LEATHER CHEMISTS' POCKET-BOOK

H. R. PROCTER


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LEATHER CHEMISTS' POCKET-BOOK

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A SHORT

COMPENDIUM OF ANALYTICAL METHODS

EDITED BY

PROF. H. R. PROCTER

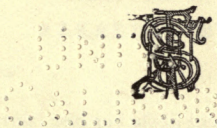
M.SC. F.I.C. F.C.S.

ASSISTED BY

EDMUND STIASNY, PH.D., & HAROLD BRUMWELL

OF THE UNIVERSITY OF LEEDS

FOUR ILLUSTRATIONS



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PREFACE

THE little book which is now presented to the public is intended not as a substitute, but as an adjunct to the Leather Industries Laboratory Book. It has been found convenient in the laboratories of our Leather Department to employ in addition to the Laboratory Book, which is the regular text-book, a series of manuscript laboratory sheets, giving the course of analysis absolutely essential to the practical student, but omitting the many details and variations which are important to the professed chemist, and which are described in the Laboratory Book. As these sheets required revision, it appeared that in a more permanent form they might have uses to a wider public, and especially to the students in evening classes of technical schools. Incidentally, they have for the moment the advantage over the Laboratory Book of revision up to date by the senior members of my staff, who have co-operated with me, and to whom my

thanks are specially due; but unfortunately many of the most recent and important developments of leather chemistry are of too abstruse a character to be included in so elementary and abridged a text-book.

HENRY R. PROCTER.

UNIVERSITY OF LEEDS:
1912

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CHAPTER I.

INTRODUCTORY.

It is assumed that the reader is acquainted with the elements of chemistry, and the ordinary manipulations of the laboratory, but the following brief notes on the general methods may not be out of place.

1. **Note Books.**—It is of the utmost importance that all weighings, measurements and calculations should be permanently recorded for further checking and reference. The laboratory note book should be used for permanent work on one side of the page only, and the other devoted to calculations and preliminary weighings. Even if the laboratory record is re-written in a neater and more concise form, these rough note books should be preserved for reference.

2. **Duplicates.**—All chemical determinations should be done in duplicate; and if in good agreement, the

average should be taken as the result. If the difference is greater than the ordinary analytical error of the method, the analyses must be repeated till concordant results are attained.

3. **Weighing.**—All weighings should be made in tared glass, porcelain, or platinum vessels, and never on the bare balance-pan. Unless the weights employed are of the highest quality, serious errors may arise from their inaccuracy, and sets should always be checked by weighing the large weights against the smaller, and the smaller against each other. If errors are serious a systematic table of corrections must be made.

4. **Measuring.**—Graduated glass vessels, and especially flasks and pipettes, are frequently seriously inaccurate, and should be checked before use by weighing water in them at 15° C. Specific gravity bottles must be similarly tested. If the water in a 10 c.c. bottle weighs, say, 9·980 grm., in most cases a sufficiently accurate correction will be made by *adding* 0·020 grm. to the weight found. Readings of graduated vessels must always be made to the lower side of the liquid meniscus, keeping the eye at the same level, reading against the light, and holding a dark card (or the finger) behind and just below, and care must be taken that the vessel is upright.

5. **Weights, Measures.**—Metric (decimal) measures are now almost invariably used by chemists. The metre = 39·37 inches. The litre (0·22 gallon)

is 1 decimetre cube or 1000 cubic centimetres, and contains 1 kilogramme of water at 4° C.; but in laboratories the so-called "Mohr's litre" is generally used, which contains 1 kilogramme at 15° C. The kilogramme weighs almost exactly 2·2 lb. avoirdupois, and the gramme 15·43 grains. It is rarely necessary, however, for chemical purposes actually to reduce one measure to the other, as in most cases the question is one of proportion, 1 grm. per litre being equivalent to 1 lb. per 100 gallons or, very approximately, to 1 oz. per cube foot. Commercially, 1 mark, or 1 fr. 25 cent., per 50 kilos is very nearly £1 per ton.

6. **Temperature.**—The Centigrade (or Celsius) thermometer scale divides the space between boiling and freezing points into 100°. The ordinary Fahrenheit scale puts freezing point 32° above an arbitrary zero, and boiling point 180° higher. Therefore Temperature Centigrade × 1·8 + 32° = Temperature Fahrenheit.

7. **Specific Gravity,** the weight of unit volume, is most accurately determined in the case of liquids by weighing a known volume. *Any* bottle with a mark on the (narrow) neck can be used for the purpose. The bottle is filled with water, usually at 15° C. (though sometimes 4° is used), and the water accurately weighed. The weight of the liquid divided by that of the water is the specific gravity. To save calculation, bottles with perforated stoppers (pycno-

meters), to contain 10, 25 or 100 c.c., are commonly used. Liquid overflows on replacing the stopper, and the bottle must be carefully cleaned and dried before weighing, and care taken that no air-bubbles are enclosed. Pycnometers are frequently inaccurate, and should always be tested by weighing with water. If the gravity of the liquid does not very widely differ from water, errors not exceeding a few milligrams are sufficiently allowed for by *adding* the error if −, or subtracting if + to, or from the weight found.

Gravity of solutions permits the calculation of their concentration by the use of tables, if the solution is clear and contains one substance only, but is affected by *all* dissolved substances and by suspended matter. In mixtures (e.g. tan-liquors) the gravity gives no reliable indication of their tanning strength, but the *loss* of gravity when hides have been put through is nearly proportional to the *loss* of tannin.

Hydrometers (Barkometers, Oleometers, Twaddell and Beaumé floats) are a rough but convenient means of determining gravity. The barkometer indicates the excess weight in grm. of a litre of liquor over water (that is, 100° = 1·100 sp. gr.). 1° Twaddell = 5° barkometer. Beaumé degrees are arbitrary, and can only be calculated from or to gravity by tables, of which several discrepant ones exist.

Where many gravities are required, "Mohr's balance" is convenient and accurate.

8. **Chemical Calculations.**—Every chemical equa-

tion is also a numerical one, since the symbols represent single atoms; and though the actual weight of any single atom is very small, and is only approximately known, their relative weights as compared to H = 1 (or practically to O = 16) have been very accurately determined, and are given in any table of atomic weights, and for calculation are all that are required. For practical purposes it is generally sufficient to employ the whole numbers (except in the case of Cl = 35·5), as the unavoidable errors of analysis, and in some cases those of the weights themselves, render the decimal doubtful. Thus the equation:—

$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$ is numerically
$2 \times 40 + 98 = 142 + 2 \times 18$

and is proportionally true for *any* quantity, and for *all* of the materials if the reaction is complete; and the calculation becomes a mere sum in rule-of-three. Thus the quantity of sodium sulphate formed from 1 ton of sulphuric acid when neutralised with soda is $98 : 142 :: 1 : x$ or $\frac{142 \text{ tons} \times 1}{98}$, and so for any quantity required or found in analysis. For instance, sulphuric acid is usually weighed as $BaSO_4$ and the SO_4 is calculated as $\frac{96}{233}$ of the weight found.

CHAPTER II.

ALKALIMETRY.

9. **Principle.**—One of the most useful applications of these facts is in volumetric analysis, of which many applications are given in succeeding sections, but the simple and general cases of the determination of acids and alkalies may be at once described.

It is obvious in the equation given above, that if we can determine the amount of sodium hydrate required exactly to neutralise any unknown quantity of sulphuric acid, we can calculate the latter. The determination is easily made, not by use of the solid sodium hydrate, but by the employment of a solution of known strength, and conveniently of 1 molecular weight in grammes, i.e. 40 grm. NaOH in the litre. As 1 molecule of H_2SO_4 neutralises 2 of NaOH, its solution must be of "equivalent," i.e. 1/2 molecular concentration, 49 grm. per litre, while an equivalent solution of HCl is molecular. Such solutions are called "normal" or N/1, while their dilutions to 10 and 100 are decinormal or N/10, and centinormal, N/100.

10. **Standard Solutions must** be accurate, and too great pains cannot be taken in their preparation, and in the purity of the water and materials used. About five minutes violent shaking is required fully to mix the contents of a "Winchester," and if too full, they cannot be adequately mixed. As far as possible one standard solution must be tested against another, acids against alkalies, and oxidising against reducing solutions (e.g. iodine against thiosulphate).

11. **Indicators** are mostly coloured substances, often dyestuffs, which are employed to show the completion of a reaction. It must be noted that, especially in alkalimetry, the point of colour-change is not that of theoretical neutrality, but some definite degree of slight alkalinity or acidity. Thus the reddening of phenolphthalein always indicates slight alkalinity, and that of litmus slight acidity; while methyl-orange only reddens at a degree of acidity which is not reached by some of the "weaker" acids (e.g. boracic) even when present in excess; and in all cases the colour-change is more or less gradual. With "strong" acids and bases this is of less importance, since the excess of acid or alkali required to produce the change is negligibly small. In titrating NaOH with HCl or H_2SO_4, no perceptible difference exists between results with phenolphthalein and those with methyl-orange; but if the acid or the base is weak, and especially in presence of neutral salts, much more acid or base is required to produce the colour-change, and great errors arise by

the use of unsuitable indicators. As a rule phenolphthalein is suitable for weak acids, and methyl-orange* for weak bases. Many salts of weak acids which are neutral to phenolphthalein are alkaline to methyl-orange. As all indicators themselves consume a minute quantity of the re-agent, it is best to work with the smallest quantity, which will give a distinct colour-change, to use the same quantity in each titration, and to go to the same tint. Titrations are best made in white porcelain basins, or in beakers on white tile or opal glass, and it is convenient to keep for comparison a beaker of distilled water, coloured with the indicator, titrated to the neutral tint. For very exact work the volume of standard solution required to do this should be noted and deducted from the amount needed for each titration.

12. **Preparation of Normal Acid and Alkali Solutions.**—In most cases these cannot be made by direct weighing of the substances, which can seldom be obtained quite pure and anhydrous. Pure dry sodium carbonate is perhaps the simplest substance to

* Congo-red may generally be substituted for methyl-orange, as it indicates a very similar degree of acidity. Its colour-change (to blue with acids) is less sharp, but more visible by artificial light or in coloured solutions. Methyl-red (dimethyaniline anthranilate) gives a colour-change similar to methyl-orange, but sharper, and may be substituted with advantage. Methyl-orange and congo-red are conveniently used in 0·1 per cent. aqueous solution, methyl-red in alcoholic solution of similar strength, and phenolphthalein in 1 per cent.

use as a standard; and caustic soda and hydrochloric acid are the most serviceable for general use.

110–120 c.c. of the strongest pure hydrochloric acid is diluted with distilled water to 1 litre, and shaken for five minutes in a stoppered bottle to ensure uniform mixing. The solution will be somewhat over normal. A few grammes (20–30) of the purest dry Na_2CO_3 is heated in an air-oven to 160° C. for some hours, with occasional stirring, or (sufficiently accurately) over a spirit lamp or Bunsen burner till the bottom of the porcelain basin is dully red, and is then allowed to cool somewhat in a desiccator, and transferred while still warm to a stoppered weighing bottle. A burette is filled with the acid solution to the zero mark; 2–3 grm. of the dry Na_2CO_3 is shaken into a beaker and dissolved in distilled water, the exact quantity being determined by weighing the bottle before and after; two drops of a 1 grm. per litre aqueous solution of methyl-orange added, and then acid from the burette, stirring with a glass rod till the pale yellow changes to a faint pink, and the quantity of acid is noted. The number of c.c. of the acid which is required to make a litre of normal solution, is found by multiplying the c.c. of acid used by 53, the equivalent of Na_2CO_3, and dividing by the weight of the latter used. This is repeated three or four times, and if the results agree closely the average is taken as the required value. Supposing this to be, say, 869·3 c.c., 130·7 c.c. of distilled water is measured by the burette into a dry clean

litre flask, which is then carefully filled to the mark with the acid, and when well mixed should be exactly normal. It is again tested against the sodium carbonate, when the result of the calculation should be 1000 c.c. Errors not exceeding 1 c.c. are negligible in ordinary work. N/1 sodium or potassium hydrate solutions are made by dissolving 45 grm. of NaOH or 60 grm. of KOH "pure by alcohol," in distilled water to 1 litre, mixing well, and repeatedly titrating with it 10 c.c. of the N/1 HCl, when the quantity of the alkaline solution required × 100 is the volume needed for 1 litre of N/1 solution. Much care should be taken to secure accuracy, as any error in these solutions would vitiate all subsequent work. The caustic alkaline solution should be preserved in a bottle with a soda-lime tube or bulbs filled with caustic soda solution in the cork, to exclude CO_2, and is best transferred to the burette with a glass syphon, also fitted through the cork and closed with a piece of rubber tube and a pinch-cock. For the titration, either phenolphthalein or methyl-orange may be used, or both together, in which case, the pink solution will become nearly colourless and then pink again, the pale yellow colour being taken as neutrality.

For certain purposes, saturated lime-water or baryta-water form valuable standard solutions, since their carbonates are insoluble and the solutions are therefore always entirely caustic. Lime (CaO) dissolves only to the extent of 0·132 grm. per litre at

15° C. (1 litre = 482 c.c. N/10 acid), and may therefore be taken for many purposes as approximately N/20, if excess of solid lime is kept in the bottle, and occasionally shaken, and the clear liquor only used. Saturated solution of $Ba(OH)_2$ is over N/3 and may therefore be easily adjusted to N/5, and keeps permanently if preserved from CO_2; but the most accurate way of using these solutions in the titration of acids is to titrate them at the time against 10 c.c. of standard N/10 or N/1 acid, and the strength of the acid tested has the same proportion to that of the standard acid as the c.c. used in each case.

