonate were ignited in the same way, likewise amounted to approximately 2 per cent, but in each case the greater part of the residue remaining after extracting with water was decomposed when treated with dilute hydrochloric acid, the potash going into solution.

When the temperature was increased to about 1,200° C., the soluble potash amounted to 5 per cent. of the feldspar, and the extracted residue was then found to be readily and completely decomposed by hydrochloric acid. From this solution was obtained the remaining portion of the potash which did not dissolve on digesting with water.

The crucible in which these ignitions were made was closed with a cap, and as this end of the crucible was not ignited, there was little tendency for the potash to escape, but when the ignition was made in an open platinum dish in a furnace at a temperature of about 1,400° C., the potash in the feldspar was found to have been completely lost by volatilization.

In carrying out this experiment the feldspar was first dried to constant weight by heating in a muffle furnace at 1,000° C. The calcium oxide used was likewise reduced to constant weight by igniting chemically pure calcium carbonate at a temperature of 1,400° C., for several hours. One gram of the feldspar and 1.68 grams of calcium oxide, equivalent to 3 grams of calcium carbonate, were then well mixed and ignited in an open dish in the furnace at 1,400° C., for one hour. The weight of the mixture was found to have decreased by 0.1606 gram, which is equal to 16 per cent. of the feldspar. The residue was then analyzed for potassium, but only a trace was found.

The experiment was then repeated, using ten times the amount of feldspar and a corresponding amount of calcium oxide. The same care was taken as before to reduce each constituent to constant weight before mixing. After igniting for one-half hour the loss in weight of the mixture amounted to 1.3912 grams, equal to 13.9 per cent. of the feldspar. On repeating the ignition for one hour a further loss in weight of 0.1630 gram took place, which was increased to 0.1768 gram on igniting for one hour longer, making a total loss of 1.5680 grams, equal to 15.7 per cent. of the feldspar. Since the feldspar was shown by analysis to contain 15.9 per cent. of $K_2O + Na_2O$, it would thus appear that the greater part of the alkalies in the feldspar were driven off in the form of oxides. This was confirmed by an analysis of the residue, which contained less than 0.2 per cent. of total alkalies.

The hardened mass remaining after ignition strongly resembled cement clinker, and that the product obtained by igniting feldspar and lime together contains all the essential elements of a cement is well known. Using the feldspar and lime in the proportions of 1 to 3, a clinker approaching the composition of Portland cement is obtained.

Thus, if 1 part of feldspar assumed to contain the theoretical amounts of potash, alumina and silica loses the first named constituent, amounting to 0.17 part when ignited with 1.68 parts of calcium oxide, or 3 parts of calcium carbonate, then the clinker which remains will equal 2.51 parts, and will have the percentage composition given in Table III. In the second and third columns are also given the minimum and maximum limits of the constituents of good Portland cement.[1]

TABLE III:—Comparison of the composition of feldspar-lime clinker with that of Portland cement.

Constituents	Feldspar lime clinker	Portland cement	
		Minimum	Maximum
Silica	25.8	19	26
Alumina	7.3	4	11
Lime	66.9	58	67
Ferric Oxide	0	2	5
Magnesia	0	0	5
Sulphuric acid	0	0	2.5
Alkalies	0	0	3

---

[1] Bleininger, Bull. Ohio Geol. Survey, No. 3, p. 197.

Table III shows that all the constituents of pure feldspar-lime clinker lie between the limits allowable in a good Portland cement, and that ferric oxide is the only necessary constituent absent. If commercial feldspar and lime were used, however, this would no doubt be also supplied in sufficient quantity, and at the same time the silica and lime would be reduced more closely to the mean of that found in a good Portland cement, providing the feldspar does not contain an excessive amount of free silica.

In order that a clay may be suited for the manufacture of cement it should have a percentage ratio of silica to alumina of from 3 to 1 to 4 to 1.[1] The ratio of these two constituents in feldspar is 3.5 to 1. In muscovite and leucite of theoretical composition the proportion of silica to alumina is less than 3 to 1, but in commercial samples of leucite-bearing rocks the ratio is usually greater than 4 to 1.

A clinker of the same ultimate composition as that which results when feldspar and lime are heated together may also be obtained when part of the lime is replaced by sufficient calcium chloride to be equivalent to the potash and soda in the feldspar, the total calcium used remaining the same as before. In carrying out this experiment the feldspar and lime were ignited to constant weight as already described, and the calcium chloride thoroughly dried by heating in an aid bath below its melting point. Ten grams of the feldspar were well mixed with 2.0050 grams of calcium chloride and 15.7895 grams of calcium oxide, and the mixture then ignited in an open dish in the furnace at 1400° C. By this treatment the alkalies are volatilized as the chlorides.[2] On igniting for one-half hour the weight lost by the ignited mass amounted to 2.5632 grams, equal to 25.63 per cent. of the feldspar. When expressed as the chlorides the percentage of alkalies in the feldspar used amounted to 25.82 per cent. It would appear, therefore, that practically the whole of the alkalies in the feldspar were volatilized during the first half hour of ignition. On continuing the ignition for one hour longer the additional decrease in weight which took place amounted to only 0.0090

---

[1] Bleininger, loc. cit., p. 223.

[2] Herstein, J. Ind. Eng. Chem., III, 426.

gram. The residue was then analyzed for potassium and chlorine, but only a trace of each was found.

This shows that the volatilization of the potash in feldspar takes place more rapidly when part of the lime is replaced by calcium chloride than when the feldspar is ignited with lime alone, but in each case the ultimate composition of the residue obtained is the same. Any excess of calcium chloride used above that equivalent to the potassium in the feldspar is slowly decomposed at the temperature at which the ignitions were made, leaving behind the oxide of calcium.

Since the clay used in making cement contains in some cases as high as 3 or 4 per cent. of potash, it might be expected that part would escape from the kiln and be collected with the flue dust, particularly in those plants where the Cottrell process for collecting dust has been installed. This has been observed by several investigators to really take place, and the potash then collected is found to be in the soluble form. By the substitution of feldspar for clay in the manufacture of cement the potash then collected would, no doubt, be greatly increased, but since the analyses of cement show the presence of alkalies, it follows that with the style of kilns now in use all the potash in feldspar could not be made available in this way. That a larger proportion of the potassium would be volatilized by substituting for a part of the lime sufficient calcium chloride to be equivalent to the potassium is evident from the experiments already referred to, and experiments are now being undertaken on a large scale to compare the practicability of this procedure with the simple ignition of feldspar and lime alone.

According to the census report for 1910 the Portland cement manufactured in the United States during the year 1909 amounted to 65,000,000 barrels, or 13,000,000 tons, valued at approximately $53,000,000. The maximum quantity of potash which it would be possible to obtain by the use of feldspar in the manufacture of this quantity of cement can be calculated if the potash content of the feldspar is known. This varies up to about 16 per cent., but if half of this, or 8 per cent., be taken as the average percentage of potash in commercial feldspar then 1 part of feldspar combined with 3 parts of lime, equal to 1.68 parts of calcium oxide, would yield 0.08 part of potash and 2.6 parts of cement. Therefore 13,000,000 tons of cement would produce 400,000 tons of potash. Again, quoting potash at 66 cents a unit, this would have a value of $26,400,000, which is three times the value of the potash salts used in this country during the year referred to and about twice the value of the imports for 1911. Whether or not this would cover the cost of the feldspar, its transportation, and the expenses incident to the recovery of the potash can only be determined by experimentation on a large scale, but the probability that potash salts can thus be obtained in large quantities as a by-product makes this method of getting at the potash in feldspar quite promising.

ORGANIC SOIL CONSTITUENTS IN THEIR RELATION TO SOIL FERTILITY[1]

BY OSWALD SCHREINER, PH.D.

U. S. Department of Agriculture, Bureau of Soils, Washington, D.C.

In 1907 the presence of dihydroxystearic acid and picoline carboxylic acid was discovered in an unproductive soil.[2] Both compounds were shown to be harmful to plant growth, the dihydroxystearic acid especially so. Since then the latter compound has been found in a large number of soils from various parts of the United States and a relation with the infertility of such soils established.[3] The compound has also been thoroughly studied in regard to its harmful effects on plants and its behavior in the presence of fertilizers.[4] Such researches showed the importance of a study of the chemistry of soil organic matter, about which nothing definite had previously been known.

In the past few years a still broader survey of the organic matter of the soil from the standpoint of biochemistry has been under way. The object has been to determine definitely as many constituents of the soil as possible and while this was tedious in the beginning as no methods of any kind existed for such work, the results have, nevertheless, been very promising in the last year or two, and as many as thirty-six different compounds have been isolated and identified.[5]

The definite recognition of these compounds has led to a fuller understanding of the chemistry of the organic matter of soils and of the biochemical changes taking place therein. It is not the purpose of the present paper to enter into this phase of the discussion, but rather to confine itself to the effect which certain of

---

[1] Published by permission of the Secretary of Agriculture.

[2] Schreiner and Shorey, Journ. Amer. Chem. Soc., **30**, 1295, 1599 (1908).

[3] Schreiner and Lathrop, Journ. Amer. Chem. Soc., **33**, 1412 (1911).

[4] Schreiner and Skinner, Bot. Gaz. **50**, 161 (1910).

[5] Schreiner and Shorey, Bulletins 53 and 74; Schreiner and Lathrop, Bulletins 80 and 89; Shorey, Bulletin 88, Bureau of Soils, U. S. Depart. of Agriculture.

these constituents have on plant growth. It should be mentioned, however, that the compounds isolated cover a wide range of chemical substances of biological origin. There are represented the hydrocarbons, consisting of carbon and hydrogen only; the acids, fats, resins, alcohols, aldehydes, sugars, glucosides, waxes, consisting of carbon, hydrogen and oxygen; a large group of nitrogenous compounds which consist of carbon, hydrogen, oxygen, and nitrogen; as well as organic phosphorus and organic sulphur compounds. The nitrogen compounds contain the nitrogen combined in different forms, as for instance with carbon only, as the amino group NH_2, or as the imino group NH. Most of the compounds isolated from the soil are decomposition products of proteins, nucleo-proteins, nucleic acids, lecithin and similar complex nitrogenous compounds of biological origin. There are included substituted ammonias, hexone bases, pyrimidine derivatives, purine bases, and pyridine derivatives.

The nitrogenous soil constituents isolated or determined in this laboratory up to the present time are creatinine, with the probability that creatine also exists, hypoxanthine, xanthine, guanine, adenine, cytosine, choline, trimethylamine, histidine, arginine, lysine, nucleic acid, and picoline carboxylic acid. The present paper is chiefly concerned with their relation to soil fertility.

As many as possible of these and related compounds have been studied in regard to their effect on plant growth, in most cases quite extensively. The first soil nitrogen compound studied in respect to its effect on plants was found to be moderately harmful. This was the picoline carboxylic acid studied in 1907. Since then most of the above nitrogenous compounds found in soils have been thoroughly studied in respect to their influence on plant growth, and the results uniformly show a more or less marked beneficial effect.[1]

In Table I some of these results are presented, the composition of the culture solutions in mineral constituents being given

---

[1] See also, Skinner, "Effect of Histidine and Arginine as Soil Constituents" presented before this Congress; and Bulletin 83, Part III, Bureau of Soils, U. S. Dept. Agric.

in the first 3 columns and the per cent. increase observed in the green weight of wheat plants on the addition of the respective nitrogenous soil constituents being given in the subsequent columns of the table. The mineral salts used were calcium acid phosphate and potassium sulphate, the creatinine, creatine and hypoxanthine were used as such, the arginine and histidine as carbonates, and the nucleic acid in the presence of calcium carbonate in the cultures as well as in the control cultures.

TABLE I. Showing relative increase in the growth of wheat produced by the addition of organic nitrogenous soil constituents to culture solutions containing potash and phosphate in different proportions.

p.p.m. = parts per million.

Composition of Culture Solution			Increase in the green weight of wheat produced by the addition of:						
Phosphate P_2O_5	Nitrate NH_3	Potash K_2O	Creatine 50 p.p.m.	Creatinine 50 p.p.m.	Histidine 50 p.p.m.	Arginine 50 p.p.m.	Hypoxanthine 100 p.p.m.	Nucleic acid 100 p.p.m.
p. p. m.	p. p. m.	p. p. m.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
0	0	80	28.5	12.6	16.8	22.5	16.2	93.2
8	0	72	37.1	50.0	16.3	26.2	57.5	71.7
16	0	64	36.6	8.0	26.8	29.3	23.3	88.2
24	0	56	50.1	30.3	28.3	38.6	64.7	66.7
32	0	48	61.1	54.4	57.3	63.6	69.5	90.1
40	0	40	60.0	67.4	25.3	58.3	59.0	130.8
48	0	32	35.9	29.7	51.6	33.3	69.0	45.5
56	0	24	48.6	55.8	72.4	41.6	24.2	84.1
64	0	16	53.1	53.7	21.4	23.0	14.8	83.4
72	0	8	44.5	50.0	10.7	13.1	39.0	30.8
80	0	0	11.4	4.6	10.5	8.3	5.5	12.9

Creatinine has a beneficial effect on growth. Its solution in pure water produced an increased growth over plants growing in pure water without creatinine. A more extended study showed that when combined with phosphate and potash, this nitrogenous soil constituent gave in solution cultures an increased growth.

This increased growth was observed in each and every culture, no matter what the proportion of potash and phosphate. The average effect in such cultures was an increase in plant growth of 36 per cent. This effect must be ascribed to creatinine, and is to be attributed to action within the plant after absorption. It is certain that creatinine disappears from solution in the course of the experiment as its diminution in the course of three days from 50 parts per million to 5 parts per million was experimentally determined, using the method of Folin for this purpose. The next question considered was its change to creatine, which would not have responded to this test. Boiling with hydrochloric acid, which would revert the creatine to creatinine, failed, however, to reveal any increase in the creatinine content of the culture solutions, hence this possibility is excluded. Tests for nitrite made with the delicate nitrite reagent of Griess, gave only negative results and tests for nitrate by means of the phenoldisulphonic acid reagent likewise showed the absence of any nitrate. Ammonia was tested for by means of Nesslers reagent. Traces only could be detected, which, however, was also the case in the control cultures.

It follows that the creatinine had not changed to creatine, but had disappeared from solution, without the production of nitrite, nitrate or ammonia, and hence must have been absorbed by the wheat plants as such, whatever its fate may have been after absorption. Moreover if the change had been one to creatine, this would not have explained the diminution of creatinine in the cultures. For creatine, when tested, behaved in exactly the same manner as creatinine toward plants, producing in solution cultures, with potash and phosphate added, an average increase of 44 per cent., again without the production of nitrite, nitrate or ammonia. Furthermore, the formation of nitrate was practically excluded in solution cultures of this kind, and ammonia, if formed, would not have had an effect even approximating that produced by these soil constituents in the solution cultures.

In the case of all the other soil compounds studied the solution cultures were tested for nitrites, nitrates and ammonia and always with the same result, total absence of nitrites and nitrates, and only traces of ammonia.

Histidine and arginine, both of which are protein decomposition products of the soil, showed this same increase in plant growth when potash and phosphate were also supplied, the average increase being 30 and 33 per cent. respectively. Nucleic acid and its decomposition product, hypoxanthine, likewise showed an average increase of 74 and 41 per cent. respectively. The other xanthine bases, xanthine and guanine, while not so completely studied, show, nevertheless, the same behavior as do also several other nitrogenous compounds not yet found in soils, notably, asparagine, which produced an average increase of 47 per cent.

The above results were obtained by the addition of compounds to the solutions containing phosphate and potash, but no nitrate, so that the compounds were the only source of nitrogen. When nitrates were also present the addition of the compounds produced a further increase in growth, but this was not as marked as when no nitrate whatever is supplied. For instance, in the culture series in which 8 parts per million of NH_3 as nitrate was present, the same compounds mentioned above produced the additional growth of 17 per cent. with creatinine, 11 per cent. with creatine, 14 per cent. with histidine, no increase with arginine, 23 per cent. with nucleic acid, and 14 per cent. with asparagine. It is obvious that the additional effect attributable to the organic compound is not as great as when some nitrate is supplied. The results for the 8 parts per million series of cultures are presented in Table II, the arrangement being the same as in Table I already considered. The mineral source of the nitrogen expressed in the table as NH_3 was sodium nitrate, the other salts and compounds were as explained in connection with Table I.

Experiments with higher nitrate content revealed the fact that as more nitrate is supplied the effect in the cultures containing the organic compounds becomes still less noticeable.

If this were the only information at hand, one would be justified in concluding that the plant absorbed and utilized the organic compound only when it could not get nitrate and that when this is supplied in sufficient quantity the compound is rejected, or at least not utilized. This supposition, is however, negatived by two experimentally determined facts. First, that

TABLE II. Showing relative increase in the growth of wheat produced by the addition of organic nitrogenous soil constituents to culture solutions containing potash and phosphate in different proportions, as well as a uniform quantity of 8 parts per million NH_3 as nitrate.

p.p.m. = parts per million.

Composition of Culture Solution			Increase in the green weight of wheat produced by the addition of:					
Phosphate P_2O_5	Nitrate NH_3	Potash K_2O	Creatine 50 p.p.m.	Creatinine 50 p.p.m.	Histidine 50 p.p.m.	Arginine 50 p.p.m.	Hypo-xanthine 100 p.p.m.	Nucleic acid 100 p.p.m.
p. p. m.	p. p. m.	p. p. m.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
0	8	72	6.8	20.3	4.1	— 5.3	22.9	25.5
8	8	64	8.8	25.1	10.4	0.0	13.6	28.9
16	8	56	24.0	14.6	47.7	— 4.4	14.8	14.1
24	8	48	16.0	17.6	2.0	11.0	31.4	40.6
32	8	40	0.6	91.7	34.0	13.6	12.6	27.7
40	8	32	5.0	11.2	27.8	16.0	16.0	29.9
48	8	24	4.0	32.2	— 1.8	19.8	11.3	12.5
56	8	16	10.5	13.8	—11.8	9.4	7.6	11.3
64	8	8	26.0	14.6	3.1	31.0	6.6	12.3
72	8	0	14.2	29.3	15.5	28.3	2.0	1.9

in the case of creatinine, where such an experiment was possible, this compound was shown to disappear from solution fully as fast from those cultures which contained plenty of nitrates as from those which contained none, thus showing that under both conditions the creatinine was absorbed by the plants. Second, by the results of the nitrate determinations in the nutrient solutions during growth. These results are briefly given in Table III.

These analyses established the fact that the plants consumed more nitrate when the nitrogenous compounds were absent, than they did when the compounds were present. This behavior was shown by all the compounds. It seems that the plants absorb and use such nitrogenous soil constituents whether nitrate be present or not, the effect on growth being much more marked in

TABLE III. Showing the decreased quantity of nitrate absorbed from the culture solutions in the presence of organic nitrogenous soil constituents.

Organic nitrogenous soil constituents in solution.	Decrease in nitrate absorbed Per cent.
Creatinine	25
Creatine	17
Hypoxanthine	45
Arginine	21
Histidine	27
Nucleic acid	23

the limiting case, where no nitrate was present, and that in the other cases the compounds replaced the effect of nitrate.

It will be clear from the above remarks that the culture work was throughout under strict chemical control, so as to establish as definitely as possible that the effects on the plants noted were produced by the absorption of the compounds as such. Nitrite, nitrate, or ammonia were tested for and found to be absent, or, in the case of ammonia, in traces only, and the removal of the compound itself was followed by chemical tests when this was possible. Although neither nitrate, nitrite, nor ammonia was found, the plants, nevertheless, grew remarkably well and the only conclusion justified by this experimental evidence is that these compounds are directly absorbed and assimilated. With the strict chemical control exercised all possibility of any extended action by bacterial or other external biological agencies seems excluded. If such effects were produced in these experiments, they were of only minor significance in the results obtained. Bacteria and other microorganisms were excluded as far as possible, but no special effort was made to maintain absolutely sterile conditions, inasmuch as this would have been a practical impossibility in experiments on so large a scale involving over a thousand plants in a single test. Moreover it may even appear questionable whether absolute sterility, as being too artificial a condition for the determination of the effect of soil constituents on plants, would be desirable. It would seem that chemical control under as normal conditions as a cultural experiment will allow, is better than conducting the experiment under the artificial condition of sterility, which, after all, is made only so that bio-chemical changes be excluded.

Moreover, some very excellent data with sterile pea cultures have recently been obtained by Hutchinson and Miller[1] which led these investigators to the conclusion that some organic nitrogen compounds were available as sources of nitrogen, even under sterile conditions. Their method of experimentation was necessarily different from that here employed and was usually confined to the growth of two pea plants in culture solutions under sterile conditions, the nitrogenous compounds being added in the cultures and the weighed plant analyzed, the increase in total nitrogen being thus determined. Proceeding in this way, they found that acetamide, urea, barbituric acid (with calcium carbonate), and alloxan, are good sources of nitrogen, while formamide, glycocoll, α-aminopropionic acid, guanidine hydrochloride,[2] cyanuric acid, oxamide and sodium aspartate are not so good. Several other compounds were doubtful or even toxic.

The soil compounds beneficial to growth, creatinine, creatine, histidine, arginine, hypoxanthine, nucleic acids, as well as others, are among the unit parts of which the complex constituents of every life cell are built; that is, they are the units obtained when one of the complex proteins, nucleo-proteins, etc., are resolved into simpler compounds by chemical means. Take for instance a nucleo-protein. This complex can be split into a protein and a nucleic acid. The protein can be further split into a number of smaller units which are known as splitting products of protein or

---

[1] Centrb. f. Bakt. **30**, 513 (1911).

[2] In the work of this laboratory guanidine as carbonate has shown itself to be a strong poison to plant metabolism in the case of wheat, corn, potatoes and cowpeas. The peculiar effect of guanidine, namely, to produce bleached spots, seems also to have occurred in the case of peas in the experiments of Hutchinson and Miller for they mention that " the guanidine plants were the first to lose their color."

primary degradation products. These units or bricks out of which the complex structure of the protein is built comprise such compounds as histidine, arginine, lysine, and others still simpler in composition. Those mentioned have all been found in soils. This process of taking the complex molecule apart into these units is accomplished by fairly simple means. To effect further decomposition of these units means more deep seated changes, and actual breaking up of the bricks themselves, as it were. In this process, ammonia, acids, phenols and the like are formed. In the soil, as is well known, the ammonia is again changed to nitrite and nitrate, and thus, according to most authorities, the nitrogen cycle is completed and ready to again start on its mission to produce plant growth.

Let us also trace the building down of the nucleic acid, which was one of the component parts of the nucleo-protein used above as an illustration. Like the protein part, nucleic acid yields smaller parts or bricks. The unit bricks of the structure of nucleic acid comprise such compounds as hypoxanthine, xanthine, guanine, adenine, cytosine, pentose sugars, phosphoric acid, and others. All of those mentioned have been found in soils. Like the splitting products of the proteins, these compounds can and do suffer further decomposition in the soil in which the nitrogen appears first as ammonia, then nitrite and nitrate as before, but again these changes mean the breaking up of the unit bricks which composed the nucleic acid structure.

The proteins, nucleo-proteins and nucleic acids are essential in all animal and vegetable growth. That the plant can build these compounds with nitrate and ammonia as the source of the nitrogen has been definitely shown. In the case of the animal it is just as certain that it cannot build up tissue with nitrate or ammonia as the source of nitrogen. The animal obtains its nitrogen for protein building from the organic nitrogen compounds of plants or other animals. Hence has arisen the popular conception that plants build up complex protein compounds from minerals, and from minerals alone, that plants are fundamentally different in their functions from animals.

The animal, in order to obtain the elements for building its own protein, resolves by the process of digestion the protein materials of ingested vegetable or animal food into the units or bricks above mentioned and then builds out of these units its own protein. If, in a restricted diet, certain of these units are excluded, improper nutrition results. All of the units must be potentially in the food of the animal or be formed in the digestive tract. It is not possible to enter into a full discussion of this problem here, except to mention in passing that there are known many intermediary complexes and that animal and plant enzymes are capable of changing these compounds one into the other, for instance guanine into xanthine or adenine into hypoxanthine.

While the plant is able to build up the complex protein substances in its tissues from nitrate and even ammonia, it does not make this complicated chemical transformation in one step. While this process is but little understood, it is certain that there must be intermediary products and that these are the same products as the degradation units above mentioned is more than probable. Many of these, such as histidine, arginine, asparagine, guanine, xanthine, etc., have been found in plant tissues as such, as have also creatine and creatinine.[1] It seems logical, therefore, that if the plant absorbs such units of tissue building from the soil that it uses them just as if they were produced within the plant itself. Nitrate (NO_3) presents nitrogen in a highly oxidized form. The nitrogen in organic combination in the plant is always in a greatly reduced form, as NH or NH_2 groups or even attached directly to carbon only. It follows that much energy must be expended in causing this chemical transformation. This energy can be expended otherwise and hence plant efficiency is increased and growth augmented, when the plant can obtain such compounds which will serve directly as tissue builders from the soil.

The results obtained in the cultural work with such nitrogenous soil constituents leads me to suggest this theory in explanation of their action when alone and in conjunction with nitrate, namely, that the compounds are absorbed as such and utilized directly for building up the proteins, nucleic acids, and the other complex nitrogenous constituents of vegetable material. It seems

---

[1] Sullivan, J. Am. Chem. **33**, 2035 (1911).

reasonable to suppose that the unit parts of the complex protein molecules, when presented to the plant, will be used by it in preference to expending energy on the nitrate to prepare these units. If a soil be liberally supplied with all these units, it is conceivable that good plant growth will result, even without nitrate. If only a limited amount or kind of the units be present the plant must have nitrate with which to supply the missing units.

In the light of this theory, it is clear that a single compound or brick cannot be used to build the whole structure. Nitrate is, therefore, required for maximum effect, so that other compounds or units can be formed. It is of course conceivable, and this conception forms a part of this theory, that the plant enzymes may be able to transform one of these units into other closely related units, such as, for instance, the change from guanine or adenine to deamidizing enzymes, to xanthine and hypoxanthine respectively, so that if guanine only were presented to the plant, it would by virtue of such an enzyme, have available both guanine and xanthine, as well as ammonium compounds. If, however, only a single compound or brick is supplied, in the absence of other sources of nitrogen, there should be a limit beyond which the plant can make no further use thereof, because of the fact that the entire protein structure cannot be thus built up. Such a limit seems, in fact, to be reached when a single compound is presented to the plant, as is shown by the following experiment.

A series of culture solutions containing 25, 50, 100, 200, and 400 parts per million of histidine carbonate were prepared. Each culture of the series contained 32 parts per million of P_2O_5 as calcium acid phosphate, and 48 parts per million of K_2O as potassium sulphate. A second series contained creatinine, and a third series contained asparagine, the concentrations ranging as before from 25 to 400 parts per million. Wheat plants grew from Dec. 21 to Jan. 3. The green weight obtained with wheat seedlings in these culture solutions are recorded in Table IV.

It will be noticed that growth was increased by all of these compounds with increasing concentration up to 50 to 100 parts per million, beyond which no further increase took place. The plants were getting all the histidine, creatinine, or asparagine that they could economically use when 50 to 100 parts per million were presented in the culture solution. A concentration of 150 parts per million can therefore be considered as fully covering the maximum effect to be obtained from any one of these compounds in such an experiment.

TABLE IV. Effect of Histidine, Creatinine, and Asparagine, used in varying concentrations.

Culture No.	Concentration in p. p. m.	Green weight of culture in grams		
		Histidine	Creatinine	Asparagine
1	Nutrient Solution (check)	1.200	1.200	1.200
2	" " 25	1.440	1.650	1.410
3	" " 50	1.750	1.800	1.600
4	" " 100	1.980	1.790	1.540
5	" " 200	2.040	1.720	1.540
6	" " 400	1.920	1.610	1.560

The next step, therefore, was to prepare culture solutions as above but containing 150 parts per million of each of these substances, and another culture solution which again contained 150 parts per million, but composed of 50 parts per million each of histidine, creatinine, and asparagine. This mixture of the three compounds was then tested against the equivalent concentration of the compounds separately. The plants grew from Jan. 10 to Jan. 23. The green weights are given in Table V.

It will be seen that histidine, creatinine and asparagine again increased growth, and in the order named, but that when all three were combined, although only one-third the amount of each was present, the growth was nevertheless greater than the best of these. In the light of the theory above expressed, this would mean that the three different units were more useful to the plant than an equivalent amount of any one kind.

The nitrogen content in these solutions bears no relation to the plant growth observed. The nitrogen content of the histidine culture was 40.8 parts per million and of the asparagine culture it was 32.1 parts per million. The culture of all three compounds had 42.9 parts per million. It was, therefore, greater than the asparagine culture, approximately the same as the histidine and considerably less than the creatinine culture, while in growth it was greater than all of these. Moreover, it is evident that there exists no relation between nitrogen content and growth in regard to these different compounds by a glance at Table IV. Creatinine culture No. 2, for instance, containing 9.3 parts per million nitrogen gave a growth which was not even equalled by asparagine culture No. 6 which had a nitrogen content as high as 42.8 parts per million. The differences in the action of these compounds either singly or in combinations, is, therefore, due to an inherent property in the compounds themselves which makes it impossible for any one to wholly replace the other in plant metabolism.

Table V. Effect of Histidine, Creatinine, and Asparagine, used singly and in concentration.

Culture No.	Culture solution			Green weight Grams
1	Nutrient Solution			1.172
2	" "	Histidine	150 p.p.m.	1.640
3	" "	Creatinine	150 "	1.575
4	" "	Asparagine	150 "	1.350
5	" "	Histidine Creatinine Asparagine	50 " 50 " 50 "	1.900

Nitrogenous compounds of biological origin exist in soils and most of those here discussed are distinctly beneficial to crop growth. It follows that their presence in soils is beneficial to crops, inasmuch as the crop can use them for increasing growth, without these constituents passing on to ammonia, nitrite or nitrate by further decomposition and synthesis. They appear to be as beneficial as nitrate and are able to replace the latter in part. It follows that a mere nitrate determination in the soil does not give a complete valuation of its readily assimilable nitrogen, for it is conceivable that nitrification may be low and yet appreciable quantities of such beneficial nitrogenous compounds as histidine, hypoxanthine, creatinine, etc., be present. To alone lay stress on the nitrate content in soils is obviously erroneous in the light of these results, although it is not unlikely that their formation also goes hand in hand with the production of these cleavage or splitting products of protein.

In the foregoing there has been presented in a general way the action of those nitrogenous compounds which acted beneficially on plants. It must not be inferred, however, that because the compounds discussed were nitrogenous, that all nitrogenous compounds were found to be beneficial, for this is not the case. The soil constituent, picoline carboxylic acid, is moderately harmful as already mentioned, and the related uvitonic acid decidedly so. Tyrosine, a splitting product of protein, is toxic to plants, and neurine is decidedly so. Picoline, piperidine and pyridine are likewise toxic. Guanidine has shown itself to be decidedly harmful to plants and to produce a very marked effect on its metabolism, producing symptoms like those of a disease.

The nitrogenous fertilizers, such as dried blood, tankage, fish scrap, etc., as well as the leguminous crops as green manure, are excellent sources of the compounds discussed in this paper. To some extent, they are already contained in such fertilizers, but especially are they formed during the process of decomposition in the soil. The results in this paper make many field observations with such fertilizing material clear, and show that the decomposition does not have to go on so far as to change all nitrogen to ammonia and nitrates before being useful for plant growth. These facts are of further significance in that such compounds are removed from the soil with the greatest difficulty by drainage waters, whereas nitrates are easily lost in this way, if the plant does not remove them as fast as formed. Nitrates do not last over from season to season but the organic compounds can do so and yet be ready for absorption and use by plants at any time. In this form the nitrogen of the soil is conserved, whereas excessive nitrification or even ammonification may result in actual loss of the soil nitrogen by leaching.

The non-symbiotic or sympiotic nitrogen fixing bacteria also furnish just such compounds to soil and plants, and thus some light is thrown on the effect of nodules in increasing so largely the growth of those plants in which they occur. While the actual process of fixing the nitrogen is but little understood, it is certain that compounds of the nature of those here discussed are formed in the nodules. It is to be regretted that so little attention has been paid to the chemical nature of the nodules. The numerous investigations have confined themselves to the determination of total nitrogen and ash constituents. Stoklasa, however, has found asparagine in such nodules and Sana[1] has found glycocoll in addition to asparagine. A more extended investigation will doubtless disclose other compounds of this nature. Both of these constituents are directly absorbed by plants, and produced increased growth in the experiments of this laboratory. It would seem logical to conclude that such compounds, produced by organisms in the nodules, pass from these to the plants as such, and in harmony with the theory proposed in this paper, are used directly for the production of more complex protein matter in the plant, just as is done when such constituents are absorbed from solution or soil by plant roots. These compounds in nodules may, therefore, serve a similar function in the direct nutrition of the plant by the nodules.

---

[1] Jour. Chem. Soc., 98, II, 993 (1910).

SOME CONSTITUENTS OF HUMUS[1]

By Edmund C. Shorey, D.Sc.

(*Contribution from the Laboratory of Soil Fertility Investigations, Washington, D. C.*)

The term humus as originally used seems to have had no especial agricultural or scientific significance having been used to designate dark colored vegetable mold, and later applied to this mold material as a constituent more or less of all soils.

As used at present by Agricultural chemists the term humus is usually intended to include that portion of the organic matter of soils soluble in dilute alkalies. Some investigators apparently assume that the organic matter so dissolved is the same, or nearly so, as the "matière noir" of Grandeau,[2] but this is not true. On acidifying the alkaline humus extract of a soil the so-called humus bodies or "matière noir" of Grandeau is precipitated, but a large proportion, sometimes more than half of the organic matter extracted, will be found in the filtrate from this material.

In a loose agricultural sense the term humus is sometimes used to include all organic matter, organized undecomposed material as well as that which is the result of decomposition. In this paper the term humus is used to designate all the organic material extracted from a soil by dilute alkali solution.

The old terms designating the constituents of this humus, ulmic, humic, geic, crenic and apocrenic acids were used by Mulder[3] in the first half of the last century, and have passed current in agricultural literature from his time to the present. Although Mulder had very definite ideas regarding the individuality of those supposed compounds, and proposed formulas for them based on elementary analysis, consideration of the data

---

[1] Published by permission of the Secretary of Agriculture.

[2] Traite d'analyse des matieres agricoles p. 148. Paris, 1877.

[3] The Chemistry of Vegetable and Animal Physiology, trans. by Fromberg, 1849, p. 146.

on which their identity as definite compounds was based, and a realization of the status of organic chemistry at his time cannot but convince one that they have no standing as definite organic compounds.

Recognizing that the humus of soils results from the additions of vegetable and animal remains to the soil, that these are made up of known organic chemical compounds or may give rise through decomposition to other organic compounds also well known, an attempt was made to investigate the alkaline or humus extract of soils by the application of methods used for the separation of organic compounds in mixtures of plant or animal origin. The first definite, organic compound isolated from soils as a result of this attempt was picoline carboxylic acid. This was first isolated from a soil from Hawaii[1] and although since isolated from other soils[2] seems to be of rather infrequent occurrence in soils. Continuing the investigation of this humus extract and using for the most part methods of separation or isolation already in use in biochemical investigations, modified often to meet difficulties presented by the material under investigation, a number of organic compounds were isolated from soils and identified. These stated in the order isolated are, dihydroxystearic acid, agrosterol, agroceric acid.[3] Later work resulted in the isolation of sixteen additional compounds.[4]

A paraffin hydrocarbon hentriacontane[5] monohydroxystearic acid,[6] paraffinic acid,[6] lignoceric acid,[6] phytosterol,[7] pentosan,[8]

---

[1] Shorey, Organic Nitrogen in Hawaiian Soils. Report of Hawaii Agricultural Experiment Station, 1906, p. 37.

[2] Schreiner and Shorey, Bulletin No. 53, Bureau of Soils, U. S. Department of Agriculture.

Schreiner and Shorey, Journ. Am. Chem. Soc., **30**, 1295 (1908).

[3] Schreiner and Shorey, Bulletin No. 53, Bureau of Soils, U. S. Dept. Agri.; Jour. Am. Chem. Soc., **30**, 1599 (1908); Jour. Am. Chem. Soc., **31**, 116 (1909).

[4] Schreiner and Shorey, Bulletin No. 74, Bureau of Soils, U. S. Dept. Agri.

[5] Schreiner and Shorey, Jour. Am. Chem. Soc., **33**, 81 (1911).

[6] Schreiner and Shorey, Jour. Am. Chem. Soc., **32**, 1674 (1910).

[7] Schreiner and Shorey, Jour. Biol. Chem., **9**, 9 (1911).

[8] Shorey and Lathrop, Jour. Am. Chem. Soc., **32**, 1680 (1910).

histidine,[1] arginine,[1] cytosine,[2] Xanthine,[2] hypoxanthine,[2] a glyceride,[3] several unidentified resin acids and a resin ester. These were followed later by the isolation and identification of creatinine.[4]

A continuation of the investigation of the humus extract of soils by the same methods has resulted in the isolation of fourteen additional organic compounds, thirteen of which have been identified. These have all been found in the acid filtrate obtained on acidifying the humus extract and filtering, that is they are a part of the humus extract but not of the " matière noir." They are: oxalic acid, succinic acid, saccharic acid, acrylic acid, salicylic aldehyde, lysine, choline, trimethylamine adenine, mannite, a glucoside yielding rhumose, trithiobenzaldehyde, nucleic acid and an unidentified aldehyde.

The methods by which these have been isolated cannot be stated in detail in this paper, but in outline the general procedure was as follows. The soil was treated with a 2% solution of sodium hydroxide with stirring for some hours, the soil allowed to settle and the extract when clear syphoned off and acidified. Several soils were included in the investigation and in most cases but one or two of the compounds mentioned were obtained from any one soil. The methods of isolation included separation with immiscible solients, precipitation with phosphotungstic acid and salts of lead, mercury, silver and copper, and distillation with steam or in a vacuum. The separation with immiscible solients was always made from an acid extract obtained by acidifying the humus extract and filtering, precipitation with phosphotungstic acid in an extract acidified with sulphuric acid and the precipitation with metalic salts in a neutral or slightly alkaline medium. The fourteen organic compounds isolated from humus and reported in this paper together with those previously reported make a total of thirty-five definite organic soil constituents which may be classified as follows: thirteen organic acids, nine

---

[1] Schreiner and Shorey, Jour. Biol. Chem., **8**, 381 (1910).

[2] Schreiner and Shorey, Jour. Biol. Chem., **8**, 385 (1910).

[3] Schreiner and Shorey, Jour. Am. Chem. Soc., **32**, 78 (1910).

[4] Shorey, Bulletin No. 83, Part I, Bureau of Soils, U. S. Department of Agriculture; Jour. Am. Chem. Soc., **34**, 99 (1912).

organic bases, three sugars, two aldehydes, two alcohols, and one each, hydrocarbon, glyceride, resin ester, acid anhydride, sulphur compound and phosphorus compound.

This list while far from representing all the organic matter in the humus extract probably indicates roughly the properties of the classes of organic compounds in soils.

Organic acids make up a large proportion of the organic matter in the soil and when the great variety of acids in plant tissues and the proportion of the organic matter of plants made up of this group of compounds is considered, as well as the fact that the other groups of compounds in both plants and animals yield acids on decomposition, this preponderance of organic acids in the organic matter of soils becomes a matter not only easily explained but one to be expected. There is no reason why any of the organic acids found in plants or found in the decomposition of plant or animal remains should not be found at some time in some soils. The great variety of organic acids possible from these sources, and their susceptibility to change under soil conditions tends to bring about an individuality of soils in respect to organic acid content much more pronounced than is possible with any other group of organic compounds.

Organic bases that occur in plants or animals or arise in the decay of the same are comparatively few in number, and the nine so far isolated from probably make up half or more of those likely or probable occurrence in soils. The demonstration of the presence of organic bases in soils is of rather more than usual interest in view of the prevailing idea that soil organic matter is primarily acid and further, from the fact that those nitrogenous compounds have been shown to be directly assimilated by plants as well as furnishing much of the material from which nitric acid is generated in the process of nitrification.

Sugars represented by pentosans, apparently a constant constituent of soils, a glucoside containing rhannose, and mannite, represent but a very small part of the carbohydrate material that is added to soils, and probably but a small part of that which persists in the soil. The susceptibility of starches and sugar, to decomposition by enzymes and microorganisms makes it likely that these plant constituents either disappear altogether or are represented by some of the products of decomposition, organic acids largely. Oxalic and saccharic acid might have their origin in this way and there are no doubt many other acids not yet found that are derived in the same manner.

Aldehyde compounds seem to be rather constant constituents of the soil organic matter. The salicylic aldehyde isolated from one soil is the only representative of this class. The unidentified aldehyde isolated or a similar body or mixture is found in nearly all soils.

Hydrocarbons represented by one paraffin hentriacontane, one representative each of glycerides, and resin esters, and two alcohols represented by agristerol and phytosterol, are usually found in the humus precipitate formed on acidifying the alkaline extract of the soil. The present investigations do not include any examination of this material additional to that presented in previous publications.

The fact that there are many soils that give tests indicating the presence of organic sulphur compounds in which trithiobenzaldehyde cannot be found indicates that there are other organic sulphur compounds in soils. The very definite way in which sulphur-containing proteins yield cystine on hydrolysis, the easy change of this to cystein on reduction and the further ready change of both these to thiolactic acids makes it probable that some or perhaps all of these will ultimately be found in soils.

Phosphorus organic compounds are represented by nucleic acid, of which there are probably several. The only nucleic acids of plant origin that have been investigated to any great extent are those from yeast and from the wheat embryo. These are said to be identical and it may be that the nucleic acids of plant origin do not present so great a variation in structure as do those of animal origin. It has been found that some nucleic acids under certain conditions split into compounds less complex than the original but more complex than the proteids usually considered as the end products, pentoses, bases, and phosphoric acid. Under certain conditions the split may result in free phosphoric acid and compounds known as nuclecsides. The nuclecsides are combinations of the pentose and purine base. Under other conditions the split may result in a compound known as a carbohydrate phosphoric acid. One of these compounds, d-Ribose phosphoric acid $C_5H_{11}O_8P$[1] results from the decomposition of inosinic acid, and thymo-hexose-phosphoric acid $C_{11}H_{17}N_2PO_{10}$,[2] results from the decomposition of thymus nucleic acid. There has been obtained some evidence of the presence of compounds of a similar nature in soils but as yet no separation in a form definite enough for identification.

There is also considerable evidence pointing to the presence in soils of both lecithin and phytin, the two other representatives of phosphorus organic compounds.

These results of the investigation of the chemical nature of the organic compounds in humus while demonstrating the complex character of this material indicate at the same time that the chemical nature of the whole of this organic material can be determined by the use of modern methods of research.

---

[1] Levene and Jacobs. Ber. deutsch. Chem. 41, 1905 (1908).

[2] Levene and Mandel. Ber. deutsch Chem. 41, 1905 (1908).

EFFECT OF HISTIDINE AND ARGININE AS SOIL CONSTITUENTS[1]

By J. J. Skinner

(*Laboratory of Fertility Investigations, Washington, D. C.*)

Introduction

This laboratory has been investigating the nature and properties of the organic matter of soils and an essential part of this survey is the effect of the isolated soil constituents on crops. While more than twenty-four compounds have been isolated and identified, not all of these have been tested culturally, but this work is progressing as fast as material permits. So far as several of these constituents is concerned, this has already been done, notably in the case of the harmful soil constituent, dihydroxystearic acid,[2] and in the case of the beneficial soil constituent, creatinine.[3] In this latter investigation it was demonstrated that creatinine and also creatine had a beneficial effect on plant growth, that this effect was most marked when other sources of nitrogen were absent, as for instance in cultures containing only phosphate and potash, that the effect was much less if large amounts of nitrate were present, and that plants growing in cultures, whether high or low in nitrate, showed a greatly diminished nitrate consumption.

Histidine, like creatinine, is a nitrogenous soil constituent, and appears to be fully as widely distributed and of as frequent occurrence. It is, therefore, fully as important as creatinine in its effect on crops, and the results obtained with this soil con-

---

[1] Published by permission of the Secretary of Agriculture.

[2] Some Effects of a Harmful Organic Soil Constituent. By Oswald Schreiner and J. J. Skinner, Bul. 70, Bureau of Soils, U. S. Dept. of Agric. (1910).

[3] Effects of Creatinine on Growth and Absorption. By J. J. Skinner, Bul. 83, part III, Bureau of Soils, U. S. Dept. of Agric. (1911).

stituent, as well as with arginine, show that both of these compounds possess the same general properties in regard to their effect on plants, as those above summarized for creatinine.

PRESENCE IN SOILS

Histidine ($C_6H_9O_2N_3$), and Arginine ($C_6H_4O_2N_4$), are primary decomposition products of protein material which have been found in soils. Their isolation and identification has already been described in earlier publications from this laboratory[1] as has also some data in regard to the frequency of its occurrence.[2] They undoubtedly occur in the soil as the result of protein decomposition. The degradation products of protein, however, do not appear in the decomposition of plant remains, but exist in very appreciable quantities at the time of germination and in the seedling plant. These compounds are found in relatively large amounts in plants, especially in members of the legume and mustard families, not only in the seedling stages of the plants, but also in the roots, root stalks, stems, buds, and in all parts which store up reserve material for the nutrition of the plant. Since plants of these families are extensively used in the practice of green manuring, they may also become soil constituents through this process.

Both arginine and histidine are constituents of meat extracts prepared by hydrolysing meat with dilute acid and are similarly produced from blood, which, in the dried form, is used as a fertilizer. In fact, dried blood is one of the best sources for the preparation of histidine. The beneficial effect of histidine on plant growth, makes its occurrence in the decomposition products of dried blood fertilizer especially significant.

---

[1] "Chemical nature of Soil Organic Matter," by Oswald Schreiner and Edmund C. Shorey, Bul. 74, Bureau of Soils, U. S. Dept. of Agric. (1910); also "The Presence of Arginine and Histidine in Soils," Jour. Biol. Chem. **8** 381 (1910).

[2] Examination of Soils for Organic Constituents, especially Dihydroxystearic Acid," by Oswald Schreiner and Elbert C. Lathrop, Bul. 80, Bureau of Soils, U. S. Dept. of Agric. (1911); also Jour. Franklin Institute, **171**, 125 (1911).

In the decomposition of protein there are two groups of nitrogenous compounds, the monoamino and diamino acids, also called hexone bases. Both contain the carboxl group COOH and in the monoamino acids there is but one NH_2 group and the compounds are mainly acid in character, although many of them have the property of forming compounds with both acids and bases. In the diamino acids or hexone bases there are two or more NH_2 groups and sometimes an NH group and the basic character usually predominates, that is, they form well defined salts with acids and show alkaline reaction.

While all protein bodies give some diamino acids on decomposition, the nature and properties of these vary with different proteins. Three of these amino acids or hexone bases occur very frequently, and usually occur together, but in varying proportions. These are histidine, arginine, and lysine. As stated above, histidine and arginine have already been found in soils, but lysine has not yet been isolated.

The monoamino acids, likewise have not been detected in soils, probably due to the fact that when formed they readily undergo further changes under soil conditions so that if present at all, they would be so only temporarily, or under special conditions only.

SEPARATION FROM SOIL

Histidine and arginine are so closely related in their properties that they are obtained together in the first stages of the process. The histidine and arginine are obtained as a silver compound from the neutral liquid obtained by precipitating the so-called humus from an alkaline extract of the soil with sulphuric acid. Separation of the two is accomplished by taking advantage of the fact that the histidine silver compound is precipitated in slightly alkalin solution, while the arginine silver compound is not precipitated except in strongly alkaline mediums. The silver is removed by hydrogen sulphide. For the details of the method, which is rather complicated, the original description in the bulletin cited must be consulted.

CHARACTERISTIC PROPERTIES

The histidine is finally obtained as the dihydrochloride which appears in very characteristic glassy plates or prisms. Histidine can further be confirmed by two color reactions. If to a solution of the histidine salt, bromine water be added until the yellow color is permanent and this solution then heated, the color disappears, to be replaced shortly by a faint red, which gradually deepens, the liquid becoming turbid, through the separation of amorphous particles. This is Knoop's test for histidine. Pauly's diazo reaction can also be applied and is very delicate. Diazosulphailic acid gives in alkaline solution with histidine a red color which does not disappear on dilution. The histidine dihydrochloride obtained from the soil gave both color reactions. The free base can be prepared from this dihydrochloride.

The arginine was obtained in the form of neutral nitrate and agreed in all respects with the description of this salt. The acid nitrate and free base were also made and had the characteristic properties of these compounds.

DISTRIBUTION IN SOILS

The soil in which both histidine and arginine were first found was a sample of Houston clay from Mississippi. The quantity of arginine was even in this case much smaller than the quantity of histidine, and histidine has since been obtained from several soils from which no arginine could be obtained. Their distribution was specifically studied and the results reported in Bulletin 80, already cited.

Twenty-four soil samples were tested, out of which number seventeen contained histidine. The soils tested were from widely distributed parts of the United States, from Maine, New York, Pennslyvania, West Virginia, Kentucky, Mississippi, and Texas. It was found in surface and in subsoils. This indicates that this hexone base is a fairly common constituent of soils and shows, therefore, that the protein change in soil is similar to that brought about by chemical or other action in laboratory investigations.

Arginine has so far been found in only two soils, one from Mississippi and one from Pennsylvania and is probably not a soil constituent which persists for any length of time.

EFFECT OF HISTIDINE ON GROWTH

The histidine, as usually prepared, is in the form of the characteristic dihydrochloride, which crystallizes nicely in glassy plates or prisms. This salt, however, hydrolyses readily, so that its solutions are rather acid in reaction. For the purpse of this cultural work, the pure dihydrochloride was, therefore, changed over to the carbonate.

In studying the effect of histidine on crops, wheat seedlings were grown in aqueous culture solutions, containing the ordinary fertilizer salts, calcium acid phosphate, sodium nitrate and potassium sulphate. The concentration of the solution was 80 parts per million of the fertilizer ingredients $P_2O_5+NH_3+K_2O$. If the culture contained only one salt, for instance, calcium acid phosphate, the concentration was 80 parts per million of P_2O_5. If two salts were present, for instance, calcium acid phosphate and potassium sulphate, the concentration was 80 parts per million of $P_2O_5+K_2O$. The wheat seedlings when used for the experiment were about one inch high. They were previously germinated on aluminum disks floated on the surface of a tank of water. Wide mouth bottles holding 250 c.c. were used for containers of the culture solutions. Ten wheat plants were grown in each bottle, and were held in place by means of a flat notched cork. The details in preparing the solutions, securing uniform seedlings, and method of experimentation have been given in Bulletin 70, already cited.

Two sets of culture solutions were prepared, the one as control, the other containing histidine. Owing to the limited supply of histidine carbonate, the extent of the cultures used was confined to four series: (1) cultures containing no nitrate; (2) cultures containing 8, (3) cultures containing 16, and (4) cultures containing 24 parts per million of NH_3 as nitrate respectively. All of the cultures contained phosphate and potash in several proportions. To one set of the cultures composed of the four series, only the nutrient salts were added, to the other set, in addition to the nutrient salts, 50 parts per million of histidine carbonate were added to each culture. The culture solutions were changed every three days and analyzed. The cultures grew from Nov. 15 to Nov. 27, 1911.

After the two sets of plants had grown for a few days, with and without the histidine, it was quite apparent that the histidine had the same effect in promoting plant growth as had creatinine and creatine. The effects in regard to the nitrate removal during growth were also strikingly the same as with the other substances, the effect of the histidine being the most marked in the series of cultures containing potash and phosphate in varying proportions, but no nitrate. The appearance of these cultures is shown in Fig. I. They are arranged in pairs of like composition in regard to mineral salts, phosphate and potash. Cultures marked with the same number, for instance 56 and 56H, have like fertilizer ratios. The cultures marked with numbers alone have no histidine; the cultures with the letter H have 50 parts per million of histidine. The composition of these culture solutions is shown in Table I.

As shown in the photograph, the plants in each culture containing histidine, regardless of the composition of the culture solution in phosphate and potash, were larger and showed a much better top and root development.

EFFECT IN CULTURES CONTAINING NO NITRATE

The green weight of the plants growing in the culture solutions containing no nitrate is shown in Table I. The larger growth in each of the histidine cultures is apparent. The average increase in the series is 30 per cent. greater than the growth without the histidine.

Figure I

Histidine and Arginine as Soil Constituents, J. J. Skinner

Figure II

Histidine and Arginine as Soil Constituents

TABLE I. EFFECT OF HISTIDINE ON GROWTH IN CULTURES CONTAINING NO NITRATE

Culture No.	Fertilizer ingredients in culture solution			Green weight of cultures	
	P_2O_5	NH_3	K_2O	Without Histidine	With Histidine
	p.p.m.	p.p.m.	p.p.m.	Grams	Grams
56	0	0	80	1.250	1.460
46	8	0	72	1.220	1.420
37	16	0	64	1.420	1.700
29	24	0	56	1.200	1.540
22	32	0	48	1.220	1.920
16	40	0	40	1.500	1.880
11	48	0	32	1.200	1.820
7	56	0	24	1.240	2.140
4	64	0	16	1.400	1.700
2	72	0	8	1.140	1.550
1	80	0	0	1.040	1.150

TABLE II. EFFECT OF HISTIDINE ON GROWTH IN CULTURES CONTAINING 8 P.P.M. OF NH_3 AS NITRATE.

Culture No.	Fertilizer ingredients in culture solution			Green weight of cultures	
	P_2O_5	NH_3	K_2O	Without Histidine	With Histidine
	p.p.m.	p.p.m.	p.p.m.	Grams	Grams
57	0	8	72	1.450	1.510
47	8	8	64	1.720	2.000
38	16	8	56	1.570	2.320
30	24	8	48	1.940	1.980
23	32	8	40	1.940	2.600
17	40	8	32	1.940	2.480
12	48	8	24	2.240	2.200
8	56	8	16	2.040	1.800
5	64	8	8	1.600	1.650
3	72	8	0	1.220	1.410

TABLE III. EFFECT OF HISTIDINE ON GROWTH IN CULTURES CONTAINING 16 P.P.M. OF NH_3 AS NITRATE.

Culture No.	Fertilizer ingredients in culture solution			Green weight of cultures	
	P_2O_5	NH_3	K_2O	Without Histidine	With Histidine
	p.p.m.	p.p.m.	p.p.m.	Grams	Grams
58	0	16	64	1.500	1.730
48	8	16	56	1.800	2.140
39	16	16	48	2.100	2.180
31	24	16	40	1.940	2.120
24	32	16	32	2.150	2.380
18	40	16	24	2.100	2.400
13	48	16	16	2.140	2.020
9	56	16	8	1.820	1.440
6	64	16	0	1.220	1.280

EFFECT IN CULTURES CONTAINING NITRATE

When some nitrate, 8 parts per million NH_3 as nitrate, was present, the additional effect of the histidine was not as great as in the case where nitrate was entirely absent. This is shown in Table II. The total green weight for the 10 cultures was 17.660 grams without histidine and 19.950 grams when this compound was present. The average increase caused by the histidine was 14 per cent. greater than that caused by the nutrient salts alone. For the series of culture solutions containing 16 parts per million this increase was still less as is shown by Table III the average increase being only 5 per cent. The total growth of the cultures without histidine was 16.770 grams as against 17.690 grams with the histidine. The total growth for the 24 parts per million NH_3 as nitrate series was 14.390 grams without histidine and 16.390 grams with histidine, the average increase being again 14 per cent. What the effect of still larger amount of nitrate would have been is not determinable by this experiment, but it seems probable that the effect is of the same character as in the case of the creatinine and creatine with higher nitrate content in which it was shown that no appreciable effect was noticed on the growth due to the creatinine, although the nitrate consumption was shown to be decreased.

INFLUENCE OF HISTIDINE ON ABSORPTION

The analysis of the culture solutions during growth also showed that this compound behaved like the creatinine and creatine already reported. The total amount of phosphate, potash and nitrate removed from the solution by the plants in the cultures containing all three constituents was 637.6 milligrams for the normal or control cultures, and 645.9 milligrams for the histidine cultures. The phosphate was 166.3 milligrams for the normal and 212.8 milligrams for the histidine cultures, an increase of 56.5 milligrams. The potash was 276.6 milligrams for the normal cultures and 290.5 milligrams for the histidine cultures, an increase of 13.9 milligrams. The greater growth in the histidine cultures caused therefore a somewhat greater absorption of the phosphate and potash. With nitrate, however, the reverse was the case. The normal cultures consumed 194.7 milligrams, whereas the histidine cultures consumed only 142.6, a difference of 47.9 milligrams, thus showing that the histidine had caused a decreased consumption of this amount of nitrate although an increase in growth had taken place in harmony with the behavior of creatinine and creatine in this respect.

It appears that histidine can replace the effect of nitrate in producing plant growth. The culture work was throughout under strict chemical control, so as to establish as definitely as possible that the effects on the plants noted were produced by the absorption of the compound as such. Nitrite, nitrate, and ammonia were tested for and found to be absent, or, in the case of ammonia, in traces only. Although neither nitrate, nitrite nor ammonia was found, the plants, nevertheless, grew remarkably well and the only conclusion justified by this experimental evidence is that this compound is directly absorbed and assimilated. With the strict chemical control exercised all possibility of any extended action by bacterial or other external biological agencies seems excluded. If such effects were produced in these experiments, they were of only minor significance in the results obtained. Bacterial and other micro-organisms were excluded as far as possible, but no special effort was made to maintain absolutely sterile conditions, inasmuch as this would have been a practical impossibility in experiments on so large a scale involving several hundred plants in a single test. Moreover, it may even appear questionable whether absolute sterility, as being too artificial a condition for the determination of the effect of soil constituents on plants, would be desirable.

It would seem that chemical control under as normal conditions as a cultural experiment will allow is better than conducting the experiment under the artificial condition of sterility, which, after all, is made only so that biochemical changes be excluded. In these experiments the bottles were sterilized before being used in making culture solutions for the various changes, the pans and other apparatus used in germinating the seed were sterilized from time to time, and corks used for the cultures were always clean and sterilized before use. Although all of these precautions were taken, it was of course not possible to exclude some micro-organisms in such work, as the solutions were exposed from time to time to the air. There was no excessive micro-organic life noticeable. While bacteria and other micro-organisms were present in the solutions to a slight extent, it can hardly be said that their influence could have been large; that is, such influence as they had was probably so slight as to be negligible so far as the general and larger tendencies which are shown to exist are concerned.

EFFECT OF ARGININE ON GROWTH

In testing the effect of arginine on plants the carbonate was used as in the case of histidine, already described, and the experiment otherwise conducted in exactly the same manner and with the same culture solutions, the arginine carbonate being added to the one set of solutions at the rate of 50 parts per million. The wheat seedling grew from Nov. 2 to Nov. 14, 1911.

Arginine, like histidine, was beneficial to plant growth and the cultures showed the same general behavior. The growth in the series of cultures containing no nitrate was again the one most influenced by the compound. This is shown by the results given in Table IV.

The total weight of the 11 cultures without arginine was 13.840 grams against 18.340 grams for the cultures with arginine. This is an increase of 33 per cent. in growth. When nitrate was present the arginine had far less effect even than the histidine in producing an additional effect, as was shown by the series of cultures containing 8, 16 and 24 parts per million NH_3 as nitrate. The growth in each of these series was approximately the same whether arginine was present or not.

The absorption too is in line with results obtained with histidine, although not so definite. The total for the cultures containing all three elements was 672.9 milligrams without arginine and 587.4 milligrams with arginine. The phosphate removal was 196.2 milligrams for the normal and 160.7 milligrams in the arginine cultures. The potash removal was 278.6 milligrams in the normal and 270.9 milligrams in the arginine cultures. The nitrate consumption was 198.1 milligrams in the normal and 155.8 milligrams in the arginine cultures.

TABLE IV. EFFECT OF ARGININE ON GROWTH IN CULTURES CONTAINING NO NITRATE.

Culture No.	Fertilizer ingredients in culture solution			Green weight of cultures	
	P_2O_5	NH_3	K_2O	Without Arginine	With Arginine
	p.p.m.	p.p.m.	p.p.m.	Grams	Grams
56	0	0	80	1.240	1.520
46	8	0	72	1.220	1.540
37	16	0	64	1.500	1.940
29	24	0	56	1.240	1.720
22	32	0	48	1.100	1.800
16	40	0	40	1.200	1.920
11	48	0	32	1.440	1.920
7	56	0	24	1.200	1.700
4	64	0	16	1.300	1.600
2	72	0	8	1.440	1.640
1	80	0	0	0.960	1.040

SUMMARY

Histidine and arginine occur as soil constituents, both having beneficial effects on plant growth. Plants grown in solution cultures containing only potash and phosphate show greatly increased growth when histidine or arginine is added.

When large amounts of nitrate are present in the culture solutions, histidine and arginine produce no appreciable effect on the growth.

Plants growing in cultures, whether high or low in nitrate, showed a greatly diminished absorption of this ingredient when histidine or arginine was present, whereas the removal of potash and phosphate was practically normal.

It appears, therefore, that histidine and arginine, like creatinine and creatine, can replace the effect of nitrate in plant growth.

THE PLASTICITY OF CLAY

By John Stewart

Chemical Laboratory, Utah Experiment Station, Logan, Utah, June, 1912

It is one of the peculiarities of human endeavor that action taken for a certain purpose often results in the accomplishment of an entirely different and unexpected result. *A priori* it would hardly be expected that a study of the organic phosphorus of the soil would have any bearing on the plasticity of clay; but such is the infinite inter-ramification of the facts of nature that they lead to strange results.

So far as the writer is aware, no satisfactory explanation of the cause of the plasticity of clay has ever been advanced. Numerous attempts to explain the phenomenon have been made, but none of the results has met with general acceptance. Hilgard[1] reviewed some of the most important of these attempts, but indicated by his treatment of the subject that the question was still an open one. Hopkins[2] mentions plasticity as a *property* of *clay*. Thorp,[3] in his exposition of the chemistry of the ceramic industries, offers no explanation of the cause of the plasticity of clay, although without this property the industry could not exist. Ashley[4] reviewed the literature of colloids and of clay, and made a study of the absorptive power of some clays for certain dyes. His work was based on the idea that " clay is . . . a mixture of granular matter and a colloid gel." and had for its purpose the development of a method of measuring the plasticity of clay by utilizing the absorptive power of colloids for this purpose. In a later publication, Ashley[5] discusses plasticity of clay on the same general lines. He says, " The colloid matter of clays may

---

[1] Soils, pp. 57-62 (1906).

[2] Hopkins' Soil Fertility and Permanent Agriculture, p. 55.

[3] Outlines of Industrial Chemistry, pp. 191-200 (1909).

[4] U. S. G. S., Bulletin 388 (1909).

[5] C. A., Vol. 5, No. 1, p. 174-5 (1911).

be considered as consisting of complex mineral and organic acids and salts." Bleininger[1] studied the effects of heating clays to temperatures under 400°. He found that the placticity was decreased and that there was *not* a corresponding change in the absorptive powers of the clay. Acheson,[2] in 1901, ground clay in a water extract of straw and found that this treatment increased the plasticity. He considered this result to be due to the *organic* matter in the water extract. In 1904 this result was claimed to be due to gallotanic acid, and seems[3] to have been regarded as a *physical* and not a chemical action. Thus the importance of Acheson's observation does not seem to have been recognized by investigators. P. Rohland[4] attributed the plasticity of clay to hydroxides of Si., Al., and Fe. He noted that fuller's earth *absorbs* unsaturated *hydrocarbons,* and he recommended the use of clay to purify factory wastes.

There are some facts relating to the plasticity of clay which have received general recognition and acceptance as being true. First, *pure* clay is *not* plastic. Hilgard[5] says " . . . it is readily mistaken for chalk (and is sometimes used as such), being powdery to the touch and entirely devoid of plasticity . . . ." Those engaged in the ceramic industries call the purer clays " lean " on account of their lack of plasticity. Second, *impure* clays are the plastic ones. These are the " fat " clays, so-called by those engaged in the ceramic industries because of their possession of plasticity. Third, it is a common practice in the ceramic industries to mine the clay and allow it to *weather*[6] for months before use. This is said to increase the plasticity. Fourth, *ignition* destroys the plasticity of clay. Attempts to restore the plasticity to an ignited clay (as by levigation) have all failed. Fifth, a pure clay is a hydrated *aluminum* silicate.

---

[1] C. A., Vol. 5, No. 1, p. 175 (1911).

[2] Some Chemical Problems of To-day, R. K. Duncan, pp. 118-119 (1911).

[3] U. S. G. S., Bulletin 388, p. 12 (1909).

[4] C. A., Vol. 4, p. 503, and other abstracts.

[5] Soils, p. 59 (1906).

[6] Thorp, Outlines of Industrial Chemistry, p. 194 (1909).

[6] Roscoe and Schorelemmer, Treatise on Chemistry, Vol. II, Part I, new edition (1883), p. 495.

Two other facts[1] which are not as generally recognized as the above may be mentioned here. First, Ries in his work on Michigan clays found examples of lean clays absorbing a greater percentage of water than fat clays absorbed. Second, Grout found that a shale increased largely in plasticity on weathering, but that the combined water remained practically constant. It is also a fact that shale loses its plasticity on being metamorphosed into slate.

During the past year the writer made an observation which is of considerable importance with reference to this subject of plasticity. The observation referred to was made during a study of humus and the organic phosphorus of the soil, in which the writer was engaged during the summer of 1911. This study resulted in some interesting data and conclusions with reference to the organic phosphorus, iron and aluminum compounds of the soil. A paper has been prepared emboyding the data and conclusions resulting from the work and not embodied in the present article.

In the study of humus, or the constituents of humus, there is a fundamental difficulty, due to the defloculation of the clay by the alkali used, which makes it almost impossible to obtain a humus solution free from suspended clay. In searching for a means of overcoming this difficulty the writer added a small quantity of alumina cream, washed free from salts, to a humus solution containing some suspended clay, and filtered the liquid. A perfectly clear humus solution passed through the filter; but the residue on the filter was dark colored, indicating that chemical action had occurred between the humus and the alumina cream. This indicated that this method could not be used for quantitative work, and, consequently, the filtered solution and residue were set aside for several days. The filtered solution was then placed in an evaporating dish to determine if the chemical action of the alumina on the humus had seriously interfered with quantitative results. After being on the water bath a short time a flaky, dark brownish colored solid separated out, leaving the humus solution almost colorless. This solid was gelatinous, and some of it floated on the liquid. As the solution evaporated,

---

[1] U. S. G. S., Bulletin 388, p. 28 (1909).

these flakes adhered to the sides of the evaporating dish and to the glass stirring rod, sticking almost like glue. The solid was then filtered off and leached with one per cent. hydrochloric acid. It proved to be rather difficult to decompose. The acid was used cold at first, then hot acid was tried; and a hot stronger acid was used before a very complete decomposition of the precipitate was obtained. The acid solution gave a heavy precipitate of *aluminum* hydroxide on adding ammonia. There was a residue of organic matter left on the filter which dissolved readily in ammonium hydroxide.

Now, taking all these facts into consideration, the writer suggests that the plasticity of clay is due to the presence of an *organic aluminum* compound (or compounds). This will satisfactorily explain all the important, established facts concerning the plasticity of clay. This explains why it is the *impure* and not the *pure* clays which are plastic. This explains why *ignition* destroys plasticity and why levigation fails to restore plasticity to the ignited clay. This explains the heretofore unexplained practice of weathering clay before using it in the ceramic industries. In 1883, Roscoe[1] and Schorelemmer said:—"It . . . is allowed to remain for a considerable length of time in a moist place, when the organic matter contained in the clay undergoes putrefactive decomposition: this seems to increase the plasticity of the mass; but the exact action which takes place under these circumstances is not well understood." This explains why shales lose their plasticity on being metamorphosed into slate. This explains the observations of P. Rohland, mentioned by Ashley,[2] to the effect that plasticity of clay is reduced by all bases and all salts of strong bases with weak acid which hydrolytically split off hydroxyl ions and that neutral salts have no effect on the plasticity; for, the aluminum organic compound observed by the writer is soluble in alkali. This gives a partial explanation of the universal observation that hydrous *aluminum* silicates are sometimes plastic, while similar hydrous silicates of other bases, as serpentine,

---

[1] Treatise on Chemistry, Vol. II, Part I, New Edition (1883), p. 495.

[2] U. S. G. S., Bulletin 388, p. 21 (1909).

are not plastic; and, taken in connection with some other facts which readily suggest themselves, makes a complete explanation of the observations.

In all probability, the writer's observation gives at least a partial explanation of the use of fuller's earth for purifying mineral and vegetable oils. The writer suggests also that the heretofore unexplained fact that vegetable oils purified in this way generally have a bitter taste, is due to the formation of an aluminum organic compound which is somewhat soluble in the oil, and to which the bitter taste is due.

It is interesting to recall in this connection an observation made by Th. Schloesing[1] in 1874. After washing a kaolin with dilute acid, he separated it into several fractions by mechanical analysis, using ammoniacal water. Out of five fractions, only one showed any marked plasticity. This was the fraction that was still in suspension after 27 days. Schloesing called this fraction "colloidal clay"; and it was so plastic as to be sticky and adhered strongly to the porcelain dish in which it was dried. In the light of the writer's observation, and considering Schloesing's method of work, it is evident that Schloesing's "colloidal clay" contained a large proportion of an *organic aluminum* compound (or compounds) to which its plastic, sticky properties were due.

In speaking of "colloidal clay" Hilgard[2] said: "(It) . . . bears more resemblance to glue than to the clay of everyday life. Like glue, too, the dried colloidal clay adheres to the tongue . . . it assumes a highly plastic and adhesive condition, so that it is difficult to handle and almost as sure to soil the operator's hands as so much pitch." Hilgard[3] also says, " . . . the several humates (of lime, magnesia, iron), which, when fresh, are colloidal (jellylike) like clay itself, but unlike the latter, when once dried do not resume their plastic form by wetting (Schloesing)." No mention of *aluminum* humates was made by Hilgard in this connection. His treatment of the subject also indicates that up to the time of his

---

[1] Compt. Rend., Vol. 79, pp. 376-380, 473-477 (1874).

[2] Soils, pp. 61 and 62 (1906).

[3] Soils, p. 110 (1906).

writing there had been no suggestion of a possible causal relationship between the plasticity of humates and the plasticity of clay. On the contrary, Hilgard[1] states: " A similar process," (viz., to that of Johnson and Blake,[2] who levigated kaolinite in a mortar for a long time in an attempt to produce plasticity) " but continued much longer by the mechanical agencies concerned in soil formation (see Chapt. 1), *is unquestionably the chief factor*[3] concerned in the formation of natural plastic clays; but whether this is the *only* process by which powdery kaolinite may be transformed into plastic clay is a question not definitely settled."

In view of the observations of the writer and of Schloesing, it is evident that if plastic clays be subjected to treatment for the removal of the humus they will lose their plasticity. These observations point the way for the development of analytical methods for estimating the plasticity of clay; and also point the way for methods of treating clays which are too " lean " (or too " fat ") for certain uses in the ceramic industries. Further research along these lines might prove very interesting and also of considerable practical value. It should probably be mentioned in this connection that Ashley[4] has already indicated some means of improving clays in accordance with these principles; but Ashley's work, in this connection, appears to be based upon the observations of Rohland,[5] for which neither of them apparently had a satisfactory explanation.

While the writer does not doubt that time will prove his explanation of the plasticity of clay to be correct and that these aluminum organic compounds are the only important ones concerned in this phenomenon—he would not be understood as claiming that in some cases other compounds may not contribute to the plasticity of *very impure* clays in a very minor degree. In this connection he would call attention to the fact that the " lime muds " obtained in purifying sugar beet juices are *very plastic.* These are composed of granular calcium carbonate and

---

[1] Soils, p. 60 (1906).

[2] Am. Jour. of Sc., 2nd Series, Vol. 43, p. 357.

[3] These italics are Stewart's.

[4] C. A., Vol. 5, p. 174-175 (1911).

[5] U. S. G. S., Bulletin 388, p. 21 (1909).

coagulated albuminous substances and *calcium organic* compounds mainly. Limestone is generally impure and there may be also magnesium, iron and aluminum organic compounds in the "lime muds." There can be no doubt that plasticity results from the mixture of a granular substance and a gelatinous substance in due proportion. There are many granular substances and many gelatinous substances; and so the plasticity of different substances is due to different components of the mixtures.

ORGANIC PHOSPHORUS IN THE SOIL

By John Stewart

Logan, Utah

Introductory Remarks

The study with which this paper deals was commenced during the past summer, and is of a supplementary nature to Bulletin No. 145, of the Illinois Agr. Expt. Sta., by Dr. Robert Stewart. It is the outgrowth of two main facts. First, there has been, and still is, a lack of agreement among investigators as to the nature of the compounds of phosphorus present in the *matiere noire* in regard to their being mainly or wholly of an organic or an inorganic nature. Pitsch and Van Bemmelen, among early investigators, and Stoddart and Fraps, among recent ones, have supported the theory that the phosphorus in the *matiere noire* is either wholly or mainly inorganic; while Grandeau, Eggertz, Nilson, Wiklund, Dumont, Schmoeger and Aso, among early investigators, and Ladd, Synder, Hopkins, Petit, and Stewart, among recent ones, have maintained that the phosphorus of the *matiere noire* is mainly or wholly organic. Second, attempts to make humus determinations at the Utah Experiment Station, according to the "Official Method," have not been entirely satisfactory. It was, therefore, desired to remedy this difficulty in the humus determination, if possible; but mainly to determine what part of the phosphorus in the *matiere noire* is organic.

Experimental Data

The work was begun by the writer on the assumption that the *matiere noire* contained both organic and inorganic phosphorus. The first difficulty which presented itself was the obtaining of a *matiere noire* free from suspended clay. How much inorganic phosphorus might be present in the colloidal mineral matter in the ordinary humus solution was an unknown quantity; and that this colloidal matter would be precipitated when the humus solution was acidified with HCl, thus contaminating with mineral matter of unknown composition a portion of the phosphorus of the humus solution, which portion was, with more certainty than any other portion, in organic combination. It was, therefore, practically useless, for the purpose of this study, to proceed until a means of removing suspended clay from the *matiere noire*, or of obtaining a *matiere noire* free from colloidal mineral matter, had been secured.

The official Method, Peters and Averett's modification and Snyder's modification were useless for the purpose. Cameron and Breazeale's modification. Fraps ammonium sulphate modifications and Mooers-Hampton's modification were all capable of removing the clay, but were objectionable because of the danger of also removing humus or of hydrolyzing it. Hilgard's modification of Grandeau's method appeared to be the most suitable of all known methods. It would give a solution practically free from suspended clay, and do so with a minimum danger of hydrolysis occurring.

The writer was very pleased to discover at this time Bulletin No. 115, of the Nebraska Experiment Station, in which F. J. Alway *et al.* very ably demonstrated the excellence of Hilgard's method, and showed that the Mooers-Hampton and the Cameron-Breazeale methods give reliable results. Alway's results by the Cameron-Breazeale method show a slight loss of humus on the average. The writer suggests that such loss probably would not occur if the filter were leached with dilute acid as well as ammonia before use.

Before learning of the existence of the bulletin of Alway *et al.* the writer had commenced the preparation of humus solutions by the Mooers-Hampton method and by the Hilgard method, making two solutions by each method; viz., Solutions Nos. 1 and 2, and 3 and 4, Table I. All the work recorded in this paper was done on one soil sample from near Nephi, in the central part of Utah. Rather unfortunately for the purpose of the study, this soil proved to be very low in humus and organic phosphorus, thus making the work considerably more difficult than would have been the case with a soil richer in these components. The

Grandeau-Hilgard method, while being excellent in most respects for the work attempted, proved to be a very tedious method, and to yield a very dilute humus solution. For the first two solutions prepared by this method; viz., Nos. 3 and 4, the time required for the completion of both the acid and the ammonia leachings was about five to six weeks. The soil samples were large. For the second two solutions, obtained at a later period, by this method; viz., Nos. 5 and 6, the time required was more than two months.

TABLE I.

	Mooers-Hampton Method		Grandeau-Hilgard Method			
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Soil used in grams	80	80	250	250	250	250
Humus solution obtained in cc.	200	200	6000 1000	7000	1000	500 900
Acid solution obtained in cc.	Thrown out	Thrown out	7000	6220	30500	32000
Wash water obtained in cc.	Thrown out	Thrown out	2000	2000	1750	1500
The soil contained, per cent.						
Phosphorus in acid solution	Not determined	Not determined	0.1741*	0.1609	0.1621	0.1643
Phosphorus in wash water			0.0008	0.0009	0.0000	0.0002
Phosphorus in *Matiere Noire*	0.0103 0.0090	0.0110	0.0108	0.0103	0.0089	0.0087
Dry *Matiere Noire*	1.29 1.31	1.06	1.25	1.09	0.82	0.87
Humus	0.98 1.10	0.76	0.77	0.81	0.65	0.63
Humus ash	0.31 0.21	0.30	0.48	0.28	0.17	0.25
Organic nitrogen in acid extract	Not determined	Not determined	0.022	Not determined	Not determined	Not determined

*Average of two determinations on the solution, one showing 0.1747%, the other 0.1736%.

While these solutions were in course of preparation, the writer did some work on small (10-gram) samples to ascertain if some means could be found of successfully removing the clay from solutions prepared by the Official Method, suitable for general routine work. He tried filtering the solutions after adding a small quantity of alumina cream, washed free from salts. By this means he secured solutions absolutely free from suspended clay; but it was evident that the solutions had acted chemically on the alumina cream. The residue of " cream " on the filter was dark colored; and after being thoroughly washed with ammonia, it was leached with 1% HCl, which dissolved aluminum and left a humus residue on the filter, which dissolved readily in ammonium hydroxide. The filtrate of perfectly clear humus was allowed to stand for about ten days, when it was put on the water bath for evaporation and determination of the humus. After heating for a short time, an organic precipitate separated, and the liquid remained almost devoid of organic coloring matter. This precipitate was gelatinous and flaky. It was filtered off and leached with 1% HCl. The acid leaching gave a heavy precipitate of $Al(OH)_3$ on adding ammonia, the humic organic matter having remained on the filter. This precipitate appeared to be very difficult to decompose with 1% HCl both cold and hot. The results of this work indicated that alumina cream could not be used as a filtering admixture for humus determinations; but the fact of this aluminum compound being formed in this way is of some importance with reference to a conclusion to be drawn later.

A number of trials indicated that the best filtering medium for humus determinations is probably the soil itself. The writer devised an apparatus for the accomplishment of this filtration under pressure and on a scale of sufficient magnitude to allow of the accomplishment of a large amount of routine work in a short time. But as he has not yet had an opportunity to make a practical application of the idea, he refrains from any further mention of it at present.

The writer also demonstrated that, while the Mooers-Hampton method gives results that agree very well with the Grandeau-Hilgard method, there is, nevertheless, a precipitation of organic matter, iron, and phosphorus during the evaporation of a humus solution by the Mooers-Hampton method. He took the residue left by evaporation and after *thoroughly* washing it with NH_4OH, he extracted it with hot 1% HCl; this gave a solution containing phorphorus among other elements. The phosphorus was not quantitatively determined. Now, on washing the residue free from acid and extracting with 4% NH_4OH, he obtained a strongly colored humus solution, from which the humus was precipitated by HCl, leaving a colorless solution. This process was repeated with the same residue, again giving the same results. One of the 250 grams residues from the Grandeau-Hilgard method was subjected to the same treatment. Phosphorus was absent from the acid solution; and ammonia extracted only the faintest tinge of organic coloring matter from the soil. This is positive proof of the precipitation of organic matter and phosphorus by the Mooers-Hampton process. Dr. Robert Stewart, in his work at Illinois, Bulletin 145, page 113, Illinois Agr. Exp. Sta., noted also an accumulation of phosphorus and carbon in the residue of evaporation by the Mooers-Hampton method, which agrees with the writer's observation. But he explained their appearance in that residue somewhat differently.

Having digressed somewhat from the main theme to give some data and make some remarks concerning methods of determining humus, I shall now return to the main topic.

The Second Difficulty

After obtaining a humus solution free from clay, the next difficulty to be encountered was the separation of inorganic phosphorus, if present, from organic phosphorus.

The work of Forbes *et al.*, as given in Bulletin No. 215, of the Ohio Agr. Exp. Sta., seemed to offer hope of the very successful accomplishment of the task. The data given by Forbes *et al.*, indicate that the method is very successful in working with phytin and nucleic acid and under the conditions of their work. But the nature of all the organic phosphorus compounds of the soil is not known, and as this method does not give a precipitate free from organic matter there is doubt as to whether the precipitate contains only inorganic phosphorus.

Column four of Table II gives some data obtained by a modification of Forbes' method. Phosphorus, in the form of sodium hydrogen phosphate, amounting to 6.72 mg., was added to the solution used. The precipitate contained all of the inorganic phosphorus added and about two-thirds of the phosphorus originally present in the solution. An attempt to remove the inorganic phosphorus in this precipitate by dissolving the $MgNH_4PO_4$ in water indicated that a large quantity of water would be necessary, that the solution would not be free from organic matter and that there was an element of uncertainty on account of the presence of iron and aluminum. Leaching the precipitate with acid (after water) extracted most of the phosphorus along with some organic matter. Precipitation of this *acid* solution with ammonium hydroxide and magnesia mixture gave a precipitate which *did not entirely dissolve in* HNO_3*, some organic matter soluble in* NH_4OH *remaining.* The use of alcohol with 1% HCl as indicated in Forbes' work (on another magnesia mixture precipitate) gave an acid solution strongly colored with organic matter. No conclusion concerning the state of combination of the greater part of the phosphorus originally present in the humus solution could be drawn from this data, partially because of the extremely small quantity of humic phosphorus present, partially because the method failed to give a precipitate or solution free of organic matter.

Column 5 of Table II gives some data concerning the use of $BaCl_2$. Definite conclusions concerning the state of combination of the greater portion of the phosphorus was again impossible. There was also again strong evidence of change in the nature of the organic compounds during the manipulations. The acid solution of the $BaCl_2$ ppt. yielded a precipitate on adding ammonia and then heating. This precipitate looked like ferric hydroxide; but iron was not present in this humus solution. This precipitate after solution in acid failed to be re-precipitated by adding ammonia to the solution. It contained 0.7 mg. of P and 1.2 mg. of alumina.

Column 3 of Table II gives data concerning the use of phenylhydrazine. The recovery of the added aluminum was quantitative. Likewise the precipitate contained more phosphorus than the inorganic phosphorus added. There was again evidence of changes in the nature of the organic matter; for, on neutralizing the acid solution (to which 0.3000 gram of potassium alum had been added) with NH_4OH, the neutral point was passed and on making quite strongly acid again the precipitate which had formed failed to entirely dissolve on standing more than 48 hours. The undissolved precipitate contained 0.18 mg. of phosphorus.

TABLE II.

	Humus Solution No. 4			Humus Solution No. 2
Solution used in cc.	100*	100*	250	75
Phosphorus in solution used in mgs.	0.71	0.71	0.92	3.09
Phosphorus added to solution in form of K_2HPO_4	None	3.36 mg.	6.72 mg.	None
$KAlSO_4$, 12 H_2O added to solution	None	0.3000 g.	None	None
Organic P precipitated by NH_4OH and not redissolved by HCl		0.18 mg.		
Precipitating agent used	Phenylhydrazine	Phenylhydrazine	Magnesia mixture	Barium chloride
Phosphorus precipitated	None	3.52 mg.	7.30 mg.	3.35 mg.
(a) Dissolved in water		Not determined	1.05 mg.	Not determined
(b) Dissolved in HCl		3.46 mg.	6.11 mg.	2.90 mg.
(c) Not dissolved in HCl		0.06 "	0.14 "	0.32 "
Phosphorus not precipitated	Not determined	0.06 "	0.10 "	0.13 "
Error	Not determined	—.30 "	—.24 "	+0.24 "
Aluminum in $KAlSO_4$, 12 H_2O added		0.0167 gm.		
Aluminum recovered in analysis		0.0171 gm.		

*These solutions were the partly concentrated filtrates from the HCl precipitate of humus, the concentration having taken place at ordinary temperature.

The use of $(NH_4)_2SO_4$ to salt out organic matter gave a precipitate probably almost indentical with that produced by adding hydrochloric acid to the humus solution. The filtrate from the $(NH_4)_2SO_4$ precipitate in all cases gave a very slight additional precipitate on adding HCl; while the filtrate from the HCl precipitate of original humus solutions did not give any additional precipitate on saturation with $(NH_4)_2SO_4$ or NH_4Cl, in either acid or alkaline solution.

A CHANGE IN METHOD OF ATTACKING THE PROBLEM

Some two months' work and study on the problem convinced the writer that there is an element of uncertainty, in some cases at least, in the differentiation of organic from inorganic phosphorus in solution, by any known method, which practically precludes definite conclusions when the quantity of phosphorus present is small. With larger quantities of phosphorus and under some conditions, some methods may make this differentiation with approximate accuracy and with practically useful results. His work also gave convincing evidence of hydrolytic change in extracting humus from the soil and in later manipulations with the solution. These facts necessitated a change in the method of attacking the problem. It appeared, therefore, that the most feasible plan of operation to separate the inorganic from the organic phosphorus was to make the separation before removing the humus from the soil. The humus when in the soil is nearly insoluble in 1% HCl, but after removal by alkali it is changed so that only about 25% to 75% is insoluble in this reagent. On the other hand, all mineral phosphates likely to be present in an agricultural soil are known to be soluble in HCl. Therefore, the acid extract, if properly obtained, should contain *all* the inorganic phosphorus.

THE ACID EXTRACT

Accordingly, two more portions of soil were weighed out and extracted with acid and alkali according to the Grandeau-Hilgard method, the purpose being to make certain of the complete removal of acid soluble phosphorus by the acid treatment. These are designated in the tables as No. 5 and No. 6. In this procedure the phosphorus was determined in measured portions of the acid extract as they were obtained, usually in 2,000 cc. portions. After about 30 litres of 1% HCl had been passed through each soil sample the phosphorus appearing in the acid solution had diminished to an almost undeterminable amount. The acid was then washed from the soil and the phosphorus determined in the wash water. The data are given in columns headed No. 5 and No. 6, in Table III. This acid leaching lasted three weeks in the case of No. 5 and four weeks in the case of No. 6, being as nearly continuous as practicable.

As a result of this new view of the problem, it became somewhat important to know whether or not the acid soluble phosphorus had all been extracted in the previous work, in which the acid leaching had ceased when all the calcium and magnesium had been removed. Fortunately the acid extracts from samples No. 3 and No. 4 had been saved, but those from No. 1 and No. 2 had been thrown out. The data for Nos. 3 and 4 are also given in Table III.

Table III. Phosphorus Extracted from Soil by Cold One Per Cent. Hydrochloric Acid.