13. **Testing of Commercial Acids.**—A weighed or measured quantity of the acid, sufficient to make a solution of approximate N/1 or N/10 strength, is made up to 1 litre, and 10 c.c. is repeatedly titrated with standard NaOH solution. If the exact number of c.c. corresponding to the equivalent weight is made up to 1 litre, each 0·1 c.c. of N/1 NaOH required to neutralise 10 c.c. will correspond to 1 volume per cent., or the number of pounds of pure acid contained in 10 gallons. Weighed quantities give percentage by weight: measured, percentage by volume. To reduce the latter to the former, divide by the specific gravity of the acid tested.

14. **Sulphuric, Hydrochloric and Nitric Acids** may be tested with almost any indicator: Congo-red, methyl-orange, or phenolphthalein. 1 c.c. of N/1 NaOH equals 49 mgr. H_2SO_4, 36·5 mgr. HCl, and

63 mgr. HNO_3. The percentage strength of HCl very closely corresponds to its degree Twaddell. A yellow colour generally indicates iron, which may be estimated as in water analysis (par. 27).

15. **Oxalic, formic, lactic, acetic, butyric,** and most other organic acids may be tested as above, but phenolphthalein must be used as indicator. Lactic acids usually contain lactones or anhydrides, which are not acid to indicators, but combine with lime or alkalies when the latter are present in excess. Consequently only the free acid is determined if the titration is made cold, and stopped when the solution is still faintly pink; but if allowed to stand for ten minutes with excess of N/1 NaOH (1–3 c.c.) and excess of standard acid added and just brought to a boil, and the titration completed with NaOH, the lactone is also estimated. The acid used is deducted from the NaOH required. Liquid organic acids sometimes contain H_2SO_4, which may be detected or estimated with $BaCl_2$. 1 c.c. N/1 NaOH equals 63 mgr. oxalic, 46 mgr. formic, 90 mgr. lactic, 60 mgr. acetic, and 88 mgr. butyric acids. For dark-coloured acids, phenolphthalein test-papers may be used.

16. **Boric** (boracic) **acid** $B(OH)_3$ may be titrated with NaOH and phenolphthalein in presence of 30 c.c. of neutral glycerin for ½–1 grm. boric acid. When the solution becomes pink 10 c.c. more glycerin is added, and if the colour disappears, more NaOH till

a faint pink is restored. 1 c.c. of N/1 NaOH = 62 mgr. $B(OH)_3$.

As boric acid, like carbonic, does not affect methyl-orange, or methyl- or congo-reds, the whole of the alkaline bases present may be titrated in borates with these indicators and standard sulphuric or hydrochloric acid, as if no acid were present. Thus borax, $Na_2B_4O_7$, 10 Aq. (= 382) may be used instead of Na_2CO_3 to make a standard alkaline solution for use with these indicators, 19·1 grm. per litre being decinormal. To determine boric acid in borates, the solution is carefully neutralized to one of these indicators with HCl or H_2SO_4, boiled to expel CO_2, and the free boric acid titrated with glycerine and phenolphthalein as just described.

Free boric acid is more or less volatile when its aqueous solution is evaporated, and still more so in presence of alcohols, but may be safely evaporated or even ignited with addition of sodium hydrate or carbonate. Free boric acid may therefore be separated from mixtures by distillation with methyl-alcohol (see Lab. Book, p. 77). Small traces are easily detected by boiling its acidified solution with a little alcohol, and igniting the vapours, which burn with a green flame. The free acid also turns turmeric paper reddish-brown, and the stain is not discharged, but blackened by acids.

17. **Sulphurous Acid.**—Hydric sulphites (bisulphites) are neutral to methyl-orange and acid to

phenolphthalein. Titration with NaOH and methyl-orange therefore converts all acid into bisulphite, and each c.c. of N/1 NaOH corresponds to 1 mol. or 64 mgr. of free SO_2. If the titration be continued with phenolphthalein, the whole of the SO_2 present is converted into Na_2SO_3, and the total standard solution in both titrations used represents the total SO_2 existing as free acid and bisulphite, each c.c. of N/1 corresponding to 32 mgr. or half a molecule. Neutral sulphite cannot be present with free SO_2, but may with bisulphites. If the liquid neutral to phenolphthalein be now titrated back with HCl till it is just acid to methyl-orange, the difference between this acid and the NaOH previously used represents the SO_2 originally present as neutral sulphite; each c.c. of N/1 = 32 mgr. SO_2.

18. **Testing of Commercial Bases.**—A solution is made as described for acids, and standard acid, generally HCl, is used for titration. For soda and potash, if phenolphthalein is used, caustic alkali and half the carbonate is estimated. If methyl-orange is now added and the titration continued, the remaining half of the carbonate is estimated, and if deducted from the phenolphthalein titration, the remainder corresponds to hydrate only. In lime and baryta, the hydrates only are estimated if phenolphthalein is used, and care taken not to go beyond the last trace of pinkness. To estimate total base, acid is used in excess, and either allowed to stand for some time or

heated, and the solution is titrated back with NaOH solution and methyl-orange.

19. **Weak Bases.**—Ammonia, amines, etc., must not be titrated with phenolphthalein. Methyl-orange (by daylight), carminic acid (1 per cent. aqueous solution), methyl-red, and less accurately Congo-red, are suitable.

CHAPTER III.

WATER ANALYSIS.

20. WATER which has to be tested as to its suitability for tanning or dyeing leather, ought not only to be investigated chemically but also as to its bacteriological behaviour, the latter being of great importance in soaking, liming, bating, puering, drenching and tanning with vegetable tan liquors. Information on bacteriological work is very briefly given in Chapter XV., and only the chemical analysis of water is dealt with here. The most important determinations for the leather trades chemist are those of temporary, permanent and magnesia hardness, sodium carbonate, free carbonic acid, chlorides, iron compounds, sulphates, suspended and organic matter.

21. **Temporary hardness** is due to the presence of hydric carbonates (bicarbonates) of calcium and magnesium, but is generally stated as an equivalent amount of $CaCO_3$, and is determined by titrating a definite volume of the water with N/10 HCl.

The chemical process going on during titration is given by the following equations :

$$CaH_2(CO_3)_2 + 2HCl = CaCl_2 + 2CO_2 + 2H_2O$$
$$MgH_2(CO_3)_2 + 2HCl = MgCl_2 + 2CO_2 + 2H_2O$$

From these equations it can be seen that 1 c.c. N/10 HCl indicates 5 mgr. $CaCO_3$ in the form of temporary hardness; and remembering that 1° of hardness is one part $CaCO_3$ in 100,000 parts of water,* we find that each c.c. N/10 HCl necessary to titrate 100 c.c. of the water represents 5 degrees of temporary hardness.

Working details:—100 (or 200) c.c. of the water are put in a porcelain basin and titrated with N/10 HCl or H_2SO_4, with a drop or two of 2 per cent. purest alizarin paste. When the violet colour gives place to pure lemon-yellow the solution is boiled, when the violet colour will return from expulsion of CO_2, and must *immediately* be destroyed by further addition of acid. Titration of the boiling solution is continued till the lemon-yellow remains unchanged. In place of alizarin in boiling solution, methyl-orange may be used in the cold, but is less accurate. The same quantity (1 or 2 drops) of the indicator is used in each titration, and a blank experiment made to ascertain the quantity (generally about 0·1 c.c.) required to change the tint of this amount of methyl-orange in 100 c.c. distilled water, which must in each case be deducted from the volume of standard solution used.

* Grains per gallon (parts per 70,000) are sometimes called degrees, and German degrees are parts of CaO per 100,000.

Example:—

100 c.c. of water required 6·5 c.c. of N/10 acid.

Each c.c. of N/10 acid corresponds to 5 mg. $CaCO_3$.

6·5 c.c. N/10 acid = 32·5 mg. $CaCO_3$ per 100 c.c. water = 32·5 parts $CaCO_3$ in 100,000 parts water.
= 32·5 degrees of temporary hardness.

22. **Permanent hardness** is due to any calcium or magnesium salts except bicarbonates. It is best determined by the method of Pfeifer and Wartha, which is based on the action of a mixture of NaOH and Na_2CO_3 on the water; this mixture is used in excess, and titrated back with N/10 HCl, and reacts with the permanent hardness according to the following equations:—

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$
$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$$

the sodium carbonate converting the Ca salts into $CaCO_3$, while the NaOH precipitates the Mg salts in form of $Mg(OH)_2$.

The NaOH reacts also with the temporary hardness, but without increasing the alkalinity of the solution, as equivalent amounts of Na_2CO_3 are produced:

$$CaH_2(CO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O$$
$$MgH_2(CO_3)_2 + 4NaOH = Mg(OH)_2 + 2Na_2CO_3 + 4H_2O$$

It is therefore only the permanent hardness which removes alkali, and this alkali corresponds to 5 mg. $CaCO_3$ per 1 c.c. N/10 HCl.

Working details:—200 c.c. of the water are boiled in a Jena flask so as to expel most of the CO_2; 50 c.c. of a mixture of equal parts N/10 NaOH and N/10 Na_2CO_3 are then added and the whole boiled down to about 70 c.c., cooled, and made up to 100 c.c. and, if possible, allowed to stand for some hours to settle, and 50 c.c. filtered off and accurately titrated with N/10 HCl or H_2SO_4. It is not essential that the alkaline solution should be accurately N/10, but the N/10 acid required for neutralising 25 c.c. must be exactly known. The titration may be made cold with methyl-orange, using the precautions mentioned above (see temporary hardness), but alizarin, boiling, is to be preferred.

Example:—

25 c.c. of the N/10 alkalies consume 25·2 c.c. N/10 acid

50 c.c. of the filtered water consume 19·5 c.c. N/10 acid

25·2 − 19·5 = 5·7 c.c. N/10 acid corresponds to permanent hardness in 100 c.c. original water.

Each c.c. N/10 acid corresponds to 5 mg. $CaCO_3$

5·7 c.c. N/10 acid = 28·5 mg. $CaCO_3$ per 100 c.c. water = 28·5 parts $CaCO_3$ in 100,000 parts water = 28·5 degrees permanent hardness.

23. **Magnesia hardness** is due to any magnesium salt, and, as far as $MgH_2(CO_3)_2$ is present, is included in temporary hardness, while the other magnesium salts are expressed in the figure of permanent hardness.

The determination of magnesium hardness is done after the temporary hardness is removed with N/10 HCl.

Such water, containing magnesium and calcium salts as permanent hardness only, is treated with a known quantity of lime water, which precipitates magnesium salts without acting on calcium salts.

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2$$
$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$$

The decrease of alkalinity expressed in c.c. N/10 HCl is therefore only due to magnesium salts, and is usually expressed in degrees of magnesia hardness, that is, as the equivalent amount of $CaCO_3$.

Working details:—100 c.c. of the water, accurately neutralised with N/10 HCl in presence of alizarin (that portion used in determining temporary hardness may be employed), is boiled down till all CO_2 is expelled and the bulk reduced below 100 c.c. and is mixed in a 200 c.c. Jena flask with 100 c.c. of filtered lime-water, the value of which in N/10 acid is accurately known. The whole is raised to 100° C. in the water-bath, corked or stoppered and allowed to cool,

and made up to the mark with well boiled distilled water, thoroughly mixed and allowed to stand till settled. It is then filtered rapidly, covered to prevent absorption of CO_2, or preferably 100 c.c. is pipetted off perfectly clear, and titrated with N/10 HCl and phenolphthalein.

Example:—

50 c.c. of the lime-water require 22·5 c.c. N/10 acid
100 c.c. of the mixture require 20·1 c.c. N/10 acid

22·5 − 20·1 = 2·4 c.c. N/10 acid correspond to magnesia hardness in 50 c.c. original water.

Each c.c. N/10 acid corresponds to 5 mg. $CaCO_3$

2 × 2·4 × 5 = 24 mg. $CaCO_3$ per 100 c.c. water
= 24 degrees of magnesia hardness.

If the magnesia hardness has to be expressed in parts MgO per 100,000 parts water, the above figure (24) must be multiplied by 24/100 (= $MgO/CaCO_3$) corresponding to 9·6 parts MgO in 100,000 parts water.

24. **Sodium Carbonates or other alkaline carbonates** can only be present in absence of permanent hardness, and are found in determining this when more alkali is titrated back than was added to the water; 1 c.c. N/10 HCl corresponding to 5·3 mg. Na_2CO_3. In such cases, which are rather exceptional, the excess of acid required must be calculated as

"sodium carbonate," and a similar amount deducted from that returned for temporary hardness before calculating the latter.

25. **Free Carbonic Acid** can be determined by titrating 100 c.c. of the water with N/10 Na_2CO_3, using phenolphthalein as indicator, the soda solution being added very slowly until a final permanent pink is produced.

$$H_2CO_3 + Na_2CO_3 = 2NaHCO_3$$

The bicarbonate produced is neutral to phenolphthalein, and each c.c. N/10 Na_2CO_3 used for titration corresponds to 2·2 mg. CO_2 (or 3·1 mg. H_2CO_3). The sample of water must be preserved in a tightly closed and full bottle, as the carbon dioxide readily escapes.

26. **Chlorine** is determined by titrating 100 c.c. of the water with N/10 $AgNO_3$ using a few drops of a solution of yellow potassium chromate as indicator. The $AgNO_3$ combines first with the chlorides present in the water, and subsequently with the potassium chromate producing a brick-red coloration or precipitate, which serves as the end point.

$$CaCl_2 + 2AgNO_3 = 2AgCl + Ca(NO_3)_2$$
$$K_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3$$

Each c.c. N/10 $AgNO_3$ corresponds to 3·55 mg. chlorine or 5·85 mg. of sodium chloride.