Grandeau-Hilgard Method								
Portion Extracted	No. 3		No. 4		No. 5		No. 6	
	Volume of solution	Per cent. phosphorus on soil	Volume of solution	Per cent. phosphorus on soil	Volume of solution	Per cent. phosphorus on soil	Volume of solution	Per cent. phosphorus on soil
1st			2.5	0.1344	2.5	0.0301	2	0.0254
2nd			2.5	0.0281	2.0	0.0215	2	0.0240
3rd			1.2	0.0024	2.0	0.0166	2	0.0237
4th					2.0	0.0238	2	0.0247
5th					2.0	0.0167	2	0.0190
6th					2.0	0.0207	2	0.0136
7th					2.0	0.0106	2	0.0091
8th					2.0	0.0077	2	0.0072
9th					2.0	0.0046	2	0.0075
10th					2.0	0.0045	2	0.0025
11th					2.0	0.0018	2	0.0020
12th					2.0	0.0016	2	0.0020
13th					2.0	0.0008	2	0.0010
Wash water					1.0	0.0001		
14th					2.0	0.0008	2	0.0012
15th					2.0	0.0002	2	0.0006
16th					None		2	0.0008
Totals	7	0.1741*	6.2	0.1609	30.5	0.1621	32	0.1643

*Average of two analyses of the solution; one showing 0.1736%, the other 0.1747%.

This table shows that the average phosphorus in the four acid extracts is 0.1653% on air dry soil (the soil contained 2.56% moisture); the highest result is shown by No. 3, being 0.1741%, and the lowest by No. 4, being 0.1609%. The variation is 0.0132%. Now, by reference to Table I, it will be seen that this variation is greater than the total amount of phosphorus in the humus extract, which averages, for the solutions Nos. 1, 2, 3, and 4, 0.0103% on soil, and for solutions 5 and 6 the average is 0.0088% on soil. It is therefore important to locate the cause of the variation. (It may be stated here that the considerable number of determinations of phosphorus in the humus solutions made both directly and indirectly by adding together the phosphorus in several portions of the humus; as, the HCl precipitate and the filtrate, some of these being made in duplicate and all closely agreeing, leaves absolutely no room for doubt as to the reliability of the phosphorus determinations in the *matiere noire*).

The results indicate that in some cases the acid extraction may not have been complete. This is especially the case with solution No. 4. But the author is convinced that the acid extraction was practically complete in the cases of No. 5 and No. 6. This is indicated by the very low phosphorus content of the last acid leachings, and by the absence of phosphorus in one wash water and the minute quantity in the other. The results are a little lower in these cases than they should be, though, on account of the slight solubility of the ammonium-phospho-molybdate. In the case of sample No. 6, the filtrates from the yellow ppt. in fifteen determinations were combined, after having evaporated to small volume. The iron was then precipitated with ammonium hydroxide. The phosphorus in this ppt. was found to be 0.48 milligram. Now, as the volume of the solution from which this quantity of phosphorus was obtained represented 1/20 of the total acid extract the per cent. of phosphorus in this acid extract should be increased by 0.0038% on the basis of the soil. By making a corresponding correction to the phosphorus in the other acid extracts after giving due consideration to the ratio of the volume used in the determinations to the total volume of the extracts, and also adding the phosphorus in the wash waters—the percentages would become: for No. 3, 0.1757; for No. 4, 0.1628;

for No. 5, 0.1659; and for No. 6, 0.1683. Averaging these, the result is 0.1683% on soil.

Mr. C. T. Hirst, not working in connection with this study at all, made three determinations of the total phosphorus in this soil by the sodium peroxide ingition method. The writer made three determinations by the same method and two by igniting with magnesium nitrate. Five grams of soil were used in each case. Mr. Hirst made his precipitations with the ammonium molybdate solution in duplicate. The writer made his in triplicate on aliquot parts of the solution, except in the cases of ignition with magnesium nitrate, where it required four successive extractions with acid to extract the phosphorus completely. All the solution resulting from each extraction was used for the precipitation, the results being added. The average of all these determinations of the total phosphorus is 0.1814% on the basis of the soil. The average of the two ignitions by magnesium nitrate method is 0.1808%, one being 0.1800%, the other being 0.1816%. The difference between the total phosphorus and the acid soluble phosphorus is therefore 0.0156%, or 0.0132%, according as we choose to consider 0.1658% or 0.1682% the average per cent. for the acid soluble.

It is important to note that where the determination of acid soluble phosphorus shows a low result, as in No. 4 the determination of the ammonium hydroxide soluble phosphorus does *not* show a high result, and vice versa. That is, the ammoniacal soluble phosphorus does not exhibit any definite relation to the acid soluble. For instance, the acid extract for No. 3 shows a result 0.0132% on soil higher than No. 4, but the ammoniacal extract in the two cases differs very slightly. The acid extracts in No. 5 and No. 6 show lower results than in No. 3, but the humic phosphorus is also lower in Nos. 5 and 6 than in No. 3, and bears unmistakable evidence of diminution by the long continued acid extraction. This is directly opposite to what would be true if the humic phosphorus were derived from the mineral acid soluble phosphorus.

The phorphorus found in the wash waters shows positively, when compared with that in the ammoniacal extract, that the phosphorus remaining in the soil after acid treatment is very much *more soluble* in ammonia than it is in acid. Some of the ammonia soluble phosphorus is slightly soluble in acid as shown by samples Nos. 5 and 6, the humic phorphorus being in these cases 0.0088% on air dry soil. Organic matter is also slightly soluble in the acid as shown by the organic nitrogen determination given for sample No. 3, Table I.

In Bulletin No. 124, p. 375, Iowa Agr. Exp. Sta., the statement was made that the washing with water to remove acid from the soil after the acid leaching dissolved some humus toward the end of the process. This statement was based upon the fact that the wash water came through slightly colored at this stage of the washing. The writer observed a similar coloration of the wash water in his work; but after standing over night the coloring material had settled and was filtered off. It then failed to dissolve in 4% NH_4OH and contained no phosphorus.

INSOLUBILITY OF SOIL PHOSPHORUS IN AMMONIA

Now, at the beginning of this work, two 40 gram samples of this soil were placed in two ordinary acid (2 litre) bottles and treated with 2,000 cc. each of 4% NH_4OH. They were shaken at intervals for two days. At the end of that time it was evident from the color of the solution and the results of evaporating to dryness 100 cc. of each solution that only traces of humus had been dissolved. The two solutions were than set aside and are now standing in contact with the soil. But after changing the method of attacking the problem as noted above, it became very important to know whether ammonia would dissolve phosphorus from this soil without previous leaching with acid. The phosphorus was determined in 100 cc. of each of these solutions after they had been in contact with the soil more than two months. There was *no* phosphorus present in the ammoniacal solution. (The method used is capable of measuring with considerable accuracy an absolute amount of phosphorus to within 0.10 milligram).

THE AMMONIACAL SOLUTION

While the above contains the proof that all the phosphorus in the *matiere noire* is derived in this ase from organic phosphorus compounds, still it is of some importance to make further study of the *matiere noire*; because, apparently it contains some phosphorus in inorganic form, and the presence of iron and alumina in it is not accounted for.

By reference to Table I, it will be seen that the humus in samples Nos. 2, 3 and 4 are in close agreement, No. 2 being slightly lower than the average of Nos. 3 and 4. The humus in No. 1 is about 0.25% on soil higher than Nos. 2, 3 and 4; and the humus in No. 5 and No. 6 is almost exactly the same in each case, but is about 0.15% lower than Nos. 2, 3 and 4. The lower results in Nos. 5 and 6 are undoubtedly due to the greater extraction of humus in the *acid* solution in these cases, due to the long continued extraction. The explanation for the high result in sample No. 1, which, according to the proof of precipitation of organic matter in the Mooers-Hampton process given above, should be lower than No. 3 and No. 4—is not perfectly apparent to the writer. The most probable explanation seems to be that in that case; viz., No. 1, the *acid* had removed less organic matter than in the others, and that the extraction of humus in Nos. 3 and 4, by the Grandeau-Hilgard method was not quite complete. The final ammoniacal leachings in the case of Nos. 3 and 4 were still slightly colored. The writer does not consider the difference to be due to analytical operations on the solutions after they were obtained.

The humic ash is in all cases less than 0.30% on soil except in the case of No. 3. The reason for the higher result in No. 3 is partially due to a greater amount of colloidal matter present in this case. No. 4, which shows a lower humus ash and which was obtained in the same way as No. 3, had stood more than a month before the determination was made.

Table IV gives some data concerning the results of precipitating the humus solution with several reagents. The $(NH_4)_2SO_4$ precipitates were washed with a saturated solution of ammonium sulphate. The $BaCl_2$ precipitates were washed with dilute ammonia and then leached with 1% HCl. The residue is, therefore, probably almost identical with the precipitate formed by treatment with HCl.

TABLE IV. Humus Components Precipitated by the Several Reagents Indicated.

A. Parts per Hundred of Soil

	Mooers-Hampton Method				Grandeau-Hilgard Method						
	No. 1		No. 2		No. 3	No. 4			No. 5		No. 6
Precipitating reagent used	HCl	$BaCl_2$	$BaCl_2$	$(NH_4)_2SO_4$	HCl	HCl	$(NH_4)_2SO_4$	Magnesia mixture	HCl	HCl*	HCl
Dry *matiere noire*	0.65	0.72			0.69						
Humus	0.62	0.64			0.56						
Humus ash	0.03—	0.07			0.13						
Phosphorus	0.0014	0.0023	0.0011	0.0016	0.0028	0.0012	0.0027	0.0015	0.0010	0.0007	0.0010

B. Parts Per Hundred of Each Humus Component

	No. 1 HCl	No. 1 $BaCl_2$	No. 2 $BaCl_2$	No. 2 $(NH_4)_2SO_4$	No. 3 HCl	No. 4 HCl	No. 4 $(NH_4)_2SO_4$	No. 4 Magnesia mixture	No. 5 HCl	No. 5 HCl*	No. 6 HCl
Organic matter	57.15	58.98			77.20						
Humus ash	12.38	35.71			32.35	25.00†					
Matiere noire	50.00	55.24			61.13						
SiO_2	22.80	68.42			34.31				27.24		36.79
xFe_2O_3, yAl_2O_3									56.70	47.00	67.81
Fe_2O_3									60.63		76.44
Al_2O_3											45.07
Phosphorus	13.79	22.66	10.56	15.84	26.34	11.31	26.87	14.00	12.47	8.71	16.75
Colloidal ash precipitation										6.80	
xFe_2O_3, yAl_2O_3 in HCl precipitation + Fe_2O_3 in Colloidal ash										60.00	

*This HCl precipitant was redissolved in NH_4OH and reprecipitated with HCl. The colloidal ash is the mineral matter left on the filter after solution of first precipitate in NH_4OH, it being ignited before weighing.

†Includes only SiO_2, Fe_2O_3 and Al_2O_3.

Part B shows that the HCl precipitate from solution No. 1 contained 57.15% of the total organic matter present in the *matiere noire.* This agrees approximately with the results for precipitation with $BaCl_2$ from the same solution. But the HCl precipitate in solution No. 3 contains 77.20% of the total organic matter. As these two solutions contained the same humus from the same soil, the results indicate beyond the possibility of doubt that the chemical nature of the organic matter had been changed by the operations to which it had been subjected. And as *all* the organic matter in the *matiere noire* had passed through one treatment with HCl, while in the soil, without going into solution in the acid, and now only a portion of it in both cases is precipitable by acid, the change has occurred in both solutions, but to a greater extent in one than in the other. The solution showing the greater change is the one prepared by the Mooers-Hampton process. Known facts concerning hydrolysis would lead us to expect exactly this kind of result, if hydrolysis had occurred in extracting the humus and in its subsequent treatment.

Less than one-third of the humic ash appears in the HCl precipitate; and, in the solution by the Mooers-Hampton process, the amount is very much less than one-third. Approximately one-half to two-thirds of the iron and alumina appear in the HCl precipitate; while the amount of the phosphorus appearing in this precipitate is very much less, being about 10% to 25% of the total phosphorus present in the humus solution.

Column 11 of Table IV gives some data concerning some of the components of the HCl precipitate, after it has been re-dissolved in NH_4OH and re-precipitated with HCl. The table shows plainly that variations in the treatment produce variable results.

The literature relating to humus shows that there has been a rather general sub-conscious idea that the humus ought to be completely precipitable by acid; because it did not dissolve in acid while in the soil. Methods of determining humus have been based on this idea. Stoddart[1] recently did this. There has at the same time been a rather general observation of the fact that the

---

[1] J. Ind. Eng. Chem. 1, 72.

acid did not completely precipitate the humus from ammoniacal solution. So far as the writer is aware, the observed fact has generally been explained as due to a *slight* solubility of the humus in acid, and the variation of results by different investigators as due to a difference in the humus itself in different soils before being subjected to analytical operations. This is an explanation used by Sherman Leavitt[1] in June, 1910.

The writer's observations, noted above, show that this explanation can, at most, be only partially true. That it is part of the true explanation he does not doubt, but his work indicates that the greater and more important cause of the observed fact is *change in the chemical nature of the humus during the analytical operations.* This conclusion has been forced upon the writer at almost every move in his analytical work. This kind of change in chemical nature is well illustrated by the following account of some operations. It was mentioned above that humus dissolved alumin cream, and that on heating the solution an aluminum organic compound was precipitated. This compound was decomposed with hot 1% HCl; some organic matter also dissolved in the HCl. The acid solution was evaporated to dryness, after which the residue failed to dissolve completely in HCl. The insoluble residue was organic and dissolved readily in NH_4OH. The part which had dissolved in HCl, on evaporation to dryness on the water bath, again left a residue which was only partly soluble in HCl, the other part being again organic and soluble in NH_4OH. This process was repeated three more times with the respective acid solutions with the same result in each case.

THE PHOSPHORUS IN THE FILTRATE FROM THE HCl PRECIPITATE

The fact that most of the phosphorus associated with the *matiere noire* appears in the filtrate from the HCl precipitate has apparently led some investigators to the conclusion that nearly all the phosphorus associated with the *matiere noire* is derived from mineral phosphates. Stoddart[2] considered ⅘ to be inorganic;

---

[1] J. Ind. Eng. Chem. 2, 6.

[2] J. Ind. Eng. Chem. 1, p. 71.

Fraps[1] considered ⅔ to be of inorganic origin. Other investigators have considered all of it, or the greater part of it, to be organic in origin.

In a later publication,[2] Fraps reiterates his former conclusion. His fundamental proposition[3] in this publication is a negative one; viz., " We have at present no method for estimating the organic phosphoric acid of the soil." In support of this proposition, it is claimed that a portion of the phosphorus of the *matiere noire* is derived from mineral phosphates. A method is proposed for determining the *minimum* amount of phosphorus in the *matiere noire* " which must be inorganic." For an exposition of this method, the writer refers those interested to the bulletin[4] noted, where the method is explained in its author's own language.

This method is based upon the assumption that phosphorus dissolved by ammonia from an ignited soil passed through the ignition unchanged. Comey, in his dictionary of solubilities, mentions two modifications of ferric pyrophosphate, one of which is insoluble in acids but soluble in ammonia. Leavitt and LeClerc[5] demonstrated that the ignition of phosphorus compounds in the presence of organic matter results in the formation of pyro and meta phosphates, although the phenomenon was not understood by them at the time of their work but explained later.[6] The application of Fraps' method to 27 soils[7] shows a variation in the *minimum* amount of phosphorus in the *matiere noire* " which must be inorganic " to be (after some clerical errors are corrected) from 12% to 177% of the total phosphorus present in the *matiere noire*, and the average minimum for the data presented to be 51%, but which, properly corrected, should be 36%.

In another table[8] data are given which indicate that the phosphorus dissolved by ammonia from some *ignited* soils is only

---

[1] Am. Chem. J. Vol. 39, p. 579 (1905).

[2] Bulletin 136, Texas Agr. Exp. Sta. (1911).

[3] Ibid. p. 31.

[4] Bulletin 136, Texas Agr. Exp. Sta. (1911), pp. 21-25.

[5] Journal of the Amer. Chem. Soc., 30, p. 391 (1908).

[6] Ibid. 30, p. 617.

[7] Bulletin 136, Texas Agr. Exp. Sta. p. 24, Table 17.

[8] Bulletin 136, Texas Agr. Exp. Sta. Table 10, p. 13.

21% of that dissolved by ammonia from the same soils without ignition. That is, the destruction of the organic matter by ignition was accompanied by a destruction of 79% of the solubility of phosphorus in ammonia. Fraps also presents two series of determinations of the ammonia soluble phosphorus in the *same ignited* soils. These may be tabulated as follows:—

Soil No.	From Table[1] 17 % P_2O_5	From Table[2] 11 % P_2O_5
831	0.0063	0.0056
344	0.0102	0.0230
832	0.0082	0.0200
869	0.0080	0.0076
876	0.0100	0.0103
741	0.0058	0.0069
744	0.0104	0.0078
992	0.0158	0.0450
Averages	0.0093	0.0155

The differences in these averages is 0.0062% P_2O_5 on the basis of the soil used.

" Table 18 " in Fraps'[3] presents another two series of determinations of the ammonia soluble phosphoric acid in the same ignited soils. The averages of these two series are: 0.0123% and 0.0060% respectively. The difference in these averages is 0.0063% on the basis of the soil used. In " Table 17,"[4] he presents 0.0074% phosphoric acid on the basis of the soil used as being the average percentage dissolved by ammonia from 27 ignited soils. It thus appears that the experimental error is nearly equal to or much greater than the absolute quantity of phorphorus involved in the determinations.

The average absolute amount of the element phosphorus which is involved in the determination of the ammonia soluble phos-

---

[1] Bulletin 136, Texas Agr. Exp. Sta., p. 23.

[2] Ibid., p. 14.

[3] Ibid., p. 24.

[4] Ibid., p. 23.

phorus in 27 ignited soils which Fraps[1] gives—is 0.2 of a milligram. As no compound is absolutely insoluble, it might be conceived that even ferric phosphate is 100% soluble in ammonium hydroxide, provided a small enough quantity of ferric phosphate be used with a large enough quantity of solvent. The writer, therefore, suggests that this data concerning ammonia soluble phosphorus in ignited soils would be better expressed as a function of the volume of solvent, and not as a function of the quantity of soil used or of the phosphorus in the soil. Looked at from this point of view, the data which Fraps presents in his " Table[2] 11 " show that in one series of determinations he obtained a maximum of 4 parts of phosphorus per million of solvent with a minimum of 0.5 parts and an average of 1.25 parts per million. In the other series of determinations he obtained a maximum of 2 parts, a minimum of 0.05 part, and an average of 0.6 part of phosphorus per million of solvent. Therefore, *if* a soil contains inorganic phosphates when it is being extracted with ammonia, the ammoniacal solution may derive phosphorus from the inorganic source to the extent of approximately 0.5 to 1.0 part of phosphorus per million of solvent. Data presented by Dr. J. E. Greaves[3] indicate that if the soils contain considerable quantities of soluble salts, the phosphorus dissolved from inorganic phosphates may be greater, about 2 or 3 parts per million. This is evidently due to hydrolytic and mass action.

The writer's work indicated to him that the phosphorus in the *matiere noire* was all derived from organic compounds, but that hydrolysis occurred during its extraction from the soil. Hydrolysis need not necessarily have converted the phosphorus into the inorganic form. It might still be present in combination with organic matter. It was therefore still of interest to apply some methods of separating inorganic from organic phosphorus to the filtrate from the HCl precipitate. Table V gives some data obtained by use of 250 cc. in each trial of solutions No. 5 and No. 6, in which the phosphorus was present in sufficient quantity to give reliable analytical data.

---

[1] Bulletin 136, Texas Agr. Exp. Sta., p. 23.

[2] Ibid., p. 14.

[3] Journal of Biological Chemistry, Vol. VII, No. 4, pp. 287-319.

TABLE V. Distribution of Humic Phosphorus, Iron and Aluminum in the Precipitates and Solutions Indicated.

Humus Solution by the Grandeau-Hilgard Method																		
	Solution No. 5										Solution No. 6							
	Used 250 cc.			Used 250 cc.							Used 250 cc.							
	Phosphorus			xFe_2O_3 yAl_2O_3	Fe_2O_3		Phosphorus				xFe_2O_3 yAl_2O_3	Fe_2O_3	Parts per 100 of total in *Matiere noire*		Phosphorus		
	Milligrams titrated	Per cent. on soil[1]	Parts per 100 of total P. in *Matiere noire*	Grams weighed	Grams titrated	Parts per 100 of total in *Matiere noire*	Milligrams titrated	Per cent. on soil[1]	Parts per 100 of total in *Matiere noire*	Grams weighed	Grams titrated	Fe_2O_3	Al_2O_3	Milligrams titrated	Per cent. on soil[1]	Parts per 100 of total in *Matiere noire*
In the HCl Precipitate	[2]0.440	[2]0.0007	[2]8.71	0.0148	0.0077	60.63	0.630	0.0010	12.47	0.0178	0.0146	76.44	45.07	1.240	0.0010	16.75
In the Acid Washings of PPt.	0.090	0.0002	1.78	Not determined	......	.....	0.050	0.0001	0.99	Not determined	......	......	......	0.120	0.0001	1.62
In the Filtrate from the HCl Ppt.																
Added to filtrate	0.3000 gram $KAlSO_412H_2O$			0.3000 gram $KAlSO_412H_2O$						Magnesia Mixture and Ammonium Hydroxide						
Pptng. Agent added to filtrate	Phenylhydrazine			Ammonium Hydroxide												
Not precipitated from "filtrate"	0.150	0.0002	2.97	0.0062	0.0012	9.45	0.930	0.0015	18.42	0.0024	0.0014	7.33	14.08	2.650	0.0021	35.81
Precipitated and:																
(a) Soluble in NH_4OH	2.514	0.0040	49.78	None	......	.....	None	......	......	None	......	......	......	None	......	......
(b) Soluble in 1% HCl	[3]1.214	[3]0.0019	[3]24.04	0.0362	0.0017	13.38	1.004	0.0016	19.88	0.0038	0.0018	9.42	28.17	1.834	0.0015	24.78
(c) Insoluble in 1% HCl but soluble in NH_4OH	......	....	......	0.0012	0.0021	16.53	0.520	0.0008	10.30	0.0022	0.0013	6.81	12.67	1.120	0.0009	15.13
(d) The fractional ppt. which formed in filtrate on heating it. Purified by solution in HCl and re-pptn. by NH_4OH, repeated several times.	0.330	0.0005	6.53	......	......	.....	......	......	......	......	......	......	......	......	......	......
(e) The combined filtrate and washings from (b) and (d)	0.020	0.0000	0.40	......	......	.....	......	......	......	......	......	......	......	......	......	......
(f) Error (loss)	0.292	0.0005	5.78	Not determined	......	.....	1.916	0.0031	37.94	Not determined	......	......	......	0.423	0.0003	5.91

[1] The sum of the numbers in these columns do not represent the total humic phosphorus in the soil, because the solutions worked with were not aliquots of the total humus solutions.

[2] Re-dissolved in NH_4OH and again precipitated with HCl.

[3] Re-precipitated with ammonium hydroxide.

The second, third and fourth columns give data regarding the use of phenylhydrazine as a precipitating agent, when applied to the filtrate from the HCl precipitate to which 0.3000 gram of potassium alum had been added. The precipitation of phosphorus was practically complete, but organic matter was also precipitated in large amount. The precipitation might be considered a fractional one; for, the part which came down immediately in the cold was filtered off, and then the filtrate on being placed on the hot plate for the purpose of evaporation so as to determine the phosphorus not precipitated, gave an additional precipitate in the course of a half hour's heating. This precipitate looks somewhat like ferric hydroxide, but was largely or wholly organic. It was dissolved, after filtration, in HCl and re-precipitated with NH_4OH. This process was repeated about four or five times. It contained 6.53% of the total phosphorus as indicated in (d); and, as the combined filtrates and washings from the purification as indicated in (e) contained only 0.40% of the total phosphorus, this may have been a pure organic, phosphorus compound. In the part of the precipitate produced in the cold 49.78% of the total humic phosphorus was soluble in NH_4OH, evidently on account of the presence of organic matter; and 24.04% was soluble in HCl after the ammonimum hydroxide treatment.

Columns 5 to 10, inclusive, give data concerning the use of NH_4OH, as a precipitating agent, using the filtrate from the HCl precipitate after adding 0.3000 gram of potassium alum. The phosphorus data are incomplete owing to an unexplained loss of 37.94% of the total phosphorus. The most probable explanation of this loss appears to the writer to be that it was volatilized during an ignition; and if so, it represents organically combined phosphorus. The writer aimed to have $Mg(NO_3)_2$ present in all ignitions so as to avoid loss of phosphorus, but he is not infallible and may accidentally have omitted the $Mg(NO_3)_2$ in one case. All of the aluminum added to the solution, as well as some of that originally present in the solution, was recovered in the precipitate by NH_4OH; but only 30.18% of the total phosphorus appeared in this precipitate. 10.30% of the total phosphorus, precipitated by NH_4OH, was not dissolved by treatment on the filter with HCl, but did dissolve in NH_4OH along with organic matter after the acid treatment. The precipitation of the phosphorus with NH_4OH, in the presence of added inorganic aluminum, was not as complete as in the precipitation by phenylhydrazine under the same conditions.

Columns 11 to 17 contain data relating to the use of magnesia mixture as a precipitating agent. In this case also the precipitation of phorphorus was not as complete as with phenylhydrazine, and the precipitate was not entirely soluble in HCl. The insoluble part dissolved readily in NH_4OH along with organic matter.

Either iron or aluminum appeared along with every precipitate or solution of phosphorus. Table V contains some data concerning this appearnce of iron or aluminum. But the absolute amount of iron and aluminum was in some cases very small—too small, in fact, for very accurate determination, although the precipitates were in general redissolved and re-precipitated, and the ignited iron and aluminum oxides were fused with $KHSO_4$ and corrected for the SiO_2 present. A platinum crucible may change in weight more than 1.0 milligram during an ignition and the amount of moisture condensed on its surface is not always the same during several weighings. The correct determination of an absolute amount of iron and aluminum as oxides of about 1.0 milligram is a difficult thing to do, while on the other hand the volumetric method used by the writer for phosphorus determinations is capable of measuring the phosphorus fairly accurately to within an absolute amount of about 0.1 milligram. Although either iron or aluminum was present with phosphorus in every phosphorus determination, it is a noteworthy fact that iron was entirely absent from solutions No. 1 and No. 2, prepared by the Mooers-Hampton process.

Definite conclusions regarding the state of combination of the phosphorus in the filtrate from the HCl precipitate can not be drawn from the above data. It is probable that some of the phosphorus is present in inorganic form. The data in Table V indicate that some iron and aluminum have been hydrolyzed to inorganic form; for they are precipitated by the reagents used. The presence of inorganic phosphorus in the filtrate from the HCl precipitate is not conclusive evidence of inorganic origin.

The study of the soil humus is attended with the same difficulty as attends the study of the protein molecule. The humus is composed largely of protein bodies and protein decomposition products.

SOME EVIDENCE OF ORGANIC COMBINATION OF IRON AND ALUMINUM IN THE HUMUS SOLUTION

The solution of iron and aluminum in ammonium hydroxide is practically conclusive evidence that they are *not* inorganic in this case. This reagent precipitates iron and aluminum when they are in known inorganic condition on account of the presence of the $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, and $Al^{\cdot\cdot\cdot}$ ions. When iron is not precipitated by this reagent it is because these ions are not present. This occurs with $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, which are organic compounds. Iron and aluminum are not precipitated by NH_4OH in the presence of sugar and certain other organic compounds; because chemical action between the organic matter and the iron and aluminum had occurred and the $F^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, and $Al^{\cdot\cdot\cdot}$ ions are not present in the solution. Ammonium hydroxide does not dissolve aluminum with the formation of an $(NH_4)_3Al0_3$[1]. *Complex inorganic ions,* for instance, ions containing SiO_2 and iron and aluminum might account for the phenomena; but they are not known to exist under the conditions of the work. Potassium and sodium aluminates are decomposed by NH_4OH and ammonium chloride.

The writer determined iron and alumina in the humus solution; by dissolving the humus ash in nitro-hydrochloric acid and then precipitating iron and aluminum by NH_4OH in a volume of solution equal to, or *greater than,* the original volume of humus solution used to prepare the ash.

Ammonium sulphide failed to produce a precipitate in the humus solution, and this reagent is known to precipitate iron in the presence of tartaric acid.

Alumina cream dissolved in a cold humus solution, and an aluminum organic compound was precipitated on heating the solution. A similar behavior was noted when some humus solu-

---

[1] Hillebrand, Bulletin 422, U. S. G. S., p. 99.

tion was accidentally mixed with tap water containing Ca and Mg.

It is a recognized fact that the humus in the soil is combined with Ca and Mg, also with iron and aluminum. It is not particularly remarkable that some of these iron and aluminum organic compounds should be soluble in ammonium hydroxide and that the organically combined phosphorus should go into solution with the rest of the molecule. The writer suggests that it was probably on account of the existence of such organic iron and aluminum compounds, as well as free humic acids that Dr. Stewart[1] obtained a partial solution of the soil humus, with some phosphorus, without making an acid extraction of the soil before subjecting it to the extraction with NH_4OH. If the Illinois soil had been very rich in limestone, which it was not, the humus (and phosphorus) would probably have been practically insoluble in NH_4OH until the lime had been removed with acid.

SOME EVIDENCE OF ORGANIC COMBINATION OF PHOSPHORUS

The experimental data presented in this paper in regard to the organic nature of the phosphorus of the *matiere noire* speaks for itself. The organic nature of the phosphorus of the *matiere noire* is also testified to by Grandeau, Eggertz, Nilson, Wiklund, Schmoeger, Aso, Dumont, Schultz, Snyder, Ladd, *et al.*

It has been noted by many that an increase in the soil humus is often accompanied by an increase in the ammoniacal soluble phosphorus or the ignition soluble phosphorus. Eggertz and Nilson noted that a peaty soil contained 90% of the total phosphorus present in the ignition soluble form.

Dr. Stewart[1] made a partial extraction of the humus without first extracting the soil with acid; and after extracting the soil with acid he made a complete extraction of the humus. In the two cases the phosphorus extracted varied in almost exact direct proportion with the *matiere noire* and with the organic matter. For instance, the *matiere noire* obtained without acid extraction was 45.8% of that obtained with acid extraction, while the phosphorus in the former case was 46.1% of that in the latter. The

---

[1] **Illinois Agr. Exp. Sta. Bulletin 145, pp. 113-115.**

carbon obtained without acid extraction was 42.0% of that obtained with acid extraction, while the nitrogen in the former case was 58.0% of that in the latter case.

Fraps[1] presents average data on 27 soils showing an almost exact agreement between the ammoniacal soluble phosphorus and the ignition soluble. His averages are 0.0208% and 0.0192% on the basis of the soil. For the amount of soil worked with these results show an absolute difference of 0.07 of a milligram of the element phosphorus.

Well known and thoroughly established facts in regard to solubilities of phosphates point strongly to the conclusion that the phosphorus of the *matiere noire* is in organic combination. The phosphates of calcium, magnesium, iron and aluminum—the only inorganic phosphates (except possibly those of sodium, potassium and ammonium) which are likely to be present in an agricultural soil—are soluble in hydrochloric acid, according to Dana. Dana mentions a phosphate of *lead* which is insoluble, or difficultly soluble, in HCl; but pyromorphite is not likely to be present in an ordinary soil, neither is it soluble in ammonium hydroxide. If, therefore, the action of hydrochloric acid on soil phosphates is complete, in the humus determination, there should be no mineral phosphates left for ammonia to dissolve. Some confusion has arisen, apparently, as a result of incomplete removal of acid soluble phosphates, by which some mineral phosphates are left in the soil as *acid* phosphates.

Ammonium phosphomolybdate is an inorganic phosphate which is soluble in ammonia and insoluble in nitric acid, although somewhat soluble in HCl and chlorides. This fact shows that insolubility in acids and solubility in alkalies is not *positive* proof that a phosphorus compound is organic. But it will be noted that the phosphorus in this compound is part of a *complex ion*, and that neither this compound nor any other inorganic phosphorus compound in which the phosphorus is part of a complex ion has ever been found in soil. While, on the other hand, some organic phosphorus compounds are known to be insoluble in acids but readily soluble in alkalies; as for instance the nucleic acids.

---

[1] Bulletin 136, Texas Agr. Exp. Sta., p. 23.

Again, calcium, magnesium, iron and aluminum phosphates are known to be insoluble in ammonia. Well known, quantitative analytical methods are based upon these facts. The writer is aware of the fact that no compound is known to be absolutely insoluble and that phosphorus exists in the ocean to the extent of probably less than one part per million. Some salts are known to increase the solubility of phosphates and some to decrease that solubility. Ammonium salts[1] have been found to increase the solubility of rock phosphates; but to a very slight degree, say, to about 1 to 3 parts per million of solvent. This, the writer considers to be due to hydrolytic and mass action, the weak base ammonium being replaced to a slight extent by the bases calcium, etc. This explains a *slight* solubility of mineral phosphates in ammonia.

Phosphorus, in the form of phosphotungstic acid, is known to combine readily with di-amino acids.

The fundamental principle upon which Fischer[2] worked in his synthesis of the polypeptides is this: Chemical action is a result of properties which we designate by the terms "acidic" and "basic," and there is practically an infinite variation in the degree of acidity or basicity. When, therefore, two compounds, which he had reason to think would react in a certain way, did not do so to his satisfaction, he changed the "acidity" or the "basicity" of one of them by means of another reaction, also depending on a certain, but different relation between the basic and acidic properties of the reacting compounds, then the desired reaction generally proceeded to his satisfaction. Fischer never lost sight of some fundamental facts, and he did not attempt to make quantitative measurements where quantitative measurements are impossible.

Now, if we remember some fundamental facts, it will not be difficult to conceive of the union, chemically, of inorganic soil phosphoric acid and the decaying matter of the soil. Why should not mineral bases act upon organic acids in the soil?

---

[1] J. E. Greaves, Journal of Biological Chemistry, 1910, Vol. VII, No. 4, pp. 287-319.

[2] A. W. Stewart's Recent Advances in Organic Chemistry, 1908, pp. 211-219.

Why should not mineral acids act upon organic bases in the soil?

It appears to the writer that the chemistry of soil organic matter in relation to its action on mineral soil phosphates could probably be better studied by the synthetic method than by the analytical method. The chemistry of the action evidently depends on the NH_2, COOH and OH groups mainly, and a study of the behavior of amino acids on mineral phosphates ought to throw some light on the problem. The chemical relation of potassium to the humus appears also to be worthy of study. Some analysis of the humus ash indicate an accumulation of potassium in the humus.

CONCLUSIONS

1. The Grandeau Method for determining organic phosphorus of the soil gives results lower than the true amount present; for, part of the organic matter is dissolved by the acid treatment and part is not dissolved in either the acid or alkali used.

2. All of the phosphorus of the *matiere noire* is derived from organic sources.

3. A part of the phosphorus in the *matiere noire* is present as inorganic phosphorus, due to hydrolysis having occurred during the extraction with alkali.

4. The Grandeau method is one of the best yet proposed for determining organic phosphorus of the soil. It gives results which are approximately quantitative, and is a useful method when intelligently handled.

5. The testimony of those who have used the Ignition Method of Eggertz and the Autoclave Method of Schmoeger is that these methods give results which agree approximately with the results by the Grandeau Method.

6. The data given by Fraps[1] in determining the *minimum* amount of phosphorus in the *matiere noire,* " which must be inorganic " show anomalous results. The method is evidently faulty.

7. The Factor Method, proposed by Hopkins and Petit and studied by Stewart is evidently capable of giving approximate

---

[1] Bulletin 136, Texas Agr. Exp. Sta., pp. 21-25.

and useful data regarding the organic phosphorus of the soil in some cases. It is evident on its face that it could not have been intended as an exact quantitative and generally applicable method.

8. Some mineral matter may be present in the *matiere noire* in the colloidal form, the amount varying with the method used. The writer considers that his solutions of *matiere noire* prepared by the Mooers-Hampton method were free from mineral matter in colloidal solution; but those prepared by the Grandeau-Hilgard method contained some colloidal mineral matter, the data indicating this to vary from about ten per cent. to 50% of the total ash of the *matiere noire.* (This conclusion is not in harmony with Van Bemellen's theory that the *matiere noire* is a "colloidalen-silicate-humate-complex.")

9. All the iron and aluminum present in the *matiere noire* (except the small quantity present in colloidal form) are organically combined.

10. The decaying organic matter of the soil reacts with calcium, magnesium, iron and aluminum phosphates of the soil to form a variety of complex organic compounds containing phosphoric acid and the several bases mentioned. Acidic and basic mineral phosphates are probably intermediate steps in this process.

11. Barium chloride in alkaline solution, magnesia mixture in alkaline solution, phenylhydrazine in presence of aluminum and in faintly acid solution, and ammonium hydroxide in presence of sufficient iron or aluminum, reprecipitate inorganic phosphorus quantitatively in the presence of organic matter, in some cases at least. But the writer, in his work, did not get a precipitate with any reagent used, which was free from organic matter. It can not therefore be certain that precipitates produced by these methods do not also contain organic phosphorus.

12. Attempts to separate the inorganic phosphorus in these precipitates by means of the solvents, 1% cold aqueous HCl; 1% cold alcohol HCl; water; and 4% cold NH_4OH solution, did not result in sharp, definite separations.

DIE STEIGERUNG DER WIRKUNG DES CYANAMIDS AUF DEN ERTRAG LANDWIRTSCHAFTLICHER KULTURPFLANZEN UNTER DEM EINFLUSS VON EI-SEN OXYD

Dr. A. Stutzer

Professor Universität Königsberg, Deutschland

Das billigste Verfahren, um den Stickstoff der Atmosphäre in Dünger zu verwandeln besteht darin, dass man Cyanamid herstellt. Jedoch haben wir beim Gebrauch von Cyanamid einige Schwierigkeiten zu überwinden. Beim Ausstreuen auf dem Felde staubt die Masse sehr, sie belästigt die Arbeiter und die Pferde, die an der Streu-maschine tätig sind. Ein anderer Uebelstand besteht darin, dass das Cyanamid nicht in allen Bodenarten so gut wirkt als Ammoniak.

Ich habe mich seit mehreren Jahren mit Versuchen beschäftigt, um festzustellen, in welcher Weise die erwähnten Uebelstände zu beseitigen sind. Zur Verbesserung der mechanischen Beschaffenheit des Düngers erzielte ich dadurch den besten Erfolg, dass ich Calcium-Nitrat mit Cyanamid mischte. Das Nitrat wird durch schwaches Erwärmen auf ungefähr 40° C. weich gemacht und mit dem Cyanamid zerrieben. Söderbaum in Stockholm berichtet über Düngeversuche mit einer solchen Mischung und er erhielt durch ein Gemenge von 1 Teil Calciumnitrat mit 2 Teilen Cyanamid besonders gute Erfolge.

Andre von mir ausgeführte Versuche hatten den Zweck, die Wirkung des Stickstoffs zu verbessern und hierüber teile ich folgendes mit.

Die Pflamzen können Cyanamid nicht direkt verwerten, es muss zuvor in Ammoniak umgewandelt sein. Nach Untersuchungen, die in meinem Laboratorium ausgeführt wurden (Biochem. Zeitschrift. Bd. 25 S. 476) bildet sich Carbamid (Harnstoff) und aus diesem durch die Tätigkeit von Bakterien Ammoniak. Die Entstehung von Harnstoff geschieht durch chemische Umsetzung und wir beobachteten, dass Eisenoxyd die Bildung sehr beschleunigt, indem dieses wahrscheinlich katalytisch wirkt. Gleichzeitig stellte C. Ulpiani in Portici bei Napoli die Bildung von Harnstoff fest. (Rendiconti della societa chim. italiana 1910).

Ist Calcium-Cyanamid in den Boden gebracht, so scheidet Kohlensäure das Calcium als Carbonat ab. In Bodenarten, die an Humus und an Kohlensäure arm sind, wirkt Calcium-Cyanamid deshalb schlecht, weil zu wenig Kohlensäure vorhanden ist, um die Trennung vom Cyanamid herbeizuführen und das ausserdem vorhandene Calcium-oxyd mit Kohlensäure zu vereinigen.

Ich führte Versuche in Vegetationsgefässen aus. Der Boden war sandiger Lehm, die Pflanze Hafer. Der Stickstoff wurde in Form von Calcium-Cyanamid gegeben, teils mit, teils ohne Zusatz einer organischen Substanz, nämlich Melasse. In allen Fällen war die Ausnutzung der Stickstoffe nach dem Gebrauch von Melasse besser, weil die Produktion von Kohlensäure erhöht und dadurch die Zersetzung des Calcium-Cyanamids beschleunigt wurde.

Dann haben wir viele Versuche auf Feldern gemacht. Im Jahre 1910 bauten wir Hafer in sandigem Lehm. Das Wetter war in jenem Sommer heiss und trocken. Der Boden auf einem Felde trocken, auf einem andern feucht. Auf 1 Hectar berechnet, sind (bei Verwendung von 40 Kilogr. Stickstoff) an Körnern geerntet:

Dünger:	Boden trocken	Boden feucht
Kali, Phosphorsäure, Cyanamid	1692 kilogr.	4205 kilogr.
Desgleichen mit 80 kg. Eisenoxyd	1811 “	4633 “
“ “ “ “ “ und 25 kg. Melasse	1867 “	4812 “

Unter günstigen Verhältnissen konnte der Ertrag an Körnern durch die Zugabe von wenig Eisenoxyd um 328 Kilogr. und durch Eisenoxyd mit Melasse um 607 kilogr. gesteigert werden. Das ist für 1 acre berechnet 2 cwt. und 60 pounds bezw. 4 cwt. 90 pounds. Die Ausnutzung des Stickstoffs stieg durch diese Zusätze in trocknen Boden von 27 auf 47% und im feuchten Boden von 52 auf 90%.

Ein anderer Versuch ist bei Roggen gemacht. Durch die Zusätze ist ebenfalls der Ertrag gesteigert.

Als die Menge des Stickstoffs von 40 auf 60 Kilogr. erhöht war (das ist von 35 auf 53 pounds per acre) fand eine Steigerung des Ertrages unter dem Einfluss von Eisenoxyd und Melasse nicht statt, weil auch ohne diese Zusätze der Höchstertrag erzielt war, der unter den Verhältnissen des Bodens, des Klimas und der Witterung erreichbar war.

Im Jahre 1911 haben wir die Versuche unter ganz anderen Boden Verhältnissen fortgesetzt, aber keine Melasse gegeben, sondern nur Eisenoxyd in Form von billigem Raseneisenstein. (Bog ore).

Bei Hafer wurde der Ertrag an Körnern um 100 bis 180 Kilo für 1 Hectar gerechnet, gestiegert. Der Roggen hatte im Frühjahr bei einem Versuch während der Blüte durch Frost sehr stark gelitten, ich erhielt durch 40 Kilo stickstoff von 1 Hectar nur 2500 – 2700 Kilo Körner. War dem Cyanamid Eisenoxyd zugesetzt, so stieg der Mehrertrag um 118,220,223,309 und 343 Kilo Körner. Das Eisenoxyd hatte gut gewirkt. Auf einem anderm Felde, in einer andern Gegend, erntete ich ohne Zusätze zum Cyanamid 3700 Kilo Körner (das sind 29 cwt. von 1 acre). Hier liess durch Eisen eine weitere Steigerung des Ertrages sich nicht bewirken, auch ohne die Zusätze war der Höchstertrag erreicht, der unter den Verhältnissen des Klimas und der Witterung erzielbar gewesen ist.

Die eigentümliche Wirkung des Eisenoxyds ist nach meiner Ansicht dadurch bedingt, dass Cyanamid in Carbmid (Harnstoff) übergeht. Ausserdem liegt vielleicht zum Teil eine Reizwirkung vor, wie sie Mangan und andere Metalloxyde geben können.

Die billigste eisenhaltige Substanz, die wir anwenden können, ist gemahlener Raseneisenstein (Bog ore).