Working Details:—The N/10 $AgNO_3$ solution is made by dissolving exactly 4·25 grm. of purest $AgNO_3$ and making up to 250 c.c. with distilled water at 15° C.; and must be kept in the dark. The chromate must be free from chlorides (acidify with nitric acid and test with silver nitrate). The solution in which the chlorine is to be determined must not be acid, but may be neutralised with pure magnesia, free from chlorides, or where the acidity is slight, sodium acetate solution may be added.

27. **Iron** may be tested for by acidifying the water with nitric acid, and adding an alkaline thiocyanate (sulphocyanide), when its presence is indicated by red coloration. For exact colorimetric estimation evaporate 100 c.c. to dryness in a porcelain basin, with a drop or two of dilute sulphuric acid, add a drop of concentrated nitric acid, ignite *gently* to destroy organic matter. Re-dissolve in water with a little nitric acid, and make up to 25 c.c.; mix 10 c.c. of dilute nitric acid (1 c.c. concentrated HNO_3 free from iron) 5 c.c. of 5 per cent. solution of potassium thiocyanate, as many c.c. of the residue solution as will give a convenient colour for matching in a Nessler glass, make up to 50 c.c. with distilled water, and stir thoroughly. To a similar solution of thiocyanate in another glass, add a 0·01 grm. per litre solution of ferric nitrate till the colour is matched. Repeat several times, varying the quantity of residual solution used, and calculating the iron required to match 100 c.c. of the original

water in mg. (parts per 100,000), and take the average. The standard iron solution is made by dissolving 0·496 grm. of pure crystallised ferrous sulphate in a little concentrated nitric acid in a flask, heating (in the draught-chamber) till no more red fumes come off, making up to one litre, and diluting 1 : 10 before use.

The following determinations of sulphates, suspended matter and organic matter are gravimetric.

28. **Sulphates** are determined by slightly acidifying 250 c.c. (or 500 c.c.) of the water with hydrochloric acid and concentrating the bulk by evaporation to about 100 c.c., when about 5 c.c. of a hot 10 per cent. barium chloride solution are added drop by drop to the boiling liquid. After allowing it to stand for some hours in a warm place, the clear liquid is poured through the filter, into which the precipitate is finally transferred and well washed, dried, ignited and weighed. This weight ($BaSO_4$) multiplied by $96/233 = 0{\cdot}41$ gives grm. SO_4 in the original volume of water.

29. **Suspended matters** are determined by filtering 500 c.c. (or 1 litre), taken after carefully mixing a large quantity of the water, through a dried and tared quantitative filter paper. The filter is washed with distilled water, dried at 105°–110° C. till constant, and weighed; the gain of weight being "mud and suspended matter." The filter is now ignited, the residue being "inorganic suspended matter," while the difference between the two last figures gives the "organic suspended matter."

30. **Organic Matter.**—500 c.c. of the filtered water

are evaporated to dryness on the water-bath, in a large porcelain crucible, and dried, first at 100–105° for one hour, and then at 170–180° C. for about two hours, when the crucible containing the total solubles is weighed. The whole is now ignited, in order to destroy organic matter; and as the carbonates of calcium and magnesium at the same time are converted into oxides, the residue after cooling must be damped with water saturated with carbonic acid (or with a solution of ammonium carbonate), and subsequently evaporated, dried at 100–105 and 170–180° C. as above, and weighed. The difference between this weight and the weight above will give the dissolved organic matter. A great amount of such organic substance is not desirable for a tannery-water, as bacteria are usually present in large numbers.

31. **Softening Water with Lime alone** (Clark's method) removes temporary hardness and magnesia hardness, but does not remove permanent hardness. The action of lime is given by the following equations :—

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$

$$MgH_2(CO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2 + 2CaCO_3 + 2H_2O$$

$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$$

It can be seen that magnesium bicarbonate requires twice as much lime as calcium bicarbonate, and fur-

ther that magnesium sulphate is replaced by the corresponding calcium salt, so that the amount of permanent hardness is not reduced. Temporary hardness cannot be reduced below about 5°, the solubility of $CaCO_3$ in water.

Considering that 1° of hardness corresponds to 1 grm. $CaCO_3$ in 100 litres of water and that the molecular weights of $CaCO_3$ and CaO are 100 and 56 respectively, we come to the following conclusions:—

1° of hardness due to $CaH_2(CO_3)_2$ requires 0·56 grm. CaO per 100 litres water.

1° of hardness due to $MgH_2(CO_3)_2$ requires 2 × 0·56 grm. CaO per 100 litres water.

1° of hardness due to $MgSO_4$ (or MgCl, etc.) requires 0.56 grm. CaO per 100 litres water. *

The $MgH_2(CO_3)_2$ hardness, as has been stated above, forms a part of the temporary hardness as well as of the magnesia hardness. If we take the sum of temporary hardness and magnesia hardness, that due to magnesia will be included twice, so that the lime required for 100 litres will be obtained by multiplying this sum by 0·56 grm.

In addition, the free CO_2 consumes lime, 44 parts of CO_2 requiring 56 parts of CaO for its removal.

* 1 grm. per 100 litres equals 1 lb. per 10,000 gallons, or practically, 1 oz. per 100 cubic feet.

Example:—

temporary hardness = 16°
magnesia hardness = 5°

(16 + 5) 0·56 = 11·76 grm. CaO per 100 litres water
= 11·76 lb. burnt lime for 10,000 gallons.

As the calculation is somewhat complicated, it is often best to make direct experiment, by adding known excess of a titrated lime-water to a litre of the water, allowing to stand, and titrating back as in the estimation of magnesia hardness, par. 23. On the larger scale, the reaction and settling are facilitated by warmth and by thorough mixture, especially in presence of the precipitate of previous operations, and the best practical results are often got by somewhat less than theoretical quantities.

32. **Softening Water with Lime and Soda.**—Lime removes temporary hardness and converts magnesium salts into calcium salts (see Clark process); sodium carbonate removes permanent hardness (i.e. the calcium salts originally present, and those formed from the magnesium salts).

The following reactions take place:—

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$

$$MgH_2(CO_3)_2 + 2Ca(OH)_2 = Mg(OH)_2 + 2CaCO_3 + 2H_2O$$

$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$$

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

The amount of lime required is equal to that according to Clark's process (temporary hardness and magnesia hardness) × 0·56 grm. CaO per degree, for 100 litres water.

The amount of soda required per degree for permanent hardness is :—

1·06 grm. Na_2CO_3 or 2·86 grm. Na_2CO_3 $10H_2O$ (soda crystals) per 100 litres water

Example:—temporary hardness 10°
magnesia hardness 4°
permanent hardness 6°

(10 + 4) × 0·56 = 0·784 grm. CaO per 100 litres water.

6 × 2·86 = 17·16 grm. Na_2CO_3 $10H_2O$ per 100 litres water.

It is sometimes convenient on the small scale to substitute caustic soda for lime in the Clark process, when the sodium carbonate formed re-acts further and also removes its equivalent of permanent hardness.*

33. **Suitability of Water for Tanning Purposes.**—In judging a water as to its suitability for leather

* In place of sodium carbonate, tribasic sodium phosphate (Payne) may be used to remove permanent hardness; barium hydrate will remove temporary hardness and sulphates; and "permutit" (a sodium aluminium silicate) will remove *all* hardness, but is unsuitable for tanneries, since it replaces it with sodium bicarbonate, which is almost equally injurious.

manufacture, the following points must be remembered.

Considerable temporary hardness makes soaking slower; has no effect on liming as long as lime is used either alone or in mixture with other agents; interferes very much with the hair-loosening action of sodium sulphide (if this is used alone); is unsuitable for deliming, because $CaCO_3$ is formed in the hides and especially in the grain; causes loss of tannin in the process of leaching and in the tan pits, and darkening of both tan liquors and leather; it also leads to the formation of insoluble calcium and magnesium soaps when used for fat-liquoring or for scouring with soaps. It further causes loss of aniline dye if used for dyeing, and produces stains (separation of calcium sulphate in the grain) on glove leather in the process of washing out excess of alum before staining, etc., etc. Besides these, the action in a boiler water (furring) has to be considered.

Considerable permanent hardness is of less influence. It does not interfere with soaking, liming and deliming, and causes only small loss of vegetable tannins or dyestuffs, but is equally injurious as regards soaps and for boiler feeding.

Free CO_2 and Na_2CO_3 have similar effects on deliming to temporary hardness. Both can be prevented by adding some lime liquor to the water before use. Sodium carbonate has also a darkening effect on vegetable tan liquors.

Iron salts produce a bad colour with vegetable tan liquors and make the water unsuitable for dyeing.

Chlorine present as common salt tends to prevent proper swelling of sole leather in the liquors, and if abundant, as in tidal rivers, interferes with the extraction of tanning materials.

Organic matter. A great amount of organic substance is in most cases objectionable, as such waters form a good nutrient for bacteria of pernicious kinds and usually contain putrefactive organisms. Such water would cause loss of hide substance in soaking and liming, while sweating, bating, puering and drenching would be rendered dangerous.

CHAPTER IV.

LIMING, DELIMING AND BATING.

34. **Analysis of a Quicklime.**—The amount of "available" lime is what the tanner is most interested to know. A sample is drawn by breaking off small pieces from a number of lumps of the bulk, coarsely pulverising them in a mortar, and then grinding a portion as fine as possible and transferring it at once to a stoppered bottle for weighing. A portion of this, not exceeding 1 grm., is shaken into a stoppered liter flask, which is filled up with hot and well-boiled distilled water, and allowed to stand for some hours with occasional shaking. When cold it is filled to the mark with recently boiled distilled water, and well shaken again and allowed to settle, or filtered with as little exposure to the air as possible, and 25 or 50 c.c. withdrawn with a pipette and titrated with N/10 hydrochloric or sulphuric acid and phenolphthalein. Each cubic centimeter of N/10 acid equals 0·0028 grm. CaO. The presence of a small quantity of insoluble sediment in the liquid titrated, does not affect the phenolphthalein.

The total bases existing as oxides, carbonates and easily decomposable silicates of alkalies, calcium and magnesium, are readily determined by treating 1 grm. of the finely powdered sample with 50 c.c. of N/1 HCl and titrating the excess of acid. If these total bases are expressed in grm. CaO and the available lime deducted from it, the difference will be practically due to calcium carbonate and magnesium compounds, other salts usually being present in traces.

The alkalinity of a saturated solution of the quicklime is not without interest for the tanner, and impure limes often show a higher alkalinity than pure ones, the impurities reacting with lime and forming alkali hydrates which are much more soluble than lime. About 1 grm. of the finely powdered lime is shaken with about 100 c.c. of water, and the solution treated as in the determination of available lime. In the case of pure lime, 50 c.c. of the saturated solution (at a temperature of 15°C.) will consume 23·6 c.c. N/10 HCl (at higher temperatures the solubility is less), and any higher figure will be due to the above mentioned reactions. A determination of iron can be made in a separate sample, by dissolving about 0·5 grm. in hydrochloric acid, boiling with a few drops of nitric acid, making up to 100 c.c. and determining the iron colorimetrically with potassium thiocyanate. (See Water Analysis, par. 27.)

35. **Analysis of Sodium Sulphide.**—Sodium sulphide is brought on the market in a crystallised form,

$Na_2S.9H_2O$ containing 32·5 per cent. Na_2S, the brown crystals being oxidised and carbonated on long exposure to air, and colourless salts formed, principally sodium thiosulphate and sodium carbonate.

Another form of commercial sodium sulphide is a fused salt which contains much less water, and about 60 per cent. Na_2S. The most frequent impurities of sodium sulphide are polysulphides, sodium sulphate, sodium hydrate, and the above named products of oxidation and carbonation.

It will generally be sufficient to determine the alkalinity to methyl red* or methyl orange and the amount of H_2S produced by acidification. The total alkalinity is easily determined by titrating 25 c.c. of a solution containing about 12 grm. sodium sulphide in 1 litre water with N/10 HCl and methyl orange as indicator. Sodium sulphide is, in aqueous solution, to a great extent hydrolysed according to the equation $Na_2S + H_2O = NaOH + NaSH$ and both products of hydrolysis are titrated with HCl, methyl orange not being sensitive to H_2S. Each c.c. N/10 HCl is equal to 3·9 mg. of Na_2S or 12 mg. of $Na_2S, 9H_2O$, assuming that no excess of NaOH was present in the sample.

The amount of H_2S produced by acidification is of interest to the tanner because this amount is

* Methyl red may in most cases be substituted for methyl orange with advantage, its sensitiveness being very similar, and the change of colour sharper.

responsible for the sharpening effect of the sodium sulphide. It is not the total amount of sulphur which works in this way, as the polysulphides (which are present in most commercial samples) do not react with their total sulphur, but only with that part which gives H_2S after acidification. The determination of this sulphide-sulphur can be made by distilling the acidified sodium sulphide solution into a known amount of N/10 iodine solution, the latter being in excess, and titrated back with N/10 sodium thiosulphate. A simpler way, which is quite satisfactory, is the titration with ammoniacal zinc sulphate solution, using lead acetate as an external indicator. The zinc sulphate solution is made either by dissolving 14·35 grm .of pure crystallised $ZnSO_4$ 7 Aq. in water, adding ammonia until the precipitate which is at first formed, is redissolved, and making the whole, with the addition of 50 grm. ammonium chloride,* up to a litre: or by dissolving 3·25 grm. of pure zinc in dilute sulphuric acid with a piece of platinum foil, and then adding excess of ammonia and 50 grm. of ammonium chloride, and making up to a litre.