Hiervon werden 50-100 kg mit derjenigen Menge von Calciumcyanamid gemischt, die zur Düngung von 1 Hectar dienen soll. In dem meisten Fällen werden 50 Kilo genügen; ich habe den betreffenden Mindestgehalt an Eisen noch nicht festgestellt. Der bei unsern Versuchen benutzte Boden hatte 1-2% Eisenoxyd, er war also nicht arm an Eisen, aber dieses Eisen genügte nicht, um die gesteigerte Wirkung hervorzubringen. Mischt man 200 Kilo Calciumcyanamid mit 50 Kilo Eisenoxyd, so ist die katalytische Wirkung eine andere als wenn der Dünger mit Boden in Berührung kommt, der nur 1-2% Eisenoxyd hat. Eine Wirkung wird nicht eintreten, wenn der Boden sehr reich an Eisen ist, oder wenn man soviel Cyanamid gibt, dass auch ohne Zusatz von Eisenoxyd der erzielbare Höchstertrag erreicht wird. Geben wir normale Mengen von Cyanamid (25-45 kilo für 1 Hectar), so wird in sehr vielen Fällen der Zusatz von Eisenoxyd eine gute Wirkung haben, es ist aber zu erwarten, dass gewisse Arten von Pflanzen eine höhere Verwertung des Cyanamids zeigen als andere. Dies muss durch weitere Versuche festgestellt werden.

Ich hoffe, dass es möglich sein wird, den billigen Stickstoff des Cyanamids durch Beimischung von Eisenoxyd zu einer besseren Ausnutzung zu bringen, so dass er in allan besseren Bodenarten den gleichen Wert hat wie Stickstoff im Ammoniak.

BIOCHEMICAL FACTORS IN SOILS[1]

BY M. X. SULLIVAN, PH.D.

U. S. Department of Agriculture, Washington, D. C.

(Contribution from the Laboratory of Soil Fertility Investigations)

The soil, as is generally agreed at the present day, is not merely a reservoir for the nutrients of plants, but is rather the seat of complex chemical, physical, and biological actions which directly and indirectly influence fertility.

The various factors at work in soils have been extensively studied with the main stress, until recently, upon the physical and chemical sides. Within the last decade or two, however, much attention has been given to the biochemical side of soils and much valuable work has been done along this line, especially in the field of soil bacteriology. Even in soil bacteriology, however, the work has been limited, for the most part, to the study of the nitrogen problem, to denitrification, non-symbiotic and symbiotic fixation of nitrogen, and to ammonification.

On the other hand, biochemical factors in soils, such as the nature of the organic matter, the changes produced in soil constituents by microorganisms, the synthesis of organic compounds in soils, the presence of enzymes, the effect of plant growth on the soil and soil constituents, the physiological action of organic soil constituents on plants, the action of fertilizers, the oxidizing, reducing, and catalyzing powers of the soil, and the general metabolic activity of microorganisms have received less consideration until recently in this and other laboratories.

As regards the organic matter of soils it may be said that recent researches of this Bureau[2] have shown that it consists of a mixture of substances. Over thirty-five distinct bodies have been isolated thus far. Some of these bodies, such as picoline car-

---

[1] Published by permission of the Secretary of Agriculture.

[2] Buls. 53, 74, 80 and 83, Bureau of Soils, U. S. Dept. of Agric.

boxylic and dihydroxystearic acid,[1] are harmful to plants, while others, such as creatinine,[2] histidine,[3] etc., are beneficial. These bodies arise in soils either from the decomposition of plant and animal debris or by synthesis by microorganisms. The biochemical processes through which they arise in the soils has hitherto been little studied. In this laboratory, however, considerable advance has been made in the study of the biochemical factors in soils and much attention has been given to the enzymotic activities of plant roots, enzymes in soils, semi-enzymotic functions in soils, such as oxidation and catalysis, and the metabolism of microorganisms. In the present paper are given the main results of the study of the oxidizing and catalyzing powers of soils, of soil enzymes, and metabolism of molds in reference to the origin of certain soil constituents.

The oxidizing power of soils. Not only do plant roots and microorganisms of the soil possess oxidizing functions, but the soil *per se* has also semi-enzymotic functions, in that it possesses both oxidizing and catalyzing powers. In testing the oxidizing power aloin was found the best reagent. When twenty grams of soil are shaken with 50 cc. of a 0.125 per cent. water solution of aloin, the aloin solution is changed in a few minutes from a bright yellow to a cherry red. After the soil has settled, the somewhat turbid solution is decanted and centrifuged, the supernatant liquid poured off and the depth of color of the solution compared by means of a colorimiter. In experiments already reported upon[4] and in subsequent experiments it was found that soils known to be of good productivity give as a rule good oxidation of the aloin, while soils of poor productivity as a rule have poor oxidative power. Subsoils, which in general are of poorer productivity than surface soils, have little oxidizing power. The oxidizing power is increased by adding water up to the optimum moisture content of the soil and by the commonly used fertilizers in conjunction with plant growth.

---

[1] Schreiner and Shorey, J. Amer. Chem. Soc., 30, 1295, 1599 (1908). Schreiner and Skinner, Bot. Gaz. **50**, 161 (1910).

[2] Bul. 83, Bureau of Soils, U. S. Dept. of Agric.

[3] Bul. 87, Bureau of Soils, U. S. Dept. of Agric.

[4] Bul. 73, Bureau of Soils, U. S. Dept. of Agric. (1910).

Catalytic power of soils. Associated with the oxidizing power of plant and animal tissue is the power to decompose hydrogen peroxide with the evolution of oxygen. This property of the tissue to decompose hydrogen peroxide has been generally attributed to the enzyme catalase and the process is known as catalysis. In testing the catalytic power of soils, five grams of air-dried soil were placed in a large test-tube having a capacity of 90 cc. provided with a two-holed rubber stopper, through which passed a small dropping funnel and a glass tube connected with a gas measuring tube. The peroxide used was a slightly acid rather stable solution containing approximately 3 per cent. hydrogen peroxide by weight. Before using the peroxide it was made faintly alkaline to phenolphthalein by means of dilute sodium hydroxide. The neutralized peroxide, one-half strength, was dropped upon the soil by means of the funnel and the oxygen was collected in the gas measuring tube. The criterion for the catalytic power of the soils was the time required to evolve 50 cc. of oxygen. In the experiments, each tube was shaken once every minute for fifteen seconds. In this way many soils, productive and non-productive, surface soils and subsoils, greenhouse soils and field soils, were tested. The catalytic power is greater in strong vital soils than in weak soils, in surface soils than in subsoils, and persists for years in air-dried soils.

Enzymes in soils. From the presence in soils of compounds such as histidine, arginine, cytosine, xanthine, etc., it is apparent that enzymes, either intracellular or extracellular, are working in soils. Thus far, however, no extract of soil has been found to contain diastatic, inverting, lipolytic, proteolytic, oxidizing, or catalyzing enzymes, though many soils have been extracted with water and with twenty per cent. gylcerine solutions. Since no trace of 0.05 grams of commercial diastase added to five pounds of soil could be found in an extract one week later it appears that the enzymes are so absorbed by the soil that they cannot be extracted or that extracellular enzymes do not exist long in soils. Whatever change is brought about is probably produced by the intracellular enzymes, of soil organisms. As regards the oxidizing and catalyzing powers of soil it may be said that these powers do not seem to be due to enzymes but rather to the organic and inorganic matter of the soil working separately or conjointly. Both the oxidizing and catalyzing power persist in air-dried soils for years.

Metabolism of molds. Filter paper placed on soils and kept damp disappears more or less quickly, depending on the soil. In most cases the paper becomes covered with a fine mold growth. Since the mold spores seem to be abundant in soil a study of the metabolism of molds has begun in these laboratories with especial attention to the origin of various bodies found in soil. As a medium for the growth of the molds, the customary Raulin's solution was used either alone or reinforced at times by 0.2 per cent. of peptone. Molds taken from soil were first developed in a small amount of Raulin's solution and from this culture, 50 to 70 liters in bottles, 350 cc. in each large bottle, were inoculated. The mold growth soon covered the surface. After two or three weeks the solution was filtered and the mold air-dried. The solution and the air-dried mold were then analyzed.

The air-dried mold was extracted for several hours with 2 liters of boiling alcohol containing 2 per cent. sodium hydroxide and the hot alcoholic solution was filtered off. After evaporation of the alcohol, the residue was taken up with hot water and filtered hot. The alkaline filtrate was acidified with dilute sulphuric acid and allowed to cool. The brownish fatty, oily matter was filtered off and dissolved in alcohol. The alcohol solution was treated with alcoholic lead acetate. The lead soap was partly soluble in ether, partly insoluble.

The lead soap soluble in ether was freed from lead and consisted almost entirely of an unsaturated light yellow oil solifying at 4° C. which proved to be oleic acid. Treated with nitrosyl sulphuric acid it was converted to elaidic acid, which after recrystallizing, melted at 50-51° C.

The ether insoluble lead soap was freed from lead and recrystallized several times from alcohol. From this sample two fatty acids were obtained by fractional crystallization out of 90, 85, and 70 per cent. alcohol. One acid melted at 62° C. and one at 54° C. The acid melting at 62° was mixed with an equal part of palmitic acid of a melting point of 60 and the melting point of the mixture was 60-61°. This acid is undoubtedly palmitic acid.

The filtrate from the fatty acids was tested for dihydroxystearic acid, purine bases, and histidine, cytosine, and thymine.

Dihydroxystearic acid. The filtrate spoken of yielded to ether a small amount of a crystalline fatty acid which was soluble in hot water and alcohol, rather insoluble in cold water and resembled dihydroxystearic acid in crystalline shape. The amount was small and could not be definitely identified.

Purine bases. The mold after extraction with the alcoholic soda was heated two hours on the steam bath with 2 liters of 8 per cent. sulphuric acid. On cooling, the acid filtrate was combined with the acid filtrate from the fatty acids after shaking out with ether as above mentioned. The solution was made nearly neutral with barium hydroxide and filtered hot from the barium sulphate. The filtrate was concentrated to about a liter and was extracted with ether. The main solution was then made 5 per cent. acid with sulphuric acid and precipitated by a 10 per cent. solution of phosphotungstic acid in 5 per cent. sulphuric acid. The precipitate was analyzed for purine bases and cytosine, the filtrate for thymine.

The precipitate produced by the phosphotungstic acid was freed from phosphotungstic acid by barium hydroxide and from barium by the careful addition of sulphuric acid. The practically neutral solution was then made slightly acid with nitric acid and was precipitated by 20 per cent. silver nitrate. The precipitate of silver nitrate contained the purine bases, the filtrate the cytosine.

The silver nitrate precipitate of the purine bases was digested with warm 5 per cent. ammonia water and again filtered. The precipitate was suspended in boiling water and the bases converted to chlorides by means of hydrochloric acid. The silver chloride was filtered off and the solution brought to dryness at a moderate temperature. The mass was then dissolved in hot water and treated with an excess of warm 10 per cent. ammonia. A precipitate occurred. This precipitate was filtered after 24 hours and was washed with 2 per cent. ammonia and then dissolved in dilute sodium hydroxide. On acidifying with acetic acid a slight precipitate occurred. This precipitate gave Strecker's test for xanthine or guanine, a characteristic hydrochloride with strong hydrochloric acid, and a picrate when the solution of the hydrochloride in water was treated with picric acid. The method of isolation and the reactions fix the compound as guanine.

The ammoniacal filtrate from guanine was brought to dryness and after the removal of ammonia was treated with dilute hydrochloric acid. The slightly acid solution was treated with sodium picrate until a precipitate no longer occurred. After twenty-four hours, the presumably adenine picrate was filtered off and dissolved in hot ammonia. To the ammoniacal solution ammoniacal copper sulphate was added. The filtrate from the copper picrate contains the adenine if present. This filtrate was evaporated to dryness on the water bath and the residue was dissolved in dilute sulphuric acid and freed from copper by hydrogen sulphide. On concentrating the filtrate from the copper sulphide crystals separated out in prisms. The mixture was then treated with ammonia in slight excess. The crystals dissolved in the ammonia. The excess of ammonia was driven off on the water bath and the solution tested for adenine again. The solution gave a red color with ferric chloride, a reaction shown by adenine. On addition of potassium ferricyanide and acetic acid a precipitate of brownish green prisms arranged in bunches separated out. Treated with ammoniacal silver nitrate a precipitate formed. From the mode of separation of the compound, the formation of a picrate, a crystalline sulphate, a ferricyanide, and the color reaction with ferric chloride, the compound in question must have been adenine.

For the isolation of xanthine and hypoxanthine the filtrate from the adenine picrate was made ammoniacal and precipitated by ammoniacal silver nitrate. The precipitate after a thorough washing with dilute ammonia was decomposed by hydrochloric acid. The filtrate from the silver chloride was brought to dryness and digested with warm water (40° C.). The parts soluble in water was found to contain hypoxanthine by its precipitation with ammoniacal silver nitrate, the formation of a characteristic hydrochloride, and the color reaction with bromine and nitric acid and sodium hydroxide. The small amount insoluble in water was likewise found to be hypoxanthine, but later traces of xanthine were found in examining the dried mold.

The filtrate from the silver precipitate of the purine bases was tested for histidine and cytosine by the method of Kossel and Kutscher[1] and Kutscher.[2] Cytosine was not present. Histidine was present in small amounts as was proved by the formation of the characteristic diochloride and the color reactions with bromine and with diazosulphanilic acid.

The filtrate from the phosphotungstic acid precipitate was tested for thymine. Freed from phosphotungstic acid by barium hydroxide and from barium by careful addition of dilute sulphuric acid, the filtrate was evaporated to a syrup. The syrup was extracted repeatedly with cold alcohol and the alcohol evaporated. After taking up with cold alcohol several times the residue from the evaporation of the alcohol was extracted with ether. The ether extracted matter was soluble in hot water; insoluble in cold water and resembled in crystalline shape the crystals of the thymine described by Gulewitsch,[3] and sublimed as does thymine. Evaporated with fuming nitric acid, crystals closely resembling alpha-oxynitrohydrothymine, described by Johnson[4] formed.

Since in previous experiments[5] it was shown that plants leave material in the water and soil where they are grown, the solution in which the molds had grown was tested for definite chemical bodies. By methods similar to those already described, there were found in the solution a small amount of fatty material and purine bases, guanine, adenine, and hypoxathine, and histidine, especially in that solution which contained peptone, and thymine. The work shows that many of the substances found in soils arise in the metabolism of microorganisms and are let in the medium as a result of excretion, leaching, or as mold disintegration, just as in the case of plants but to a greater degree.

---

[1] Zeit. physiol. Chem., **31**, 166 (1900).

[2] Zeit. physiol. Chem., **38**, 170 (1903).

[3] Zeit. physiol. Chem., **27**, 292 (1899).

[4] Jour. Biol. Chem., **4**, 407 (1908).

[5] "The Origin of Creatinine in Soils," Bul. 83, Part II, Bureau of Soils, U. S. Dept of Agric.; Sullivan, J. Am. Chem. Soc., **33**, 2035 (1911).

SUMMARY

The soil possesses oxidizing and catalyzing powers which are stronger in the more productive soils and are more manifested in soils than in subsoils.

There are evidence of enzyme action in soils but as yet no good method has been obtained for extracting enzymes from soil.

Many of the substances found in soil undoubtedly arise to a considerable degree as a result of the metabolism of microorganisms. In mold cultures have been found fatty acids, especially oleic and palmitic, purine bases, such as guanine, adenine and hypoxathine, histidine, and probably thymine.

In the solution in which molds have grown were found fatty bodies, guanine, adenine, hypoxathine, histidine, and probably thymine.

A NOTE ON THE DISTILLATION OF KELP

By J. W. Turrentine

Department of Agriculture, Washington, D. C.

The destructive distillation of kelp for the recovery of valuable distillation products and the extraction of potassium salts from the unvolatilized residue was first proposed by Stanford,[1] in England and more recently by Balch[2] in this country. These processes, together with other proposed methods of utilizing kelps, have been discussed in Appendix Q, of Senate Document, 190, 62nd Congress, 2nd Session, which is a report on the "Fertilizer Resources of the United States." Green and Johnson[3] distilled specimens of kelp from the Atlantic and Pacific coasts, obtaining results at variance with these described by Stanford and by Balch.

The destructive distillation of kelp described briefly in this paper was effected in a modified Hornsey rotary still, designed and constructed for the distillation of wood on a laboratory scale, and the experiments were conducted in the laboratories of John W. Hornsey, Consulting Engineer, 27 William Street, New York.

The apparatus. The cylindrical retort, instead of being rotated, as in the case of the larger apparatus from which it was modeled, was provided with stirrers. These were operated through a suitable arrangement of gears, by means of a small electric motor and served to keep the charge thoroughly stirred, thus insuring uniform heating. Temperatures were recorded by means of a pyrometer. The retort was enclosed in a chamber of fire-brick and was heated by means of kerosene burners.

The distillate was led from the retort through a series of water cooled, glass condensers arranged in two sets of two each. The condensers were vertical and conducted the condensate into glass

---

[1] Cf. Senate Doc. 190, p. 271, appendix S. " Reference List of Papers Concerning the Economic Uses of Algae," etc.

[2] J. Ind. Eng. Chem. I., 777 (1909).

[3] Chem. Eng. **15**, 55 (1912).

bulbs. The latter resembled separatory funnels with two necks—to accommodate two condensers. The distillate could be withdrawn as desired from the bulbs through the opening in their bottoms.

The uncondensed portion of the distillate passed from the condensers through a series of two scrubbers where it was forced to bubble under water. Thence it passed through a gas meter, graduated in thousandths of a cubic foot, and thence to gas burners.

The charge distilled consisted of two samples of the Pacific kelp, *Macrocystis pyrifera,* from Stations No. 17 and 20.[1] These had been dried until their moisture content was 2.89 per cent. (= ave. of 2.67 per cent. and 3.12 per cent.).

The distillation continued until the evolution of distillation products had practically ceased. In tabular form below is given the log of the run.

TABLE I. Log of Run.

Hour	Retort Temp. F.	Meter Temp.	Meter	Cu. Ft. per hr.	Total cu. feet	Remarks
10.20 A.M.			80.873			Started.
.30 "			80.878		.005	Bubbles.
11.00 "			81.145	.534	.272	Bubbles, mist.
.03 "			81.250	2.100	2.377	Pyrom. moved.
.06 "						Distillate.
.16 "			81.900	3.000	1.027	Wash water turning green.
.25 "	300	80.5	82.750	3.864	1.877	Tested gas: CO_2 present.
.26 "						Rapid Dist.
.33 "	320		83.600	6.075	2.727	Samp. 1 not combustible at burners.
.39 "			84.175	5.760	3.302	Dist. water in scbr. opaque.
.45 "	340		84.800	6.240	3.927	
.47 "	360		85.100	9.000	4.227	Rapid dist.
.53 "	370	8.15				
.56 "	380		86.100	6.666	5.227	Mist yellow

---

[1] Cf. Sen. Doc. 190, p. 213; J. Ind. Eng. Chem. 4, 434 (1912).

TABLE I. Log of Run—*Continued*

Hour	Retort Temp. F.	Meter Temp.	Meter	Cu. Ft. per hr.	Total cu. feet	Remarks
12.00 M.	390	82.0	86.450	3.715	5.577	Dist. brown, gas.
.06 P.M.	410	82.	87.173	2.220		Slightly combust.
.09 “	420					Sample 2.
.12 “	430					Brown distillate.
.15 “	440		88.393	8.100	7.520	Heavy black dist.
.25 “	480	83.	89.965	9.432	9.092	Samp. 3 lights at burners.
.30 “			90.234		9.361	Samp. 4, burns luminous flame.
.35 “	570					
.37 “	590		90.933	4.836	4.836	Sample 5.
.41 “	640		91.223	4.320		Shut off burners.
.43 “	670					Exothermic react.
.45 “	700					
.46 “	710		91.480	1.870		Dimin. flow of gas.
.48 “	725		91.533	1.590		Dimin. flow distil.
.49 “	740	84.	91.563		10.69	
.51 “	760		91.606	1.260		Luminous gas.
.54 “	780					
.58 “	800		91.669	.540		Started burns.
1.05 “	820					No more dist.
.07 “	820	85.	91.717	.318	10.834	No gas mist.
.09 “	820	85.	91.763	1.580	10.89	Gas mist.
.15 “	830		91.913	1.400	11.04	More gas.
.19 “	850	85.	92.113	3.000	11.24	
.24 “	880	85.	92.433		11.56	
.28 “	900	85.	92.653	3.300	11.78	Sample 7.
.31 “	920		92.853	3.946	11.96	Dim. flow gas.
.37 “	950	85.5	93.107	2.436		
.45 “	980		93.430	2.418	12.557	
.50 “	1000		93.430	2.418	12.645	Sample 8.
.51 “	1000	86.	93.607	1.740	12.734	Shut off.
.54 “	1010		93.650	.840	12.777	
2.05 “	1000		93.717	.360		
.13 “	970		93.717			
.33 “	870		93.717			
3.13 “	710					

Samples of gas were taken at frequent intervals. These were withdrawn at a point between the retort and the first condenser. The analysis of four alternate samples are given below. These, as were the other analyses reported here, were made in the Hornsey laboratories.

TABLE II. Analyses of Gas Samples. Results in Per Cent.

Sample No.	1	3	5	7
CO_2	80.0	70.0	44.0	20.2
Illuminants	2.0	4.0	10.0	3.3
O_2	0.5	1.5	0.8	0.5
CO	10.5	8.5	6.7	4.0
H_2		10.6	23.5	32.0
Methane	2.88	4.8	4.4	7.6
Nitrogen (by difference)	4.12	0.6	10.6	32.4
Total	100.00	100.00	100.00	100.00
Wt. per cu. ft.	0.106040	0.094	0.074150	0.057600
Cal. value	107.45	196.70	352.05	282.54

The liquid portion of the distillate, yet to be examined, consisted of a watery and an oily portion. The former was of reddish color and gave a neutral action to litmus. The oily portion was black and had a persistent and penetrating odor. The oils were lighter than water. In the earlier stages of the experiment the condensate was largely watery. The proportion of oil increased as the distillation proceeded. The proportion of oil to water was roughly, 1:4.

The coke resulting, representing 50.10 per cent. of the weight of the original kelp, was light and porous. Its analysis showed it to contain 77.79 per cent. potassium chloride. On the basis of this analysis, it is evident that from the three kilograms of kelp distilled, 751.5 grams potassium chloride were obtained.

The summarized results of the experiment are given in table III.

TABLE III

Item	Percentage	Weight
Kelp out in retort	100%	3000. grms.
Weight of distillate	19.90	597. grms.
Wt. from Scrubber No. 1—wash water and distillate less wash water used	1.74	52.20 grms.
Wt. from Scrubber No. 2	8.40	252.00 grms.
Gas	16.15	484.50 grms.
Weight of charcoal	50.10	1503.00 grms.
Moisture	2.895	86.85 grms.
Loss	.815	24.45 grms.
Total	100.00	3000.00 grms.

THE SALINES OF THE UNITED STATES AS A SOURCE OF POTASSIUM SALTS

By J. W. Turrentine

Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.

For the sake of convenience the salines of the United States may be divided into the following groups:

(1) Rock salt and the brines prepared therefrom (artificial brines).

(2) Natural brines (subterranean).

(3) Salt lakes and desiccated remains of salt lakes (playas, salt marshes, salt crusts, etc.)

(4) Ocean brines.

While, strictly speaking, among the salines may be included other natural products, in this discussion are considered only those masses of salts and brine which are great enough to be recorded as workable on a commercial scale.

(1) Immense deposits of rock salt are known to underlie portions of New York, northeastern Ohio, the southern peninsular of Michigan, Kansas and parts of Louisiana and Texas. In New York, Michigan, Kansas and Louisiana the deposits are entered by shafts and the salt is removed by mining methods. Also, in these regions and in northeastern Ohio the salt is recovered by solution methods.

Solution methods consist in drilling a hole to the salt beds. Through this a pipe is inserted, which, together with the circular space between it and the casing of the boring, constitute two courses through one of which fresh water is admitted to the salt and through the other brine is withdrawn. Brines obtained in this manner are spoken of as artificial brines.

(2) Natural Brines (subterranean) are found in the porous strata underlying numerous areas in the United States, but are utilized for the manufacture of salt on a commercial scale, principally in southern Ohio, West Virginia, and Michigan.

Natural brines are obtained by drilling a hole to the containing strata, " shooting " to form a cavity for its accumulation and pumping.

(3) Salt lakes and their desiccated remains are found in the arid and semi-arid regions of the western part of the United States. The lakes are of widely varying degree of salinity, some of them being practically saturated solutions; while others have gone almost to complete dryness and are represented by brine-impregnated saline and alluvial deposits; and the nature of their saline contents varies widely, depending, among other things, on the nature of the rocks constituting their drainage area.

(4) Ocean brine constituted a source of potassium salts before the development of the Stassfurt deposits. Potassium chloride was obtained from the mother-liquors resulting in the manufacture of salt from sea-water by means of solar evaporation.

On the Pacific coast of the United States there are a number of manufacturers engaged in the preparation of salt from ocean water by means of solar evaporation or a combination of solar and artificial evaporation. The mother-liquors resulting have found no very important use, though, for the most part, they are preserved. Their possible utilization will be discussed in a following paragraph.

The Bureau of Soils of the United States Department of Agriculture has investigated the principal bodies of salines of the United States to determine their content in potassium salts. Some of the analytical data obtained in the investigation are given in the subjoined tables.

TABLE I. ROCK SALT FROM NEW YORK, MICHIGAN, KANSAS AND LOUISIANA

Results in per cent.

No. Sample	Source	Description	K	KCl
1	Retsof Mining Co., Retsof, N. Y.	From near floor at working face	Trace	Trace
2	Sterling Salt Co., Cuylerville, N. Y.	Rock salt dust	"	"
3	Sterling Salt Co., Cuylerville, N. Y.	Through full depth of working face	"	"
4	Detroit Mining Co., Detroit, Mich.	Through full depth of working face	"	"
5	Crystal Salt Co., Kanopolis, Kan.		"	"
6	Royal Salt Co., Kanopolis, Kan.		0.1	0.2
7	Bevis Rock Salt Co., Lyons, Kan.	From 16-ft. bed	Trace	Trace
8	Bevis Rock Salt Co., Lyons, Kans.	Fine salt screened from coarse	"	"
9	Avery Rock Salt Co., Avery Island, La.		"	"

TABLE II. ARTIFICIAL BRINES FROM NEW YORK

Results in parts per thousand

No. Sample	Source	Description	K	KCl
1	Worcester Salt Co., Silver Springs, N. Y.		0.3	0.6
2	Rock Glen Salt Co., Rock Glen, N. Y.		Trace	Trace
3	Star & Crescent Salt Co., Saltvale, N. Y.		0.8	1.5
4	Genessee Salt Co., Genessee, N. Y.		0.5	1.0
5	Watkins Salt Co., Watkins, N. Y.		11.8	22.5
6	International Salt Co., Watkins, N. Y.		12.0	23.9
7	Genessee Salt Co., Genessee, N. Y.		2.0	3.8
8	Remington Salt Co., Ithaca, N. Y.		0.4	0.8
9	Onondaga Pipe Lime Co., Liverpool, N. Y.		0.2	0.4

TABLE III. ARTIFICIAL BRINES OF OHIO

Results in parts per thousand

No. Sample	Source	Description	K	KCl
1	Colonial Salt Co., Akron, O.	From well No. 6	0.4	0.8
2	Columbia Chemical Co., Barberton, O.		0.2	0.4
3	Columbia Chemical Co. Barberton, O.		0.8	1.5
4	Cleveland Salt Co., Cleveland, O.	Composite brine from 2 wells	0.4	0.8
5	Union Salt Co.,Cleveland, O.	Brine from one well	1.0	1.9
6	Ohio Salt Co., Wadsworth, O.	Composite brine from 2 wells	3.0	5.7

TABLE IV. ARTIFICIAL BRINES OF MICHIGAN

Results in parts per thousand

No. Sample	Source	Description	K	KCl
1	Delray Salt Co., Delray, near Detroit, Mich.	Direct from well	Trace	Trace
2	Michigan Alkali Co., Detroit, Mich.	Direct from well	Trace	Trace
3	Louis Sands Salt & Lumber Co., Manistee, Mich.	Direct from wells	0.1	0.2
4	R. G. Peters Salt & Lumber Co., East Lake, Manistee, Mich.	Composite brine from 6 wells	0.1	0.2
5	Filer & Son, Filer City, Mich.	Direct from wells	0.2	0.4
6	State Lumber Co., Plant No. 2, Manistee, Mich.	Composite brine from 2 wells	0.1	0.2
7	Stearns Salt and Lumber Co. Ludington, Mich.	Composite brine from 4 wells	0.2	0.4

TABLE V. ARTIFICIAL BRINES OF MICHIGAN AND CANADA

Results in parts per thousand

No. Sample	Source	Description	K	KCl
1	Diamond Crystal Salt Co., St. Clair, Mich.	Brine from one well	Trace	Trace
2	Davidson, Wonsey Co., Marine City, Mich.	Composite brine from 2 wells	1.4	2.7
3	Michigan Salt Works, Marine City, Mich.	Brine from 1 well	0.6	1.2
4	Worcester Salt Co., Ecorse, Mich.	Composite brine from 2 wells	Trace	Trace
5	Western Canada Flour Mills Co., Goderich, Canada	Brine from 1 well	1.4	2.7
6	Mulkey Salt Co., Detroit, Mich.	Composite brine from 3 wells	3.8	7.2

TABLE VI. BITTERNS FROM NEW YORK ARTIFICIAL BRINES

Results in parts per thousand

No. Sample	Source	Description	K	KCl
1	International Salt Co., Myers, N. Y.	Bittern after 22 hrs. evaporation	Trace	Trace
2	International Salt Co., Myers, N. Y.		Trace	Trace
3	Remington Salt Co., Ithaca, N. Y.	Represents evaporation of 350 tons to 25 tons	1.0	2.0
4	Remington Salt Co., Ithaca, N. Y.	From centrifuges at end 1st hr. centrifuging	0.2	0.4
5	Remington Salt Co., Ithaca, N. Y.	From centrifuges at end 7th hr. centrifuging	0.6	1.2
6	LeRoy Salt Co., LeRoy, N. Y.	Bittern from continuous run-off	0.2	0.4
7	Solvay Process Co., Syracuse, N. Y.		0.6	1.2

TABLE VII. BITTERNS FROM NEW YORK ARTIFICIAL BRINES (*Cont'd*)

No. Sample	Source	Description	K	KCl
8	Worcester Salt Co., Silver Springs, N. Y.	From vacuum pans	1.7	3.2
9	Worcester Salt Co., Silver Springs, N. Y.	From grainer	2.8	5.3
10	Rock Glen Salt Co., Rock Glen, N. Y.	Represents 10 days' evaporation	1.9	3.6
11	Rock Glen Salt Co., Rock Glen, N. Y.	Represents 6 weeks' evaporation	9.4	17.9
12	Star and Crescent Salt Co., Warsaw, N. Y.	Represents evaporation 85,000 gals. to 350 gals.	1.8	3.4
13	Genessee Salt Co., Piffard, N. Y.	Represents evaporation of 30,000 gals. to 15,000 gals.	1.3	2.5
14	Genessee Salt Co., Piffard, N. Y.	Represents 2 weeks' evaporation	2.2	4.2

TABLE VIII. BITTERNS FROM ARTIFICIAL BRINES OF MICHIGAN

No. Sample	Source	Description	K	KCl
1	Delray Salt Co., Detroit, Mich.	Drippings from salt from vacuum pans	0.1	0.2
2	Delray Salt Co., Detroit, Mich.	Represents 12 days' evaporation	Trace	Trace
3	Pennsylvania Salt Co., Wyandotte, Mich.	From dripping vats	0.4	0.8
4	Diamond Crystal Salt Co., St. Clair, Mich.	Represents 23 days' evaporation	Trace	Trace
5	Davidson, Wonsey Co., Marine City, Mich.	Drippings from vacuum pan salt	Trace	Trace
6	Michigan Salt Works, Marine City, Mich.	Represents 6 weeks' evaporation	2.0	3.8
7	Mulkey Salt Co., Detroit, Mich.	Represents 30 to 35 days' evaporation	1.6	3.1
8	Filer & Son, Filer City, Mich.	Drippings from salt	2.0	3.8
9	Peters Salt and Lumber Co., East Lake, Manistee	Represents 19 days' evaporation	0.5	1.0
10	Buckley Douglas Lumber Co., Manistee, Mich.	Represents 4 weeks' evaporation	0.2	0.4
11	Louis Sands Lumber Co., Manistee, Mich.	Represents 3 weeks' evaporation	0.7	1.3
12	Stearns Salt and Lumber Co., Ludington, Mich.		Trace	Trace

TABLE IX. BITTERNS FROM ARTIFICIAL BRINES OF CANADA, OHIO AND KANSAS

Results in parts per thousand

No. Sample	Source	Description	K	KCl
1	Western Canada Flour Mills Co., Goderich, Can.	Represents 5 weeks' evaporation	1.4	2.7
2	Colonial Salt Co., Akron, O.	Represents 5½ weeks' evaporation	2.8	5.4
3	Union Salt Co., Cleveland, O.	Represents 5 days' evaporation	1.2	2.3
4	Ohio Salt Co., Wadsworth, O.	Represents 35 days' evaporation	0.7	1.3
5	Ohio Salt Co., Wadsworth, O.	From vacuum pan at boot	1.8	3.4
6	Western Salt Works, Hutchinson, Kan.	Represents 25 days' evaporation	1.0	2.0
7	Sterling Salt Co., Sterling, Kan.	Represents 30 days' evaporation	Trace	Trace
8	Orient Salt Co., Anthony, Kan.	Represents 8 days' evaporation	0.2	0.4

TABLE X. NATURAL BRINES OF MICHIGAN

Results in parts per thousand

No.	Source	Description	K	KCl
1	Bliss, Van Auken Co., Saginaw, Mich.	Composite brine from 3 wells	Trace	Trace
2	Edward Germain, Saginaw, Mich.	From well No. 1 (750 feet deep)	0.4	0.8
3	Mershon, Eddy, Parker & Co., Saginaw, Mich.	Composite brine from 2 wells	1.4	2.7
4	S. L. Eastman Flooring Co., Saginaw, Mich.	Composite brine from 2 wells	0.8	1.5
5	Saginaw Plate Glass Co., Saginaw, Mich.	Composite brine from 10 wells	1.0	1.9
6	Dow Chemical Co., Midland, Mich.	Composite brine from 12 wells	Trace	Trace
7	Daw Chemical Co., Mt. Pleasant, Mich.	Composite brine from 5 wells	1.2	2.3
8	Saginaw Salt Co., St.Charles, Mich.	Brine from 1 well	Trace	Trace
9	Saginaw Salt Co., St.Charles, Mich.	Composite brine from 2 wells. Plant No. 2	Trace	Trace
10	Port Huron Salt Co., Port Huron, Mich.	Brine from shallow well	0.8	1.5

TABLE XI. NATURAL BRINES FROM OHIO AND WEST VIRGINIA

No. Sample	Source	Description	K	KCl
1	Colonial Salt Co., Akron, O.	From strata above rock salt	3.2	6.1
2	Columbia Chemical Co., Barberton, O.	From strata above rock salt	3.2	6.1
3	Diamond Alkali Co., Fairport Harbor, O.	From stratum 300 ft. above rock salt	5.8	11.1
4	Diamond Alkali Co., Fairport Harbor, O.		3.9	7.4
5	Dixie Salt Works, Mason, W. Va.	Composite brine from 4 wells	0.2	0.4
6	Pomeroy Salt Ass'n, Pomeroy, O.	Composite brine from 2 wells	0.2	0.4
7	Pomeroy Salt Ass'n, Pomeroy, O.	Brine from spring	1.0	2.0
8	Hartford City Salt Co., Hartford, W. Va.	Composite brine from 5 wells	Trace	Trace
9	Liverpool Salt Co., Hartford City, W. Va.	Composite brine from 5 wells	Trace	Trace

TABLE XII. BITTERNS FROM NATURAL BRINES OF MICHIGAN

No. Sample	Source	Description	K	KCl
1	Hine & Co., Bay City, Mich.	Represents 5 days' evaporation	1.3	2.5
2	Bliss, VanAuken Co., Saginaw, Mich.	Represents 5 days' evaporation	1.6	3.1
3	Edward Germain, Saginaw, Mich.	Represents 14 days' evaporation	4.2	8.0
4	Mershon, Eddy, Parker & Co., Saginaw, Mich.	Represents 4 days' evaporation	2.6	5.0
5	Saginaw Chemical Works, Saginaw, Mich.	Solid calcium chloride. Results in per ct.	0.3	0.6
6	Saginaw Chemical Works, Saginaw, Mich.	Represents 85% volume of original brine	10.2	19.5
7	Dow Chemical Co., Mt. Pleasant, Mich.	After removal of bromine	1.2	2.3
8	Van Schaack Calcium Wks., Mt. Pleasant, Mich.	Solid calcium chloride. Results in per cent.	0.2	0.4
9	Saginaw Salt Co., St. Charles, Mich.	Represents 4 days' evaporation	Trace	Trace
10	Port Huron Salt Co., Port Huron, Mich.	Represents 2 weeks' evaporation	Trace	Trace

TABLE XIII. BITTERNS FROM NATURAL BRINES OF OHIO AND WEST VIRGINIA

No. Sample	Source	Description	K	KCl
1	Pomeroy Salt Ass'n., Pomeroy, O.	Bittern just before going to bromine still	3.2	6.6
2	Eureka Calcium Works, Pomeroy, O.	Calcium chloride. Results in per cent.	0.7	1.4
3	Hartford City Salt Co., Hartford, W. Va.		0.4	0.8
4	Dixie Salt Works, Mason, W. Va.	Bittern just before going to bromine still	2.7	5.4
5	Hartford City Salt Co., Hartford, W. Va.	Solid calcium chloride. Results in per cent.	Trace	Trace
6	Liverpool Salt and Coal Co., Hartford, W. Va.	Solid calcium chloride. Results in per cent.	0.8	1.5
7	Liverpool Salt and Coal Co., Hartford, W. Va.	Bittern just before going to bromine still	2.9	5.8

TABLE XIV. BRINES FROM REMNANTS OF DESICCATED LAKES

Results in per cent. of total salts

No. Sample	Source	Description	K_2O
1	Searles Lake, San Bernadino Co., Cal.	Average of 7 analyses	6.73
2	Railroad Valley, Nev.	Average of 19 analyses	6.25

TABLE XV. BITTERNS FROM SEA-WATER

Results in parts per thousand

No. Sample	Source	Description	K	KCl
11b 198	Leslie Salt Refining Works, San Mateo, Cal.	From mother liquor pond	8.2	15.6
11b 199	Leslie Salt Refining Works, San Mateo, Cal.	From different parts same pond	13.4	25.5
11b 200	Leslie Salt Refining Works, San Mateo, Cal.	From salt-making pond	13.2	25.2
11b 201	Oliver Salt Works, Mt.Eden, Cal.	Represents accumulation of 5 years	14.6	27.8
11b 202	Oliver Salt Works, Mt.Eden, Cal.		21.5	41.0
11b 204	California Salt Co., Alvarado, Cal.	Represents 3 years' accumulation	35.0	66.7
11b 205	Pioneer Salt Co., San Francisco, Cal.	Represents 1 year's accumulation	11.8	22.5

The results of the analyses show that the rock-salt of these deposits so far exploited contain but very small amounts of potassium salts. As the history of these deposits is unknown as is likewise, the nature of the brine from which they were crystallized, it is impossible to say whether there is any likelihood of segregations of potassium salts underlying or overlying them. From all theoretical considerations it appears quite improbable that the known deposits of rock salt of the United States east of the Rocky Mountains are associated with potassium salts other than those small amounts occluded and absorbed during the crystallization of the sodium chloride.

The natural (subterranean) brines, being less pure solutions of sodium chloride, contain more potassium than the artificial brines. But in no instances do the artificial or natural brines, or the concentrates thereof, contain sufficient potassium salts to make them of commercial value as a source of potash. This is especially true in view of the fact that from none of the systems represented by the brines and mother-liquors can other than double salts of potassium be separated by simple evaporation processes.

The brines from the western desert basins present interesting commercial possibilities. Among the large number of brines from those regions analyzed by this Bureau the two reported in Table XIII show largest content in potassium salts. The possibility of obtaining from them useful by-products, enhance their commercial value.

When the bitterns from sea-water are evaporated to dryness, it is seen from Table XIV, a mixture of salts is obtained which contains sufficient potassium salts to make the mixture of value as a so-called "manure salt." However, the amounts in which these mother-liquors are produced are so small, that the amount of "potash" obtainable from them is inconsiderable when compared with this country's total annual consumption.

SUR L'"HÉRÉDITÉ" DE LA RICHESSE EN FÉCULE DES TUBERCULES DE POMMES DE TERRE

PAR M. M. PH. DE VILMORIN ET F. LEVALLOIS

Aimé Girard, dans ses " Recherches sur la culture de la pomme de terre industrielle et fourragère" avait montré "qu'aux tubercules formant la récolte totale d'une touffe déterminée, la mère, c'est-à-dire le tubercule de plant, impose des qualités héréditaires, qu'au pied de chaque touffe à produit abondant et riche, on est sur de rencontrer une génération qui elle aussi fournira des récoltes abondantes et riches et qu'il y a proportionnalité entre la puissance de la végétation aérienne et l'abondance de la récolte souterraine."

L'hypothèse d'une relation directe entre la richesse féculente d'un tubercule et l'abondance de la récolte que ce tubercule fournit " ne l'avait jamais séduit." " Si elle était vraie, disait-il, il semble que la dégénérescence progressive de toutes les variétés en devrait découler fatalement. Il est des années (1892 par exemple) où nombre de variétés, les variétés tardives surtout, ne mûissent pas; les tubercules restent pauvres en fécule, en matières azotées, en matiéres minérales, et, à la levée, par la suite, ils offriront à la jeune plante une proportion de matiéres nutritives moindre que de coutume. Et cependant, si la saison est favorable, les récoltes que ces tubercules pauvres fourniront seront abondantes en poids et riches en fécule."

A la suite d'un long travail publié dans les Annales de la Science agronomique, A. Girard concluait que l'opinion suivant laquelle il existe un rapport régulier entre la richesse du plant en fécule et l'abondance comme aussi la richesse des récoltes n'était pas justifiée jusqu'àlors.

L'hérédité des qualtités constatées dans un tubercule de pomme de terre ne semble pas plus probable aujourd'hui qu'à l'époque des expériences d'A. Girard, mais une apparente contradiction existe dans le travail de cet auteur: D'une part il admet la transmission de qualités " héréditaires," d'autre part il n'admet pas la transmission de la richesse en fécule: Or, en ce qui concerne la pomme de terre le terme hérédité n'est pas strictement juste, car toutes les variétés de pomme de terre quels que soient leur âge ou leur dispersion proviennent chacune d'un individu unique et indéfiniment divisé, sans qu'il y ait eu jamais reproduction sexuelle, et l'on comprend mal que si la propriété de produire la fécule ne se transmet pas dans les dérivés on puisse espérer avoir des récoltes abondantes et "*riches*" en partant d'une touffe abondante et riche. En admettant même qu'il s'agisse de la valeur d'un ensemble de tubercules et qu'un même plant riche donne des tubercules riches et pauvres, il faut accepter implicitement la prédominance des tubercules riches soit dans le nombre, soit dans le poids, puisque la résultante de ces deux facteurs est une récolte de qualité supérieure à la moyenne par " sa richesse."

Depuis A. Girard certains auteurs ont donné à la richesse en fécule des plants de pomme de terre une importance particuliéré, citons par exemple M. Garola qui conseille de sélectionner les tubercules méres suivant leur richesse qu'il mesure par la densité. (Petit Journal agricole 1909, p. 229). La question ne semble donc pas résolue.

Par ailleurs, une erreur existe dans le mémoire de A. Girard: La dégénérescence progressive de toutes les variétés ne découle pas nécessairement de l'" hérédité " des qualités féculières des tubercules.