The solution is decinormal and each c.c. equals 1·6 mg. sulphur or 12 mg. crystallised sulphide. The standard solution is added with constant stirring, to, say, 25 c.c. of the sodium sulphide solution (containing 12 grm. in 1 litre) in a beaker, and after each addition

* J. R. Blockey and P. V. Mehd, J.S.C.I., pp. 369–372, 1912.

a drop is taken from the beaker and placed on a pair of filter papers so that the zinc sulphide precipitate is left on the upper paper, which the filtrate passes through, and wets the lower paper. Turning over the pair of papers, a drop of lead acetate solution is placed on the wet spot of the paper, and a black or brown colour will be produced so long as any sulphide is present. When all sodium sulphide is converted into insoluble zinc sulphide, no darkening of the spot on the lower filter paper will be produced by lead acetate

A somewhat more delicate lead indicator may be made by dissolving lead acetate in a solution of sodium tartrate or tartaric acid made strongly alkaline with sodium hydrate and filtering. Instead of using a lead salt as indicator, a solution of sodium nitroprusside may be employed, drops of which are simply spotted on a white tile and give a strong purple reaction with the least trace of alkaline sulphide.

Polysulphides are not determined by this method, but only that part of the sulphur which liberates H_2S on treatment with an acid. The proportion of NaOH to NaSH, which is important for the unhairing effect, can be found by the two determinations, namely, the titration with N/10 HCl (methyl orange) (a c.c.), and the zinc sulphate titration (b c.c.)

$\left(a - \frac{b}{2}\right)$ 0·004 is the amount of NaOH, and $\frac{b}{2}$ × 0·0056 the amount of NaSH; and if $a > b$, alkali

is present in the sample of sodium sulphide. (Sodium carbonate is here expressed as NaOH.)

36. **Analysis of Red Arsenic.**—Red arsenic is a mixture of As_2S_2 and As_2S_3 and contains often As_2O_3 and free sulphur, which impurities are of no value to the tanner.

The depilatory power can be measured by determining the amount of soluble sulphides produced by the action of alkali on the red arsenic. One gram of the finely powdered sample is digested for some hours with 50 c.c. of 10 per cent. caustic soda solution with frequent shaking, and made up to 100 c.c. with water and filtered. 50 c.c. of the filtrate are titrated with N/10 ammoniacal zinc sulphate solution, as described in par. 35, p. 34. The result can be expressed in per cent. active sulphur by multiplying the c.c. N/10 zinc sulphate with 0·32 (2 × 0·0016 × 100).

For further information on the analysis of Red Arsenic, see Lab. Book, p. 58.

37. **Analysis of a Lime Liquor (Fresh or Used).**—The lime liquor in the pit must be well stirred and about one litre taken for analysis.

The lime liquors before analysis must be filtered, which is not always an easy problem, especially in old limes, as the colloidal particles of dissolved hide substance fill the pores of the filter paper (and of other filtering substances), or pass through the filter together with finely suspended particles of undissolved lime.

In such cases, it is best to allow the lime liquors

to settle (at least to stand over night in a stoppered conical flask), and to pipette off the clear supernatent solution in a dry flask, or to pour the upper layers through a dry (folded) filter, the funnel being covered to prevent carbonation as much as possible. The filtrate is taken for the following determinations.*

38. **Alkalinity of a Lime containing no Sulphides.**—25 c.c. of the filtered lime are titrated with N/5 HCl, using methyl red (or phenolphthalein) as an indicator. Pure, saturated calcium hydrate solutions consume 5·9 c.c. of N/5 HCl,† and any higher figure found will be due either to ammonia formed by putrefaction, or to other alkalies being present by addition of carbonates or other salts which react with lime.

For works control the alkalinity figure is of considerable value, if unsharpened limes are used.

For gravimetric determination of total lime, caustic lime and other alkalies, see Lab. Book, p. 86.

39. **Free Ammonia.**—For exact determination, according to Procter and McCandlish's method, see Lab. Book, p. 60.

A short and for most purposes accurate method (the results of which are a little too low) consists of slightly acidifying 50 c.c. of the lime (which need not necessarily be filtered clear) in a distilling flask with hydrochloric acid, using phenolphthalein as indicator,

* The mixture may also be centrifugated; see Wood and Law, Collegium, 1912, p. 121 *et seq.*

† See also par. 34, p. 32, as to alkalinity of impure lime solutions.

and subsequently adding excess of magnesia. The flask is connected with a Liebig condenser and the liberated ammonia distilled into a known amount of N/10 HCl, the excess of which is titrated back with N/10 NaOH. Each c.c. N/10 HCl, neutralised by the ammonia equals 0·0017 grm. NH_3.

40. **Dissolved Hide Substance.**—There are many different products of hydrolysis present in old limes, derived from the easily attacked mucous layer, the hairs and horny layer, the cementing substance, and from the hide fibres themselves. Further, both the products of alkaline treatment and of putrefaction have to be considered, viz. calcium albuminates, calcium salts of mucins, albumoses, peptones, amino-acids and ammonia.

Some of these products, all of which contain nitrogen, are necessary constituents of any used lime, others again are only present in a putrid lime, causing loss of valuable hide substance. We have not yet a method to distinguish between the necessary and the objectionable splitting-up products, and hence the following methods are of limited value.

41. **Total Nitrogen by Kjeldahling.**—25 c.c (or more, according to the amount of nitrogen expected) of the filtered lime (hairs and microscopic particles must be removed, but the filtrate need not be clear), are pipetted into the Kjeldahling flask, acidified with sulphuric acid and evaporated nearly to dryness before adding 10 c.c. of concentrated sulphuric acid for the

actual digestion. This is easily accomplished by gently boiling over a small Bunsen flame, and no addition of an oxidising agent or even of potassium sulphate will be found necessary. When the liquid has turned quite colourless, which will be the case after 1–2 hours boiling, the flask is allowed to cool down, and after diluting with 200 c.c. water and connecting the flask with a distilling apparatus, a sufficient quantity of strong caustic soda solution is run in the flask, to render its contents alkaline, and the NH_3 produced by boiling, allowed to pass into a known quantity (25 c.c) of N/5 HCl, the excess of which is then titrated back with N/5 NaOH using methyl orange or carminic acid as an indicator. The distillation is carried out slowly, so that in $\frac{3}{4}$ hour about 200 c.c. have passed over into the receiver.

Each c.c. N/5 acid required for neutralisation of the ammonia formed will correspond to 2·8 mg. nitrogen, or 15·72 mg. hide substance.

For further details of the method, see Lab. Book, p. 64–69.

42. A method which gives an idea of the amount of amino-acid present, is based on the fact that amino-acids are neutral to phenolphthalein, but turn acid by addition of formaldehyde, which reacts with the amino groups and liberates the carboxyl group.

$$R\begin{matrix}\diagup NH_3 \\ \\ \diagdown COO\end{matrix} + HCHO = R\begin{matrix}\diagup N = CH_2 \\ \\ \diagdown COOH\end{matrix} + H_2O$$

By titrating these carboxyl groups with N/5 NaOH and phenolphthalein, a figure is obtained which is in relation to the amount of amino-acids present.

25 c.c. of the filtered lime liquor (containing no sulphides), is neutralised with acid, and a faint pink colour produced by a few drops of N/5 NaOH. 10 c.c. of 40 per cent. formaldehyde are then added, and the acidity thus produced titrated with N/5 NaOH. The formaldehyde solution must be neutralised to phenolphthalein before use, or the acidity of it allowed for.

A definite factor cannot be given, because of the variety of amino-acids (mono- and di- amino-acids) present; but the figure obtained in c.c. N/5 NaOH for each 25 c.c. lime liquor, will be useful in a works control for comparison of different limes.

43. Another method for determining dissolved hide substance (in absence of sulphides) and which measures calcium compounds of any hide-splitting-up products of acid character, viz. of mucins, albuminates, amino-acids, is based on the fact that these weak acids do not produce a colour change on methyl orange or methyl red, while they decolorise reddened phenolphthalein.

25 c.c. of the filtered lime liquor are titrated with N/5 HCl using phenolphthalein as indicator, then methyl orange is added and the titration continued until the colour changes from yellow to red. This last figure again will be useful for comparative works control,

though no exact relation between it and the nitrogen of the lime can be expected, and no constant factor can be suggested.

As a disadvantage of this method the indefinite end point given by very old limes, especially with methyl orange, must be mentioned.

44. A practical test of little accuracy, which has the object of measuring dissolved hide substance, as far as it is salted out from acid solution by means of saturated salt solution, is carried out in the following way :—50 c.c. of the filtered lime liquor are placed in a graduated 100 c.c. cylinder, some drops of phenolphthalein added, and after neutralising with 33 per cent. acetic acid an excess of 5 c.c. of this acid is added, and the whole made up to 100 c.c. with a clear saturated solution of common salt. After shaking the cylinder, the liquor is allowed to stand for one hour, and the volume of the precipitate, which rises to the top, is taken as a measure of the dissolved hide substance present. This method, apart from its rough nature, does not determine amino-acids, peptones or any splitting-up products which are not salted out under the given conditions, but the method is not without value for comparative works control.

45. **Analysis of Lime Liquors (Fresh or Used) containing Sulphides.**—The methods used in such cases are in their principle identical with those given in pars. 37–44, but need in several cases alterations and remarks, especially as to the determination of the

alkalinity of dissolved hide substance and of the amount of sulphides present.

46. **Alkalinity of a Lime containing Sulphides.** The titration with phenolphthalein as indicator gives not only the amount of lime and other alkalies present, but also half of the sulphides, according to the hydrolysis of sulphides into hydrates and hydrosulphides. The end point of this titration is also very indefinite, owing to the fact that the H_2S formed gradually escapes and allows the phenolphthalein to be reddened again.

Titrating with methyl orange as indicator gives not only the amount of alkali, but also that of the total sulphide, and of the calcium salts of acid splitting-up products of hide. In very old limes where much dissolved hide substance is present, the end point is not sharp.

47. Free ammonia is determined in the same way as given in par. 39, and as to the total nitrogen, the reader may be referred to par. 41.

48. The formaldehyde method of determining amino-acids in limes which contain sulphides, must be altered from that given in par. 42, because formaldehyde reacts with sulphides, increasing the alkalinity of the liquor.

$$HCHO + NaSH + H_2O = HCH\begin{matrix}OH\\SH\end{matrix} + NaOH$$

The sulphides can easily be removed by addition of

iodine, and the method has then to be carried out in the following way :—

To 25 c.c. of the filtered lime liquor a few drops of phenolphthalein and enough acetic acid are added to render the solution slightly acid; then an iodine solution of about N/10 strength is run into the liquor until a slight excess of iodine is seen by the remaining yellowish colour. The sulphides thus being removed ($NaSH + I_2 = NaI + HI + S$), N/5 NaOH is now added until a distinct pink colour is reached, and after addition of 10 c.c. formaldehyde, the titration with N/10 NaOH is carried out as described in par. 42.

49. The determination of dissolved hide substance by measuring the difference of phenolphthalein and methyl orange figure (see par. 43), is not applicable for limes which contain sulphides.

The practical test (par. 44) needs no alteration on this account.

50. Sulphides in limes are determined by the zinc sulphide method described in par. 35.

51. The analysis of the sludge of lime pits is done in the same way as the analysis of quick lime, see par. 34.

52. **Determination of Lime in Pelt.**—*Caustic lime* is determined by cutting the pelt in thin shavings, which are weighed into a stoppered bottle containing distilled water free from CO_2. After adding a few drops of phenolphthalein, N/10 HCl is run into the bottle until the red colour disappears, and the bottle

shaken and allowed to stand, when the diffusing lime will again redden the phenolphthalein. Further additions of acid are made very slowly and over many hours, till the red colour seen in the shavings just disappears. Each c.c. N/10 HCl equals 0·0028 grm. CaO present as caustic lime.

53. *Total lime* is determined by drying and igniting a weighed sample of the pelt, dissolving the ash in excess of N/10 HCl and titrating back with N/10 NaOH and phenolphthalein as indicator.

54. **Deliming.**—The amount of acid necessary for complete deliming is determined according to par. 52.

If this acid is applied in the form of a weak organic acid, and a considerable amount of its lime salt (sodium ammonium salt, etc.) is present, the deliming capacity of this mixture will be found by titrating 25 c.c. with N/10 NaOH and phenolphthalein, while the desired incapacity of swelling is ascertained by testing with methyl orange or congo red, to which the liquor ought not to be acid.

A more accurate method is the electrometric method as described by Sand and Law,* according to which the actual hydrion concentration ought to be less than 10^{-5} if the deliming liquor can be used without any danger of using excess.

55. Another method, which does not require the special apparatus, consists of determining the free and

* Collegium, 1911, p. 150 *et seq.*

combined acids, the proportion of which ought to be $1 : >1$.

If volatile acids, like acetic or butyric are used, this determination can be made by first distilling the free acid until the volume is reduced to about one-third,* the receiver containing a known amount of N/10 NaOH, the excess of which is titrated back with N/10 HCl; and then adding oxalic acid (or sulphuric or phosphoric acid) to the distilling flask and continuing the distillation, using another portion of N/10 NaOH as a receiver, and again titrating back with N/10 HCl. Each c.c. N/10 NaOH used in this last titration equals 0·006 grm. acetic acid (or 0·0088 grm. butyric acid) present in form of salts, while a similar calculation of the first portion of N/10 NaOH gives the amount of free acid.

56. **Drenches.**—The acids present are determined by—

(*a*) Titrating a measured volume of the filtered liquid with N/10 NaOH and phenolphthalein (total acidity), and –

(*b*) Boiling the same quantity of the filtered liquid until its volume is reduced to about 1/3, and then titrating with N/10 NaOH and phenolphthalein (non-volatile acids). The difference of *a* and *b* gives the free volatile acids.

* Distillation to one-third will give comparative results of value, but for accurate estimation of total volatile acid, must be repeated, with addition of water or steam, until the fractions coming over show only negligible traces of acid.

57. For more detailed analysis of drenches, see Laboratory Book, p. 94.

As to the investigation of puers and bates, the reader must also be referred to the Laboratory Book, p. 92, and Wood's "Puering, Bating and Drenching of Skin" (Spon, 1912).

CHAPTER V.

THE QUALITATIVE RECOGNITION OF VEGETABLE TANNINS.

58. THE qualitative recognition of tannins has become a subject of increasing importance since the use of extracts has reached such considerable dimensions. In judging the quality of a tanning material, as barks, fruits, leaves, etc., the mere appearance of the material will be sufficient to indicate what sort of tannin one has to deal with, and the ordinary gravimetric analysis will give all necessary information as to the tanning value of the sample. Adulterations will not easily occur, or—in cases of ground material—will be recognised by microscopic examination.

For judging the purity of an extract or for identifying a tannin in form of an extract, chemical tests must be applied, and though our knowledge of useful tests is unfortunately not as yet sufficient to allow us to answer all possible questions on the qualitative composition of an extract or extract mixture, the following tests will prove useful.

We may distinguish colour tests, precipitation and solubility tests. Colour tests can be of value if a single tannin is given, but they are almost useless in cases of mixtures. The following will therefore be principally precipitation- and solubility-tests. All figures given are to be taken as approximate, if not stated otherwise.

59. **The Gelatin Test.**—To 2–3 c.c. of the tannin-solution (0·4 per cent. tan) a solution of gelatin is added drop by drop. The formation of a precipitate or turbidity is observed with all tannins, though the sensitiveness of the test is not the same for different tannins. A precipitate is obtained in extremely dilute solutions with gallotannic acid and all fruit-tans, while bark-tans give the test in not too weak solutions, and pine bark and gambier are least sensitive towards gelatin. The gelatin solution is prepared by dissolving 10 grm. gelatin and 100 grm. salt in one litre of water.

Excess of gelatin must be avoided, because the precipitate is soluble in such excess, and might be overlooked.

The gelatin test is the most characteristic test for tannins in general, and is used to notify the presence of any tannin in a solution, to differentiate tannin from non tans, especially in the hidepowder-filtrate of the official method (see p. 87) or in the extraction of a tanning material (see p. 96).

Substances which are like tannins in most other

reactions, but which do not give the gelatin test, must be regarded as non-tans.

60. **The Iron Test.**—3–5 drops of a 1 per cent. solution of iron alum are added to 2–3 c.c. of the tannin solution (0·4 per cent.).

A blue or bluish violet colour is produced by many tannins (by the so-called pyrogallol tans, and also by mimosa and malet), while other tannins (catechol tans) give a green colour. In stronger solutions a precipitate of bluish black or greenish black colour is formed.

The iron test must be carried out in neutral tannin solutions; strong mineral acids prevent the test, weak organic acids cause a green colour even with pyrogallol tans; while a slight alkaline reaction (easily obtained by addition of sodium bicarbonate or sodium acetate) produces bluish violet coloration even with catechol tans.

The use of ferric chloride is not to be recommended, as its aqueous solution is always strongly acid.

An excess of iron alum must be avoided, lest the oxidising action of the ferric salt should lead to olive or brown products which make the test less distinct.

The iron test is not only given by tannins, but also by phenolic non-tans, and tans and non-tans of the same material behave comformably. In some materials (e.g., oak bark) both iron-greening and iron-blueing tannins are present.

61. **The Lead acetate Test.**—Both normal and

basic lead acetate form precipitates with all tannins. The precipitation with basic lead acetate is used in the method of sugar determination in tanning materials (see par. 184) for the removal of tannin, which is so complete that the filtrate of this precipitation remains colourless after addition of excess of strong sodium hydrate. Normal lead acetate (sugar of lead) gives as complete a precipitation with some pyrogallol tans (chestnut and oakwood), while extracts of most other tanning materials give a darkening after adding sodium hydrate to the filtrate of the lead acetate precipitation, probably due to some phenolic non-tans.

62. **The Acetic acid lead acetate Test.**—Presence of acetic acid prevents the lead acetate precipitation of all catechol tans, while the pyrogallol tans are totally or partially carried down.

Take 5 c.c. of 0·4 per cent. tan solution in a test tube, add 10 c.c. acetic acid (10 per cent.) and 5 c.c. lead acetate (10 per cent.). If no precipitate is formed, catechol tans are present only, and copious precipitates prove the presence of pyrogallol tans.

63. **The Bromine Test.**—Bromine water (4–5 grm. bromine per litre) is added drop by drop to 2–3 c.c. of the 0·4 per cent. tan solution in a test-tube, until the solution smells strongly. The tannin solution should be faintly acid, acetic acid being added if required.

Catechol tans give immediate precipitation, while pyrogallol tans give soluble brom-derivatives, but are

sometimes gradually oxidised by the bromine to insoluble products. Hence no notice need be taken of any precipitate which only forms after long standing.

Strongly sulphited extracts of catechol tans give no distinct bromine test, and the presence of wood pulp also diminishes, or even prevents, the precipitation.

The bromine test is very useful for finding catechol tans as adulterants in pyrogallol tans, e.g. pistacia lentiscus in sumach, quebracho in chestnut, etc.

64. **The Formaldehyde Test.**—Add 10 c.c. formaldehyde (40 per cent.) and 5 c.c. hydrochloric acid to 50 c.c. of the tan solution (0·4 per cent. tan) in a flask and boil half an hour with the reflux condenser.

Observe if the solution remains clear, or if a copious precipitate is formed during boiling. Then cool thoroughly, filter, and take 10 c.c. of the filtrate in a test tube, add 1 c.c. iron alum (1 per cent.) and 5 grm. sodium acetate (solid), and observe if a strong bluish violet coloration appears.

Catechol tans are completely precipitated with formaldehyde and hydrochloric acid, the filtrate giving no violet coloration with iron. Some pyrogallol tans (oakwood, chestnut, etc.) remain quite clear during boiling, while others are partially precipitated, but all pyrogallol tans can be detected by the iron test in the filtrate of the formaldehyde precipitate. This test has proved to be useful for the detection of myrobalans (or other pyrogallol tans) in quebracho (or other catechol tans).

65. **The Ammonium sulphide Test.**—Add 2–3 drops of strong sulphuric acid to 25 c.c. of a strong tannin solution (2·5 per cent. tan) in a flask, boil 1–2 minutes, and cool down; then add about 5 grm. salt, shake, and allow the mixture to stand for 5–10 minutes, when the precipitate has to be filtered off. In a test tube add 10–15 drops ammonium sulphide to about 15 c.c. water, and then 2–3 c.c. of the above filtrate. All pyrogallol tans give a copious precipitate (of different colours), while most catechol tans cause no precipitation, even after standing over night. Mimosa and malet behave like pyrogallol tans towards this test, and can therefore be easily detected even in mixtures with other catechol tans.

66. **The Ethyl acetate Figure.**—Determine the total solubles in 25 c.c. of the analytical tannin solution (0·4 per cent. tan) by evaporating and drying at 100–105° till constant weight. Take another 25 c.c. and shake out repeatedly with ethyl acetate. This can be done in a small separating funnel, using about 25 c.c. ethyl acetate at a time, and running the aqueous layer into another funnel, where the shaking out is repeated with fresh ethyl acetate. The process is repeated (usually three times) until the ethylacetate layer remains quite colourless. A more convenient way of extracting the tannin solution is by means of the apparatus shown in Fig. 1. The flask A contains the ethyl acetate, and is heated by means of a water bath. A wide tube leads the vapours

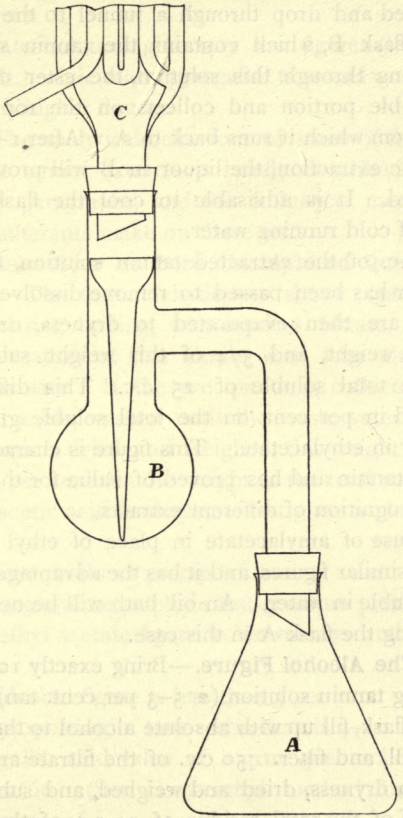

FIG. 1.

through B into the reflux condenser C, where they are condensed and drop through a funnel to the bottom of the flask B, which contains the tannin solution. In passing through this solution, the ester dissolves the soluble portion and collects on the top of the liquid, from which it runs back to A. After 1–2 hours automatic extraction, the liquor in B will prove to be exhausted. It is advisable to cool the flask B by means of cold running water.

20 c.c. of the extracted tannin solution, through which air has been passed to remove dissolved ethyl acetate, are then evaporated to dryness, dried till constant weight, and 5/4 of this weight subtracted from the total soluble of 25 c.c. This difference, expressed in per cent. on the total soluble gives the solubility in ethylacetate. This figure is characteristic for each tannin and has proved of value for the qualitative recognition of different extracts.

The use of amylacetate in place of ethyl acetate leads to similar figures, and it has the advantage of not being soluble in water. An oil bath will be necessary for heating the flask A in this case.

67. **The Alcohol Figure.**—Bring exactly 10 c.c. of the strong tannin solution (2·5–3 per cent. tan), into a 100 c.c. flask, fill up with absolute alcohol to the mark, shake well, and filter. 50 c.c. of the filtrate are evaporated to dryness, dried and weighed, and subtracted from half of the total residue of 10 c.c. of the above strong tannin solution. This difference expressed in

per cent. on the total soluble gives the alcohol precipitation figure.

All catechol tans give very low figures (less than 5 per cent.), while many pyrogallol tans and wood pulp give much higher figures.

68. The analytical behaviour of some of the more important tannin extracts is briefly described in the following paragraphs, and the influence mentioned, which adulterants make on these tests.

69. **Behaviour of Pure Unsulphited Quebracho Extract.**—The formaldehyde test shows copious precipitate during boiling, a colourless filtrate and no violet coloration of this filtrate with iron alum and sodium acetate. If the precipitate is collected in a Gooch crucible, washed until the wash water is free from chlorine, dried and weighed, this weight will be about 95 per cent. on the weight of the total solubles.

The acetic acid lead acetate test gives a clear solution.

Bromine produces precipitation.

The ammonium sulphide test gives no precipitate.

The ethyl acetate figure is between 70 and 80 per cent.

The alcohol figure is less than 5 per cent.

The proportion of tans : non-tans is 9–10 : 1.

The gallic acid value of 1 grm. quebracho tannin is 0·58–0·60. (See Loewenthal method for tannin analysis, par. 126.)

70. The presence of mangrove extract in unsul-

phited quebracho extract is indicated by the following tests :—

The ethyl acetate figure is lowered, owing to the fact that the ethyl acetate figure of pure mangrove is less than 5 per cent.

The non-tans are slightly increased, so that the proportion of tans and non-tans is $< 9 : 1$.

In pure mangrove this proportion is 3–4 : 1.

The fact that mangrove always contains considerable amounts of salt, can be made use of in deciding a quebracho extract free from mangrove if the ash contains little or no sodium chloride. A positive chlorine test may not necessarily be due to mangrove, but to chlorides from other sources.

71. The presence of myrobalans in unsulphited quebracho extract is easily detected by the following reactions :—

The filtrate from the formaldehyde precipitation gives a distinct bluish violet with iron alum and sodium acetate.

The acetic acid lead acetate test gives a precipitate.

The ammonium sulphide test also causes a precipitate.

72. The presence of wood pulp (sulphite-cellulose) liquor in unsulphited quebracho extract is found by the following tests, of which the aniline test must be particularly mentioned as a general lignine test.

5 c.c. of the tannin solution (0·4 per cent. tan) and

(exactly) 0·5 c.c. aniline are violently shaken in a test tube, and (exactly) 2 c.c. of strong hydrochloric acid added. In absence of pulp liquor a clear liquid is produced; presence of pulp liquor causes more or less dense turbidity, which increases on standing. Not longer than fifteen minutes should be allowed before making the decisive observation. Extracts which are prepared by means of pressure, especially in presence of alkalis or sulphites, often give the lignine test, even if no wood pulp has been purposely added, the alkaline treatment being responsible for lignine-like substances brought into solution.

The following tests also indicate the presence of pulp liquor in unsulphited quebracho: the formaldehyde precipitate will be less than 90 per cent. on the weight of the total solubles if not less than 10 per cent. of pulp liquor is present.

The ethyl acetate figure is considerably lowered, pulp extract being practically insoluble in ethyl acetate.