Le fait que dans une années défavorable les pommes de terre sont pauvres en matiéres nutritives n'implique nullement qu'elles ont perdu la propriété de produire de la fécule; disons qu'elles se sont trouvées dans de mauvaises conditions, qu'elles n'ont pas donné la mesure de leurs qualités; mais elles n'ont pas pour cela dégénéré; les influences extérieures atmosphériques ou culturales ne causent pas nécessairement une variation *transmissible* des qualités biologiques d'une plante.

La méthode expérimentale suivie par A. Girard était la suivante: Il choisissait dans une touffe des tubercules ayant très sensiblement le même poids, les pesait très exactement, puis déterminait leur densité qui donnait la mesure de leur richesse en fécule. Les tubercules choisis au nombre de deux ou trois, étaient soigneusement conservés, plantés dans des conditions identiques, et les touffes résultantes examinées quant au poids et duant à la richesse.

En dehors des objections de principe que nous avons faites plus haut, quelques raisons nous ont déterminés à reprendre ou plutôt à vérifier de plus prés le travail de A. Girard: Le fait de ne prendre dans une touffe que des tubercules très voisins comme poids, présente l'inconvénient, tout fortuit, d'ailleurs que dans certaines expériences on élimine presque tout une catégorie de sujets: nous en avons fait l'expérience personnelle, et les résultats de Girard le démontrent. Par exemple dans un essai avec la variété Abundance de Sutton, le poids moyen calculé des tubercules est de 82 gr, or, dans cet essai ne figurent que trois Tubercules sur 29 dont let poids soit compris entre 72 gr et 92 gr., c'est-à-dire dans les limites où l'on peut admettre sans exagération que la moyenne naturelle puisse s'écarter de la moyenne arithmétique. Dans d'autres essais, c'est le contraire qui se produit, les tubercules de poids extrémes forts ou faibles sont en nombre très réduit. Cet inconvénient n'enléve rien de la valeur des expériences de Girard, mais il nous a paru qu'au point de vue de la généralisation, il était préférable de pas chercher à simplifier et, par suite, d'accepter tous les tubercules de toutes les touffes, dut la comparaison des résultats être beaucoup plus compliquée.

De plus, la méthode densimêtrique appliquée à l'analyse des pommes de terre peut donner des indications, mais pas de certitude sur la teneur en fécule. Il n'est pas inutile de signaler que Behrend, Maercker, Morgen ont démontré le peu de précision de cette méthode dans laquelle l'erreur absolue, atteint facilement 2 per cent. de fécule en plus ou en moins, de sorte qu'il est bien difficile de dire si une pomme de terre titre 16, 18 ou 20% d'amidon. En admettant que les erreurs se compensent dans un ensemble de tubercules, on n'en est pas moins exposé quand il s'agit d'un seul, à commettre une erreur qui dans certains cas est du même ordre de grandeur que la moyenne des variations de teneur en fécule entre les tubercules d'une même variété.

Partie expérimentale. L'étude a port sur les variétés suivantes: Saucisse, Géante de Reading, et Schultz-Lupitz. Environ 150 tubercules de chaque sorte ont été coupés en deux, une des deux moitiés a été analysée, l'autre moitié conservée, numérotée et plantée.

L'analyse a été faite de la façon suivante: Les pommes de terre épluchées ont été réduites en une bouillie très fine au moyen de la presse "Sans-Pareille," la pulpe obtenue a été bien mélangée, puis on en a prélevé un échantillon pesé à 5mmg. près. Au moyen d'un peu d'eau la pulpe a été transvasée dans un petit creuset de Gooch, garni d'un fond d'amiante pressée, puis au moyen du vide on a filtré le mélange et soumis le résidu à un lavage au moyen d'eau distillée. De cette façon, les sucres solubles ont été éliminés. Cette précaution nous parait indispensable, car, d'une façon courante leur présence dans la pomme de terre peut fausser le dosage de 1 à 2% en valeur relative. A chaque fois on s'est assuré que le liquide filtré ne contenait pas d'amidon; nous y avons rencontré en dehors des sucres réducteurs un peu de produits dextriniformes. Ces jus ont un pouvoir oxydasique marqué et d'autant plus net que les tubercules sont moins mûrs.

Le contenu du creuset étant transvasé avec l'amiante dans une fiole jaugée, l'hydrolyse a été pratiquée au moyen d'une solution picrique, dans les conditions qui ont été indiquées par M. Buisson (Bulletin de l'Association des Chimistes de Sucrerie et Distillerie, Avril 1909). Nous avons en soin de vérifier que dans les conditions indiquées par ceauteur, il n'y avait pas lieu de craindre l'hydrolyse simultanée de la cellulose contenue dans les pommes de terre. La lecture polarimètrique nous a permis de déduire immédiatement la richesse en amidon des produits examinés, à une unité près de la première décimale.

La culture de nos pommes de terre a été faite dans un terrain plutôt argileux, dans les conditions habituelles, ce terrein avait reçu une bonne fumure de fumier de ferme (70.000 kilogs à l'hectare plus 600 kilogs de superphosphate, 200 kilogs de potasse et 200 kilogs de nitrate).

Pendant toute la durée de la végétation, des notes ont été prises sur chaque plante, sur son état, sa vigueur etc., puis pour chaque espèce on a procédé à l'arrachage en temps convenable après maturité. Une partie seulement des touffes a été analysée, pour les autres, on n'a pris en considération que le nombre et le poids des tubercules récoltés Au cours de ces expériences, on a fait également quelques prélèvements sur le terrain pour prendre note des relations entre la formation des jeunes tubercules et la disparition de l'amidon dans les tubercules mères, relations qui feront l'objet d'un autre mémoire.

Nous ne reporterons pas ici tous nos résultats nous ne donnerons que ceux relatifs aux plantes dont l'étude a été faite complètement. On trouvera à la fin de notre exposé les conclusions relatives à l'ensemble du travail.

POMME DE TERRE SAUCISSE

	Plant		Fécule mise en oeuvre	Végétation	Récolté		Fécule récoltée
	Poids	Richesse			Poids	Richesse	
9	55	17,79	9,78	faible	270	16,7	45,09
13	55	16,59	9,12	moyenne	900	17,2	154,8
15	57	11,98	6,82	moyenne	640	18,4	117,76
25	100	18,58	18,58	moyenne	620	19,4	120,28
28	41	18,11	7,42	faible	380	18,5	70,3
37	57	19,95	11,37	moyenne	770	18,5	142,45
39	60	17,19	10,31	faible	350	16,8	58,8
47	70	12,44	8,7	moyenne	870	19,5	169,65
51	57	15,94	9,08	forte	1070	14,9	159,43
63	42	17,65	7,41	forte	1090	19,5	212,55
67	52	18,71	9,72	moyenne	420	18,7	78,54
80	60	18,11	10,86	forte	880	17,7	155,76
94	75	19,63	14,72	faible	540	17,6	95,04
97	55	19,95	10,97	faible	410	17,6	72,16
107	50	15,67	7,83	moyenne	760	16,8	127,68
119	72	19,63	14,13	moyenne	970	15,2	147,44
125	45	19,36	8,71	faible	480	17	81,6
127	87	17,33	15,07	moyenne	890	17,3	153,97
139	70	17,33	12,13	forte	1360	14,1	191,76
145	62	12,57	7,79	moyenne	645	18,3	118,03
147	48	14,42	6,92	moyenne	630	16,9	106,47

Les poids indiqués pour le plant sont ceux des demi-tubercules.

POMME DE TERRE GÉANTE DE READING

	Poids	Plant Richesse	Fécule mise en oeuvre	Végétation	Poids	Récolte Richesse	Fécule récoltée
10	227	15,72	35,68	forte	890	14,5	129
13	108	15,34	16,56	faible	290	17,1	49,59
31	48	13,36	6,36	forte	700	12,8	89,6
34	83	16,26	13,5	faible	310	14,6	45,26
38	60	13,4	8,04	faible	390	16	62,4
47	65	11,06	7,18	moyenne	580	15,5	89,9
48	58	16,26	9,43	moyenne	730	16	116,8
54	92	16,41	15,09	forte	910	15	136,5
71	52	11,52	5,99	moyenne	240	16,3	39,12
76	148	16,13	23,87	faible	230	17,7	40,71
88	93	15,03	13,97	forte	1040	16	166,4
91	110	16,13	17,74	moyenne	1000	13,6	136
98	58	12,57	7,29	moyenne	790	15,8	124,82
99	45	16,13	7,25	moyenne	740	14,5	107,3
104	82	18,90	15,49	moyenne	630	14	88,2
107	100	17,95	17,95	moyenne	630	16,8	105,84
117	107	18,11	19,37	faible	600	15	90
121	45	19,16	8,62	faible	360	15	54
129	45	14,29	6,43	moyenne	670	16,8	112,56
130	40	17,51	7	moyenne	720	17,1	123,12
139	55	14,29	7,85	moyenne	940	21,4	201,16
140	50	19,49	9,74	faible	70	18,6	13,02

Le poids indiqués pour le plant sont ceux des demi-tubercules.

POMME DE TERRE SCHULZ-LUPITZ

	Poids	Plant Richesse	Fécule mise en oeuvre	Végétation	Poids	Récolte Richesse	Fécule
9	150	24,56	36,84	forte	820	21,6	177,12
10	105	20,41	21,43	faible	210	20,9	43,89
12	122	23,79	29,02	faible	370	19,3	71,41
15	137	18,44	25,26	moyenne	360	18,5	66,6
19	118	21,88	25,81	forte	400	19	76
21	167	24,1	40,24	moyenne	510	19,4	98,94
25	167	21,88	36,53	forte	450	19,4	87,3
26	148	16,41	24,28	forte	790	20,1	158,79
30	95	19,16	18,2	moyenne	920	19,4	178,48
31	93	21,47	19,96	moyenne	570	21	119,7
36	98	16,59	16,25	forte	1130	21	237,3
38	83	20,74	17,21	forte	1240	19,5	241,8
42	100	21,2	21,2	moyenne	700	18	126
44	120	19,96	23,95	faible	350	22,5	78,75
47	65	23,97	15,58	faible	260	19,3	50,18
49	82	21,2	17,38	moyenne	310	19	58,9
72	63	21,66	13,64	moyenne	220	22	70,4
73	68	23,05	15,67	forte	900	21	189
103	100	24,57	24,57	forte	1060	20,6	218,36
104	98	19,36	18,97	moyenne	730	18,9	137,97
115	87	20	17,4	forte	860	20,4	175,4
126	45	15,21	6,84	moyenne	340	19,9	67,66
135	60	16,63	9,97	moyenne	380	19,5	74,1
137	48	14,42	6,92	moyenne	390	19	74,1

INTERPRETATION DE CES RESULTATS

Pour la commodité de l'interprétation nous avons divisé les poids et les richesses des plants et des récoltes en trois catégories; forts, moyens, faibles. Ces catégories ont été déterminées comme suit: on a déterminé la moyenne arithmétique de chaque valeur, puis on a considéré comme rentrant dans cette moyenne tous les nombres qui ne s'en écartaient qu'en dedans d'une limite de tolérance, supérieure ou inférieure à la moyenne théorique d'une même quantité. Quel que soit donc l'arbitraire avec lequel on ait établi la tolérance, les conclusions restent les mêmes; les nombres sont d'ailleurs en général assez différents pour ne pas donner d'incertitude sur leur classement.

RELATION ENTRE LA RICHESSE DU PLANT ET LA VIGUEUR DE LA VÉGÉTATION; RAPPORTÉE À 100 TUBERCULES

Saucisse				Géante de Reading				Schultz-Lupitz			
100 Tub.	Végétation Forte	Moy.	Faib.		Végétation Forte	Moy.	Faib.		Végétation Forte	Moy.	Faib.
100 Rich.	16	50	35	Riche	29	38	32	Rich.	50	31	19
100 Moy.	30	44	27	Moyen	16	43	41	Moy.	12	64	24
100 Pauv.	25	56	19	Pauv.	13	48	38	Pauv.	30	47	24

RELATION ENTRE LA RICHESSE DU PLANT ET LE POIDS DE LA RÉCOLTE

Tuber.	Récolte								
	Saucisse Forte	Moy.	Faib.	Reading Forte	Moy.	Faib.	Schultz-Lupitz Forte	Moy.	Faib.
100 Rich.	16	31	53	28	40	32	41	14	45
100 Moy.	49	26	26	38	21	41	21	42	37
100 Pauv.	48	40	12	50	12	38	34	8	57

RELATION ENTRE LA VIGUEUR DE LA VÉGÉTATION ET LE POIDS DE LA RÉCOLTE

Végétation	Récolte								
	Saucisse Forte	Moy.	Faib.	Reading Forte	Moy.	Faib.	Schuitz-Lupitz Forte	Moy.	Faib.
100 Fort	85	15	0	77	16	7	70	17	12
100 Moy.	34	43	23	51	28	21	23	26	51
100 Faib.	0	13	87	4	21	75	0	14	86

On a pu voir par le tableau général N° 1 qu'il n'y a aucun rapport entre le poids ou la richesse du tubercule de plant et le poids ou la richesse de la touffe résultante: Les variations qu'on observe sont du même ordre et aussi irrégulières. La quantité de fécule mise en oeuvre n'est liée par aucun rapport fixe à la quantitée récoltée. Il semblerait à l'inspection du tableau 2 que la pomme de terre Schultz Lupitz, d'introduction plus récente, ait une tendance à donner une végétation vigoureuse quand le plant est riche en fécule, il n'en est pas moins vrai qu'à nombre égal (tableau 3) cette variété donne avec du plant riche moins de fortes que de faibles récoltes.

En somme ce sont les tubercules moyens en richesse et en poids qui semblent maintenir les qualités de la variété à laquelle ils appartiennent. Une seule conclusion ressort avec une admirable netteté, elle avait été signalée déjà par A. Girard: C'est qu'entre la partie aérienne et la partie souterraine de la plante il y a la relation la plus étroite dans plus de 85% des cas, une belle plante, bien feuillue, bien vigoureuse est l'indice d'une bonne récolte au-dessus de la moyenne Quant à savoir si ce seul indice extérieur suffit pour affirmer que les tubercules de cette récolte assureront dans l'avenir une bonne production, c'est ce que de nouvelles expériences en cours nous apprendront; il serait téméraire de rien préjuger.

RECHERCHES SUR LA FUMURE MINERALE DE LA BETTERAVE A SUCRE

A. Vivier

Melun, France

1° Comparaison des nitrates et des sels ammoniacaux.
2° Influence de la Soude.
3° Influence du Chlore.
4° Comparaison de la Betterave à différentes époques de son développement.

Le présent travail fait partie d'une série d'études sur la fumure minérale de la Betterave à sucre que j'ai poursuivies depuis 1892; les essais de culture qui y sont relatés datent de 1907: ce sont ceux de ma dixième année de recherches sur la Betterave.

Les résultats culturaux et les analyses des jus ont été publiés en 1908 dans le *Bulletin de la Société d'Agriculture de Melun*; quant aux analyses des récoltes feuilles et racines à trois époques du développement de la plante, qui ont exigé un travail matériel considérable et des calculs très longs, elles ont été retardées par les exigences du service courant du laboratoire.

Je me suis proposé dans ce travail:

1° De comparer l'action des nitrate de soude, de potasse et de chaux, et du sulfate d'ammoniaque, sur la rendement en poids et sur la composition de la Betterave.

2° De rechercher l'influence de la soude, pour vérifier, le cas échéant, la loi formulée par M. E. Saillard au Congrès du Syndicat des Fabricants de sucre de France (1er Mai 1903), savoir: " Plus les betteraves sont riches en sucre, moins elle contiennent de soude pour cent. de cendres abstraction faite de la partie insoluble dans l'acide chlorhydrique."

3° De rechercher l'influence du chlore apporté par les engrais en particulier par le chlorure de potassium.

4° Tout en suivant le programme précédent, de comparer la composition de la betterave à différentes époques de son développement.

Pour les détails culturaux, je renvoie le lecteur au Bulletin précité; cependant je reproduis ci-dessous sommairement les conditions et le plan des essais, les résultats des pesées des récoltes et l'analyse des jus.

PLAN ET CONDITION DES ESSAIS

Le champ d'expérience ètait divisé en 8 parcelles formant deux séries parallèles de 4 parcelles (voir le croquis ci-après).

I		II	
Nitrate de chaux	294	Nitrate de chaux	294
Sulfate de potasse	313	Chlorure de potassium	268
Superphosphate	600	Superphosphate	600
III		IV	
Nitrate de soude	306	Nitrate de soude	306
Sulfate de potasse	313	Chlorure de potassium	268
Superphosphate	600	Superphosphate	600
V		VI	
Nitrate de potasse	364	Nitrate de potasse	364
Superphosphate	600	Chlorure de sodium	210
		Superphosphate	600
VII		VIII	
Sulfate d'ammoniaque	238	Sulfate d'ammoniaque	238
Sulfate de potasse	313	Chlorure de potassium	268
Superphosphate	600	Superphosphate	600

Toutes les parcelles ont reçu les mêmes quantités d'azote, d'acide phosphorique et de potasse: l'azote a été employé sous la même forme dans chaque paire de parcelles: nitrate de chaux, nitrate de soude, nitrate de potasse, sulfate d'ammoniaque, en telles quantités que la fumure en azote fût de 50 kilogs à l'hectare dans chaque parcelle; la potasse a été fournie sous forme de sulfate dans trois des parcelles impaires et sous forme de chlorure dans les trois parcelles paires correspondantes; les deux autres l'ont reçue sous forme de nitrate de potasse; la dose de potasse dans chaque parcelle correspondait à 170 kilogs à l'hectare; la parcelle VI a reçu en outre 210 Kilogs de *Chlorure de sodium,* qui apportait dans cette parcelle, autant de chlore et de soude que la chlorure de potassium et le nitrate de soude en apportaient dans les autres.

Enfin, les 8 parcelles ont reçu une dose uniforme de 600 kilogs de superphosphate minéral à 15.2 pour cent. d'acide phosphorique par hectare.

En résumé, la fumure de chaque parcelle comportait:

Azote	50 K par hectare (sous différentes formes)
A. phosphorique	90 K par hectare (superphosphate)
Potasse	170 K (sous différentes formes)

De plus certaines parcelles ont reçu:

Chlore	127, 5	par hectare	(chlorures de potassium et de sodium)
Soude	95	“ “	(chlorure de sodium et nitrate de soude)

La disposition adoptée permet donc:

1° de comparer l'action de l'azote des nitrates de chaux, de soude de potasse et du sulfate d'ammoniaque;

2° de rechercher l'influence de la soude dans diverses conditions;

3° de rechercher l'influence du chlore, également dans diverses conditions.

SOL–FAÇONS CULTURALES

Le terrain consacré aux essais était un sol d'éboulis de consistance moyenne, graveleux, en pente légère du N.O. au S.E.; il ètait cultivé en luzerne depuis 3 ans.

L'analyse a donné les résultats suivants:

Pour 1000 de terre sèche	
Azote	2,11
Acide phosphorique	2,33
Potasse	3,40
Chaux	66,22

La terre contient 20,1 pour cent de graviers et pierres.

C'est un sol sain, de culture facile, enrichi de longue date.

La luzerne a été défrichée par un labour profond, les racines ont été extripées avec soin et enlevées.

Les engrais ont été semés le 22 Mai, la graine a été semée le lendemain: c'était une graine de betterave blanche à collet vert, de richesse moyenne, utilisée dans la région pour la distillerie.

La levée s'est effectuée du 28 Mai au 6 Juin. Les binages ont été donnés le 13 Juin et le 11 Juillet; ce dernier a coïncidé avec le démariage, qui a été fait de façon à laisser 75,000 betteraves par hectare, les rayons étant distants de 0m40. A la récolte on a constaté un nombre moyen de 74,100 racines par hectare.

RESULTATS CULTURAUX

Dans le but de suivre la marche de l'absorption des éléments fertilisants au cours de la végétation, des échantillons de plantes entières ont été prélevés le 17 Juin, le 10 Juillet et à l'arrachage, le 25 octobre.

Nous reviendrons plus loin sur ces échantillonages; nous allons d'abord examiner le résultat de la récolte et la composition du jus des racines des différentes parcelles.

Le tableau I donne les rendements rapportés à l'hectare ainsi que la composition des jus.

TABLEAU I. RESULTATS CULTURAUX. ANALYSE DES JUS

Nos. des parcelles	Nombre des betteraves à l'hectare	Rendement racines à l'hectare	Poids moyen d'une racine	Densité du jus	Sucre par décilitre de jus	Sucre pour cent de betteraves	Quotient de pureté	Coefficient salin
		K.	GR.	°	GR.			
1	80100	38720	483.4	7.1	14.97	13.27	79.5	23.3
2	74800	39190	524.5	7.3	14.47	12.80	74.8	17.5
3	74800	33135	443.0	7.2	15.02	13.30	78.6	23.5
4	75800	33550	442.6	7.2	15.13	13.40	79.2	20.8
5	73700	34735	471.3	7.05	14.86	13.18	79.5	20.9
6	66200	34780	525.4	7.0	14.48	12.85	78.1	17.8
7	76900	35260	458.5	7.1	14.82	13.13	78.7	20.0
8	70500	36550	518.4	7.1	15.11	13.39	80.5	21.3

Ces résultats motivent les observations suivantes:

1° la plantation était assez régulière, sauf dans la parcelle 1 où le nombre des racines dépasse la moyenne et dans les parcelles 6 et 8 où il est notablement inférieur à cette moyenne qui est de 74100, néanmoins les différences de densité de plantation ne nous paraissent pas suffisantes pour retentir d'une façon marquée sur les rendements: elles agissent sur les poids moyen des racines (comparez 1-2, 5-6, 7-8) elles agissent légèrement sur la densité, mais d'une façon peu régulière et peu marquée, et aussi sur la richesse en sucre d'une façon plus sensible (1-2, 5-6).

2° Si l'on compare deux à deux les rendements dans les parcelles impaires (sans chlore) et paires (avec chlore) on ne constate que des différences insignifiantes;

la moyenne des rendements sans chlore est de 35462 kg
la moyenne des rendements avec chlore 36017 kg

Nous verrons plus loin que le chlore des engrais a été cependant absorbé par la plante en quantité considérable (80 pour cent. environ du chlore contenu dans l'engrais).

Le coefficient salin des jus des betteraves des parcelles paires est dans trois cas sur quatre (parcelles avec nitrate) plus faible que dans les parcelles impaires, ce qui parait être dû à la présence des chlorures.

3° Si l'on totalise les rendements des parcelles impaires et paires deux à deux, et que l'on prenne les moyennes, on obtient les rendements ci-après qui classent l'action des différents engrais azotés essayés.

	Rendements moyens
Nitrate de chaux	38955 k
Sulfate d'ammoniaque	35905
Nitrate de potasse	34757
Nitrate de soude	33342

Sans accorder à ces chiffres, qui ne répresentent que les résultats d'une seule année et d'un seul champ, une valeur absolue, on doit remarquer que le sulfate d'ammoniaque et le nitrate de chaux surtout, se sont montrés sensiblement supérieurs au nitrate de soude.

4° La densité des jus ne présente que des variations peu importantes quel que soit l'engrais azoté employé; la présence ou l'absence de soude et de chlore dans l'engrais n'agit pas non plus de façon sensible sur elle.

5° La pureté et surtout le coefficient salin paraissent meilleurs dans les parcelles fumées aux nitrates qui n'ont pas reçu de chlorures; le même effet ne s'est pas produit, au contraire, dans les parcelles au sulfate d'ammoniaque.

Nous verrons plus loin les rapports entre la proportion de soude des cendres et la richesse en sucre.

COMPOSITION DE LA PLANTE À DIFFÉRENTES ÉPOQUES

Echantillons du 17 Juin. (25 jours après le semis.)

Les betteraves étant très petites (la racine ne représentait que 5 à 6 pour cent. du poids des feuilles) on a analysé la plante entière; le poids moyen a été déterminé sur des échantillons de cent plants.

L'analyse a donné les résultats ci après:

TABLEAU II. COMPOSITION DE LA MATIÈRE SÈCHE ET DES CENDRES
25 jours après le semis.

Parcelles	1	2	3	4	5	6	7	8
	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.
Poids moyen d'une plante fraiche	1.722	0.972	2.415	1.549	2.005	1.840	1.992	1.820
Matière sèche pour cent.	9.72	15.65	9.25	8.07	10.92	8.63	10.33	8.91
Cendres pour cent. de matière sèche	24.20	25.97	24.55	27.07	23.99	26.45	24.87	26.60
Azote	4.97	4.83	4.95	4.73	4.65	4.73	4.59	4.51
Acide phosphorique de matière sèche	1.32	1.51	1.29	1.49	1.29	1.22	1.28	1.28
Chlore do	0.38	1.44	0.26	1.53	0.27	1.54	0.25	2.18
Potasse do	7.96	8.19	6.01	7.16	7.91	7.37	8.04	8.49
Soude do	1.77	2.09	4.33	4.30	1.92	3.70	2.41	2.51
Chaux do	3.75	3.98	2.71	3.27	3.68	3.07	3.16	3.86
Acide phosphorique pour cent. de cendres	5.45	5.80	5.25	5.50	5.37	4.61	5.14	4.81
Chlore do	1.57	5.53	1.06	5.64	1.12	5.82	1.00	8.19
Potasse do	32.90	31.50	24.48	26.42	32.95	27.86	32.28	31.91
Soude do	7.89	8.03	17.63	15.86	8.00	13.98	9.67	9.43
Chaux do	15.49	15.30	11.03	12.06	15.33	11.60	12.69	14.51

On observe:

I° que les cendres des parcelles paires sont notablement plus riches en chlore que celles des parcelles impaires;

2° que la soude remplace la potasse, et qu'elle augmente lorsque celle-ci diminue (parcelles à soude 3-4-6).

3° que la chaux semble suivre les mêmes fluctuations que la potasse.

Il est utile de calculer également les quantités d'éléments contenus dans la jeune betterave par hectare; pour simplifier le calcul, nous avons admis le nombre de 70000 betteraves à l'hectare dans toutes les parcelles.

Tableau III. Quantités d'Éléments Nutritifs Prélevés par Hectare

pour la Betterave 25 jours après le semis

Parcelles	1	2	3	4	5	6	7	8
	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.
Poids moyen d'une plante sèche	0,167	0.152	0.223	0.125	0.219	0.159	0.206	0.162
	K.	K.	K.	K.	K.	K.	K.	K.
Mat. sèche á l'hectare	11.725	10.647	15.645	8.753	15.323	11.123	14.406	11.354
Ac. phosphorique	0.155	0.161	0.202	0.130	0.193	0.136	0.184	0.145
Chlore	0.044	0.153	0.041	0.134	0.041	0.171	0.036	0.247
Potasse	0.933	0.872	0.940	0.626	1.212	0.819	1.158	0.963
Soude	0.207	0.222	0.677	0.376	0.294	0.411	0.347	0.285
Chaux	0.439	0.423	0.424	0.286	0.564	0.341	0.455	0.438
Azote	0.582	0.514	0.774	0.414	0.712	0.526	0.661	0.512

Au bout de 25 jours, les quantités d'éléments fertilisants absorbés sont très minimes; mais les *taux* d'azote, d'acide phosphorique, de potasse sont très élevés.

ECHANTILLONS DU 10 JUILLET
48 jours après le semis

Pendant les 23 jours écoulés depuis le premier échantillonnage, la croissance de la betterave a été excessivement rapide: le poids moyen d'une plante est devenu 80 à 100 fois plus grand.

Voici les poids moyens de 10 feuilles et racines choisies de manière à représenter l'ensemble aussi exactement que possible.

TABLEAU IV. POIDS MOYENS DES FEUILLES ET DES RACINES
48 jours après le semis

Numéros des Parcelles	Poids moyens			Racine % de plante
	Feuille	Racine	Plante	
	GR.	GR.	GR.	
1	75.17	13.13	88.30	14.87
2	86.75	13.45	104.20	12.90
3	78.07	10.63	88.70	11.98
4	79.94	8.86	88.80	9.97
5	71.01	9.89	80.90	12.22
6	127.98	20.22	148.20	13.64
7	87.94	13.86	101.80	13.61
8	87.62	12.88	100.50	12.81

Il a été procédé séparément à l'analyse des racines et des feuilles: les résultats figurent dans le tableau ci-après:

TABLEAU V. COMPOSITION DE LA MATIÈRE SÈCHE ET DES CENDRES, 48 JOURS APRÈS LE SEMIS

	1		2		3		4		5		6		7		8	
	R	F	R	F	R	F	R	F	R	F		F	R	F	R	F
Matière sèche %	14.12	9.32	13.01	7.77	14.44	8.15	14.44	7.74	14.13	9.14	13.65	7.67	14.50	8.37	14.55	8.27
Cendres % m. sèche	9.21	23.76	11.07	25.80	9.48	23.56	9.67	24.83	10.64	23.33	10.82	26.59	8.69	24.43	9.23	25.43
Ac. phosphs. m. sèche	1.13	1.26	1.05	1.16	1.09	1.23	0.95	1.03	0.95	1.07	0.89	1.01	0.81	1.12	0.66	0.97
Chlore m. sèche	0.11	0.28	0.79	2.27	0.11	0.26	0.76	2.38	0.11	0.26	0.73	2.77	0.09	0.30	0.67	2.60
Potasse m. sèche	3.60	6.87	4.65	7.45	3.41	5.38	4.07	7.39	4.00	7.24	4.29	8.12	3.37	8.05	3.28	8.01
Soude m. sèche	0.71	2.04	1.03	3.90	0.89	3.87	1.00	3.49	0.57	2.12	1.00	4.05	0.63	3.07	0.65	4.06
Chaux m. sèche	0.35	4.11	0.34	4.00	0.25	3.06	0.19	2.92	0.38	3.60	0.32	2.86	0.33	3.26	0.37	3.69
Azote m. sèche	2.50	4.68	2.58	4.50	2.32	4.45	2.37	4.14	2.18	4.69	2.52	4.06	2.21	4.51	2.15	4.32
Ac. phosph. % de cendres	12.26	5.29	9.48	4.50	11.28	5.22	9.82	4.14	8.92	4.58	8.22	3.80	9.32	4.62	7.15	3.81
Chlore % de cendres	1.19	1.17	7.13	8.79	1.16	1.10	7.85	9.58	1.03	1.11	6.74	10.41	1.03	1.22	7.25	10.22
Potasse % de cendres	39.08	28.86	42.00	28.87	35.97	22.83	42.29	29.76	37.59	31.03	39.64	30.53	38.78	32.95	35.53	31.49
Soude % de cendres	7.70	8.57	9·30	15.11	9.38	16.42	10.34	14.05	5.35	9.08	9.24	15.23	7.24	12.56	7.04	15.96
Chaux % de cendres	3.80	17.26	3.07	15.50	2.63	12.98	1.57	11.76	3.57	15.43	2.95	10.75	3.79	13.34	4.00	14.51

L'examen de ces chiffres montre:

1° Que le chlore a été absorbé dans les parcelles paires qui en ont reçu, et que le taux de chlore des cendres est plus élevé dans les feuilles que dans les racines;

2° Que la soude fournie par les engrais a été absorbée (3-4-6) elle remplace en partie la potasse; de plus, dans les parcelles ayant reçu du chlore (parcelles paires), même en l'absence de soude dans l'engrais, les cendres sont plus riches en soude que dans les parcelles sans chlore.

Pour faciliter les comparaisons, on a calculé la composition des cendres des échantillons du 10 Juillet pour la plante entière. Elle figure dans le tableau ci-après: on y a joint la teneur en azote de la matière sèche, ainsi que le poids moyen d'une plante fraiche et sèche, le taux de matière sèche et le taux des cendres.

TABLEAU VI. COMPOSITION DE LA PLANTE ENTIÈRE ET DE SES CENDRES

48 jours après le semis

Parcelles	1	2	3	4	5	6	7	8
	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.
Poids moyen d'une plante fraiche	88.30	104.20	88.70	88.80	80.90	148.20	101.80	100.50
Poids moyen d'une plante sèche	8.86	8.49	7.90	7.47	7.80	12.58	9.37	9.12
Matière sèche %	10.03	8.14	8.90	8.41	9.64	7.81	9.20	9.07
Azote % mat. sèche	4.22	4.10	4.03	3.83	4.23	3.72	4.01	3.87
Cendres mat.sèche	20.67	22.76	20.84	22.23	21.04	23.13	21.06	22.09
Ac. phosph. % cendres	5.93	5.00	5.82	4.56	4.97	4.25	5.03	4.09
Chlore % cendres	1.17	8.62	1.11	9.44	1.11	10.03	1.20	9.96
Potasse % cendres	29.81	30.18	23.99	30.68	31.62	31.40	33.46	31.84
Soude % cendres	8.48	14.52	15.79	13.76	8.73	14.61	12.08	15.19
Chaux % cendres	16.00	14.21	12.15	10.98	14.34	9.94	12.49	13.60

Les teneurs en chlore des cendres des parcelles paires, qui ont reçu des chlorures, sont vraiement remarquables; de même les taux de soude dans les parcelles 3-4-6 qui ont reçu des sels de soude, et dans les parcelles 2 et 8 qui n'en n'ont pas reçu, mais qui ont reçu du chlorure de potassium.

Quant aux poids totaux de feuilles et de racines et d'éléments fertilisants contenus dans chacun d'eux par hectare, ils figurent dans le tableau ci-après, le calcul étant fait comme pour les échantillons du 17 Juin, sur la base de 70000 betteraves par hectare.

TABLEAU VII. QUANTITÉS D'ÉLÉMENTS NUTRITIFS PRÉLEVÉS PAR HECTARE PAR LES FEUILLES ET LES RACINES, 48 JOURS APRÈS LE SEMIS

	1		2		3		4		5		6		7		8	
	R	F	R	F	R	F	R	F	R	F	R	F	R	F	R	F
	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.
Matière sèche à l'hectare	129.8	490.7	122.5	471.8	107.4	445.9	89.6	433,3	97.8	448.0	193.2	687.5	140.7	515.5	131.2	507.1
	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.
Poids moyen par pied (sec)	1.85	7.01	1.75	6.74	1.53	6.37	1.28	6.19	1.40	6.40	2.76	9.82	2.01	7.36	1.87	7.24
	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.
Ac. phosph. à l'hectare	1.47	6.19	1.29	5.47	1.17	5.48	0.85	4.46	0.93	4.79	1.72	6.95	1.14	5.77	0.87	4.92
Chlore	0.14	1.37	0.97	10.71	0.12	1.16	0.68	10.31	0.11	1.16	1.41	19.05	0.13	1.55	0.88	13.19
Potasse	4.67	33.7	5.69	35.15	3.66	24.00	3.65	32.02	3.91	32.43	8.29	55.84	4.74	41.50	4.30	40.62
Soude	0.92	10.02	1.26	18.40	0.96	17.26	0.90	15.12	0.56	9.50	1.93	27.85	0.89	15.83	0.85	20.59
Chaux	0.45	20.18	0.42	18.87	0.27	13.65	0.17	12.65	0.37	16.13	0.62	19.67	0.46	16.81	0.48	18.71
Azote	3.04	22.98	3.16	21.23	2.49	19.85	2.12	17.94	2.13	21.01	4.87	27.92	3.11	23.25	2.82	21.91

En totalisant les chiffres relatifs aux feuilles et aux racines, on obtient le tableau suivant qui donne les résultats pour la plante totale, à l'hectare.

Tableau VIII. Quantités d'Éléments Nutritifs Prélevés par Hectare par la Plante Entière

48 jours après le semis

Parcelles	1	2	3	4	5	6	7	8
	K.	K.	K.	K.	K.	K.	K.	K.
Matière sèche à l'hectare	620.5	594.3	553.4	522.9	545.9	881.0	656.2	638.3
	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.
Poids moyen d'une plante sèche	8.8	8.5	7.9	7.5	7.8	12.6	9.4	9.1
	K.	K.	K.	K.	K.	K.	K.	K.
Azote à l'hectare	26.0	24.4	22.3	20.0	23.1	32.7	26.3	24.7
Ac. phosph. l'hectare	7.6	6.7	6.6	5.3	5.7	8.7	6.9	5.8
Chlore l'hectare	1.5	11.6	1.3	11.0	1.3	20.4	1.6	14.0
Potasse l'hectare	38.4	40.8	27.6	35.6	36.3	64.1	46.2	44.9
Soude l'hectare	10.9	19.6	18.1	16.0	10.0	29.7	16.7	21.4
Chaux l'hectare	20.6	19.3	14.0	12.8	16.5	20.3	17.3	19.2

On voit combien sont considérables les exigences de la betterave en potasse dans la première période de son développement elles dépassent notablement les exigences en azote.

En 38 jours (en moyenne) de végétation, la betterave a absorbé autant de potasse qu'une bonne récolte de blé en exporte à la fin de sa végétation.

Echantillons du 25 Octobre

155 jours après le semis

Donnons d'abord les poids moyen des feuilles et des racines de chaque parcelle, ainsi que le pourcentage du poids de la racine dans le poids total de la plante.

TABLEAU IX. POIDS MOYENS DES FEUILLES ET DES RACINES À LA RÉCOLTE

Parcelles	Poids Moyens			Racine % de plante
	Feuille	Racine	Plante	
	GR.	GR.	GR.	
1	281.3	483.4	764.8	63.2
2	348.6	524.5	873.1	60.0
3	327.0	443.0	770.0	57.5
4	312.7	442.6	755.3	58.6
5	273.9	471.3	745.2	63.2
6	322.6	525.4	848.0	61.9
7	250.0	458.5	708.5	64.7
8	283.3	518.4	801.7	64.6

L'analyse séparée des racines et des feuilles a fourni les résultats ci-après:

TABLEAU X. COMPOSITION DE LA MATIÈRE SÈCHE ET DES CENDRES À LA RÉCOLTE

	1		2		3		4		5		6		7		8	
	R	F	R	F	R	F	R	F	R	F	R	F	R	F	R	F
Matière sèche %	19.23	10.46	19.62	10.54	19.35	9.98	19.14	9.39	19.17	10.46	19.06	9.94	18.93	10.86	19.19	10.77
Cendres % mat. sèche	4.51	19.51	3.68	23.26	3.89	20.38	4.43	24.40	3.88	22.00	4.73	24.56	4.23	21.98	4.46	23.76
Ac. phosph. mat. sèche	0.42	0.84	0.32	0.60	0.32	0.68	0.38	0.67	0.44	0.69	0.39	0.56	0.40	0.71	0.42	0.56
Chlore mat. sèche	0.05	0.56	0.28	3.57	0.03	0.29	0.22	3.98	0.03	0.37	0.27	4.44	0.03	0.44	0.25	3.71
Potasse mat. sèche	1.39	5.22	1.14	6.39	1.20	4.74	1.79	7.32	1.53	6.16	1.83	7.16	1.64	6.86	1.57	6.70
Soude mat. sèche	0.27	2.58	0.31	1.98	0.26	3.03	0.33	3.74	0.28	3.31	0.31	2.48	0.41	2.46	0.30	1.67
Chaux mat. sèche	0.46	2.26	0.30	3.49	0.45	2.66	0.33	2.53	0.33	2.99	0.29	2.68	0.31	3.09	0.31	3.53
Azote mat. sèche	1.77	3.82	1.79	3.24	1.47	3.23	1.54	3.14	1.70	3.55	1.74	3.18	1.38	3.30	1.45	3.22
Ac. phosph. % de cendres	9.31	4.30	8.69	2.58	8.22	3.33	8.57	2.74	11.34	3.13	8.14	2.28	9.45	3.23	9.41	2.35
Chlore % de cendres	1.10	2.92	7.60	15.35	0.77	1.42	4.96	16.31	0.77	1.68	5.70	18.07	0.70	2.00	5.60	15.61
Potasse % de cendres	30.82	26.75	30.97	27.47	30.84	23.25	40.40	30.00	39.43	28.00	38.68	29.15	38.77	31.21	34.30	28.19
Soude % de cendres	5.98	13.22	8.42	8.51	6.68	14.86	7.44	15.32	7.21	15.04	6.55	10.09	9.69	11.19	6.72	7.02
Chaux % de cendres	10.19	11.58	8.15	15.00	11.56	13.05	7.44	10.36	8.50	13.59	6.13	10.91	7.32	14.05	6.95	14.85

Les résultats consignés au tableau X motivent les observations suivantes:

1° Le taux de chlore des cendres a généralement diminué dans la racine et augmenté très notablement dans la feuille.

2° Le taux de soude ne présente plus la même régularité que dans les échantillons antérieurs: ses variations sont irrégulières mais l'ensemble parait correspondre à une diminution générale.

3° Le taux de potasse a aussi diminué, sauf dans deux cas où les différences très minimes sont de l'ordre des erreurs d'analyse;

4° Le taux de chaux a augmenté notablement dans toutes les racines, et diminué dans les feuilles, sauf deux exceptions marquées par des différences de l'ordre des erreurs d'analyse.

5° Le taux de matière sèche a augmenté fortement dans les racines et faiblement dans les feuilles.

6° Le taux d'azote a diminué sensiblement tant dans la racine que dans les feuilles.

Les conclusions 3-4-5-6 tendent à faire admettre que dans la dernière période de la végétation, l'absorption de la potasse, de la chaux, de l'azote se ralentit, alors que s'accentue la formation des corps hydrocarbonés; le chlore seul continuerait à être absorbé, la chaux ferait retour de la feuille à la racine.

Nous donnons dans le tableau XI la composition des cendres des échantillons du 25 octobre pour la plante entière; nous y avons joint le poids moyen d'une plante fraiche et sèche, les taux de matière sèche, de cendre et d'azote.

Tableau XI. Composition de la Plante Entière et de ses Cendres à la Récolte

Parcelles	1	2	3	4	5	6	7	8
	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.
Poids moyen d'une plante fraiche	764.8	873.1	770.0	755.3	745.2	848.0	708.5	801.7
Poids moyen d'une plante sèche	122.4	139.6	118.3	114.1	118.9	132.2	113.9	130.0
Matière sèche %	16.0	15.9	15.3	15.1	15.9	15.5	16.0	16.2
Azote % de matière sèche	2.26	2.47	1.95	1.94	2.13	2.08	1.83	1.86
Cendres matière sèche	8.11	8.81	8.42	9.57	8.23	9.53	8.44	8.99
Ac. phosph. % de cendres	6.20	4.46	4.96	4.83	6.26	4.67	5.81	5.18
Chlore % de cendres	2.22	12.95	1.20	12.23	1.32	13.00	1.44	11.60
Potasse % de cendres	28.30	28.54	25.85	33.81	32.36	33.04	34.35	30.70
Soude % de cendres	10.46	8.48	12.10	12.48	12.04	8.64	11.86	6.89
Chaux % de cendres	11.04	12.88	12.51	9.30	11.64	8.96	11.25	11.65

En examinant les tableaux II, V et XI en ce qui concerne les taux des cendres pour cent. de matière sèche de la plante entière, on constate que dans tous les cas, aux trois époques de la végétation étudiées, le taux des cendres est plus élevé dans les parcelles paires: on est en droit d'en conclure que la présence du chlore dans ces parcelles conduit à l'absorption d'un excès de matières minérales pour la production d'un même poids de matière sèche.

Le chlore entre évidemment en compte dans l'augmentation du taux des cendres; nous allons voir que la potasse le suit.

Voici maintenant les quantités d'éléments fertilisants contenus tant dans les feuilles que dans les racines par hectare calculées pour un nombre moyen de 70000 pieds.