The alcohol figure is much increased, as pulp extract shows figures from 40–70 per cent.

The proportion of tans to non-tans is altered in favour of non-tans.

The gallic acid value of 1 grm. tannin is distinctly lowered, pulp extract giving figures of 0·09 to 0·14 only.

73. **Behaviour of Sulphited Quebracho Extract.** The formaldehyde test shows a copious precipitate ; uring boiling, the filtrate is in most cases colourless,

but there are methods of sulphiting by which the formaldehyde precipitation gets a more colloidal nature and passes partially through the filter, thus colouring the filtrate more or less yellowish. Even in these cases no distinct violet colour is produced by addition of ferric alum and sodium acetate to the filtrate.

A quantitative determination of the formaldehyde precipitate cannot be carried out, because the precipitate, after carefully washing in the Gooch crucible and drying at 100° C. decomposes, sulphuric acid splitting up and charring the precipitate: no constant weight can be obtained.

The acetic acid lead acetate test gives no precipitation, a whitish turbidity being due to the formation of lead sulphate.

Bromine produces a precipitate, but this test is less delicate in strongly sulphited extracts, and may even fail.

The ammonium sulphide test produces no precipitation.

The ethyl acetate figure depends on the degree of sulphiting, and may vary between 0 per cent. (completely sulphited quebracho) and 70 per cent. (The highest figure hitherto found in slightly sulphited extracts was 40 per cent.).

The alcohol figure is less than 5 per cent.

The proportion of tans : non-tans depends on the amount of inorganic matters present, and gives no characteristic figure.

The gallic acid value of 1 grm. sulphited quebracho tan is 0·58–0·60 (the same figure as unsulphited quebracho).

74. The presence of mangrove in sulphited quebracho extract cannot be proved with certainty by the methods hitherto known. The following tests recently proposed by E. Schell, A. W. Hoppenstedt and B. Kohnstein still require confirmation.

Schell's Test.—20 c.c. of the tannin solution (0·4 per cent. tan) are heated to boiling-point in order to expel air, rapidly cooled and covered with a layer of petrol-ether; then 1 c.c. of a 20 per cent. cobalt chloride solution and 1 c.c. strong ammonia are added, and the liquid mixed by gently stirring with a glass rod. Quebracho extracts which contain no mangrove are said to give a green or greyish green colour, while presence of mangrove is shown by a brownish violet shade.

Hoppenstedt's Test.—Add 25 c.c. of a 1 per cent. quinine hydrochloride solution slowly while stirring to 25 c.c. of the tannin solution (0·4 per cent. tan). Place 5 c.c. of the clear filtrate in a test tube, then add 1 c.c. of concentrated acetic acid, 2 c.c. of acetone, and 5 c.c. of ethyl acetate, and mix thoroughly after each addition. The lower layer is yellow brown in presence of mangrove, but colourless with all the other tannins.*

* Different mangrove extracts seem to give different intensity of colour, and pulp extract produces also a distinct yellow colour.

Kohnstein's Test.—Add 5 c.c. of a 10 per cent. solution of Alcutin * to 10 c.c. of the tannin solution (0·4 per cent. tan), filter, add a little ammonia to the filtrate and boil. In the presence of mangrove a dark red colour appears.†

75. The fact that mangrove contains quite considerable amounts of sodium chloride in the ash has also been used to distinguish a pure from an adulterated quebracho extract. But it must be remembered that salt may be present from other causes than the addition of mangrove, as the water used for extracting the quebracho wood may have been rich in chlorides. Hence only a negative chlorine test (or mere traces of chlorides) can be taken as a proof of the absence of mangrove. (Even this deduction may become invalid if mangrove, growing far from the sea coast, should be found to contain no considerable amounts of chlorides.)

76. The **presence of myrobalans** in sulphited quebracho extract is indicated by the formaldehyde test, a deep bluish violet being obtained in the filtrate of the precipitation after adding iron alum and sodium acetate.

Other tests are: the acetic acid lead acetate test, which leads to a copious precipitate in presence of myrobalans; and the ammonium sulphide test, which also gives a precipitate.

* From Dr. Meyersberg, Vienna, Stumpergasse 27.

† Pollak states, that the presence of myrobalans and other tannins which give yellow precipitates, make the test doubtful.

77. The **presence of pulp extract** in sulphited quebracho extracts is shown by the aniline test, the increased alcohol figure and the gallic acid value of 1 grm. tannin, which appears distinctly lowered. The other tests mentioned in the case of unsulphited quebracho extract are not applicable to sulphited extracts.

78. **Behaviour of pure mimosa bark extract.**— The formaldehyde test shows copious precipitate during boiling, a colourless filtrate and no violet coloration of this filtrate with iron alum and sodium acetate. Excess of sodium hydrate added to the filtrate of the formaldehyde precipitation gave no darkening in any case hitherto investigated. The weight of the precipitate, which is collected in the Gooch crucible, and dried to constant weight, comes to about 86 per cent. on the weight of the solubles.

The acetic acid lead acetate test gives a clear solution.

Bromine produces precipitation.

The ammonium sulphide test produces a distinct precipitation (which, however, in some cases takes some hours to appear). This test is characteristic for mimosa and malet, as it distinguishes these two catechol tans from all others.

Ammonium acetate produces no precipitate in strong mimosa liquors.

The solubility in ethyl acetate amounts to 30–40 per cent.

The alcohol figure is less than 5 per cent.

The proportion of tans to non-tans is 2·5–3 : 1.

The gallic acid value of 1 grm. mimosa tan is 0·529.

79. Mixtures of mimosa with **myrobalans, mangrove** or **wood pulp** are detected similarly to those described in the case of quebracho.

80. **Behaviour of Pure Chestnut Extract.**—The formaldehyde test shows clear solution after fifteen minutes boiling.

Acetic acid and lead acetate give a precipitate which is almost complete, so that the filtrate shows but a very faint bluish violet coloration with iron alum.

Bromine gives no precipitate.

The ammonium sulphide test gives a strong precipitate.

The ethyl acetate figure is between 0 and 12 per cent., and depends apparently on the mode of manufacturing the extract.

The alcohol figure varies between 10 and 20 per cent.

The proportion of tans to non-tans is 3–4 : 1.

The gallic acid value of 1 grm. chestnut-wood tannin is 0·604.

81. The presence of **oak-wood** extract in chestnut extract cannot be recognised with certainty and all tests hitherto described (colour tests only), fail.

82. The presence of any **catechol tan** is determined by the formaldehyde test, which shows a distinct precipitate during boiling; further by the bromine test which produces a precipitate.

83. The presence of **myrobalans** and other **fruit tannins** is not easily to be recognised, but the acetic acid lead acetate test will give some information in the hands of an experienced worker, as the fruit tans are but very incompletely preciptated and the filtrates give (especially in the case of myrobalans), a deep violet with iron alum.

84. The presence of **pulp extract** in chestnut extract can be detected by the aniline test, by the gallic acid value, which is distinctly lowered, and by the incompleteness of the lead acetate precipitation; 5 c.c. of the tannin solution (0·4 per cent.) are taken in a test-tube and 5 c.c. lead acetate (10 per cent.) added, shaken and filtered; with pure chestnut the filtrate gives neither an iron test nor a darkening by adding excess of sodium hydrate (to redissolve the lead hydrate formed). Presence of pulp extract can be detected by the brown colour of the filtrate after adding the alkali.

85. **Pure Oak Wood Extract** behaves very similarly to pure chestnut extract; the somewhat lower percentage of tannin, the ratio of tans to non-tans (2–2·5 : 1) and the lower gallic acid value (0·527), being the only slight differences. A gradual difference in the salting out of oak-wood and chestnut solutions may in some cases be found valuable for the distinction.

86. For mixtures of oak-wood extract with other tannin materials, the same applies as has been said for chestnut in mixtures.

87. The purity of **sumach** will best be stated by the microscopical investigation (see Sect. XXIV. Laboratory Book, p. 407 *et. seq.*), and by the official analysis which, in case of considerable adulteration, will show a lower tannin figure.

For sumach extracts the following chemical tests may be recommended:—

Bromine gives no precipitate, while *Pistacia lentiscus* is precipitated by this reagent.

The ethyl acetate figure amounts to 50–60 per cent. (*Pistacia lentiscus* gives less than 5 per cent. and consequently diminishes the figure considerably.)

The alcohol figure is 10–15 per cent. (*Pistacia lentiscus* gives about 30 per cent.).

The proportion of tans to non-tans is 1·5–2 : 1.

The gallic acid value of 1 grm. sumach tan is 0·66.

88. **Scheme for Qualitative Recognition of a Vegetable Tannin.**—As a first test, the formaldehyde one is made; and three different kinds of behaviour are possible, according to which the tannin is placed into Group I., II., or III.

Group I.—Complete precipitate: the filtrate gives neither gelatin test nor iron test. (See par. 64).

Tests for confirmation: bromine test (precipitate) and acetic acid lead acetate test (no precipitate).

Group II.—No precipitation during fifteen minutes boiling.

Tests for confirmation: bromine test (no precipitate) ammonium sulphide test (precipitate).

Group III.—Considerable precipitate during boiling, but distinct iron test of the filtrate.

To Group I. belong: quebracho, mangrove, ulmo, gambier, pinebark, hemlock, mimosa, malet.

To Group II. belong: oak-wood, chestnut-wood, valonia, myrobalans.

To Group III. belong: oakbark, pistacia lentiscus, sumach, divi-divi, algarobilla, teri, bablah, galls.*

89. Having found to which group the tannin belongs, the following further testing is done in each group:—

Further Testing of Group I.—The ammonium-sulphide test (see par. 65) allows a subdivision, in so far as no precipitate is obtained with quebracho, mangrove, ulmo, gambier, pinebark, hemlock (Group I*a.*), while a precipitate is shown by mimosa and malet (Group I*b.*)

Group I*a.* is also characterised by the green coloration produced with iron alum.

Group I*b.* gives a bluish violet with iron alum.

The further way of identifying the tannin in I*a.* or I*b*, demands the carrying out of all the tests mentioned in pars. 60–67, and especially by determining the ethyl acetate and alcohol figure, the proportion of tans to non-tans, and—in case of suspicion of pulp extract—the aniline test and the gallic acid value (Loewenthal).

A single tannin will easily be identified in this way, and even mixtures will in many cases be found out.

* Galls give only a slight precipitate.

90. **Further Testing of Group II.**—The acetic acid lead acetate test allows a subdivision, as no distinct coloration is given by the addition of iron alum to the filtrate of the lead precipitation, in the case of oak-wood, chestnut-wood and valonia (Group II*a*.), while a deep violet coloration is obtained with myrobalans (Group II*b*.).

The further testing in these groups is done according to the method described with regard to I*a*. and I*b*.

91. **Further Testing of Group III.**—The bromine test allows a subdivision, a precipitate being obtained with oakbark and pistacia lentiscus (Group III*a*.) while sumach, divi-divi, algarobilla, etc. give no precipitate (Group III*b*.).

Here again, all tests given above must be applied to identify the tannin; and this is less easily done in this than in the other groups.

The table on next page gives a view of the scheme of qualitative testing.

92. TABLE I.

50 c.c. TANNIN SOLUTION (0·4 PER CENT.) BOILED WITH 25 c.c. OF THE HCHO–HCl MIXTURE FOR 30 MIN., THOROUGHLY COOLED AND FILTERED.

Complete precipitate: filtrate + iron alum + sodium acetate: no violet coloration	No precipitate after 15 minutes boiling	Considerable precipitate after 15 minutes boiling; deep violet coloration of the filtrate + iron alum + sodium acetate
Group I.	*Group II.*	*Group III.*
Confirming tests: + bromine: precipitate + acetic acid + lead acetate: no pp.	Confirming tests: + bromine: no pp. Ammonium-sulphide test: pp.	
25 c.c. tannin solution (2·5 per cent.) + ammonium-sulphide test (par. 65).	5 c.c. tannin solution (0·4 per cent.) + acetic acid lead-acetate test. The filtrate of the pp. gives + iron alum	5 c.c. tannin solution (0·4 per cent.) + bromine test
no pp. pp.	no distinct coloration / distinct coloration	pp. / no pp.
Group I*a*. Group I*b*.	Group II*a*. Group II*b*.	Group III*a*. Group III*b*.
Confirming tests: + iron alum		
green / bluish violet		

93. TABLE

—	Formaldehyde-test (par. 64)		Bromine-test (par. 63)	Ammonium-sulphide-test (par. 65)	Lead-acetate-test (par. 61) Filtrate + NaOH
	During 15 min. boiling	Filtrate + iron alum + sodium acetate			
Quebracho .	pp.	no coloration	pp.	no pp.	yellowish
Sulphited Quebracho	,,	,,	(par. 73)	,,	,,
Mangrove .	,,	,,	pp.	,,	colourless
Ulmo . .	,,	,,	,,	,,	yellowish
Gambier . .	,,	,,	,,	,,	—
Mimosa . .	,,	,,	,,	pp.	colourless
Oakbark . .	,,	violet	,,	,,	,,
Hemlock .	,,	no coloration	,,	pp. (after standing over night)	yellowish
Pistacia . .	,,	deep bluish violet	,,	pp.	yellow
Chestnut . .	no pp.	,,	no pp.	,,	colourless
Oakwood .	,,	,,	,,	,,	,,
Myrobalans .	pp.	,,	,,	,,	,,
Sumach . .	,,	,,	,,	,,	yellow
Valonia . .	turbid	,,	,,	,,	colourless
Divi-Divi .	,,	,,	,,	,,	,,
Algarobilla .	,,	,,	,,	,,	,,
Wood pulp .	no pp.	no coloration	,,	not characteristic	deep yellow

II.