Tableau XII. Quantités d'Éléments Nutritifs Prélevés par Hectare par les Feuilles et les Racines à la Récolte

	1		2		3		4		5		6		7		8	
	R	F	R	F	R	F	R	F	R	F	R	F	R	F	R	F
	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.
Matière sèche à l'hectare	6520.	2058.	7203.	2569.	5999.	2282.	5929.	2058.	6321.	2002.	7007.	2247.	6076.	1897.	6965.	2135.
	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.
Poids moyen par pied sec	93.0	29.4	102.9	36.7	85.7	32.6	84.7	29.4	90.3	28.6	100.1	32.1	86.8	27.1	99.5	30.5
	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.	K.
Ac. phosph. à l'hectare	27.2	17.3	23.0	15.4	19.2	15.5	22.5	13.8	27.8	13.8	27.3	12.5	24.3	13.5	29.2	11.9
Chlore à l'hectare	3,2	11.5	20.1	91.7	1.8	6.6	13.0	81.8	2.0	7.4	18.9	99.6	1.8	8.3	17.4	79.2
Potasse à l'hectare	90.2	107.5	82.1	164.2	72.0	108.3	106.1	150.5	96.8	123.2	128.3	160.7	99.6	130.3	109.8	143.0
Soude à l'hectare	17.5	53.1	22.3	50.9	15.6	69.2	19.5	76.9	17.7	66.2	21.7	55.6	24.9	46.7	20.9	35.6
Chaux à l'hectare	29.8	46.5	21.6	89.7	27.0	60.8	19.5	52.0	22.0	60.0	20.3	60.1	18.8	58.7	21.6	75.3
Azote à l'hectare	114.8	78.7	128.9	83.3	88.2	73.8	91.3	64.5	107.5	71.0	122.0	71.3	83.8	62.7	101.0	68.6

Ces résultats confirment ce que l'on sait de la distribution des éléments fertilisants dans la betterave à maturité: l'azote et l'acide phosphorique sont surtout abondants dans la racine, alors que le chlore, la potasse, la soude et la chaux sont plus abondants dans la feuille.

Le tableau suivant donne les quantités totales des éléments fertilisants contenus dans la récolte:

Tableau XIII. Quantités d'Éléments Nutritifs Prélevés à l'Hectare par la Récolte Entière

Parcelles	1	2	3	4	5	6	7	8
	K.	K.	K.	K.	K.	K.	K.	K.
Matière sèche à l'hectare	8568	9772	8281	7987	8323	9254	7973	9100
	GR.	GR.	GR.	GR.	GR.	GR.	GR.	GR.
Poids moyen par pied sec	122.4	139.6	118.3	114.1	118.9	132.2	113.9	130.0
	K.	K.	K.	K.	K.	K.	K.	K.
Acid phosphorique	44.5	38.4	34.7	36.3	41.6	39.8	37.8	41.1
Chlore	14.7	111.8	8.4	94.8	9.4	118.5	10.1	96.6
Potasse	197.7	246.3	180.3	256.6	220.0	289.0	229.9	252.3
Soude	70.6	73.2	84.8	96.4	83.9	77.3	71.6	56.5
Chaux	76.3	111.3	87.8	71.5	82.0	80.4	77.5	96.9
Azote	193.5	212.2	162.0	155.8	178.5	193.3	146.5	169.6

L'étude du tableau XIII conduit aux conclusions suivantes:

1° L'absorption du chlore apporté par les engrais a été presque totale: sur 127 Kg. fournis par hectare dans les parcelles paires, 95 Kg. en moyenne ont été absorbés par la récolte.

2° L'absorption de la potasse suit celle du chlore: la récolte des parcelles paires contient de 22 à 76 Kg. de potasse de plus que celle des parcelles impaires, en moyenne 54 Kg.

Le tableau XII montre que la potasse ainsi prélevée en excès se localise en plus grande quantité dans la feuille que dans la racine.

Comme la production à l'hectare est sensiblement la même avec chlore que sans chlore, comme la richesse en sucre est plus faible en présence du chlore (ou tout au plus égale) comme enfin, le quotient de pureté et surtout le coefficient salin sont moins bons dans les parcelles ayant reçu du chlore, on doit conclure que l'emploi du chlorure de potassium comme fumure de la betterave n'est pas avantageux dans les conditions où il a été fait, c'est-à-dire immédiatement avant le semis de la graine, suivant la pratique générale de la culture dans le Département de Seine-et-Marne.

La présence du chlore dans l'engrais conduit dans le cas présent à une consommation supplémentaire de 54 Kg. de potasse en moyenne par hectare sans aucun avantage.

Evidemment ces 54 Kg. de potasse ne sont pas perdus; cependant il y en a en moyenne le tiers, soit 18 Kg. dans la racine, qui sont perdus en totalité si la betterave est livrée à la sucrerie, et qui ne sont récupérés qu'en partie, si la betterave est distillée à la ferme.

Les deux tiers, soit 36 Kg. contenus dans les feuilles feront retour au sol si celles-ci sont enterrées; il y aura une déperdition plus ou moins grande si les feuilles sont consommées par les animaux.

L'emploi du chlorure de potassium dans les conditions précitées a donc été nettement désavantageux par rapport à celui du sulfate de potasse au point de vue de l'utilisation de la potasse.

Il faut ajouter que si la betterave était destinée à la sucrerie, la diminution du coefficient salin des racines ayant reçu des chlorures viendrait en diminuer sensiblement la valeur réelle.

3° L'absorption de la soude est irrégulière à la fin de la végétation, ainsi que celle de la chaux, et je n'ai pas trouvé d'explication de cette irrégularité.

Peut-être que le dosage de la magnésie, que je regrette de n'avoir pas fait, en permettant de comparer la basicité totale des cendres des betteraves des différentes parcelles, aurait pu fournir à cet égard des indications précieuses.

RELATIONS ENTRE LA RICHESSE EN SOUDE DES CENDRES ET LA RICHESSE EN SUCRE DE LA BETTERAVE

Le tableau XIV ci-après donne pour chaque parcelle la densité des jus, leur richesse en sucre, le taux de sucre pour cent de betteraves calculé au coefficient 0,95 et les taux centésimaux de soude dans les cendres des racines.

TABLEAU XIV ANALYSE DU JUS—RICHESSE EN SUCRE—TAUX DE SOUDE DES CENDRES

Numéros des Parcelles	Densité du Jus	Sucre % de Jus	Sucre % gr. de Jus	Sucre % gr. de Betterave	Soude % de cendres de la racine
	°	GR.	GR.	GR.	
1	7.1	14.97	13.97	13.27	5.98
2	7.3	14.47	13.48	12.80	8.42
3	7.2	15.02	14.01	13.30	6.68
4	7.2	15.13	14.11	13.40	7.44
5	7.05	14.86	13.88	13.18	7.21
6	7.0	14.48	13.53	12.85	6.55
7	7.1	14.82	13.83	13.13	9.69
8	7.1	15.11	14.10	13.39	6.72

On constate que les variations des taux de soude sont considérables, alors que celles des taux de sucre sont faibles; de plus les variations ne se suivent pas; la loi énoncée par M. Saillard: "Plus les betteraves sont riches en sucre, moins elles contiennent de soude pour cent. de cendres, abstraction faite de la partie insoluble dans l'acide chlorhydrique" n'est donc pas confirmée.

(Extrait)

INFLUENCE DU BICHRÔMATE DE POTASSE EMPLOYÉ COMME CONSERVATEUR DU LAIT SUR L'ÉCRÊMAGE ET LE BARATTAGE ET SUR LA COMPOSITION DU BEURRE

M. Vuaflard

Pas de Calais, France

M. L. Vuaflart, directeur de la Station agronomique d'Arras, France, fait remarquer que la comparaison avec un beurre suspect d'un échantillon de contrôle préparé par l'expert ou sous sa surveillance ne sera possible que quand on aura élucidé les trois points suivants:

Le beurre provenant d'une seule traite a-t-il la même composition que celui qui a été préparé en mélangeant le produit de plusieurs traites?

Le degré de maturité de la crême a-t-il une influence sur les résultats de l'analyse du beurre?

Le bichrômate de potasse, ajouté au lait comme agent de conservation, permet-il de procéder comme à l'ordinaire à l'écrêmage et au barattage et modifie-t-il la composition du beurre?

Dans une première contribution à l'étude de ces questions, l'auteur cite les résultats de quelques expériences. A la dose de 5 décigrammes par litre de lait et même aprés 15 jours de conservation à la température du laboratoire, au mois de Mai, en bidons fermés, le bichrômate ne gêne aucunement l'écrêmage et le barattage et il semble que son action sur la composition du beurre puisse être négligée. Le degré de maturité de la crême ne paraît pas non plus avoir une grande influence sur les résultats de l'analyse du beurre.

SUR L'HÉRÉDITÉ DES DÉFECTUOSITÉS DU GLUTEN

PAR L. VUAFLART

Directeur de la Station Agronomique, Arras, France

La farine de l'un des blés de 1910 que j'ai étudiés, un Nursery, était défectueuse au point de vue de la panification: son gluten était mou, visqueux, sans élasticité et d'une extraction très-difficile. Le blé dont il s'agit était fort humide et on sait que les conditions climatériques de l'année 1910 ont été très-défavorables; la défectuosité observée pouvait donc être attribuée à un défaut de matûrité et il était intéressant de rechercher si elle n'était qu'accidentelle et passagère ou si, au contraire, elle se retrouverait dans les produits des récoltes suivantes.

Ce Nursery de 1910 a été employé comme semence par plusieurs cultivateurs et j'ai pu examiner les produits de la récolte de 1911 provenant de trois arrondissements différents et de localités assez distantes entre elles et assez éloignées du lieu d'origine pour que le changement de terrain et, jusqu'à un certain point, de climat, soit bien marqué.

Les trois farines de 1911 étaient tout aussi défectueuses que celle de 1910. La pâte collait aux doigts, puis devenait liquide; l'extraction du gluten n'a pu être menée à peu près à bien qu'en faisant le pâton à l'eau chaude, le lavant à l'eau chaude (30° C.) après un long repos et en opérant très-lentement; le gluten était mou, visqueux et manquait d'élasticité.

A l'analyse, rien ne pouvait faire soupçonner cette mauvaise qualité du gluten.

Si l'on consulte les tableaux ci-contre, on voit que d'une année à l'autre le grain a grossi et que le poids à l'hectolitre a augmenté. Les blés de 1911 étaient plus beaux et plus colorés que celui de 1910; celui d'Arras était même fort beau. Les matières azotées et l'acide phosphorique ont diminué, mais l'acide phosphorique pour cent d'azote est élevé, plus fort même que la moyenne des blés de l'année.

Pour les farines, elles ont été préparées en septembre, novembre et décembre sans que le grain ait subi aucune altération visible, et les analyses ont été faites en février-mars. Ni l'ancienneté, ni une mauvaise conservation ne peuvent donc être mises en cause. D'ailleurs, d'autres farines, préparées et analysées en même temps que celles des Nursery, ont donné des glutens d'excellente qualité.

A l'analyse, on constate que le gluten est moins abondant en 1911; IL est même tombé à un chiffre très-bas à Arras et à Saint-Pol, mais de pareils chiffres ne sont pas le signe certain d'un gluten défectueux et, inversement, la farine de Saint-Omer, plus

BLÉ NURSERY

Analyse des Grains

	Poids de l'hecto litre	Poids de 1.000 grains	Matières azotées*	Acide phosphorique[1]	Acide phosphorique pour cent d'azote
	K	GR.	%		
Récolte de 1910	75.4	42.	11.0	0.924	52.5
Récolte de 1911. Arras	80.5	49.8	9.9	0.842	52.9
— — Saint-Pol	78.0	48.8	9.6	0.890	58.1
— — Saint-Omer	77.5	49.1	10.6	0.856	50.6

*Chiffres ramene's à l'humidité uniforme de 15%.

Analyse des farines à 70% d'extraction et à 15% d'humidité

	Gluten		Matières azotées		Acide phosphorique	Acide phosphorique pour100 d'azote	Acidité
	Humide	Sec	Totales	Solubles			
Récolte de 1910	29.4	8.2	9.4	1.2	0.239	15.9	
Récolte de 1911. Arras	22.3	6.5	8.9	2.4	0.245	17.2	0.024
— — Saint-Pol	22.4	6.5	8.5	2.0	0.287	21.0	0.027
— — Saint-Omer	28.2	8.1	9.5	1.4	0.280	18.3	0.030

riche que les deux autres, n'a pas un meilleur gluten qu'elles. Deux des farines de 1911 paraissent contenir beaucoup de matières azotées solubles; mais l'extraction du gluten a été si difficile que des pertes ont pu se produire; il ne faut donc pas attacher trop d'importance à ce fait. De même, pour les raisons exposées dans une autre communication, l'augmentation de l'acide phosphorique ne saurait être retenue. Enfin, l'acidité n'est pas celle d'une farine altérée; d'ailleurs, des farines entièrment comparables à celles-ci sous le rapport des dates de mouture et d'analyse, mais dont le gluten était de bonne qualité, nous ont donné des chiffres semblables: 0,018 0,018 0,021 0,024 et 0,027. Pas plus que l'analyses des grains, celle des farines ne pouvait donc faire prévoir que le gluten était défectueux.

Un seul caractère physique attitrait l'attention: les trois farines de 1911 étaient nettement plus jaunes que celles des autres blès; mais je connais un cas où des farines absolument jaunes provenant de blé Japhet grêlé puis échaudé ont donné un gluten normal.

En réumé voici un blé qui, en 1910, sans que rien dans son aspect ni dans la composition du grain et de la farine paraisse anormal, sans que l'ancienneté ou une mauvaise conservation puissent être invoquées, a un gluten de mauvaise qualité. Le même fait se reproduit en 1911 dans la descendance de ce blé cultivé dans trois localités différentes. L'année 1910 avait été très-défavorable pour le blé; 1911, au contraire, a donné des blés très-beaux et de très-bonne qualité. Malgré ces conditions climatériques favorables et dans des conditions de sol et, jusqu'à un certain point, de climat autres que celles de 1910 et différant entre elles, on retrouve en 1911 la même défectuosité du gluten. L'infériorité au point de vue de la valeur boulangère du Nursery de 1910 s'est donc transmise à celui de 1911; l'étude des produits des récoltes futures nous montrera si elle est définitive.

AZOTE ET ACID PHOSPHORIQUE DANS LE BLÉ ET DANS LA FARINE

L. Vuaflart

Directeur de la Station Agronomique, Arras, France

Dans le blé, comme dans la farine, le rapport entre l'azote et l'acide phosphorique (dosé par voie humide) est assez constant. Les déterminations que j'ai effectuées dans ces dernières années, sur 15 à 20 échantillons de chaque récolte, me permettent de dresser le tableau ci-dessous.

	Acide phosphorique pour 100 d'azote		
	Moyennes	Maxima	Minima
Blés			
1908	54,5	59,8	49,8
1909	47,5	52,3	42,8
1910	47,4	56,7	37,4
1911	49,9	58,1	44,2
Farines à 70 % d'extraction			
1908	15,3	18,1	14,1
1909	14,4	17,9	12,1
1910	13,7	16,7	11,3
1911	17,9	22,1	12,8

On voit que, pour chaque année, les extremês ne s'écartent pas trop de la moyenne, mais que la valeur du rapport varie un peu suivant les années. Aussi bien pour la moyenne que pour le maximum et le minimum, dans le blé comme dans la farine, 1909 et 1910 donnent des rapports inférieurs à ceux de 1908. Le blé de 1911 se classe entre celui de 1908 et ceux de 1909 et 1910; quant à sa farine, c'est elle qui semble fournir la plus forte moyenne et le maximum le plus élevé.

Or les années 1909 et 1910 ont donné des blés plus riches en azote que 1908 et 1911. On trouve, en effet, comme moyenne des blés auxquels se rapporte le tableau précedent et en ramenant tous les chiffres à une humidité uniforme de 15% dans le grain:

	Azote	Acide phosphorique
blés de 1908	1,61	0,876
blés de 1909	1,86	0,882
blés de 1910	1,87	0,884
blés de 1911	1,67	0,832

Il semble donc qu'il y ait, pour chaque année, une relation assez constante entre l'azote et l'acide phosphorique et que le rapport " acide phosphorique pour 100 d'azote " soit moins élevé dans les années où les blés sont riches en azote. L'étude des farines conduit à la même hypothèse.

Si le rapport dont il s'agit est plus faible lorsque l'azote est abondant, c'est parceque dans les années à gluten l'azote a augmenté plus vite que l'acide phosphorique. C'est bien ce que montre le tableau suivant, qui n'est que la reproduction sous une forme plus claire du précédent.

	Azote	Acide phosphorique
blés de 1908	100	100
blés de 1909	115	100,6
blés de 1910	116	100,9
blés de 1911	103,7	95

Par rapport à 1908, les variations de l'azote en 1909 et en 1910 ont plus d'amplitude que celles de l'acide phosphorique; mais elles se produisent dans le même sens.

En 1911, les variations sont de sens opposés: diminution pour l'acide phosphorique, augmentation pour l'azote.

L'examen des farines à 70% d'extraction issues des mêmes blés conduit également à des constatations intéressantes.

	Azote	Acide phosphorique
farines de 1908	100	100
farines de 1909	112	105
farines de 1910	115	102
farines de 1911	102,7	119

Pour 1909 et 1910, les variations sont, comme pour le blé, dans le même sens et plus importantes pour l'azote que pour l'acide phosphorique. Pour 1911, au lieu de diminuer comme dans le blé, l'acide phosphorique augmente, mais je ne saurais affirmer que cette augmentation soit bien réelle. Les grains de 1911 étaient, en effet, beaucoup plus secs que ceux des années précédentes et il est possible qu'ils se soient comportés un peu différemment à la mouture, les enveloppes se segmentant plus facilement et passant en plus grande quantité dans la farine. Le grain contenant environ 0,850% d'acide phosphorique alors qu'on n'en trouve que 0,220% dans la farine à 70% d'extraction, les issues en renferment 2,3% environ; le remplacement dans la farine de 1% de parties provenant de l'amande par la même quantité de débris de l'enveloppe suffit pour augmenter de 1/10 l'acide phosphorique. Il est donc plus prudent de ne pas tenir compte de l'augmentation d'acide phosphorique que semble révéler l'analyse des farines de 1911.

Dès lors, il semble qu'on puisse se hasarder à avancer que, en général, l'acide phosphorique est plus constant que l'azote. L'année 1911 diffère un peu sous ce rapport de ses devancières, mais peut-être ne faut-il voir là que la conséquence de conditions climatériques exceptionnelles qui ont amené une matûration hâtive et inégale.

Du fait que l'acide phosphorique est moins variable que l'azote, on peut déduire que l'effet des fumures phosphatées sur la teneur en phosphore sera moins marqué que celui des fumures azotées sur la teneur en azote. Voici, à ce sujet, les résultats d'une expérience faite en 1910-1911 sur un blé Japhet semé après trêfle sur deux parcelles absoluement semblables sous tous les rapports, sauf que l'une avait reçu 1200 kilogs de superphosphate à l'hectare et l'autre 600 kilogs seulement.

	Blé		Farine	
Superphosphate	1200 K.	600 K.	1200 K.	600 K.
Matières azotées totales	11,1	11	9,7	10,1
Acide phosphorique	0,841	0,804	0,251	0,249
Gluten sec	"	"	8,1	7,8
Acide phosphorique % d'azote	47,2	45,5	16,2	15,4

La forte fumure phosphatée n'a pas enrichi la farine en acide phosphorique mais seulement le grain; elle n'a pas non plus exercé une action favorable sur la richesse en azote. Si la chose vient à être confirmée, il faudra renoncer à l'espoir d'améliorer la valeur boulangère des farines par de fortes fumures phosphatées. On varra, il est vrai, dans une autre communication, qu'une teneur en phosphore normale et même plutôt élevée n'est pas incompatible avec un gluten défectueux.

Voyons enfin s'il y a une relation entre la teneur du grain en matières azotées (et celle de la farine en gluten) et les conditions météorologiques. Il faut considérer pour cela les trois mois pendant lesquels se forme le grain.

Mois de Mai, Juin et Juillet	Température moyenne	Pluie totale	Heures de soleil
1908	16,11	166,1	521
1909	13,78	193,1	516,5
1910	14,94	323,8	511
1911	16,67	124,2	777

Rapprochant ces données des chiffres cités plus haut, on voit que les années froides et humides semblent favorables à la richesse en azote. Cette conclusion ne vise, d'ailleurs, que le pourcentage de matières azotées ou de gluten et non la production de matière azotée par hectare, pour le calcul de laquelle il faudrait faire intervenir le rendement. Dans des années telles que 1909 et 1910, la richesse en azote n'est, en quelque sorte, qu'apparente et résulte de ce fait que, pour une quantité d'azote donnée, il s'est formé moins d'amidon; mais il se peut très-bien que la matière azotée à l'hectare soit moins abondante que dans une année chaude et éclairée comme 1911 où le pourcentage en azote et en gluten sera moins élevé par suite d'une production d'amidon plus considérable.

ALUNITE AS A SOURCE OF POTASH

By W. H. Waggaman

Bureau of Soils, U. S. Dept. of Agriculture, Washington, D. C.

With a view to testing the commercial possibilities of the mineral alunite, a number of experiments were carried on in this laboratory, the results of which present some features of interest.

Alunite is a double sulphate of potassium and aluminum which on heating, first gives off water and sulphur trioxide leaving a residue consisting largely of potash alum. Upon increasing the temperature this latter compound decomposes with a further evolution of the oxides of sulphur, the final residue being chiefly potassium sulphate and alumina.

The Alunite used in the experiments was a rather pure sample having the following analysis: K_2O-10.86 per cent.; So_3-36.18 per cent.

In order to determine the temperatures at which the decompositions took place the apparatus shown in figure 1 was constructed.

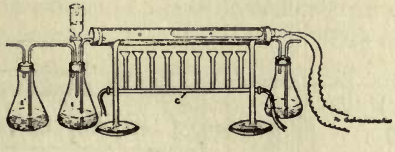


Fig 1

The pyrometer A was introduced into the tube B (preferably made of quartz) containing the sample of Alunite and heated by the burners or furnace C. A solution of sodium carbonate was contained in the dropping funnel D. The flask E containing water colored with a few drops of methyl orange was connected with an aspirator.

The burners were lighted and a gentle stream of air drawn through the apparatus, while the temperature shown by the pyrometer and the color of the methyl orange in the flask, E, were carefully watched.

At 520° C. the oxides of sulphur began to come over and the color of the methyl orange changed to red. The acidity was neutralized by dropping in a little sodium carbonate from the funnel D.

At 530° C. the evolution of gas became quite copious and the methyl orange again changed color. A drop or two of sodium carbonate was added and the temperature was kept at this point for 20 or 30 minutes. It was then increased to 670° C. where the methyl orange again became red. Another drop of sodium carbonate was added and the temperature slowly increased to 750° C.

Apparently no more gas was evolved above a temperature of 700° C.

The residue in the tube was then emptied out and washed repeatedly with hot water. It was found very difficult to wash the residue entirely free from soluble sulphates. The washings, however, gave no precipitate with ammonia or lime water, thus showing the absence of soluble aluminum compounds and indicating that the decomposition was practically complete.

In order to see how much sulphur trioxide could be actually recovered by treating alunite and collecting the evolved gases, a sample of 10 grams was ignited in a combustion tube drawn out and attached to an absorption train as shown in figure 2. Both the flask B and the absorption bulbs C′ C″ contained a solution of caustic potash. The furnace was started and a gentle stream of air drawn through the apparatus. Great care had to be exercised to prevent the gases evolved from the alunite from passing through the entire train and escaping.

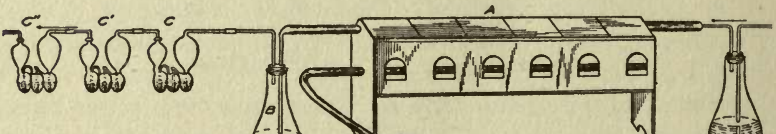


Fig. 2

After heating the charge for a part of two days (eventually carrying the temperature to 700° C.°) the contents of the absorption train were emptied into a beaker, the bulbs and flask were carefully rinsed into the same beaker, the solution rendered slightly acid with hydrochloric acid and made up to definite volume. Aliquots of this were then taken for analysis.

The temperature at which the final decomposition of the alunite takes place (viz. 700° C.) is far above that at which sulphur trioxide is decomposed. Much of the gas evolved, therefore, was sulphur dioxide. Upon acidifying the potash solution, a strong odor of sulphur dioxide was noticed. A little hydrogen peroxide and nitric acid were added, but considerable sulphur was lost which could have been saved by a suitable oxidizing agent.

In Commercial practice, platinized asbestos or some other catalytic substance could be introduced into the cooler end of the tube where the temperature is about 400° C. The sulphur dioxide and oxygen passing over this would be again converted into the trioxide and thus saved. The absence of such impurities as arsenic and chlorides would obviate the necessity of washing the gases before passing them over the contact substance.

The determination of sulphur trioxide in the alunite used in these experiments showed 26-88 per cent. over and above that necessary to combine with the potash present. Theoretically this should all be evolved on ignition. The mean of two determinations, however, made as outlined above, gave an amount of sulphur trioxide recovered equal to only 23.05 per cent. which is 85.75 per cent. of that theoretically recoverable.

The ignited residue was then analyzed both for potash and sulphur. The results are given below:

K_2O in residue,	15.95 per cent.
SO_3 in residue,	15.37 per cent.
So_3 in residue over and above that combined as K_2SO_4,	1.83 per cent.

Alunite has been used heretofore for the manufacture of potash alum.[1] Either by heating to 400° or 500° C. and leaching out the

---

[1] Guyot, M. P., Compt. Rend. Acad. Sci., Paris, 95, 693-694, 1001-1003. Thorp, F. H., Outlines of Ind. Chem., p. 259-260.

alum thus produced, or by ignition at a higher temperature and subsequently treating the ignited residue with sulphuric acid and potassium sulphate.

The production of potassium sulphate and alum by ignition of alunite, and the collection of the evolved oxides of sulphur by absorption in some suitable medium are covered by French patent No. 419,854.

In this patent, however, it is stated that the decomposition should not be carried to the end, but that the ignited residue should contain both potash alum and potassium sulphate, a separation of which can be afterwards made by lixiviating the residue and crystallizing the solution thus obtained. Although no reason is given why the decomposition should not be carried to an end it is probably on account of the residue, which it is claimed after lixiviation is an excellent artificial bauxite. The average price of natural bauxite in 1910, according to the figures of the U. S. Geological Survey, was $4.89 per ton.

Unless the alunite used is very pure it is doubtful if the leaching out of the potassium sulphate is economical. The experience of the author has been that an enormous volume of hot water is required to entirely free the ignite residue from soluble salts. The subsequent evaporation of this water is both tedious and expensive.

Pure alunite, according to Dana, has the following composition:—

SO_3,	38.60 per cent.
Al_2O_3,	37.00 per cent.
K_2O,	11.40 per cent.
H_2O,	13.00 per cent.

Figuring, therefore, the amount and value of the products obtained from 1 ton (2,000 lbs.) of pure alunite, we obtain the following figures:—

Products from 1 ton (2,000 lbs.) pure alunite.

Potash (K_2O), 220 lbs., at 4 cents per lb.,	$8.80
Sulphuric Acid (52°B), 1090 lbs., at $6 per ton,	3.27
Alumina, 740 lbs., at $4.89 per ton,	1.81
	$13.88

From an economic standpoint it would seem more practical to use the ignited alunite (free from soluble aluminum compounds) directly as a fertilizer either alone or in mixed goods, since the expense of separating the soluble salts from the alumina would probably more than counterbalance the value of the alumina obtained.

MITTEILUNG AUS DEM LABORATORIUM FÜR CHEMIE UND BAKTERIOLOGIE DER MILCH AN DER UNIVERSITÄT GÖTTINGEN

BEITRAG ZUR KOLLOIDCHEMIE DER MILCH

VON DR. G. WIEGNER

Privatdozent für Agrikulturchemie an der Universität Göttingen

Die Prüfung der Milch ist eine schwierige Aufgabe und stellt an den Untersuchenden hohe Anforderungen. Die Schwierigkeit der Untersuchung scheint mir im wesentlichen in 2 Umständen begründet: Die Milch ist das Sekret aus der Milchdrüse, das seine Zusammensetzung ständig ändert mit Individualität, Rasse, Haltung, Fütterung und Laktationsperiode des Tieres, ferner mit äusseren Bedingungen wie Temperatur, etc., so dass es nicht möglich ist, eine feste, allgemeingültige Zusammensetzung der Milch anzugeben. Dazu kommt eine 2. Schwierigkeit[1]: Die Milch ist ein Gemenge aus Kolloiden und Krystalloiden, in dem ausserdem Fett in Emulsion zerteilt ist. Es lagern sich also über die natürlichen Schwankungen in der chemischen Zusammensetzung die Unterschiede in der Zerteilung der einzelnen Milchbestandteile. Nun ist die Zerteilung bei allen echten Lösungen ziemlich gleichmässig, nämlich nahezu maximal bis zu Molekülen oder Jonen. Die physikalischen Eigenschaften solcher echter Lösungen variieren nicht wesentlich mit dem Zerteilungsgrade, der konstant maximal ist. Die physikalischen Eigenschaften der Kolloide und Emulsionen dagegen stellen sich als abhängig nicht nur von den Mengen, sondern auch vom *Zerteilungsgrade* der Stoffe dar. Die Zerteilung vor allem der Eiweisskörper und auch die des Fettes ändert sich von selbst ständig und

---

[1] Vergl.: *G. Wiegner*, Milchwirtschaftl. Zentralbl. 5,473 und 521 (1909).
Zeitschr. f. Unters. der Nahrungs- und Genussm. 20,70 (1910).
Zeitschr. f. Chemie und Ind. der Kolloide 8,227 (1911).
Milchwirtschaftl. Zentralbl. 7,534 (1911).

zwar tritt fortwährend eine Vergröberung der Teilchen ein, z.B. der Teilchen des Butterfettes durch Entrahmung, der des Kaseins durch die Säuerung. Damit müssen sich stetig die physikalischen Eigenschaften des Gemenges ändern. Hinzu kommt, dass die Fettkügelchen allmählich aus dem flüssigen in den festen Zustand übergehen, wodurch Äenderungen bedingt werden. Konstante, mit der Zeit unveränderliche Eigenschaften zeigen nur die maximal zerteilten oder molekular-resp. jondispersen Krystalloidlösungen oder die echten Lösungen. Selbstverständlich ändert auch eine Milchzuckerlösung ihre Eigenschaften, sobald der Milchzucker durch Mikroorganismentätigkeit in Milchsäure übergeht. Das ist eine chemische Umsetzung, verursacht durch Aufspaltung des Zuckermoleküls, die nicht verglichen werden kann mit den physikalischen Zustandsänderungen der Eiweisspörper beim Koagulieren, wobei durch sehr geringe primäre Aenderungen im Elektrolytgehalt, in unserm Fall für die Milch im Säuregehalt, sehr beträchtliche physikalische Aenderungen im Zustand der Kolloide ausgelöst werden, die von bedeutendem Einfluss auf den physikalischen Zustand des ganzen Gemenges, also den der Milch sind.

Die Milch enthält die hauptsächlichen Bestandteile in folgender Form, wobei vom Globulin und den stickstoffhaltigen Extraktivstoffen abgesehen ist:

(1) *Wasser* als *Dispersionsmittel,*

(2) *Butterfett* in Form von *Mikronen* oder mikroskopisch sichtbaren Teilchen (1,6-10),

(3) *Kasein* in Form von *Submikronen* und *Amikronen,*

(4) *Albumin* in Form von *Amikronen* (höchst wahrscheinlich),

(5) *Milchzucker* in Form von *Einzelmolekülen,*

(6) *Mineralbestandteile* in Form von *Ultramikronen* (jedenfalls Amikronen, doch liegen noch keine Bestimmungen vor) und von *Einzelmolekülen* und *Jonen.*

Milch ist also ein Gemenge von Kolloiden und Krystalloiden, in dem ausserdem Fett in unbeständiger Emulsion sich befindet.

Besonders interessant ist die Zerteilung des Kaseins in der Kuhmilch.

Es enthält 1 c.c.m. Kuhmilch 3 bis 6. 10^{12} Submikronen (ausgezählt im Spaltultramikroskop nach Siedentopf-Zsigmondy bei Beleuchtung mit Bogenlicht), neben vielen Amikronen. Es enthielten ferner:

Ziegenmilch mit 2,40% Eiweiss in 1 c.c.m.
1,62.10^{12} Submikronen
Stutenmilch mit 2,27% Eiweiss in 1 c.c.m.
1,74.10^{12} Submikronen
neben zahlreichen Amikronen

Frauenmilch enthielt gar keine mit Bogenlicht aufzulösenden Submikronen. Das Kasein war vollkommen gleichmässig fein in Amikronen aufgeteilt.

Kuhmilch und Frauenmilch unterscheiden sich also wesentlich durch die Zerteilung des Kaseins. J. *Alexander*[1] wies darauf hin, dass die feine Verteilung des Kaseins in der Frauenmilch bedingt sei durch den hohen Gehalt an Albumin, das als Schutzkolloid für Kasein wirkt und die Teilchenvergröberung hindert. Es würde die Säurekoagulation des Kaseins der Milch quantitativ unter dem Ultramikroskop studiert und gefunden, dass sich die Submikronenzahl während des Koagulationsverlaufs *nicht* nennenswertändert, dass aber die Grösse der Submikronen durch Anlagerung von Kaseinamikronen bedeutend zunimmt. Diese Untersuchung wurde auch auf andere Kolloide und Elektrolyte ausgedehnt und führte zu dem Schlusse, dass die Elektrolytkoagulation von Kolloiden so verläuft, dass sich nicht Ultramikronen der gleichen Grössenordnung zusammenlagern, sondern dass gewisse grosse Ultramikronen für die kleineren als Koagulationskerne wirken und sich durch Anlagerung von kleineren Ultramikronen ständig vergrössern. Der Unterschied in der Gerinnung von Frauenmilch und Kuhmilch ist z.Teil auf diese Verschiedenheit der Ultramikronenzerteilung und damit der Zahl der Koagulationskerne zurückzuführen. Die Milchbestandteile unterscheiden sich also wesentlich durch den Grad der Zerteilung oder durch den Dispersitätsgrad, Es scheint nun eine für die Untersuchung der Milch wichtige Regel zu sein, dass die einzelnen Milchbestandteile um so konstanter in ihrer

---

[1] Jerome Alexander, Journ. of Soc. of chem. Ind. 28,280 (1909), Journ. of the Amer. med. Assoc. 55,1196 (1910).

Menge auftreten, d.h.dass um so weniger Schwankungen im Laufe der Laktationsperiode eines Tieres und auch Schwankungen in der Milch verschiedener Tiere vorkommen je höher dispers die Milchbestandteile sind. Das Fett, das am gröbsten in der Milch zerteilt ist, ist den grössten Schwankungen unterworfen, weniger schwankt die Menge des Kaseins, noch weniger die des Albumins (vergl. Cornalba).[1] Relativ am konstantesten treten Milchzucker und Aschenbestandteile in ihrer Menge auf und zwar die Aschenbestandteile, die in hochdisperser Form in der Milch vorkommen. Ein Mass für die Summe der hochdispersen Milchbestandteile, also von Milchzucker, Aschen bestandteilen in Jonenform und Spuren von hochdispersem Eiweiss, ist das Brechungsvermögen oder das spezifische Gewicht des sog. Chlorkalziumserums der Milch, das nach *Ackermann*[2] durch Versetzen von 30 c.c.m. Milch mit 0,25 c.c.m. Chlorkalziumlösung (spez. Gew. 1,1375 bei 17,5°) und Erhitzen auf 100° während 15 Minuten in ganz bestimmten Gefässen hergestellt wird und nach dem Koagulieren leicht abgegossen werden kann. Die Zahlen für das Brechungsvermögen, für das spezifische Gewicht und für die Summe der hochdispersen Milchbestandteile schwanken nur innerhalb sehr enger Grenzen, was aus den zahlreichen Untersuchungen vor allem von *Mai* und *Rothenfusser*[3] hervorgeht. Da die Gesetze für die echten Lösungen gut bekannt sind, lassen sich die Beziehungen zwischen den physikalischen Eigenschaften des Chlorcalciumserums theoretisch ermitteln.

Bezeichnet $n_D^{17,5}$ das Brechungsvermögen des Chlorcalciumserums bei 17,5°, $R_{17,5}$ die Refraktionszahl in Skalenteilen (zur Ermittlung eignet sich zweckmässig das Eintauchrefraktometer nach Zeiss) $d\frac{15}{15}$ das spezifische Gewicht bei 15° bezogen auf Wasser von 15°, entsprechend $d\frac{20}{4}$ das spez. Gewicht bei 20° bezogen auf Wasser von 4° und t_c die Summe der hochdispersen Bestandteile in 100 g. Serum, so gilt:

---

[1] Milchw. Zentralbl. 5,30 (1909).

[2] Ztschr. z. Unters. der Nahrungs- und Genussmittel 13,186 (1907).

[3] Ztschr. z. Unters. der Nahrungs- und Genussmittel 16,7 (1908) 18,737 (1909) 21,23 (1911).

1, $\frac{({}^{n}D^{17,5})^2-1}{({}^{n}D^{17,5})^2+2}\cdot\frac{1}{d^{15}_{15}} = 0,2056$

2, $R_{17,5} = 970,88 d^{15}_{15} - 957,06$

3, $d^{15}_{15} = 0,00103 R_{17,5} + 0,98578$

4, $t_C = 245,36 - 244,92 \cdot \frac{1}{d^{20}_{4}}$

Ist das oben gegebene Leitmotiv bei der Untersuchung, nämlich dass die Bestandteile um so konstanter in der Milch auftreten je höher dispers ihr Zerteilungsgrad ist, annähernd richtig, so muss der Jonengehalt im Chlorcalciumserum ausserordentlich konstant sein. Den Jonengehalt in Milch direkt durch Leitfähigkeit zu ermitteln, ist unmöglich, da die in swechselnden Mengen auftretenden Kolloide die Messung in unuberschbarer Weise komplizieren. Für hiesigen Laboratorium stellte Herr R. *Hischer* einige diesbezügliche Messungen im Chlorcalciumserum an, die allerdings noch der Erweiterung bedürfen. Wir bestimmten das spezifische Leitvermögen der Milch einzelner Kühe (Glaner Rasse), die sich in verschiedenen Laktationsstadien befanden:

	$R_{17,5}$ Lichtbrechungs vermögen in Skalenteilen des Zeiss' schen Ein Lauchtefrakto meters bei 17,5°		t_C Sümme der hoch dispersen Bestandteile iw 100g Serum		$\Lambda_{25} . 10^{-3}$ Λ_{25} = spezifische Leitfähigkeit des Serums bei 25°	
Datum	Kuh I (fristhmelkend)	Kuh II (allmelkend)	Kuh I	Kuh II	Kuh I	Kuh II
18 May	36,35	36,70	5,56	5,64	8,17	8,03
19 "	36,50	36,80	5,59	5,67	8,13	8,00
20 "	36,40	36,70	5,57	5,64	8,10	7,97
21 "	36,30	36,70	5,55	5,64	8,13	7,93
22 "	36,80	36,70	5,67	5,64	8,00	7,96
23 "	36,60	37,00	5,62	5,71	8,00	7,72
24 "	36,70	36,60	5,64	5,62	8,06	8,12
25 "	36,60	36,80	5,62	5,67	8,05	7,91

Die Leitfähigkeit des Serums ist, wie erwartet werden konnte, sehr konsant.

Die Leitfähigkeit der ganzen Milch schwankte zwischen 5,39.10-[3] und 5,57.10-[3] bei 250. Da dieselbe Chlorcalciumlösung zur Herstellung des Serums in allen Fällen verwandt würde, ist deren Einfluss im Grossen und Ganzen auf die Leitfähigkeit des Serums der gleiche.

Natürlich ist die geringe Zahl der Beobachtungen, die auch den Jonengehalt im Serum konstant erscheinen lässt, bei weitem nicht genügend, um einen absolut bindenden Schluss zu ziehen, immerhin ist es zu erwarten, dass diese Messungen, die weiterhin im grösseren Umfange fortgesetzt werden, zur Lösnug der Frage, welchen Schwankungen der Jonengehalt des Serums unterworfen ist und wie weit die oben angeführte Regel von der relativen Konstanz der hochdispersen Milchbestandteile gilt, beitragen werden. Alle diesbezüglichen Untersuchungen wurden im Laboratorium für Chemie und Bakteriologie der Milch an der Universität Göttingen (Direktor Geheimrat W. Fleischmann) angestellt, und wir danken Herrn Geheimrat Fleischmann für das Interesse, das er den Untersuchungen entgegenbringt, die sich mit Erforschung des Wesens der Milch von kolloid chemischen Gesichtspunkten aus beschäftigen, und für die Bereitwilligkeit, mit der er die neuen Apparate zur Untersuchung in isenem Laboratorium an Khaffen liep.

ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS OF APPLIED CHEMISTRY

Washington and New York
September 4 to 13, 1912

SECTION VIIIa: HYGIENE

VOL. XVI.

ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS OF APPLIED CHEMISTRY

Washington and New York

September 4 to 13, 1912

SECTION VIIIa: HYGIENE

VOL. XVI.

The matter contained in this volume is printed in exact accordance with the manuscript submitted, as provided for in the rules governing papers and publications.

La matière de ce volume a été imprimée strictement d'accord avec le manuscrit fourni et les règles gouvernant tous les documents et publications.

Die in diesem Heft enthaltenen Beiträge sind genau in Übereinstimmung mit den uns unterbreiteten Manuskripten gedruckt, in Gemässheit der für Beiträge und Verlagsartikel geltenden Bestimmungen.

La materia di questo volume e stampata in accordo al manoscritto presentato ed in base alle regole que governano i documenti e le publicazioni.

THE RUMFORD PRESS
CONCORD·N·H·U·S·A·

ORIGINAL COMMUNICATIONS
TO THE
EIGHTH INTERNATIONAL CONGRESS
OF
APPLIED CHEMISTRY

APPROVED

BY THE

COMMITTEE ON PAPERS AND PUBLICATIONS

IRVING W. FAY, CHAIRMAN

T. LYNTON BRIGGS	JOHN C. OLSEN
F. W. FRERICHS	JOSEPH W. RICHARDS
A. C. LANGMUIR	E. F. ROEBER

A. F. SEEKER

SECTION VIIIa. HYGIENE

Executive Committee.

President: W. P. Mason, M.D., LL.D.
Vice-President: C. E. A. Winslow, M.S.
Secretary: Daniel D. Jackson, M.S.
Robert S. Weston, A.M.
Leverett Mears, Ph.D.

Sectional Committee.

Edward Bartow, Ph.D.
H. W. Clark
J. W. Ellms,
B. R. Fitz-Randolph, A.C.
T. C. Graham-Rogers
George W. Fuller, B.S.
Geo. A. Johnson
Edwin O. Jordan, Ph.D.
Ernst J. Lederle, Ph.D., Sc.D.
Hermann C. Lythgoe, S.B.
Herbert D. Pease, M.D.
Earl B. Phelps, S.B.
B. R. Rickards, B.S.
Geo. A. Soper, Ph.D.
F. F. Wesbrook, M.D.
Geo. C. Whipple, S.B.

and the Sectional Executive Committee.

VOLUME XVI

SECTION VIIIa: HYGIENE

CONTENTS

EXAMPLES OF THE EFFICIENCY OF CALCIUM HYPOCHLORITE IN TREATING TURBID WATERS

By Edward Bartow

University of Illinois, Urbana, Illinois

We have recently had the privilege of noting the action of calcium hypochlorite in the purification of turbid waters in some of the plants in the North Central United States. Results from two of the plants illustrate in different ways the efficiency of the chemical. In one case the chemical was added at the end of a long sedimentation period, during which some reduction had taken place. The chemical reduced the number of bacteria very materially, and filtration was able to effect a still greater reduction. In the other case, owing to failure to receive a shipment of the chemical none could be used for six days. There was at once a decided increase in the number of bacteria, followed by a decrease when the chemical was again applied even though the water, as shown by the turbidity, was the worst for years.

The results obtained in the first case are shown in Table 1. The colony counts were obtained on gelatine at 20°. The water treated was from the Mississippi River.

The number of colonies in the raw water is shown in the first column. The number of colonies in the effluent from a settling basin of twenty-four hours capacity is shown in the second column. As a rule, the number was reduced. The average reduction was 65%. The number of colonies in the water after treatment with calcium hypochlorite and approximately one and one-half hours additional sedimentation is shown in the third column. The number of colonies was further reduced 97.6% or 99.1% from the number in the raw water. The number of colonies obtained from the water after filtration is shown in the fourth column. There was a further reduction of 82% or a total bacterial removal of 99.8%.

TABLE 1.

COLONIES GROWING ON GELATINE AT 20° C. IN 48 HOURS

Date	Raw	After Sedimentation	After Hypochlorite	Filter Effluent
1910				
Oct. 17	28,000	9,700	95	75
Nov. 23	2,300	2,200	47	17
Dec. 18	5,600	1,200	70	31
1911				
Feb. 6	46,500	11,000	690	44
May 4	26,500	3,300	370	40
Aug. 15	13,000	280	50	8
Sept. 12	19,000	5,000	37	17
Oct. 18	5,400	2,800	170	72
1912				
Jan. 25	500	17,000	45	12
Mar. 29	67,000	22,000	260	10
	213,800	74,480	1,834	326

Tests for gas forming bacteria were made on the same samples of water and the results correspond very well with the reduction in the number of bacteria. The results are shown in Table 2. The treatment with calcium hypochlorite has entirely eliminated the gas formers from the .1 c.c. samples, from 86% of the 1 c.c. samples and from 50% of the 10 c.c. samples. The filtration has improved conditions by increasing the removal to 91% of the 1 c.c. samples and to 73% of the 10 c.c. samples. From these observations we may conclude that the calcium hypochlorite acts most efficiently in the removal of free bacteria, that the filters still further reduce the numbers by removing aggregates or bacteria which are surrounded by or enclosed in sediment.

In the second example of the efficiency of calcium hypochlorite none of the chemical was used for six days owing to the failure to receive a shipment. In the treatment plant lime and iron sulphate were used as coagulants. The amounts used were varied in such a way as to furnish a clear water. The calcium hypochlorite was used as an adjunct. There is approximately one hours sedi-

TABLE 2.
FORMATION OF GAS IN DEXTROSE BROTH AT 37½° C.

Raw	10 c.c.	11+	1−
	1 c.c.	20+	3−
	0.1 c.c.	18+	4−
After Sedimentation	10 c.c.	10+	0−
	1 c.c.	18+	2−
	0.1 c.c.	14+	7−
After Hypochlorite	10 c.c.	6+	6−
	1 c.c.	3+	18−
	0.1 c.c.	0+	22−
Filter Effluent	10 c.c.	3+	8−
	1 c.c.	2+	20−
	0.1 c.c.	0+	22−

mentation after the lime and iron sulphate are added. The calcium hypochlorite is added not more than five minutes before the water reaches the filters.

The water during the three six day periods, before, during and after the failure to receive the calcium hypochlorite, was especially bad (See Table 3.) as was shown by the high turbidity and the large number of colonies that developed from the raw water during forty-eight hours on gelatine at 20° C. After the first two days of the first period the number of bacteria in the raw water were never lower than 20,000. Only once was the turbidity below 200, reaching a maximum of 4,000 during the latter part of the period. As shown in Table 3, the bacterial removal during the six days preceding the period without calcium hypochlorite was 99.9% and gas formers were entirely absent in the general effluent from the filters. During the period without calcium hypochlorite the bacterial removal was only 93.9% and gas formers were present in the effluent with the exception of the test made on the first day without calcium hypochlorite. During the six days following the period without calcium hypochlorite the bacterial removal was again 99.9% and gas formers were absent in all of the samples tested.

TABLE 3. OPERATING RESULTS WITH AND WITHOUT CALCIUM HYPOCHLORITE*

Date 1912	Turbidity	Bacteria		Gas Formation		Parts per million chlorine
		Raw	Filter Effluent	Raw	Filter Effluent	
Mar. 13,	25	1600	3	+	–	.51
" 14,	25	3900	10	+	–	.51
" 15,	210	90000	200	+	–	.55
" 16,	230	400000	275	+	–	.45
" 17,	500	27000	50	+	–	.53
" 18,	800	125000	20	+	–	.48
Average six days preceding period without hypochlorite.........	298	107917	93	100%+	None+	.50
1912						
Mar. 20,	300	112000	8400	+	–	00
" 21,	400	110000	7500	+	+	00
" 22,	150	60000	2000	+	+	00
" 23,	825	44000	1700	+	+	00
" 24,	400	56000	2000	+	+	00
" 25,	320	20000	3000	+	+	00
Average during period without hypochlorite.........	399	67000	4100	All +	83.3%+	None
1912						
Mar. 26,	200	20000	30	+	–	.48
" 27,	220	160000	120	+	–	.57
" 28,	450	75000	80	+	–	.55
" 29,	4000	300000	120	+	–	.60
" 30,	4000	300000	550	+	–	.47
" 31,	350	250000	200	+	–	.47
Average six days following period without hypochlorite.........	1537	184170	183	All +	None +	.52

These results show very decidedly the advisability of using calcium hypochlorite under conditions similar to those existing in the plant in question.

---

* Analyses by H. M. Ely, Danville, Illinois.

SUR LA STERILISATION DES EAUX POTABLES

PAR MONSIEUR H. HINARD

Paris, France

Des différents procédés physiques qui réclament actuellement l'attention des hygiénistes pour la Stérilisation des eaux potables, la filtration sur corps poreux apparaît comme le plus simple; c'est aussi le plus ancien, et il a fait depuis longtemps ses preuves.

Si l'on examine cette question de près, on voit qu'une bougie filtrante doit répondre à une double condition. Il faut que ses pores soient assez ténus pour retenir les germes les plus subtils, assez nombreux aussi pour que le débit d'eau filtrée ne s'abaisse pas au-dessous d'une certaine limite. De plus, le corps filtrant doit pouvoir s'opposer au passage des germes pendant un temps très long, ce qui est une condition de sécurité.

Dès le début de cette fabrication, on put obtenir des parois poreuses, en porcelaine dégourdie, capables d'arrêter les bactéries de l'eau, c'est-à-dire de livrer une eau stérile, mais durant un temps limité. Or, c'est là le principal, sinon le seul écueil du procédé. Toutes les pâtes poreuses se laissent pénétrer à la longue par les bactéries ou leurs spores; il faut nécessairement les soumettre à un nettoyage, à une stérilisation périodique. Si la pénétration est prompte, la "régénération" de la bougie devra se renouveler très fréquemment; et comme cette opération devient vite fastidieuse, comme le public a toujours tendance à s'en dispenser le plus possible, la filtration perd toute efficacité. Si, au contraire, la pénétration est très lente, l'entretien du filtre est peu de chose, et celui qui en fait usage peut compter sur lui avec assurance, pourvu qu'il en prenne seulement quelque soin.

Le grand souci des fabricants de bougies poreuses fut donc toujours d'augmenter la durée d'efficacité de leurs filtres, tout en leur conservant un débit suffisant pour les usages pratiques.

Dans cette voie, un perfectionnement important fut réalisé par la substitution à la porcelaine ordinaire (ou plus exactement, à la faïence) d'une porcelaine spéciale à base de silicate de magnésie, dont le prototype est la bougie Mallié. Présentée pour la première fois à l'Académie des Sciences en 1891, par Jungfleisch, puis en 1893 par Berthelot, cette porcelaine spéciale se distingue essentiellement par la ténuité extrême de ses pores, beaucoup plus fins, plus réguliers et beaucoup plus nombreux que ceux du biscuit de porcelaine ordinaire. Il s'ensuit que la pénétration du corps poreux par les bactéries, sans doute inévitable au bout d'un certain temps et sous l'influence de la pression, est considérablement ralentie. D'autre part, cette finesse de pores empêche le colmatage interne de la bougie, de telle sorte qu'un simple brossage de temps en temps, pour enlever le dépôt superficiel, suffit à lui conserver son débit.

Au point de vue bactériologique, les effets obtenus furent dès l'origine excellents. Messieurs Bordas et Durand-Fardel, qui eurent à étudier le filtre Mallié, il y a une dizaine d'années, constatent qu'il fournit de l'eau parfaitement stérile, qu'il ne se laisse traverser ni par les bactéries vulgaires de l'eau, ni par le bacille typhique, ni par la bactéridie charbonneuse (Note de Monsieur Jungfleisch à l'Académie de Médecine, Séance du 9 Février, 1892). De son côté Monsieur Miquel, ayant fait fonctionner un filtre Mallié, sans aucun nettoyage, pendant deux périodes de douze jours consécutifs, pour la filtration de l'eau de l'Ourcq (eau stagnante, boueuse, et où les bactéries pullulent) obtenait, le dernier jour comme le premier, de l'eau completement stérile, ce que ne pouvait à l'époque donner aucun autre filtre (*Annales de Micrographie*, Avril, 1893). A la suite d'une enquête faite par Messieurs les Docteurs G. Sims Woodhead et G. E. Cartwright Wood, à l'instigation du *British Medical Journal*, enquête qui dura quatre années (1894–1898) et porta sur tous les systèmes de filtres, les savants anglais placent le Filtre Mallié au premier rang, "Il constitue, disent-ils, contre la transmission des maladies par l'eau, la garantie la plus parfaite qu'il soit possible d'obtenir."

Enfin plus récemment, le même filtre fut soumis à une très longue étude de Monsieur le Docteur Tiraboschi, à l'Institut d'Hygiène de l'Université Royale de Gênes (*Annales d'Hygiène Expérimentale,* 1905, fascicule IV.). Les expériences, conduites avec des eaux artificiellement contaminées par des cultures de bacille typhique, de vibrion cholérique, de bacilles de la dysenterie, durérent un mois et donnérent toutes le même résultat: absence de germes dans les eaux filtrées.

Depuis cette époque, de nouveaux perfectionnements ont encore été apportés à la fabrication de ce filtre, toujours dans le but d'augmenter sa durée d'efficacité.

J'ai eu moi-même à examiner dernièrement une nouvelle bougie poreuse, à base de silicate de magnésie, de la marque Mallié. Les résultats remarquables que j'en ai obtenus me paraissent être de nature à intéresser la Section d'Hygiène du Congrès.

Il s'agissait, en l'espèce, d'une bougie de forme courante, cylindrique, ayant 220 m-m de longueur, 45 m-m de diamètre extérieur et 5 m-m d'épaisseur. Elle fut montée, comme on le fait d'ordinaire pour les filtres domestiques, dans un manchon métallique de dimensions convenables, et établie sur une canalisation d'eau de la Ville de Paris. Du commencement à la fin de l'expérience, le filtre demeura jour et nuit sous pression, sans être vidé une seule fois, et sans que la bougie en fût sortie ou fût nettoyée par quelque moyen. Le débit, rapide à l'origine, se ralentit au bout de quelques jours, puis il s'établit un régime qui se maintient sensiblement constant pendant toute la durée de l'expérience.

Mis en observation, le 18 novembre 1911, ce filtre fonctionna sans interruption jusqu'au 30 janvier 1912. A cette date, il donnait encore de l'eau stérile (ensemencements de 1, 2 et 3 cc. sur gélatine en boîtes de Pétri, examen des boîtes au bout de 12 jours). L'eau de la canalisation, analysée quantitativement à deux reprises, le 18 novembre et le 23 decembre 1911, renfermait: la première fois, 55 bactéries, la seconde fois, 1200 bactéries par centimètre cube.

Le 9 décembre 1911—soit 21 jours après le début de l'expérience—j'envoyai sur le filtre 15 litres environ d'une eau dans laquelle j'avais délayé une culture de colibacille, de telle sorte qu'elle contenait 345,000 bactéries environ par centimètre cube. L'eau filtrée était absolument exempte de coli; et elle continua de se montrer stérile quand le filtre, sans nettoyage quelconque, eut été de nouveau branché sur la canalisation urbaine. (Je dois ajouter que la seconde analyse d'eau de la Ville y dénotait la présence du coli-bacille, qui put être découvert dans 2 cc.)

Des prélèvements d'eau filtrée étaient effectués tous les cinq ou six jours. Ils montrèrent que la bougie donnait continuellement de l'eau exempte de bactéries. Au bout de 73 jours, l'analyse bactériologique ne révélait la présence d'aucun germe dans l'eau filtrée. Je n'ai pas poussé plus loin l'expérience, la résultat acquis me semblant satisfaire amplement aux nécessités de la prâtique. En effet, les fabricants recommandent de "régénérer" les bougies poreuses au moins une fois par mois. Le filtre Mallié que j'ai examiné résiste à la pénétration, dans les circonstances indiquées, pendant un mois et demi pour le moins; et l'on considérera que durant tout ce temps il est demeuré sous pression, ce qui n'est pas d'ordinaire le cas. Il offre donc toutes les garanties désirables au point de vue de la sécurité. Je ne crois pas qu' aucun autre système de filtre ait pu fournir de résultat meilleur, voire même équivalent.

Une coupe que j'ai faite de la bougie après cette expérience, m'a montré l'intérieur du corps poreux intact, parfaitement net, sans une tache, alors que la surface extérieure était enduite d'une couche glaireuse épaisse, très compacte et cohérente. Un simple nettoyage à l'eau courante, avec un tampon de coton, suffit d'ailleurs à enlever ce dépôt et rendre à la bougie son aspect primitif, comme aussi son débit.

La Stérilisation de ces bougies peut s'effecteur par différents moyens. Monsieur le Docteur Tiraboschi a constaté que la chaleur ne les crevasse pas, pourvu que la température de 170° C. soit atteinte graduellement. J'ai vérifié le fait, en soumettant à cette temperature une bougie Mallié dont je m'étais servi, et y faisant ensuite passer de l'eau polluée: l'eau filtrée se montrait absolument stérile. De plus, étant faites d'une matière relativement dure, elles peuvent supporter sans usure appréciable et sans danger de fissures un grand nombre de nettoyages et de cuissons, ce qui leur confère une supériorité réelle sur les bougies en terre d'infusoires et même sur les bougies en porcelaine ordinaire (Tiraboschi).

Un procédé de stérilisation plus simple, très économique, à la portée de tous, et d'efficacité certaine, consiste à traiter la bougie, préalablement nettoyée à la brosse ou autrement, par une solution concentrée de permanganate de potasse. On peut ensuite éliminer le permanganate par un passage en bisulfite de soude, ou bien remonter tout simplement le filtre sur la canalisation qui le dessert et attendre pour consommer l'eau qu'elle filtre tout-a-fait incolore.

J'ai pu m'assurer également que la filtration sur bougie Mallié ne modifie pas la composition chimique de l'eau. D'ailleurs les silicates qui la constituent sont indifférente à l'action de la plupart des agents chimiques.

On sait que l'une des causes auxquelles est imputé l'encrassement des filtres, est la précipitation dans leurs pores d'une certaine quantité de carbonate de chaux. Cela peut être. Mais de l'expérience dont je parle, il ressort que ce dépot calcaire est si faible (du moins, avec les bougies en question), qu'il n'influence, pas la composition de l'eau. J'ai trouvé, en effet, exactement la même proportion de chaux totale dans l'eau non filtrée et dans l'eau filtrée. De même pour la magnésie, pour les acides chlorhydrique, sulfurique et carbonique.

En terminant, je noterai que les fabricants du Filtre Mallié sont parvenus à établir pour l'usage domestique des bougies à très grand débit, donnant un véritable courant d'eau stérilisée. Cela permet d'avoir instantanément de l'eau exempte de tout germe et de l'avoir aussi fraîche que peut la donner la canalisation. On y trouve encore l'avantage de ménager les bougies, que l'on se contentera le plus souvent de laisser en fonction pendant quelques minutes chaque jour, avant les repas, pour les besoins stricts de la consommation d'eau.

Les faits que je viens de relater me semblent propres à éclairer l'opinion de certains de mes confrères, peu au courant des perfectionnements réalisés dans ce domaine, et qui ont gardé quelque méfiance contre la stérilisation des eaux par filtration. C'est pourquoi je crois bon de les signaler au Congrès et de solliciter l'insertion de la présente note dans ses comptes-rendus.

THE APPLICATION OF CHEMISTRY TO INDUSTRIAL HYGIENE

C. T. Graham Rogers, M.D.

Medical Inspector of Factories, New York State Department of Labor, Albany, N. Y.

From an economic standpoint the question of industrial hygiene is of importance not only to the worker and manufacturer, but also to the State, for upon the State, and by that we mean the people, falls the burden of paying for the results of faulty industrial hygiene.

For many years the dangerous nature of an industry or occupation was determined from the tabulation of carefully compiled morbidity or mortality statistics, but this alone was not sufficient evidence to decisively prove that an industry itself, or the various processes of manufacture were to blame, for there was always the question of the personal hygiene of the worker to be considered, so it became necessary to determine the specific cause, whether due to the materials used, the process of manufacture, or present in the dust, fumes, vapors or gases generated during such process; this meant careful analytical measures must be resorted to, and so chemistry became an important ally to the worker in the field of industrial hygiene.

While there has been considerable research work carried on in the field of chemistry as applied to the determination of processes and materials dangerous to the health of the workers, the work as a rule, has been undertaken by independent investigators limited to one subject, or by special committees or commissions appointed to investigate certain definite processes or industries, notably the report of the Commission on Hygiene made to the Ministere Du Commerce, De L'Industre, etc., of France 1901 and entitled "Poison Industriels," and the various Committees on Dangerous Trades in Great Britain, but so far ascertainable the application of Chemistry to routine work carried on by a department or bureau charged with the enforcement of labor laws or inspection of factories and workshops, is not carried on.

Belgium has a laboratory in connection with its medical inspection service, a part of the labor department and under direction of Dr. Glibert, chief medical inspector, wherein research work is carried on as to fatigue and industrial poison.

Through the courtesy of the directors of St. Bartholomew's clinic, New York City, the New York State Department of Labor has since 1909 enjoyed laboratory facilities for research work, and as a matter of routine work has made chemical analysis of the air of factories and workrooms as well as mercantile establishments, secured temperature and humidity readings, tabulated and published them as part of the department's annual report. The courtesies of laboratory facilities for such work has also been extended to the department by the Department of Chemistry of the University of Rochester, Rochester, New York.

The method of promulgating and administering laws in relation to factories, workshops and mercantile establishments differs in the various countries. The method pursued in the various states of this country being vastly different from that of the foreign countries where power is vested in the head of a department to issue special regulations for special industry, whereas in this country such powers are as a rule entirely vested in the legislature.

In the work relating to industrial hygiene and enforcement of The Labor Laws relating to sanitation and hygiene it was deemed by the department of labor to be of the utmost importance first to discover the specific cause and the point of origin of danger from poisoning or disease to which the worker might be exposed before the proper remedy or safeguard could be applied; this meant a careful analysis of all the conditions surrounding the process of manufacturing.

In beginning the work it was found that chemical analysis of the air was one of the most necessary measures to be undertaken, this required a trained chemist so Inspector John H. Vogt, B. S. of the Bureau of Factory Inspection was assigned to assist in this work and has collaborated in this paper.

At the outset it was found that the chemistry of the air, especially in relation to industrial hygiene had been almost untouched and it was with fear and trembling that the authors entered into the work.

As a rule, methods for examination of the air have usually been confined to laboratories where numerous apparatus was at hand, and where bulk, weight and time to determine results were of small moment. The difficulties encountered by the authors were in perfecting apparatus that would be portable as well as accurate, so that the methods for analysis could be carried out in the factories, especially where a large number of determinations were to be made in a short time, this oftentimes resulted in the authors' having to resort to special methods of their own.

In the analytical work the methods have been based upon formulae as found in the accepted standard textbooks for analytical chemistry, and no claim is made for originality except as to perfection of methods and apparatus, and their adoption to portable use. In their work the authors sought for the presence of carbon dioxide, carbon monoxide, ammonia, oxidizable organic matter, total solids, bacteria and moulds, as well as for irritating the poisonous dust and acids in the air of workrooms. The apparatus and methods used in their work are described as follows.

Carbon Dioxide: The method is based upon affinity of Potassium Hydrate for Carbon dioxide, removing the carbon dioxide from the air and noting the contraction caused thereby.

The apparatus consists of measuring burette of 25 cubic centimetres capacity, 17 degrees C. with a capillary tubing graduated in parts of ten thousandths of the capacity of the burette. A compensating burette of equal capacity, and Orsat absorption bulb containing saturated solution of Potassium Hydrate, all parts of which are set in a water bath. The compensating burette and absorption bulb are connected directly with a Pettersson monometer. Mercury is used as a medium in the measuring burette for displacing and taking in air into the burette.

The process of making a determination is as follows. The stop-cock on the air burette is open, the stop-cock leading to the monometer and absorption bulb being closed, air is taken into the burette by lowering the mercury reservoir. After the burette is filled with the air sample the stop-cock is closed, the stop-cock to the monometer is open and the monometer reading is noted, the stop-cock to the monometer is now closed and is open to the absorption bulb, the air in the burette being now passed into absorption bulb and washed in the potash solution by means of raising and lowering the mercury reservoir, this operation being repeated several times, and finally brought back into the air burette; during this process the water bath is kept at a constant temperature as near as that of the room temperature by means of constantly stirring through forcing air in a fine spray throughout the water bath. After the air has been brought back into the air burette the cock to the absorption bulb is closed and opened to the monometer. The monometer reading is brought to that point first noted in taking the sample of air and is accomplished by means of a small fine adjustment screw. The contraction in the air burette is then noted which indicates the amount of carbon dioxide in parts per ten thousand volumes without further calculation.

While the determination of carbon dioxide has always been accepted as a good indicator of stagnant air where the impurities resulting from products of respirations and combustion are to be dealt with, the determination of ammonia, total solids, oxidizable organic matter, bacteria and moulds is equally important and should always be made.

While it is possible to make determinations directly in the factory, it is usually the practice when in the immediate vicinity of laboratory facilities to secure samples of the air and complete the determinations in the laboratory. For the purpose of securing samples special carrying cases and bottles were designed by the authors. (See photograph accompanying.)

The means used in securing samples consisted in the arrangement of a series of wash-bottles two or three in number each of about two hundred c.c. capacity, containing 100 c.c. of doubly distilled water, all connections being by means of ground-in joints, stoppers and tubing being of glass. The air is passed through the water and relieved of suspended matter, ammonia, bacteria, etc., and any part of the combined contents of the bottles may be examined. The method used in drawing the air through the bottles consists in a specially made air pump, the capacity of the cylinder being known and tested for accuracy every little while. For absolute accuracy a portable gas meter is used in the work. The best results are obtained by aspirating 500 to 1000 liters of air through the bottles. The use of corks or rubber stoppers and rubber tubing in connection with the bottles has been found by the authors to be objectionable in that particles may become detached and affect the analytical results. Another method for determination of dust has been in drawing air through specially designed bottles which have been previously weighed at a known temperature and a known humidity; the filtering medium being sterilized cotton and silk. The bottles are handled entirely by means of nickel forceps, all connections are glass ground-in joints. After aspirating a known quantity of air the bottles are again weighed, at the same temperature and humidity, the suspended materials in the atmosphere being indicated by the increase in weight.

For the purpose of determining the number of particles of dust in the atmosphere a cylinder of glass about 8 centimeters in diameter and about 20 centimeters in length is employed, the top and bottom of which is closed by means of two glass stoppers having ground joints. In the center of the glass tube a small Petrie dish, ruled off in squares, is suspended midway between the two ends. From one to two c.c. of pure glycerine is placed upon the Petrie dish and by means of the air pump a known quantity of air is drawn upon the surface of the glycerine. The Petrie dish is placed under the microscope of high power, the number of dust particles counted upon one square, and this multiplied by the number of squares in the Petrie dish results in the total number of dust particles in the air aspirated.

Carbon Monoxide: The method for determination in the atmosphere is based upon the reducing power of carbon monoxide in palladous chloride and water, palladium, hydrochloric acid, and carbon dioxide being formed, the carbon dioxide being estimated by means of the Pettenkofer method. The apparatus consists of three U tubes and two wash bottles. The first U tube contains potassium hydroxide, the second concentrated sulphuric acid, the third dry cotton,—the latter serves to dry the air and prevent any sulphuric acid from getting in to the palladium solution. The potassium hydroxide serves to remove carbon dioxide from the atmosphere, the sulphuric acid serving to remove the dust, ammonia, and certain hydrocarbons. Carbon monoxide not being affected by these solutions passing on and reducing the palladous chloride, being in turn oxidized to carbon dioxide, whence it is estimated as such and calculated as carbon monoxide. This method is sensitive to one part in one hundred thousandth of air, and can be readily determined. This method has the advantage over the following method which has also been employed by the department in that it obviates the use of an oil bath which has to be heated to a high temperature.

The principle is based upon the fact of the oxidation of carbon monoxide to carbon dioxide by anhydrous iodic acid, iodine being liberated, the iodine being freed is titrated with a thousandth normal sodium thiosulphate. As in the above method, potassium hydrate and sulphuric acid are used in U tubes to remove unsaturated hydrocarbon, hydrogen sulphide, ammonia and some other reducing agents. The anhydrous iodic acid is also placed in the U tubes along with three or four times the amount of large pieces of pumice stone and immersed in an oil bath heated to 150° C. The results when using three or four liters of air are able to determine one part of the gas in forty thousandth parts of air. Temperature and barometric corrections should be made to read to zero C and 760 mm.

Ammonia: The presence of ammonia in the atmosphere is suggestive of decomposition of nitrogenous organic matter in the vicinity where found. According to Mott one part in twenty-eight million is normal. The amount in the air of crowded rooms, poorly ventilated, varies, the authors having found as high as five parts per million, thus showing ammonia to be an excellent indicator of vitiated conditions. The quantitative determination of ammonia is conducted by taking 50 c.c. of the water contained in the combined contents of the sample bottles placed in a Nestlerizing cylinder held over a sheet of white paper, to this is added one c.c. of a Nestler solution, and allowed to stand five minutes. To another cylinder is added one or two c.c. standard ammonium chloride solution and brought up to the same tint as the sample being analyzed, by adding doubly distilled water free from ammonia, one c.c. of the Nestler reagent added, and after standing five minutes the color compared with the cylinder containing the original, or water being tested. The tube should be held at an angle of about 60 degrees and the color observed by looking down into the liquid. The amount of standard solution of ammonium chloride used shows the amount of ammonia present in the sample being analyzed. Should the comparing color be too weak or too strong another trial cylinder must be prepared. From the result obtained in the fractional part of the solution used it is easy to calculate the amount of ammonia present per cubic meter.

Oxidizable Organic Matter: This requires one one-hundredth of normal solution of potassium permanganate, a one one-hundredth normal solution of oxalic acid, and a twenty-five percent solution of sulphuric acid, the method of preparation may be found in any advanced standard work on volumetric analysis or water analysis. The apparatus used by the authors (see Photograph) consists of two burettes, each of which having reservoirs connected with tops of burettes with ground-in connections and sealed in such a way that no dust from the atmosphere may enter the burette or reservoirs at any time, insuring accurate determinations. The portion to be tested is placed in a flask of 150 c.c. capacity, fitted with a ground-glass stopper having a small hole in the top through which the end of the burette can pass; this small hole should also have a stopper. The stopper has a small glass vent-tube bent at right angles. The object of the hole and tube is to prevent any dust from getting into the flask during the manipulation. Ten c.c. of the standard permanganate solution is run into the flask which contains 50 c.c. of water and sufficient of the sulphuric acid to keep the manganous salts in solution. The flask is then placed over a flame and the solution boiled for five minutes. While still hot 10 c.c. of the oxalic acid solution is run into the flask, and it should be noted that the strength of the oxalic acid should exactly equal that of the permanganate solution. Again add carefully the permanganate solution drop by drop until a faint color of pink appears, the amount of permanganate solution used should then be read off, the strength of which multiplied by the number of c.c. used indicates the amount of oxygen required to oxidize the organic matter, from which, the amount of carbon dioxide formed can be calculated and finally the amount of carbon, the terminal results being oxidizable organic matter calculated as carbon. This method is not applicable where iron and substances whose oxalates are insoluble in water are present.

Dust, both organic and inorganic, play an important part in the etiology of disease. While the amount of carbon dioxide and ammonia present in the atmosphere of a factory may be low on account of open windows, vent pipes, etc., if dust be created in the process of manufacture it may fill the air of such room to such an extent as to make it unfit to breathe. Analyses of such dust can be readily determined by taking a fractional part or the entire contents of a sample bottle evaporating to dryness in a platinum crucible which has been accurately weighed before using and again after complete evaporation, the additional weight denoting the amount of suspended material, or the small dust bottles as described in the foregoing portion of the paper may be used.

The presence of wood alcohol in the atmosphere of factories is often present, particularly where lacquers are used. The method used in determining the quantity present is based on the fact of converting the alcohol into formic acid. For this purpose a known quantity of air from 250 to 500 liters is aspirated through the wash bottles containing properly distilled water placing a fractional part of the contents in a flask with four or five grams of potassium dichromate and three or four c.c. of concentrated sulphuric, allow to stand one half hour and still nearly all. Formic acid is thus formed, which can be determined by the ordinary method of acidemitry, or the acid formed may be saturated with pure barium carbonate and the formate of barium percipitated as a sulphate, if quantities are sufficiently large to so determine. Colorimetric comparison can be made with known quantities of barium sulphate in solution.

In certain industries an element of danger to the worker consists of the presence of acids in the atmosphere, among them being that of sulphuric acid. The method used in departmental work for the detection of sulphuric acid is as follows: A known quantity of air according to the amount apparently present is aspirated through the wash bottles containing the doubly distilled water to a fractional part of these combined wash bottles' contents, two drops of methyl orange are added and comparing same to a similar quantity of distilled water to which the same amount of methyl orange has been added and a sufficient number of c.c. of a ten-thousandths normal of sulphuric acid added, until the colors compare in shade. The use of methyl orange is employed in this test for the reason that it is not affected by carbon dioxide.

In the course of routine work and investigation it becomes necessary at times to determine the presence of minute quantities of toxic material suspended in the atmosphere. The method pursued is to aspirate a known quantity of air through our sample bottles, either that containing the doubly distilled water or the dry filter medium and then by means of gravimetric, volumetric or colorimetric methods determinations are completed. Among the substances determined by the Department analyses were lead, mercury, copper, zinc, arsenic and phosphorus.

Temperature: The temperature of air should be taken by means of accurate mercurial thermometers. It is needless to say accuracy of such thermometers should be established before making such tests, by the national government at Washington. Such thermometers should have a scale etched on the thermometer itself. When taking a temperature the instrument should be moved about as the zone of air surrounding the thermometer will become cooled or warmed on account of the heat contained in the instrument.

Humidity: Several devices are on the market for determining humidity among which the Swing Psychrometer serves the best purpose from which tables give the correct reading of the percentage of the humidity both actual and relative are readily obtainable.

In conclusion it is desired to draw attention to the need of research work in the chemistry of contaminated atmosphere resulting from the products of respiration, combustion, or processes of manufacture, especially where it becomes necessary to deal with small quantities of suspended or contaminating material, so that definite standards may be determined upon resulting in the enactment of better laws for the protection of the workers from poisoning or industrial diseases.

The authors desire to call attention to the importance of securing distilled water absolutely free from ammonia and suspended material and have found in practice that this may be obtained only through the use of glass through the entire process of distillation, entirely eliminating the use of corks or rubber tubing and repeatedly testing for the presence of ammonia. At no time should the air come in contact with the distilled water unless it has been filtered. The reservoir used by the authors is fitted up entirely with glass connections and ground-in joints and in drawing off the distilled water the entering air is obliged to pass through a water seal, thus protecting the supply from any contamination from without.

BIBLIOGRAPHY

Prescott & Johnson, Qualitative Analysis
The Journal of the American Chemical Society
Hemple, Gas Analysis
Sutton, Volumetric Analysis
Prescott, Organic Analysis
Cook, Select Methods
Publications of the Smithsonian Institute
Fownes, Elementary Chemistry

EPURATION DES EAUX RESIDUAIRES DE PEIGNAGES DE LAINES

PAR M. E. ROLANTS

Chef du Laboratoire d'hygiène de l'Institut Pasteur de Lille

La laine, pour être peignée, cardée, puis blanchie ou teinte doit être débarrassée de toutes les matières étrangères qui l'entourent. Ces matières sont composées de corps éliminés avec la transpiration du mouton, d'excréments et de terres.

A. Buisine a montré que les matières éliminées par la peau du mouton comprennent des composés, les uns solubles, les autres insolubles dans l'eau. En traitant la laine brute avec de l'eau distillée, on dissout des composés de potasse, les composés insolubles se dissolvent dans les alcalis. Il a trouvé les composés suivants: acide carbonique libre, carbonate d'ammoniaque provenant de la décomposition de l'urine, carbonate de potasse, acides gras volatils, acides gras plus complexes, graisses émulsionnées, phénols, acides lactiques, benzoïque, oxalique, succinique, urique, acides amidés matières colorantes. En solution aqueuse on retrouve les constituants de l'urine, et leurs produits de décomposition.

Le suint d'une laine d'Australie contenait pour 100 de residu sec: 7, 1 d'acide acétique, 4 d'acide propionique, 2, 6 d'acide benzoïque, 2, 5 d'acide lactique et 1 d'acide caproïque.

Chevreul le premier a donné une analyse de la laine brute:

Matières terreuses	26.06%
Suint soluble dans l'eau distillée froide	32.74%
Graisses neutres solubles dans l'éther	8.57%
Matières terre uses adhérant à la graisse	1.40%
Fibres de laine	32.25%

Marcker et Schulze ont donné les analyses suivantes:

	Laine de mouton		
	de Loweland	de Rambouillet	Pitchy
Humidité	23.48%	12.28%	13.28%
Graisse	7.7%	14.66%	34.19%
Matières solubles dans l'eau	21.13%	21.83%	9.76%
Mat. solubles dans l'alcool	0.35%	0.55%	0.89%
Mat. solubles dans HCl dilué	1.45%	5.64%	1.39%
Mat. solubles dans éther alcool	0.29%	0.57%	
Fibre de laine pure	43.20%	20.80%	32.11%
Poussières	2.93%	23.64%	8.38%

On donne généralement à la laine une composition moyenne plus simplifiée:

Laine dégraissée	40.0%
Potasse	4.5%
Acides gras	14.0%
Sables, terres, humidité	41.5%

Dans les petites usines de jadis on opérait le lavage à la main en placent les laines dans des paniers suspendus dans un courant d'eau. Avec l'augmentation de l'importance de cette industrie se multiplièrent les procédés et de nombreux appareils furent inventés.

Généralement l'épuration se fait en trois phases: le désuintage par lequel les laines sont débarràssées des matières terreuses et des matières solubles dans l'eau, le dégraissage effectué au moyen de solutions de savon, enfin le lavage proprement dit ou rincage. (1).

Eaux Residuaires.—La diversité de provenance des laines et des méthodes de lavage ne permet pas d'envisager la composition des eaux résiduaires comme ayant une fixité relative, c'est au

---

(1). On a aussi tenté de dégraisser la laine au moyen de dissolvants tels que l'éther de pétrole, le toluène, le sulfure de carbone, etc., mais on a reconnu que certains avaient l'inconvénient de trop crauser et de dénaturer la fibre.

contraire la variation qui est de règle et qui est très grande, comme on le remarquera dans les exemples que nous rapporterons à propos de résultats obtenus dans certaines usines.

Quoi qu'il en soit ces eaux sont toujours plus considérablement polluées que les eaux d'égoût des villes. Ce qui rend encore plus grave leur rejet dans les cours d'eau, c'est que les matières grasses qu'elles renferment se décomposent avec une extrême lenteur, si bien que les eaux sont entraînées à une très grande distance de leur point d'origine sans subir d'auto-épuration sensible, ce qui les différencie nettement des eaux d'égoût des villes. Le mal que causent ces déversements est d'autant plus grand, que, pour différentes raisons, que nous n'avons pas à étudier ici, l'industrie lainière s'est concentrée généralement en certaines villes, il s'en est suivi que les eaux d'égoût de ces villes reçoivent des volumes considérables de ces eaux résiduaires qu'elle ne savent comment triater pour satisfaire les populations échelonnées en aval de rivières qui les reçoivent.

L'ingéniosité des inventeurs s'est pourtant exercée à résoudre ce problème et les solutions proposées ont été nombreuses comme nous le verrons plus loin.

Dans l'application on a pu arriver à des rèsultats assez satisfaisants pour la prévention de la contamination des rivières, mais au point de vue industriel il n'en est pas de même. Bien que l'on puisse retirer de ces eaux des produits marchands, le prix de la vente ne compense généralement qu'en partie les dépenses nécessitées pour les obtenir, aussi les industriels ne cherchent qu'à éloigner cette éventualité.

Pour la potasse, elle ne peut être récupérée que dans les usines importantes, qui en produisent des quantités considérables; ainsi une grande usine de Roubaix en a obtenu 1250 tonnes en 1909. Pour cela les eaux de désuintage, seules traitées, sont évaporées et le résidu calciné dans des fours analogues aux fours Porion employés pour le traitement des vihasses de distilleries de mélasses.

Les eaux résiduaires que nous avons à examiner sont donc pour les petites et moyennes usines, toutes les eaux usées, pour les grandes usines toutes les eaux de lavage à l'exclusion des eaux de désuintage.

Nous avons divisé les différents procédés de traitement des eaux résiduaries de peignages de laines, que nous allons passer en revue, en plusieurs catégories:

1° Traitement mécanique;
2° Traitement par les acides;
3° Traitement par les alcalis;
4° Traitement par les sels;
5° Traitement par évaporation.

TRAITEMENT MÉCANIQUE

Procede par Battage.—Richard Lagnie.—Le procédé par battage est un procédé mécanique ne nécessitant pas l'addition aux eaux résiduaires brutes d'un acide ou d'un autre produit chimique. Les eaux sont séparées d'abord des sables et des matières terreuses dans un bassin de décantation. Elles sont pompées ensuite dans un bassin en bois étroit et très long, environ 45 métres de long et 2 métres de large, divisé en 22 compartiments. Chaque compartiment est lui-même divisé en deux parties, la plus petite d'environ Om. 70 de long sur la largeur du bassin contient l'agitateur ou batterie, la plus grande environ 1 métre de long est parcourie par une raclette qui rejette les mousses dans deux caniveaux qui courent de chaque côté du bassin. Par le battage il se produit des mousses qui entraînent les graisses insolubles contenues dans l'eau. Le courant de l'eau est réglé par une vanne à glissière, fixée transversalement dans chaque compartiment. Les eaux sont ainsi battues par les 22 appareils, mais on peut en réduire le nombre en diminuant la vitesse d'écoulement de l'eau. Chaque batteur a environ Om. 60 de diamètre et 1m. 80 de large, il est en bois sauf les axes et les dents qui sont en fer. Ces dents ont OM. 15 de long, 4 mm. 7 d'épaisseur et sont écartées de Om. 018; chaque batteur fait 80 tours par minute.

Les écumes sont pompées dans des bassins en bois où elles sont chauffées à 60° et additionnées de 1kgr. d'acide sulfurique par mètre cube, pour séparer les graisses dont l'eau contient environ 5 %. Les eaux acides sont mélangées aux eaux qui doivent subir le battage. Le magma est passé au filtre-presse.

La graisse qui s'en découle est partiellement purifiée par l'addition d'une petite quantité d'acide (1 kilogramme d'acide par 100 kilogrammes de graisse). Les tourteaux sont vendus comme engrais.

On obtient aussi trois qualitiés de graisse, les premiers compartiments fournissant la meilleure qui est couleur brun clair, la moins bonne étant brun noir provient des derniers compartiments.

Nous avons analysé les eaux résiduaires d'une usine employant le procédé par battage et nous avons obtenu les résultats suivantes:

	Eau brute	Eau décantée		Eau après traitement des mousses
		Avant battage	Après battage	
Extrait à 110°	12 gr. 760	7 gr. 730	5 gr. 230	3 gr. 840
Résidu fixe au rouge	5 gr. 950	2 gr. 390	2 gr. 180	2 gr. 420
Perte au rouge.....	6 gr. 810	5 gr. 340	3 gr. 050	1 gr. 420
Ammoniaque......	0 gr. 064	0 gr. 0315	0 gr. 0315	0 gr. 033
Azote organique en Az.............	0 gr. 1115	0 gr. 081	0 gr. 056	0 gr. 053
Alcalinité en CO3 Ca	0 gr. 490	0 gr. 540	0 gr. 540	"
Acidité en SO4 H2..	"	"	"	0 gr. 147
Matières grasses....	4 gr. 130	2 gr. 340	1 gr. 890	"
Matières grasses après traitement par l'acide.......	5 gr. 210	4 gr. 239	2 gr. 486	0 gr. 830

Dans cette usine on a préparé en 1909,770 tonnes de suintine et 1,000 tonnes de tourteaux.

Procédé de Mollins.—(1). Dans les eaux savonneuses contenant des acides gras émulsionnés, l'argile produit un précipité volumineux qui se dépose, 1 gramme d'argile bleue ou terre glaise, à 15–20 pour 100 d'eau, suffit pour le traitement d'un litre d'eau. On est ainsi parvenu à éliminer Ogr. 787 de matières organiques par litre. Les tourteaux ainsi obtenus peuvent être dégraissés par le sulfure de carbone ou brulés pour en faire du gaz d'éclairage.

(1). D'après De la Cour.

Par ce procédé on peut récupérer la majeure partie des corps gras qui ont échappé à la précipitation de l'eau résiduaire par l'acide chlorhydrique. Ce procédé nécessitant la mise en liberté des acides gras, s'ils n'y sont pas, les eaux doivent être additionnées au préalable d'acide chlorhydrique.

TRAITEMENT PAR LES ACIDES

C'est le procédé le plus généralement employé. L'acide chlorhydrique ou l'acide sulfurique décomposent les savons et mettent en liberté les acides gras insolubles qui par leur faible densité, viennent flotter à la surface des liquides, et on peut assez facilement les enlever soit par écumage, soit en laissent couler d'abord le liquide sous-jacent et en ne retenant que le magma graisseux.

Les résultats économiques ne sont pas toujours très brillants, et, si l'on s'en rapporte aux nombres donnés par Naylor, la graisse récupérée varie suivant les usines de 19, 8 à 82, 4 pour 100 laissant donc une perte de 17, 6 à 80, 2 pour 100.

Si par une opération bien conduite on peut retirer la plus grande partie des acides gras, l'épuration n'est pas parcela même obtenue. L'eau ainsi traitée est encore extrèmement polluée, et, ce qui est plus grave, elle est acide. Aussi est-on obligé souvent de la neutraliser par la chaux, comme nou sle verrons plus loin, soit par ordre des pouvoirs publics, soit pour éviter la destruction trop rapide des canalisations d'évacuation.

Nous avons pu suivre, dans une usine de Roubaix, le travail de récupération des graisses. Les eaux de lavage des laines grossièrement décantées des terres qu'elles entraînent, sont additionnées d'une certaine quantité d'acide sulfurique, puis passées au filtre-presse qui retient les acides gras avec beaucoup d'impuretés. Les eaux filtrées et les matières en suspension sont évacuées à l'égoût. Les tourteaux des filtres sont pressés à chaud et les acides gras s'écoulent en grande partie.

Le tourteau est desséché, puis dégraissé par le sulfure de carbone; le résidu est vendu comme engrais.

Les eaux de lissage sont aussi traitées par l'acide chlorhydrique, mais à part, comme les eaux de lavage.

L'expérience a montré que la température à laquelle on traite les eaux par l'acide a une grande influence sur la qualité des graisses obtenues, dont le prix varie de quinze à vingt-cinq francs les 100 kilogs. Quant à l'épuration, qui évidemment n'est pas envisagée, on peut se rendre compte par nos analyses qu'elle est à peine commencée.