Acetic acid + lead acetate test (par. 62)		Ethyl-acetate-figure (par. 66)	Alcohol-figure (par. 67)	Gallic acid value of 1 grm. tannin (see Collegium, 1909, p. 191)	tans / non-tans
—	Filtrate + iron alum				
no pp.	green	70–80	0–5	0·59	8–10
no pp. (but $PbSO_4$)	,,	0–70 (par. 73)	0–5	0·59	depends on the method of sulphiting
no pp.	,,	0–5	0–5	0·68	2·5–4
,,	,,	70–80	0–5	—	8–10
,,	,,	50–65	5–10	0·56	1·2–1·5
,,	deep bluish violet	30–40	0–5	0·53	2–3
pp.	—	12	17	—	1–1·5
no pp.	green	18	9	—	1–2
pp.	green and violet	3	29	—	—
,,	very faint violet	0–16	10–20	0·56–0·66	2–3·5
,,	colourless	0–12	20–30	0·5–0·56	1–2
,,	violet	30–50	0–15	0·55–0·60	1·5–2·5
,,	,,	40–60	5–20	0·65–0·68	1·5–1·8
,,	colourless	5–15	20–40	0·55–0·63	2–3
,,	violet	30–50	0–10	—	2
,,	,,	50–60	0–5	—	2
no pp.	colourless	0–5	30–70	0·09–0·14	0·75

CHAPTER VI.

SAMPLING AND GRINDING OF TANNING MATERIALS.

94. **Sampling.**—As the divergence between different chemists in the results of analysis of tanning materials and extracts can in most cases be traced to the inefficient manner of sampling, a few remarks on the methods which should be adopted may be useful.

Official Methods of Sampling of the I.A.L.T.C.

95. **Liquid Extracts.**—A sampling tool should be used for liquid extracts. Such an instrument as that designed and sold by Mr. Arthur Priestman, 275 Burlington Street, Liverpool, has proved of much value. Before proceeding to take the sample the extract in the barrels should be thoroughly mixed by rolling and stirring up, and if they have been standing for any lengthy period the only way of doing this satisfactorily is by removing the end of the barrel and stirring with some suitable stirrer; the mere rolling of the barrels is not sufficient in this case. When the mixing has

been satisfactorily accomplished, the sampling tool is plunged into the extract, the valve opened, and the instrument moved to all parts of the barrel whilst it fills. This procedure takes place with several barrels, the number varying according to the number of barrels in the consignment. The samples from each barrel are collected into one vessel and are mixed well together, and bottles are filled from this and sealed. It is desirable, if the barrels are numbered, to select for sampling numbers equally distributed through the parcel, as the barrels are usually filled in rotation.

The following table shows the number of barrels to be sampled from with different consignments.

TABLE III.

Number of barrels in consignment	I.A.L.T.C. official	Dr. Lepetit's suggestion (not official)*
20	1	3
50	2-3	6
100	5	9
200	10	13
300	15	16
400	20	19
500	25	22

* See Collegium, p. 382, 1911.

96. **Gambier.**—Block gambier is usually sampled by means of a tubular sampling tool similar to a large cork-borer. The blocks are perforated by means of the sampler, which should be passed completely through

each block in seven places, so as to include the inner and outer parts, and the portions mixed together with as little exposure to the air as possible. Not less than 5 per cent. of the consignment must be taken.

97. **Solid Extracts.**—Solid extracts of uneven moisture contents, such as cutch, etc., are often too hard and brittle to cut with a tool, and cannot be pulverised until dry. The blocks should be broken, and a sufficient number of portions drawn both from the "inner" and "outer" parts of the block to fairly represent the bulk. The whole sample should be weighed, air dried, and the loss of moisture ascertained. The material is then ground in a mortar, analysed in the usual way, and the results calculated to original water contents as follows:—

Original weight . .	900 grm.	
After drying . . .	765 „	
Loss	135 „	= 15 per cent.

The results must therefore be calculated by multiplying the analytical results of the air-dried sample by $\frac{85}{100}$ and 15 per cent. added to the water.

98. **Barks.**—Bark in long rind, and other material in bundles, shall be sampled by cutting a short section from the middle of 3 per cent. of the bundles by means of a saw or a pair of strong shears.

99. **Sumac.**—Great care should be taken in sampling sumac, as very often adulteration takes place in layers, pure sumac being placed at the top or mouth

of the bag. A sampler similar to a large cheese or butter sampler should be used, and should be plunged well into the bags to ensure even sampling. At least 5 per cent. of the sacks should be sampled. It is advisable, on receiving the sample at the laboratory, that it should be thoroughly mixed in a churn for half an hour.

100. **Valonia.**—The proportion of beard to cup in consignments of valonia varies very considerably, and the proportion of tannin in each part is very different. The separate analyses of the cups and beards of Smyrna and Greek valonia gave the following results: "Smyrna" cup = 32·4 per cent., beard = 43·6 per cent.; "Greek" cup = 27·4 per cent., beard 41 per cent. The proportion of beard to cup is usually about one-third of the former to two-thirds of the latter; but where samples have to be dealt with which have not been specially drawn, it is advisable to weigh an aliquot proportion of beard and whole cups, or to make the analyses on the whole cups. To sample valonia, at least 5 per cent. of the sacks should be spread on a level floor and the pile halved; the half is then halved again, and this process repeated until a sufficiently small quantity has been obtained.

101. **Myrobalans.**—The specific gravity of myrobalans varies considerably, the thin lean nuts being usually found at the top of the bag, and the plumper and richer nuts sinking to the bottom; careful note should be taken of this fact, and samples drawn con-

taining both the light and heavy nuts. A sample from 5 per cent. of the consignment should be taken.

Methods of Sampling of the American Leather Chemists' Association.

102. **Liquid Extract.**—The regulations for the American methods of sampling are as follows: 70 barrels or less, 10 per cent. of the number shall be sampled. When 71–140 barrels are to be sampled 9 per cent. of the number shall be taken, and for every increase of 70 barrels (up to 500 barrels) there shall be a decrease of 1 per cent. from which the samples shall be taken. When more than 500 barrels are to be sampled 3 per cent. shall be taken; when more than 2000 barrels, 1 per cent. shall be taken.

The samples shall be drawn as specified in the I.A.L.T.C. regulations.

103. **Solid Extracts.**—The samples shall be taken from a number of packages, according to the consignment (see Liquid Extracts). When sampling is completed the whole composite sample shall be broken up till it will pass through a sieve of 1-inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings.

104. **Crude Tanning Materials.**—Nuts, beans, pods, ground materials, etc. The number of packages shall be as specified in "extract sampling," and shall be emptied in uniform horizontal layers in a pile on some

clean surface. At least five equal samples shall be taken from top to bottom through the pile at uniformly distributed spots. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. When the number of packages to be sampled is so great as to make one pile impracticable, two or more piles may be made, and the samples from several piles properly mixed.

105. **Bark, Wood, etc., in Sticks.**—Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through, and the sawdust thoroughly mixed and sampled as in previous section.

106. **Materials Prepared for Leaching.**—Samples of equal size shall be taken at uniform intervals as the material enters the leach. These shall be thoroughly mixed and reduced to suitable bulk by quartering.

107. **Spent Materials from Leaches.**—Samples shall be taken from the top, middle, and bottom, and in each case from the centre and outer portions of the leach. Thoroughly mix and reduce the bulk by quartering.

108. **Tanning Liquors.**—The liquor shall be mixed by thoroughly plunging, and samples of at least one pint taken. The addition of 0·03 per cent. thymol or other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

109. **Grinding.**—The whole sample, or not less than 250 grm., shall be ground in a mill until it will

pass through a sieve of five wires per centimetre. When materials, such as bark and divi-divi, contain fibrous material which cannot be ground to powder, the ground sample shall be sieved and the respective parts which do and do not pass through the sieve shall be weighed separately, and the sample for analysis shall be weighed so as to contain like proportions.

A suitable mill for grinding tanning materials for analytical purposes is that made by H. R. Gläser, Wien; also drug mill No. 3 or 4, made by Burroughs, Wellcome and Co., will be found very useful. Several other good mills for laboratory purposes are on the market, among which the following may be mentioned:—"Tannina," by Robert Paessler, Freiberg, Saxony; Schmeija's, and the Hardy Pick Co's. A laboratory disintegrator is made by Grumbach and Son, Freiberg, Saxony, to the design of Dr. Koerner. It is necessary to prepare the bark by breaking or crushing it before grinding in these small mills. A thick cast-iron plate, having ledges on three of its sides, and a flat-faced heavy steel hammer will in most cases be found effective.

Some materials lose moisture when submitted to the grinding process, and it is advisable therefore to estimate the moisture both before and after grinding, and if any loss has taken place the results obtained on the drier sample should be calculated back to the original moisture, on the principle illustrated by example, par. 97.

CHAPTER VII.

ESTIMATION OF TANNINS.

110. VERY numerous methods have been suggested for this purpose, but only the gravimetric methods, founded on the absorption by hide-powder, and the Löwenthal volumetric are at present of practical importance. The earliest methods, founded on precipitation with gelatin, failed because the compound formed was not of constant composition; and the same is more or less true of precipitation by metallic salts and organic bases, the reactions being rather of the nature of colloid flocculations than true chemical compounds, and differing for different tannins. Most of these methods also failed to differentiate between tannins and allied bodies like gallic acid, and involved a second determination of these after removal of the tannins with gelatin or hide. The Löwenthal process has this defect, and also gives different values for different tannins, but from its rapidity and constancy has maintained its position for tannery control, for which purpose a rapid method free from these defects is much needed.

The hide-powder methods are rather of the nature of laboratory tanning experiments, than truly chemical reactions, and being largely empirical require the strictest adherence to detail to obtain concordant results, but have in this respect been brought to a high degree of perfection, and give indications of the utmost use to the practical tanner.

111. The hide-powder gravimetric method depends on the determination by drying of the total solids in a tannin solution and again in another portion which has been deprived of its tannin; the difference being the "tanning matters." It was first given a practical form by Simand and Weiss at the Vienna K.K. Research Institute for Leder-Industrie in 1886, who detannised by maceration with successive quantities of hide-powder. At the suggestion of Procter, this method was modified by filtration of the liquid through a layer of powder packed in a suitable tube, and this with various improvements in detail remained the standard method of the International Association of Leather Trade Chemists up to 1907. In the meantime a method was worked out in the United States by Dr. Yocum and others, depending on mechanical agitation of the liquid to be detannised with a hide-powder previously rendered insoluble by chroming. As this method permitted a thorough washing of the powder immediately before use, and was unaffected by mechanical differences of packing in a filter-tube, and not much by slight differences in the grinding of

the powder, it was found easier to obtain concordant results by it, and, with some variations in detail suggested by the work of Procter and Bennett,* was definitely adopted at the Conference of the International Association in Brussels in 1908. In the meantime the method in use in the States was gradually improved by the American Leather Chemists' Association, and their present official directions only differ in details from those of the International Association, the most important being the use of chrome alum for chroming, instead of the basic chrome chloride, which is adopted by the International Association on account of its more rapid action and the easier control of its acidity.

112. The following are the methods of the two Associations. The "General Regulations" (pars. 1–4) of the International are in conformity with those of the American method.

113. Official Method of Tannin Analysis of the International Association of Leather Trades Chemists.

General Regulations.

It has been decided by the Conference, Brussels, 1908, that any method which conforms to the conditions of paragraphs 1 to 4 of the following statement may be regarded as conforming to the recom-

* Colleg., p. 14, et seq., 1907.

mendations of the International Commission on Tannin Analysis, but that members of the International Association must work according to the detailed directions contained in paragraphs 5 to 8.

Para. 1.—"The solution for analysis must contain between 3·5 and 4·5 grm. of tanning matter per litre, and solid materials must be extracted so that the greater part of the tannin is removed at a temperature not exceeding 50° C., but if the Teas Extractor be used, the first portion of the extract shall be removed from the influence of heat as soon as possible."

Para. 2.—"The total solubles must be determined by the evaporation of a measured quantity of the solution previously filtered till optically clear both by reflected and transmitted light; that is, a bright object such as an electric light filament must be distinctly visible through at least 5 cm. thickness, and a layer of 1 cm. deep in a beaker, placed in a good light on black glass or black glazed paper, must appear dark and free from opalescence when viewed from above. Any necessary mode of filtration may be employed, but if such filtration causes any appreciable loss when applied to a clear solution, a correction must be determined and applied as described in para. 6. Filtration shall take place between the temperatures of 15° C. and 20° C. Evaporation to dryness shall take place between 98·5° C. and 100° C. in shallow flat-bottomed basins, which shall afterwards be dried until constant at the same temperature, and

cooled before weighing for not less than twenty minutes in air-tight desiccators over dry calcium chloride."

Para. 3.—"The total solids must be determined by drying a weighed portion of the material, or a measured portion of its uniform turbid solution, at a temperature between 98·5° C. and 100° C. in shallow flat-bottomed basins, which shall afterwards be dried till constant at the same temperature, and cooled before weighing for not less than twenty minutes in an air-tight desiccator over dry calcium chloride. "Moisture" is the difference between 100 and the percentage of total solids, and "insoluble" the difference between the total solids and total solubles."