En grammes par litre	Eaux de lavage Traitement par l'acide					
	AVANT			APRES		
	Maximum	Minimum	Moyenne	Maximum	Minimum	Moyenne
Extrait à 110°.....	25.010	17.380	20.120	16.400	5.605	10.455
Résidu fixe au rouge	6.680	3.960	5.220	6.890	2.165	4.485
Perte au rouge	18.330	12.350	14.900	9.510	3.445	5.970
Ammoniaque	0.217	0.115	0.170	0.205	0.096	0.155
Azote organique en Az.............	0.380	0.189	0.275	0.208	0.102	0.135
Alcalinité en CO3 Ca	2.400	2.010	2.125	“	“	“
Acidité en SO4 H2	“	“	“	1.391	0.833	1.028
Matières grasses (par éther)......	11.308	8.410	10.136	6.484	3.420	4.504

En grammes par litre	Eaux de lissage Traitement par l'acide					
	AVANT			APRES		
	Maximum	Minimum	Moyenne	Maximum	Minimum	Moyenne
Extrait à 110°.....	9.020	3.240	5.840	2.060	1.945	1.980
Résidu fixe au rouge	1.280	0.460	0.805	1.570	0.980	1.125
Perte au rouge	7.740	2.780	5.035	1.080	0.375	0.855
Ammoniaque	0.0085	0.0055	0.072	0.0085	0.0054	0.970
Azote organique en Az.............	0.154	0.0775	1.115	0.0235	0.0152	0.0215
Alcalinité en CO3 Ca	0.900	0.780	0.805	“	“	“
Acidité en SO4 H2	“	“	“	0.255	0.153	0.210
Matières grasses (par éther)......	3.460	3.060	3.150	0.580	0.305	0.41

Les procédés *Delattre* comprenaient primitivement la séparation des acides gras par addition d'acide sulfurique, puis neutralisation des eaux acides, débarrassées des graisses, par un lait de chaux. Après décantation les eaux étaient considérées comme suffisamment épurées. Ils se complètèrent plus tard par un appareil, qui, s'il avait permis d'obtenir les résultats annoncés, aurait présenté un très grand perfectionnement. Les boues obtenues par précipitation par l'acide étaient traitées à une certaine température dans des colonnes par un dissolvant. La boue cheminait de haut en bas et était mèlangée intimement avec le dissolvant qui circulait de bas en haut par des palettes.

Dans certaines usines anglaises on se contente de décanter les eaux des matières terreuses puis de les traiter à l'acide. Le magma est recueilli et livré à des industriels qui en extraient les graisses. Les résultats obtenus sont quelquefois très médiocres comme le cite M. Maclean Wilson qui a constaté que dans une usine 40 pour 100 des graisses s'échappaient avec les eaux et que pour une autre 17 pour 100 étaient récupérées.

L'auteur attribue ces mauvais résultats à deux causes principales. L'acide sulfurique était ajouté en quantité insuffisante, pour obtenir la séparation de la matière grasse, ou bien l'acide était versé dans une eau trop chaude, la séparation n'étant complète qu'à une température relativement basse. De plus, le mélange de l'acide et l'eau n'est pas réalisé d'une façon parfaite. Il serait peut-être économique, ce qui permettrait de supprimer les bassins de séparation, de filtrer les eaux acides comme cela se fait pour les autres eaux industrielles.

Toutefois, ce procédé ne peut donner un effluent qu'on puisse rejeter impunément dans une rivière, car il est acide et contient une grande quantité de matières organiques solubles qui, après saturation de l'acidité, fermentent.

Pour épurer ces eaux acides, il faut d'abord les traiter chimiquement, les meilleurs réactifs sont la chaux et le sulfate ferrique. Comme indication, il a fallu pour l'eau de l'

	Usine A	Usine B
Pour saturer l'acidité	0gr. 850 par litre de chaux et	0.930
Pour précipiter	1gr. 970	1.870
	3gr. 580 par litre de sulfate ferrique	2.000

Ce traitement produit un précipité volumineux qui formait à l'usine A 24 pour 100 du volume total du liquide, à l'usine B 16 pour 100 du volume total du liquide, mais ces volumes seraient réduits de beaucoup si les graisses étaient extraites complètement avant la précipitation. Même dans ce cas, l'auteur estime à environ 250 kilogrammes les boues à 90 pour 100 d'eau produites par mètre cube. Il serait probablement économique de passer ces eaux au filtre-presse au lieu de les abandonner à la décantation.

On peut par exemple avec un sel de fer, obtenir la précipitation des matières organiques et des graisses, ces dernières sont séparées ensuite en acidifiant les boues.

Même après précipitation et décantation parfaite, le liquide est encore fortement putrescible et on a fait des expériences, de son traitementt sur les filtres biologiques. On obtient des effluents imputrescibles en déversant à intervalles réguliers de petites quantités d'eau pendant 8 heures par jour au taux de 187 litres par mètre cube de matériaux. Au bout d'un mois les résultats étaient aussi satisfaisants, mais on constata un commencement de colmatage à la surface des lits.

Toutefois, le prix de ce traitement est considérable.

TRAITEMENT PAR LES ALCALIS

On a employé le carbonate de soude pour traiter les eaux savonneuses d'une certaine pureté, mais il ne peut en être question pour les eaux résiduaires de peignages de laines. Seule, la chaux est d'un usage courant, comme du reste pour certaines autres eaux résiduaires industrielles. Nous aurons occasion d'y revenir à propos des expériences de Grimonpont pour les eaux de Roubaix-Tourcoing.

On peut cependant employer avec avantage l'épuration à la chaux lorsque les eaux contiennent peu de matières grasses et qu'elles sont diluées par des eaux de teinture comme à Livingstone Mills Butley (Angleterre).

TRAITEMENT PAR LES SELS

On a proposé un certain nombre de réactifs chimiques qui n'ont pas été employés pour la plupart à cause de leur prix trop élevé: le chlorure ferreux (Legrand), le chlorure de manganèse (Gaillet), le ferrozone et la chaux (Howatson), le liquide provenant du lavage des lignites, sulfates ferreux, ferrique et l'alumine (Houzeau), le sulfate ferreux et la chaux, la magnésie, puis, plus tard, le phosphate de soude ferrugineux (Boblique), etc.

MM. Gaillet et Huet ont obtenu de bons résultats avec des sels acides de fer.

Les eaux sont débarrassées des boues par décantation, ces boues peuvent être utilisées comme engrais. Les eaux sont alors additionées d'une solution de perchlorure de fer, additionnée d'acide chlorhydrique; on écume les acides gras séparés qui viennent flotter à la surface et on les presse à chaud. Les eaux sont alors neutralisées par un lait de chaux qui produit une précipitation abondante, elles sortent des bassins de décantation bien clarifiées. Les boues calcaires pressées donnent des tourteaux susceptibles d'être employés comme engrais. Le traitement des eaux provenant de laines non désuintées a donné les résultats suivants; d'après les analyses publiées par M. Gaillet (par litre).

	Eau brute	Eau épurée
Matières minérales solubles.......	12 gr. 68	13 gr. 14
Mat. minérales insolubles.........	1.34 total 14.02	néant total 13.14
Mat. organiques volatiles.........	13.60	3.70
Mat. organiques fixes............	2.12 total 15.72	1.05 total 4.75
Total.....................	29.74	17.89

Ce procédé essayé à Fourmies (Nord) fut reconnu comme le meilleur et recommandé en 1881 par une Commission nommée par le Conseil de Salubrité du départment du Nord.

Les tourteaux des filtres peuvent, après sèchage, servir à la fabrication du gaz d'éclairage dont la valeur, d'après le rapport de la Commission, peut couvrir largement la dépense résultant de ce traitement.

Un procédé analogue fut employé au peignage Tordeux, à Avesnelles (Nord) jusque 1890, date de l'arrêt de l'usine.

Les eaux étaient traitées par un mélange de chaux et de sulfate de fer, puis filtrées sur des fascines et sur du sable. Le précipité, d'une épaisseur de 15 à 20 centimétres, était enlevé à la bèche et séché au soleil. On l'employait pour la fabrication du gaz d'éclairage de l'usine.

M. Tordeux nous assure, dans les renseignements qu'il a bien voulu nous communiquer, que les résultats d'épuration ont toujours été excellents. Il ajoute toutefois que l'application de ce procédé pour une grande usine lui paraît difficile par suite des grandes surfaces de terrains nécessitées pour les filtres et le séchage des boues.

TRAITEMENT PAR ÉVAPORATION

Traiter les eaux résiduaires de lavage de laines de façon à les réemployer sans avoir jamais à en rejeter; récupérer tous les produits utilisables contenus dans ces eaux, tel est le but du procédé Smith et Leach brévété en Angleterre en 1900. Les appareils employés sont un évaporateur Yaryan, un séparateur par centrifugation, et un incinérateur cylindrique rotatif.

Les eaux savonneuses, au sortir de bacs de lavage de la laine, passent dans des bassins de décantation où elles abandonnent les sables et les boues. Ces bassins sont au nombre de trois et ont une capacité totale égale au volume des eaux écoulées pendant un jour et demi, deux sont en usage, le troisiéme en nettoyage.

Les eaux sont alors évaporées dans l'appareil Yaryan (1) jusqu'à réduction à un dixième ou à un quinzième de leur volume primitif. L'évaporateur est à quadruple effet, l'ópération étant répétée quatre fois, à des températures et pressions successivement plus basses et chaque section consiste en un chauffeur, une chambre à réception et un récepteur où la vapeur est séparée du liquide concentré et s'écoule dans un bassin en attendant l'emploi. On recueille ainsi environ 80 pour 100 des eaux.

Le liquide concentré après avoir été chauffé à une température voisine du point d'ébullition est traité dans un séparateur centrifuge (2) basé sur le principe des écrémeuses de lait.

(1) et (2). Naylor signale que l'évaporateur Kestner peut donner de bons résultats et comme un très bon type de separateur celui de Fawett Presten et C° et C. M. Mathey.

On a ainsi d'un côté les boues et sables, puis les eaux savonneuses contenant toute la potasse de la laine et enfin une dernière couche consistant presqu'entièrement en graisse de laine.

Les boues et sables sont retirés de temps à autre à la main. Les liquides sont évacués par des conduites séparées; les graisses sont purifiées par chauffage avec de 'leau, puis séparation par refroidissement; les eaux savonneuses sont évaporées de nouveau de façon à réduire le volume des trois quarts. Les dernières passent alors dans un incinérateur cylindrique rotatif où la matière organique étant brulée, il ne reste que du carbonate de potasse.

On a ainsi obtenu séparément:

1° Eau distillée:
2° Graisse de laine;
3° Carbonate de potasse brut;
4° Boues et sables.

L'eau distillée n'est pas parfaitement pure, elle contient de l'ammoniaque et une trace de graisse entraînée pendant l'évaporation, mais elle est de très grande valeur pour le lavage des laines. Les inventeurs estiment qu'il faut de 15 à 30 pour 100 de savon en moins pour le travail si on emploie cette eau au lieu de celle distribuée dans les villes et si elle est utilisée à la température exigée pour le lavage des laines.

La graisse de laine ainsi obtenue a une plus grande valeur que le graisse noire du traitement des eaux par l'acide sulfurique, attendu qu'elle est obtenue des eaux non fermentées et sans emploi d'acide minéral. Elle ne contient pas d'acide gras et peut être employée sans purification comme lubréfiant ou pour tous les usages de la graisse noire purifiée. Le prix marchand de cette graisse est double de celui de la graisse noire. Elle est reconnue comme lubréfiant (1) de valeur en présence de l'eau à une température supérieure à 100° F (37°8 C).

Le carbonate de potasse contient 50 à 70 pour 100 de carbonate pur, suivant la proportion de sables et de boues entraînés et peut être employé à l'état brut pour le lavage de la laine, soit vendu pour être purifié.

---

(1). Cette graisse ne contenant ni acides gras, ni huiles, ni glycerine, n'a aucune action corrosive sur les métaux.

Le sable et les boues ont peu de valeur comme engrais mais peuvent être employés avec avantage comme amendments.

Ce procédé présente deux avantages accessoires; les eaux étant traitées à l'état frais, l'épuration s'effectue sans nuisance; de plus, l'ensemble des appareils occupe un espace très restraint comparativement à celui nécessité par les bassins de décantation indispensables pour les procédés par précipitation.

Ce procédé était installé en 1900 aux Field-Head Mills de Bradford pour traiter 55 mètres cubes par jour. Le prix de l'installation totale a été de 112.500 francs. Les dépenses en charbon et en main d'oeuvre ont été considérables. Il faut en effet, trois ouvriers et une consommation de 20 tonnes de charbon par semaine. D'un autre côté, la valeur des produits obtenus est très grande. En temps ordinaire, on lave 4.500 kilogrammes de laine par jour contenant 12 à 15 pour 100 de graisse et 6 à 7 pour 100 de carbonate de potasse. Le prix de la graisse peut être donné de 500 francs la tonne et celui de la portasse de 575 francs la tonne et comptant 0fr. 19 le mètre cube d'eau distillée, la valeur totale des sous-produits est de 400 à 500 francs par jour.

Il n'est pas économique de traiter moins de 454 litres d'eau par heure et le prix de l'installation étant très élevé il y aurait avantage pour les industriels de se grouper pour que toutes les eaux soient traitées dans une usine centrale.

D'après les affirmations de la Yaryan Company, il faut, dans ces appareils, 1 kilogramme de charbon pour évaporer 40 kilogrammes d'eau et l'eau distillée produite revient à 0fr. 55 le mètre cube en tenant compte du prix de l'appareil, de la main d'oeuvre et du charbon.

Un autre procédé de triatement par évaporation a été employé dans l'usine de Thomas Biggart and C°, à Dabry Ayrshire (Angleterre).[1]

Dans cette usine, le dégraissage des laines est obtenu par le savon de potasse seul.

Les eaux savonneuses du premier bassin contenant environ les 9-10 des graisses et de la potasse sont écoulées dans un bassin rectangulaire dans lequel elles laissent déposer les sables, etc., pendant 12 heures.

[1] D'après Naylor.

On les envoie alors dans un appareil évaporateur où on les concentre jusqu'à consistance sirupeuse. Le liquide, mis à refroidir, dans des bassines, abandonne les graisses qui surnagent et qu'on enlèvè de temps à autre. La partie semi-liquide qui reste, contenant, la potassee les matières organiques autres que les graisses, est coulée dans un four à incinérer. La chaleur dégagée par ce four, les matières organiques brulant sans addition de combustibles, est utilisée pour l'évaporation des eaux. La potasse brute est purifiée pour rentrer dans le travail.

La graisse est chauffée avec de l'acide sulfurique et peut alors être vendue ou purifiée plus complètement.

Ce procédé est paraît-il rénumérateur, il n'exige qu'un emplacement restreint et évite toute nuisance, cependant il ne paraît pass 'être répandu. On traite ainsi de 27 à 31 mètres cubes d'eau par semaine. On en retire par semaine, 350 kilogrammes de graisses à 150 francs la tonne et 500 kilogrammes de potasse à 412 fr. 50 la tonne. 100 kilogrammes de sels (sulfate et chlorure de poassium) à 175 francs la tonne. On doit employer environ, pour l'évaporation, 200 kilogrammes de charbon.

EPURATION DES EAUX D'EGOUT DES VILLES REJETANT DES EAUX RESIDUAIRES DE PEIGNAGES DE LAINES

France.—Les villes de Roubaix et Tourcoing renferment un certain monbre de peignages de laines et quelques unes de ces usines sont très importantes, nous an avons cité deux plus haut.

Si, dans quelques grandes usines, on pratique jusqu'à un certain point la récupération des graisses, il n'en est pas de même pour les autres. Aussi les eaux de l'Espierre, petit ruisseau qui reçoit toutes les eaux usées de ces deux villes, sont-elles très polluées et vont contaminer fortement l'Escaut en Belgique. A la suite de protestation du gouvernement belge on construisit une usine d'épuration à Grimonpont. Des expériences nombreuses y furent entreprises, on peut les diviser en quatre séries principales:

1° Le premier réactif et le plus employé fut la chaux dont l'usine est outillée pour produire la quantité nécessaire. L'épuration obtenue avait été jugée suffisante dans les essais faits devant la Commission internationale de 1896. Mais cette épuration est d'un prix élevé, elle est en outre très imparfaite. La décantation n'était pas toujours très bonne et, ce qui fut plus grave, on ne parvenait pas à se débarrasser des boues produites par la précipitation. Ces boues sont sans valeur comme engrais, car leur destruction est très lente dans la terre qu'elles colmatent et, de plus, leur dessication pour en permettre l'enlèvement était très difficile. Enfin on reproachait à l'effluent une alcalinité propre au développement des microbes de putréfaction.

2° En 1894, MM.A. et P. Buisine proposèrent l'emploi du sulfate ferrique à 60°. On obtint ainsi une bonne précipitation et des boues qui, seches, contenaient 30 pour 100 de graisses (dont 60 pour 100 saponifiables).

3° MM. Delattre proposèrent ensuite un procédé basé sur l'emploi de l'acide sulfurique étendu, qui déplace les acides gras des savons contenus dans les eaux de peignages et les précipite en même temps que les autres graisses et toutes les matières en suspension.

Les eaux additionnées de réactif étaient abandonnées à la décantation, puis écoulées au cours d'eau. Le dépôt boueux, sans dessication préalable, étaient alors traité dans des appareils spéciaux par la benzine ou un dissolvant analogue. La solution de matières grasses était distillée, la benzine récupérée et il restait comme résidu la graisse brute. La boue dégraissée était facilement passée au filtre-presse et les tourteaux obtenus étaient vendus comme engrais.

Les essais effectués à Grimonpont furent loin de donner les résultats annoncés par les inventeurs et firent ressortir en définitive le prix de l'eau épurée au taux excessif de Ofr. 07 par mètre cube. Ils furent abandonnés.

Nous avons fait, nous-mêmes, quelques essais au laboratoire en 1903 pour déterminer les quantités moyennes d'acide sulfurique, de chaux, ou de sulfate ferrique nécessaires pour obtenir, non pas l'épuration, mais une bonne clarification.

Dans toute précipitation chimique, il y a un rapport déterminé entre la matière à précipiter, la quantité de cette matière et la proportion de réactif pour obtenir la meilleure élimination. Nous avons reconnu que l'acide devait être employé en excès pour obtenir une clarification satisfaisante.

Après le traitement par la chaux, même à la dose optimum, les matières en suspension entraînées sont en trop grande quantité, de plus, les eaux sont très alcalines.

Par contre, le sulfate ferrique donna d'excellents résultats, l'effluent est neutre et ne contient plus de matières en suspension.

La précipitation par la chaux fournit le moins bon rennement en matières grasses. Il est vrai que les graisses ainsi obtenues sont très peu colorées et semblent, au premier aspect, plus utilisables. Les graisses à l'acide sont vert foncé, celles au sulfate ferrique sont fortement colorées en rouge par les savons de fer.

Nous conclusions à cette époque, que l'on peut obtenir une bonne clarification par l'emploi d'un réactif chimique, tel que le sulfate ferrique, mais que l'épuration proprement dite était loin d'être parfaite.

4° M. Bienvaux, ingénieur chargé du service, reprit les essais à la chaux, mais au lait de chaux concentré utilisé jusqu'alors il substitua un lait extrêmement dilué de façon qu'il ne contienne plus en suspension que des particulines très fines de chaux. Il put ainsi diminuer considérablement les quantités de chaux employées et obtenir de meilleurs résultats. Au, lieu de 2 à 3 kilogrammes par mètre cube, il montra qu'il suffisait de 400 à 500 grammes de chaux.

Après le départ de M. Bienvaux, son successeur, M. Grimpret a entrepris, sur la demande de M. Dron, Maire de Tourcoing, une série d'expériences à Tourcoing même, par la méthode proposée par M. Bienvaux, mais sur les eaux de peignages seules, non diluées par les eaux pluviales, les eaux ménagères et les autres eaux industrielles. Après quelques tâtonnements dus à la grande concentration des eaux, (12 grammes de résidu sec par litre), il obtint un effluent jaune ne contenant que très peu de matières en suspension et toutes les graisses étaient entraînées dans les boues.

L'évacuation des boues est le problème le plus difficile à résoudre. Des essais de calcination faits à l'usine à gaz de Tourcoing donnèrent un gaz plus éclairant que le gaz ordinaire mais d'un prix de revient plus élevé que ce dernier, parce que les sous-produits (coke, goudron, brai, etc.) qui constituent une des principales resources des usines à gaz, n'existent pas si on emploie ces boues.

Celles-ci étant très riches en matiéres organiques composées en majeure partie de graisses et de savons, sont très combustibles. Des essais effectués avec des gazogènes ont montré que le poids de boues nécessaires pour obtenir un cheval-heure peut être évalué à un kilogramme environ. Les cendres peuvent être utilisées car on y rencontre tous les éléments de la chaux hydraulique.

D'après les dernières expèriences sur l'épuration des eaux de peignages traitées dans les conditions indiquées ci-dessus, le prix de revient du mètre cube ne doit pas dépasser, pour l'installation complète, Ofr. 025 en comptant l'amortissement du capital de premier établissement en 30 années, évalué à 1.200.000 francs et négligeant les diverses sources de revenus: gaz pauvre, cendres, etc.

In a proposé enfin une méthode d'épuration plus complète, car si la précipitation par la chaux permet d'obtenir un liquide bien clarifié et d'éliminer les matières grasses, l'eau traitée contient encore une quantité de matières organiques putrescibles. Cette methode consisterait à traiter séparément les eaux de peignages de laines par la chaux, l'effluent de cette première opération serait réuni aux eaux ménagères et aux autres eaux industrielles et épuré par les procédés biologiques artificiels. On ne peut songer à l'irrigation culturale dans une région surpeuplée comme celle qui environne les villes de Roubaix et de Tourcoing.

Cette méthode a été expérimentée à Tourcoing en 1906 où d'une part, M. Grimpret fut chargé de traiter les eaux de peignages de laine seules comme il a été rapporté plus haut, d'autre part les eaux ménagères et industrielles furent épurées dans une installation, établie sur nos indications et analogue à celle de la station expérimentale de La Madeleine. Des deux côtés les résultats obtenus montrèrent que la solution est ainsi possible. Il semble bien probablt, en effet, que le mélange de l'effluent des eaux de peignages traitées par la chaux aves les autres eaux usées pourra être épuré facilement par les lits bactériens.

Belgique.—La ville de Verviers présente une situation analogue à celle de Roubaix et de Tourcoing, elle rejette dans la Vesdre, affluent de la Meuse ses eaux d'égoût contenant une forte proportion d'eaux résiduaires de peignages de laines. Des expériences d'épuration furent tentées en 1901 par MM. Delattre, expériences qui furent suivies à l'Institut Pasteur sur la demande de M. le Gouverneur de la Province de Liège. Ces eaux traitées par un mélange de sulfate ferrique et d'acide sulfurique donnaient un effluent bien clarifié mais encore putrescible, qu'on pouvait épurer très facilement sur les lits bactériens.

M. Schoofs a tenté d'épurer directement les eaux d'égoût de Verviers par les méthodes biologiques seules, fosses septiques et lits bactériens, sans traitement chimique préalable et a constaté une diminution des matières organiques suffisante pour que dans la plupart des cas l'effluent des lits bactériens ne soit plus putrescible.

Angleterre.—L'épuration des eaux résiduaires de peignages de laines se fait ordinairement, en Angleterre, de la façon suivante, on les envoie d'abord dans une cuve de décantation où elles abandonnent les matières terreuses et argileuses en suspension, puis on les fait traverser un tamis qui retient les filaments de laine entraînés et on les recueille dans un bassin où elles subissent la prècipitation chimique. On utilise le plus souvent pour cette précipitation, l'acide sulfurique, par exemple à Brighouse, à Pudsey, à Keighley, à Bradford, à Wakefield, à Norden Butterwort, parfois on a recours au lait de chaux et au perchlorure de fer par exemple à Norden-Kelsall et Kemp. Le mélange de l'eau et du précipitant se fait dans le bassin au moyen d'un agitateur, ou de dispositifs spéciaux tels qu'insufflation d'air comprimé, emploi de roues hydrauliques où se fait le mélange, etc. La quantité d'acide sulfurique à employer et la durée du contact à adopter dépendent de la concentration de l'eau. Dans les petites usines, on laisse souvent les bassins remplis pendant deux ou trois jours, et on laisse ensuite s'écouler le liquide décanté.

Les boues riches en matières grasses qui se précipitent dans les bassins sont le plus souvent envoyées sur des filtres de draînage formés de scories, ou pressées au filtre à toiles.

Les boues désséchées sont alors traitées en vue de la récupération des graisses, on les presse à chaud, les graisses s'écoulent sous la forme d'une huile brune qui se vend en Angleterre de 150 à 300 francs les 1.000 kilogrammes. Cette extraction ne se fait pas dans les petites usines qui vendent ordinairement leurs boues à des industriels qui les traitent et écoulent les graisses obtenues surtout dans les savonneries. Les tourteaux qui restent après le pressurage sont le plus souvent vendus parfois donnés pour l'utilisation agricole. Dans quelques villes du Lancashire, on envoie ces résidus par chemin de fer dans le Comté de Kent où ils servent pour la fumure du houblon. A Bradford, dont les eaux d'égoût renferment 13 pour 100 d'eaux résiduaires de peignages de laines, les tourteaux contiennent après pressurage, encore 15 à 25 pour 100 de matières grasses, et ne peuvent être utilisés en agriculture, on les mélange avec un septième de leur poids de charbon et on les brule. A Rochdale, où la proportion d'eaux résiduaires de peignages de laines atteint seulement 9 pour 100, les agriculteurs voisins utilisent environ la moitié des tourteaux, l'autre moitié est expédiée plus loin par chemins de fer ou canaux.

La méthode d'extraction des graisses des eaux de peignages par centrifugation est également à l'étude dans les installations anglaises. Les matières grasses séparées par l'appareil centrifuge sont fondues plusieurs fois, purifiées par ébullition dans l'eau, et finement malaxées avec de l'eau. Elles sont vendues dans le commerce sous le nom de "lanoline."

Les eaux qui s'écoulent des bassins de précipitation chimique sont envoyées dans des fosses de décantation, où elles se réunissent le plus souvent avec les autres eaux résiduaires de l'usine (eaux de lavage, eaux ménagères, matières fécales, etc.). Elles y subissent une décantation; parfois on neutralise leur acidité, puis on les laisse s'écouler dans les cours d'eaux ou dans les égoûts.

L'extraction des graisses des eaux résiduaires de peignages de laines est souvent très rémunératrice, quand il s'agit d'usines importantes; une fabrique des environs d'Halifax retire ainsi chaque année un bénéfice de 12.000 francs par l'extraction de ces graisses qui s'écoulaient autrefois dans le canal. A Bradford, on s'est plaint cependant que les fabriques de la ville n'avaient monté l'extraction des graisses que pour en retirer un bénéfice et non pas pour épurer leurs eaux, de sorte que cette partie du travail était négligée dès que le prix des graisses était trop bas pour rendre l'exploitation rémunératrice. On ne retient qu'environ les trois quarts des matières grasses, le reste s'écoule au canal avec l'excès d'acide sulfurique ou de sels de fer. D'ailleurs l'épuration est souvent considérée dans les usines comme un travail sans importance qu'on confie par suite à des ouvriers inexpérimentés et sans valeur.

Quand les eaux résiduaires de peignages de laines doivent être épurées en mélange avec d'autres eaux d'égoût, on a recours le plus souvent à un traitement préalable par précipitation chimique, par fosses septiques ou par bassins de décantation, et l'effluent est épuré par épandage ou par lit bactérien.

Amerique.—Les expériences de A. W. Clark à la station de Lawrener ont montré que la filtration des eaux de peignages seules donne de mauvais résultats, mais lorsqu'elles sont diluées dans un grand volume d'eaux d'égoûts domestiques, l'épuration par filtration intermittente peut être satisfaisante.

On peut obtenir une bonne clarification des eaux de peignages en employant des quantités assez importantes de réactifs chimiques, l'effluent est alors épuré par les lits bactériens.

Dans quelques usines on récupère les graisses par la précipitation par l'acide sulfurique comme en Europe.

RÉSUMÉ ET CONCLUSIONS

La diversité des méthodes employées pour épurer les eaux résiduaires de peignages de laines montre combien, dans la plupart des circonstances, le problème est difficile à résoudre.

Dans les usines peu importantes, le volume des eaux résiduaires étant relativement faible, l'épuration chimique est suffisante, lorsque l'effluent doit être rejeté dans un égoût de ville ou dans une rivière à grand débit. On peut pratiquer la récupération des graisses par un des procédés que nous avons décrits, mais l'effluent doit être ensuite traité par la chaux pour neutraliser l'eau et précipiter une partie des impuretés. Cette dernière précipitation est toujours facilitée et rendue plus efficace par l'addition de sulfate ferrique. Dans d'autres cas on précipite simplement par un lait de chaux dilué; les boues séchées peuvent être brûlées ou traitées dans un appareil gazogène.

Les grandes usines sont généralement plácées au centre des agglomérations enserrées par les habitations de leur nombreux personnel. De plus, elles doivent évacuer chaque jour un volume d'eau considérable; ainsi deux usines de Roubaix produisent journellement, l'une 1650 mètres cubes et l'autre 4.200 mètres cubes d'eaux résiduaires. Il est généralement difficile d'installer dans un espace relativement restreint les appareils nécessaires à une épuration réelle, sauf pour le procédé par évaporation qu'il serait souhaitable de voir se répandre, car il résoudrait le problème de la façon la plus heureuse au point de vue hygiénique.

Nous pensons cependant qu'il sera toujours plus pratique et plus économique d'épurer chimisuement les eaux de peignages de laines avant leur mélange avec les eaux d'égoût de la ville, l'épuration de ces dernières devenant relativement simple.

L'épuration chimique ou plutôt le traitement des eaux résiduaires pour en retirer les produits utiles et marchands, serait obtenue plus facilement et avec de meilleurs résultats dans un usine centrale avec un personnel spécialisé, dirigé par un ingénieur compétent. A cette usine centrale qu'il conviendrait d'organiser sous la forme coopérative, devraient être reliés par des canalisation à faible section tous les peignages qui seraient ainsi débarrassés du travail de récupération. L'effluent des bassins de précipitation chimique devrait être limpide, neutre, ou légèrement alcalin avant d'être mélangé aux eaux d'égoût. L'exécution d'un tel projet nécessitera sans doute des frais assez considérables de premier établissement à caude de la longueur des canalisations et des dispositifs de pompage indispensables dans les villes non accidentées comme Roubaix-Tourcoing. Mais on adoption s'imposera nécessairement dans un avenir prochain.

La clarification par voie chimique des eaux de peignages réalisera déjà une amélioration considérable de la salubrité des cours d'eau, et suffira sans doute à mettre fin aux réclamations incontestablement justifiées des riverains des rivières dans lesquelles ces eaux sont réjétées.

INDUSTRIAL LEAD POISONING

W. G. Gilman Thompson, M.D.

Professor of Medicine in the Cornell University Medical College in New York City

Among the numerous occupational diseases lead poisoning has long been studied more extensively than any other such disease and many monographs have been written upon this topic. This is in part due to the facts that its symptoms are often easily recognizable by laymen as well as physicians and that there are such a great variety of industries—at least 150—in which lead, or its compounds, constitute the principal disease hazard.

Although metallic lead may be the source of poisoning, as in handling lead bars or inhaling the fumes of the heated metal, it is lead salts or other compounds such as alloys, which are the common toxic agents, mainly on account of their dissemination in the workshop as dust, or their ready solubility in the blood and secretions of the body when introduced as dust or in any other form, especially that of either moist or dry paint.

The modes of entrance of lead into the body are several. As a fume it is inhaled, and as a dust it may be inhaled in the lungs or lodge in the mouth and be swallowed, or the dust may be conveyed to the mouth by unclean hands, or with food eaten in the workroom, or with chewing tobacco. Moreover, the workman's clothing may become saturated with lead fumes or dust so that he carries the poison into his home. Lead has little if any action upon the unbroken skin, but it has long been used medicinally in the form of a diluted lotion or wash to relieve inflammations of the skin, such as erysipelas and ulcers, being somewhat soothing and antiseptic. It is also given sometimes by mouth for its astringent action in diarrhoeal conditions, (hence the constipation of lead poisoning.)

Symptoms of lead poisoning. When lead enters the system it produces symptoms which may be either acute or chronic. The acute form of plumbism occurs rarely and chiefly from inhaling lead fumes which act as a violent respiratory irritant, causing asphyxia and paralysis of the heart, which may be fatal within a few hours. Several deaths have occurred in this manner in smelting works in New York City.

By far the larger number of cases are of chronic type, because lead is somewhat slowly absorbed and the structural changes which it produces in the body are of gradual development, being largely of the nature of an increase in the connective tissue of such structures as the arteries and kidneys, or changes in the nerves. Thus although in a few recorded cases serious symptoms have developed within a few weeks after entering upon a lead trade, in other cases they do not become apparent for at least six months, and in very many cases, not for several years. In fact they are often so insidious that the victim is unaware of them through any subjective sensations. It is this latter feature of lead poisoning which constitutes one of the most serious problems in dealing with the malady, for the workman keeps his employment, not knowing that he is daily adding to lesions of the arteries, kidneys and other organs which may cause his death eventually, either directly, or indirectly by undermining his constitutional resisting power against some added malady like tuberculosis or pneumonia.

The obvious symptoms of lead poisoning, i.e. those which the workman learns to recognize himself when he becomes what he terms "leaded," are three, namely: (1) a blue line made by deposit of lead in the gums; (2) attacks of very painful abdominal cramps or "lead colic," and (3) weakness of the hands, wrists and forearms, which progresses to the typical paralysis known as "drop wrist." The latter symptom, which is also accompanied by pain, prevents the workman from being able to grasp a tool, and, on attempting to raise the arms to the head, the hands fall limp at the wrists. This paralysis is exceedingly slow in recovery, and may become permanent. Exceptionally the feet are affected in a similar manner.

It is, however, a serious error to suppose that these symptoms are the only ones, or, in fact, that they are constantly present in every case of lead poisoning. This is an extremely important matter, for I have known of employers who denied that any of their workmen had plumbism, and of workmen themselves to be quite ignorant of the fact, when they were already profoundly diseased.

The other group of diagnostic symptoms which are readily recognized by the physician, are the following: (1) A remarkable change in the white blood corpuscles, whereby they show a granular structure known as "granular basophilia"; (2) Marked hardening of the arteries, whereby their elasticity disappears and the blood pressure becomes very high. As a result of the strain thus put upon the heart it becomes at first enlarged and later enfeebled; (3) As lead is excreted by the kidneys, traces of it may appear in the urine and the slow, insidious inflammation known as chronic interstitial nephritis (a form of chronic Bright's disease) is manifest through examination of the urine; (4) Decided secondary anemia; (5) Chronic gastritis and obstinate constipation.

By this second group of symptoms lead poisoning may be recognized by the physician, even without the presence of the first group.

Additional symptoms occasionally present are: temporary disturbances of the special senses, especially blindness, headache, pain in the joints, disturbances of sensation, and rarely, a somewhat more acute condition of mental derangement ("lead encephalopathy"), with vertigo, insomnia and delirium or stupor, with emaciation.

There is great personal idiosyncracy regarding susceptibility to lead poisoning, some persons being easily poisoned after short periods of exposure, and others remaining apparently immune for several years. Children are more susceptible than adults. A boy of 13 years came lately to my Clinic in the Cornell University Medical College, who had been employed for four months in cleaning paint cans, and with advanced symptoms of lead poisoning. A young man of 21 years who had been a helper for 8 years in a lead smelting works, had an enormously dilated heart, the senile arteries of an octogenarian, chronic Bright's disease and other serious symptoms, ruining his health hopelessly. On the other hand, I have seen painters who had handled white lead paints for 30 years or more before they presented symptoms of poisoning serious enough to put them out of employment.

Females are known to be much more susceptible than males to plumbism, and the wives of men who have lead poisoning either miscarry or bear children who have no stamina.

Nature of the hazardous lead industries. Consideration of all the hazardous lead trades is impossible within the limits of this brief summary and I shall allude to only a few of the gravest risks.

It has been disputed that plumbism is found among lead miners, but Dr. S. C. Hotchkiss in an investigation for the United States Bureau of mines found 39 cases treated in St. Vincent's Hospital in Leadville, Colorado within four years.

Many of the most severe and relatively acute cases occur in the manufacture of lead accumulators, in lead smelting works and in the manufacture of white lead. But by far the largest number of chronic cases originate among painters and particularly those who work in processes of enamelling, as in painting "porcelain finish" bathtubs, etc., or who paint carriages, wagons and automobiles, processes which involve the sandpapering of successive layers of paint to secure a smooth finish. This process fills the air with paint dust of extremely dangerous type. Formerly the men who finished the interiors of Pullman cars were subject to lead poisoning, but since the recent introduction of better sanitation, cases have been much less common. A man came to my Clinic last winter with paralysis of both arms and wrists, which he had had for more than six months. He was not a painter, but was hired in the Brooklyn Navy Yard to scrape red lead paint from inside the double bottoms of warships. For this purpose an automatic chisel, worked by compressed air is used and in the confined space where a number of men work together the lead paint dust becomes extremely dense. Further investigation by one of my clinical assistants, Dr. Kenney and Dr. E. E. Pratt of the New York State Factory Investigation Commission resulted in the discovery of some 20 cases among such workers.

Dr. Kenney, who has been keeping special records of all cases of lead poisoning in my Clinic reports among others, the following employments in which the patients became so severely poisoned as to require dispensary or hospital treatment: plumber (a number of cases); sheet metal worker; carrier of lead bars; steel hardener (who plunges magnetic bodies into molten lead); smelter (a number of cases); worker in white lead converting beds, (several cases); worker in brass and "composition" metal containing lead; white paint enameller; electrotyper; typesetter; paint factory hand (several cases); painter (many cases).

In this country lead poisoning from the pottery industry where the ware is glazed with lead solutions is less common than in England where it was formerly so often seen that Dr. Arlidge reported that 8 per cent of pottery glazers and polishers acquired plumbism. In the past decade, however, sanitation has reduced this percentage very much.

Extent of the lead hazard. Statistics of lead poisoning in the United States are only recently being collected upon an adequate scale. Some idea of the great prevalence of it may be gathered from the list of industries represented among the cases above reported at my Clinic, all of which were seen within a period of 6 months. I have collected further data of over 300 cases of lead poisoning serious enough to demand hospital or dispensary care, and which were met with in my personal service or that of colleagues within a period of a few years in the wards of Bellevue and the Presbyterian Hospital or my dispensary clinics.

Dr. Alice Hamilton, in her admirable and exhaustive investigation for the Illinois State Commission on Occupational Diseases, studied 23 white lead factories distributed throughout the country. Of these she writes in July, 1911, "As a result of this investigation 358 specific cases of lead poisoning, 16 of them resulting in death are known to have occurred in the 16 months from January 1, 1910 to April 30, 1911 in these 23 white lead factories." Moreover, in 33 out of 56 establishments where lead was used in manufacture, cases of plumbism were found with a yearly average of 665. Most of these latter instances were in the State of Illinois alone.

Dr. John B. Andrews in a report to the New York State Bureau of Labor, (July 1911,) found in that State alone that 60 workmen died from lead poisoning in the two years 1909–1910, 45 of whom were workers in paints, many being employed as house decorators working in confined spaces.

Prevention and relief of lead poisoning. This work may be to some extent legislative, but to a greater degree educational. Chemists should be stimulated to devise means for substituting less harmful substances for lead products, as already has been done in France to a considerable extent by the substitution of zinc for lead paints. Manufacturing chemists and all employers of workers in lead should seek improved processes of manufacture. Examining physicians should be regularly attached to all large lead works who should make compulsory periodic examinations of all employees.

I would suggest and strongly advocate as a legislative measure the compulsory labelling of all containers of lead products with a printed notice to read somewhat as follows: "*Warning!* This can contains lead paint. Lead is dangerous if taken into the mouth on food, tobacco, etc., and dangerous if breathed in the form of dry dust. Always wash your hands thoroughly before eating and never eat in your workroom. Do not inhale lead dust, but protect yourself by good ventilation. Lead poisoning may cause permanent illness and possibly be fatal. *Be careful!*"

Legislation may control to some extent the ventilation of smelting works and factories where lead is used by compelling the use of exhaust fans, prescribing modes of preventing dust, or moistening it or removing it, etc. It may further prescribe rules for hygiene such as provision for workmen to wash, bathe, change overalls, etc., but how shall it reach the independent painter who paints a house or one's barn door? Yet among painters occur fully 75 per cent of all cases of chronic lead poisoning. Obviously there are but two methods of meeting this difficulty, either to give him zinc or other non-poisonous paint, or to educate him to protect himself, a problem which in all hazardous industries is always difficult. Yet one need not despair of good results in this direction. For some time there have been issued to workmen coming to my Clinic circulars of instructions formulated by Dr. Kenney, and experience has shown that they are both studied and appreciated by them.

The circular of warning in regard to metal poisoning, especially lead, reads as follows:

MEDICAL CLINIC
CORNELL UNIVERSITY MEDICAL COLLEGE
OUT-PATIENT DEPARTMENT

(No. 5)

Instructions for persons exposed to Industrial Diseases, especially Lead.

General Information.

(1) Dusty occupations cause colds and infections, irritate the nose and throat, and weaken you.

(2) Fumes cause thin, poor blood, weak muscles, indigestion, and weak hearts.

(3) All workers exposed to dust and fumes should have good ventilation, open windows, and protective devices as Exhaust Fans, Hoods and Blowers.

Metal Poisons, chiefly Lead.

(1) Lead causes more poor health among workmen than any other metal; leads to indigestion and "colic," chronic disease of heart, blood vessels and kidneys, and paralysis of the hands—"wrist drop."

(2) Young adults are easily poisoned by lead. Young women often get the worst forms of it.

(3) Lead acts slowly and silently by constant exposure, and causes illness without the workman's knowledge of his danger. He must, therefore, be most careful.

(4) Lead enters the system through the nose, mouth and skin; that is, it may be inhaled as dust, in fumes, swallowed with food and saliva (especially if tobacco or gum is chewed), and absorbed by the skin.

(5) In New York City those trades that specially expose the workers to Lead Poisoning are: White and Red Lead manufacture, Painters, Plumbers, Typesetters, File Makers, Storage Battery Makers, Metal Hardeners and Polishers.

Rules for Prevention of Lead Poisoning Outside the Factory

(1) Keep general health always good by plenty of light, good food and fresh air in the home. Sleep at least eight hours every night.

(2) Personal cleanliness must be had. Wash with warm water and soap daily, always before eating, and at least one full hot bath a week. Remove all dirt from under finger nails.

(3) Never chew tobacco or gum when working. The lead dust on fingers is sure to be swallowed.

(4) Don't drink liquor of any kind. Alcoholic intemperance causes attacks of lead poisoning, weakens the kidneys, and causes paralysis.

(5) Never eat when you can avoid it in same room you work in.

(6) Always eat a good breakfast before going to work, especially drink milk.

(7) Do not wear same clothing on street or at home that you work in. Use overalls.

(8) Have at least one good bowel movement every day.

(9) Exercise in the fresh air. Live, when possible, some distance from work, and walk both ways.

(10) Take good care of teeth and gums. A decayed tooth favors lead symptoms. See your physician before going to work in lead factory, and at frequent intervals thereafter—at least once a month.

There should be closer co-operation in future between the chemist and physician in regard to the question of dealing with all forms of industrial poisoning, for they mutually can instruct one another before instructing the workman, and surely the problems involved are of the greatest importance alike from the humanitarian, scientific, sociological and economic points of view.

GENERAL INDEX
TO THE TWENTY-FOUR VOLUMES OF ORIGINAL COMMUNICATIONS

Martin