Para. 4. *Non-Tannins.*—"The solutions must be detannised by shaking with chromed hide-powder till no turbidity or opalescence can be produced in a clear solution by salted gelatin. The chromed powder must be added in one quantity equal to 6·0 to 6·5 grm. of dry hide per 100 c.c. of tanning solution, and must contain not less than 0·2, and not more than 1 per cent. of chromium, reckoned on the dry weight, and must be so washed that in a blank experiment with distilled water not more than 5 mgrm. of solid residue shall be left on evaporation of 100 c.c. All water contained in the powder should be determined and allowed for as water of dilution."

114. *The following paragraphs give the detailed method of carrying out the analysis adopted by the I. A. L. T. C. for the use of its own members.*

Para. 5. *Preparation of Infusion.*—Such a quantity of material shall be employed, as will give a solution containing as nearly as possible 4 grm. of tanning matter per litre, and not less than 3·5 or more than 4·5 grm. Liquid extracts shall be weighed in a basin or beaker, and washed with boiling distilled water into a litre flask, filled up to the mark with boiling water, and well mixed, and rapidly cooled to a temperature of 17·5° C.,* after which, it shall be accurately made up to the mark, again well mixed, and filtration at once proceeded with. Sumach and myrobalans extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Solid tanning materials previously ground till they will pass through a sieve of 5 wires per centimetre, are extracted in Koch's or Procter's extractor with 500 c.c.

* The cooling is best carried out in a water-bath kept at about 15° C., and care must be taken that the solution is not locally chilled by very cold water.—Ed.

of water, at a temperature not exceeding 50° C., and the extraction continued with boiling water till the filtrate amounts to 1 litre. It is desirable to allow the material to soak for some hours before commencing the percolation, which should occupy not less than three hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected, or reported separately as "difficultly soluble" substances. The volume of liquid in the flask must after cooling be accurately made up to 1 litre.

Para. 6. *Filtration.*—The infusion shall be filtered, repeatedly if necessary, till optically clear (see para. 2). No correction for absorption is needed for the Berkefeld candle, or for S. and S. 590 paper if a sufficient quantity (250–300 c.c.) is rejected before measuring the quantity for evaporation; and the solution may be passed through repeatedly to obtain a clear filtrate. If other methods of filtration are employed, the average correction necessary must be determined in the following manner. About 500 c.c. of the same, or a similar, tanning solution, is filtered perfectly clear, and after thorough mixing, 50 c.c. is evaporated to determine "total soluble No. 1." A further portion (of the filtered solution) is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible), and 50 c.c. is evaporated to determine "total soluble No. 2." The difference between No. 1 and No. 2 is the correction sought, which

must be added to the weight of the total solubles found in analysis. An alternative method of determining correction, which is equally accurate and often more convenient, is to filter a portion of the tanning solution through the Berkefeld candle till optically clear, which can generally be accomplished by rejecting 300 or 400 c.c. and returning the remaining filtrate repeatedly; and at the same time to evaporate 50 c.c. of clear filtrate, obtained by the method for which correction is required, when the difference between the residues will be the correction sought.

(*Note.*—It is obvious that an average correction must be obtained from at least 5 determinations. It will be found that this is approximately constant for all materials, and amounts in the case of S. & S. 605, 150 c.c. being rejected, to about 5 mgr. per 50 c.c. and where 2 grm. of kaolin are employed in addition, to 7½ mgr. The kaolin must be previously washed with 75 c.c. of the same liquor, which is allowed to stand 15 minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.)

Para. 7.—"Hide-powder shall be of a woolly, (fibrous) texture, thoroughly de-limed, preferably with hydrochloric acid, shall not require more than 5 c.c. or less than 2·5 c.c. of N/10 NaOH or KOH to produce a permanent pink with phenolphthalein on 6½ grm. of the dry powder suspended in water. If the acidity does not fall within these limits, it must be

corrected by soaking the powder before chroming for 20 minutes in 10–12 times its weight of water, to which the requisite calculated quantity of standard alkali or acid has been added. The hide-powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70–75 per cent. of water, and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 5 mgr. per 100 c.c. The powder when sent out from the makers shall not contain more than 14 per cent. of moisture, and shall be sent out in air-tight tins."

The detannisation shall be carried out in the following manner :—

The moisture in the air-dried powder is determined, and the quantity equal to 6·5 grm. actual dry hide-powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made, and wet back with approximately ten times its weight of distilled water.* 2 grm. per hundred of dry powder of crystallised chromic chloride $CrCl_3 6H_2O$† is now dissolved in water and made basic with 0·6 grm. Na_2CO_3 by the gradual

* Very woolly powders require slightly more than 10 times their weight of water. A powder may be considered "woolly" if it cannot be poured like sand from a beaker.—H.R.P.

† Kahlbaum. ("Chromium sesquichloride hydrate cryst.")

addition of 11·25 c.c. of N/1 solution, thus making the salt correspond to the formula $Cr_2Cl_3(OH)_3$. This solution is added to the powder, and the whole churned slowly for 1 hour. In laboratories when analyses are continually being made, it is more convenient to employ a 10 per cent. stock solution, made by dissolving 100 grm. of $CrCl_3 6H_2O$ in a little distilled water in a litre flask, and very slowly adding a solution containing 30 grm. of anhydrous sodium carbonate, with constant stirring, finally making up to mark with distilled water and well mixing. Of this solution, 20 c.c. per 100 grm. or 1·3 c.c. per 6·5 grm. of dry powder should be used.*

At the end of one hour the powder is pressed (squeezed in linen) † to free it as far as possible from the residual liquor, and washed and squeezed repeatedly with distilled water, until on adding to 50 c.c. of the filtrate, 1 drop of 10 per cent. K_2CrO_4 and 4 drops N/10 $AgNO_3$, a brick-red colour appears. 4 or 5 squeezings are usually sufficient. Such a filtrate cannot contain more than 0·001 grm. of NaCl in 50 c.c.‡

The powder is then squeezed to contain 70–75 per cent. water, and the whole weighed. The quantity

* The solution sometimes changes colour slightly by keeping; but this has been shown to have no influence on results.—H.R.P.

† See Colleg., 1910, p. 416.

‡ With powders containing much soluble organic matter, it is desirable to carry the washing somewhat further.—H.R.P.

Q containing 6·5 grm. dry hide is thus found, weighed out and added immediately to 100 c.c. of the unfiltered tannin infusion along with (26·5—Q) of distilled water. The whole is corked up and agitated for 15 minutes in a rotating bottle at not less than 60 revolutions per minute. It is then squeezed immediately through linen, stirred and filtered through a folded filter of sufficient size to hold the entire filtrate, returning till clear, and 60 c.c. of the filtrate is evaporated and reckoned as 50 c.c. or the residue of 50 c.c. is multiplied by $\frac{6}{5}$. The non-tannin filtrate must give no turbidity with a drop of a 1 per cent. gelatin 10 per cent. salt solution.

One grm. of kaolin free from solubles must be used either by mixing it with the hide-powder in the shaking bottle or with the liquid before filtration.*

Para. 8.—"The analysis of used liquors and spent tans shall be made by the same methods as are employed for fresh tanning materials, the liquors or infusions being diluted, or concentrated by boiling in vacuo, or in a vessel so closed as to restrict access of air, until the tanning matter is if possible between 3·5 and 4·5 grm. per litre, but in no case beyond a concentration of 10 grm. per litre of total solids, and the weight of hide-powder used shall not be varied from 6·5 grm."

The results shall be reported as shown by the

* The latter method seems preferable.—H.R.P.

direct estimation, but it is desirable that in addition efforts shall be made by determination of acids in the original solution, and in the non-tannin residues, to ascertain the amount of lactic and other non-volatile acids absorbed by the hide-powder and hence returned as "tanning matters." In the case of tans it must be clearly stated in the report, whether the calculation is on the sample with moisture as received, or upon some arbitrarily assumed percentage of water; and in that of liquors whether the percentage given refers to weight or to grms. per 100 c.c.; and in both cases the specific gravity shall be reported.

Para. 9.—"All evaporation shall be rapidly conducted in steam temperature in shallow flat-bottomed basins of not less than 6·5 cm. diameter to apparent dryness; and shall be subsequently dried between 98·5° and 100° C. in a water or steam oven until of constant weight, and shall be afterwards cooled in small air-tight desiccators over dry calcium chloride for at least 20 minutes, and then weighed rapidly. Not more than two basins shall be placed in one desiccator, and the basins must not be wiped after removal from the desiccator."

All analyses sent out by members or associates of the I.A.L.T.C. should be made in exact accordance with the preceding regulations, and described as "Analysed according to the Official Method of the I.A.L.T.C.," but if for any cause another method must be adopted, the exact method used and the reasons

for its employment shall be distinctly stated, such descriptions as "old official method" being prohibited.* Any copy or copies † of report of analysis, whether furnished by the analyst, or his client and agents, shall contain the entire matter both written and printed of the original report.

All analyses reported must be the average result of duplicate determinations ‡ which must agree in the case of liquid extracts within 0·6 per cent., and of solid extracts within 1·5 per cent., or the analysis shall be repeated till such agreement is obtained, and it must be clearly stated on the report that the results are the mean of such corresponding determinations.

APPENDIX.

Extract from a Publication by Prof. H. R. Procter on "The Accuracy of the I.A.L.T.C. Method of Detannisation." §

115. **The Chroming of Hide-Powder and its Testing by Blank Experiment.**—The hide-powder is weighed, its acidity adjusted, and chromed for one hour according to the I.A.L.T.C. regulations.

* Dr. Parker, "by the old official method," Coll. 1908, p. 440. (Official Minutes of the 9th Conference, Brussels.)

† Copies. Coll. 1908, p. 440.

‡ Resolution Mueller (2 analyses). Coll. 1906, p. 378. (Official Minutes of the 8th Conference, Frankfort.)

§ Coll. No. 354 (17 iv. 1909), in English in Jour. Soc. Chem. Ind. 15, iv. 1909.

The chromed hide-powder is then thrown upon a clean piece of somewhat coarse linen in the perforated vessel of a screw-press, * or in a funnel, the portions remaining on the sides of the bottle being washed on to the linen with distilled water. The liquid is allowed to drain away, and the powder and linen removed from the press, squeezed by hand, returned to the press, and pressure applied. The more liquid removed at this stage the quicker the powder is freed from chlorides, but care must be taken that pressure is not applied too suddenly, or the linen will burst. The linen with the powder is then removed, and the latter, remaining in the linen all the time, is well broken up by rubbing the cloth between the hands and returned to the press, which is filled up with distilled water. The powder is thoroughly stirred with a glass rod until all the water has run out, and is squeezed again. It is very essential to keep the powder well stirred, otherwise channels will be formed, through which the water will run with very little washing effect. This process is repeated about five times, 50 c.c. of the last portion of wash-water, which can be removed from the powder by pressing, being tested for chlorides. It is advisable after having tested the washings, and found them to comply with the I.A.L.T.C. regulations, to give one

* The ordinary German fruit-press costing 15*s.*, and holding about 1 litre is found to be very satisfactory. It is convenient to have one or two of the inner vessels varying in size for different quantities of powder.

more washing, so that two drops of N/10 $AgNO_3$ instead of four are sufficient to produce reddening in 50 c.c. of the wash-water, before the final squeezing to reduce the water to the necessary quantity ready for weighing. The washing process should be continuous, and on no account should the powder be left to stand. A quantity sufficient for four analyses in duplicate (about 60 grm. air-dried powder) can be washed free from chloride in about 30 minutes, provided the process is continuous. The powder is now ready for weighing, and is transferred from the linen with a spatula to a basin or other convenient vessel for weighing. The last traces of powder may be removed by holding the four corners of the linen together and beating it upon the bench, when the powder will collect in the centre of the cloth. The powder is now ready for employment in analysis. For a blank experiment the manipulations are precisely as for tanning analysis, but using 100 c.c. of distilled water instead of tanning liquor. The powder which has been used for a blank experiment is quite suitable for further employment in an analysis.

The following causes tend to too high residues when carrying out blanks :—

1. *Impurities in the Distilled Water Used.*—The distilled water should leave no weighable residue on evaporation of 100 c.c. to dryness.

2. *Soluble matter from the hands* when squeezing the liquid away from the powder after detannisation.

The powder in the linen might be pressed against the side of the funnel, with a spatula to expel the last of the liquid.

3. *Soluble matter from linen* used after final churning. The cloths should be washed with water alone, nothing in the nature of soap being used, and finally in distilled water before drying.

4. *Imperfect Insolubility of the Kaolin Used.*—This has caused serious errors, and the kaolin should be tested before use.

5. *Presence of dust* with the residue in the basin.—The evaporation should be carried out with as little access to dust as possible, and the basin should be transferred to the drying oven as soon as possible after evaporation is complete.

6. The employment of powder, which has been kept more than a few hours after its preparation.

It is necessary that the general Regulations (pars. 1–4), should be read in conjunction with the special (pars. 5–9), since both are binding on members of the I.A.L.T.C., and together constitute the official method. The following table gives the approximate quantities of materials to be taken per litre of infusion, both for the European and American methods, but unusual samples occasionally fall outside the perscribed limits, involving the preparation of a new infusion.

116. TABLE IV.

APPROXIMATE QUANTITIES PER LITRE FOR ANALYSES.

Barks, etc.	Grammes
Canaigre	15–18
Divi-divi	9
Hemlock bark	32–36
Mimosa bark	10–15
Myrobalans	15
Oak bark	30–36
Oak wood	50–100
Quebracho wood	20–22
Sumach	15–16
Pistacia Lentiscus	20–30
Pine bark	32
Willow bark	36
Chestnut wood	45
Mangrove bark	10
Valonia	14–15
Valonia beard	10–11
Spent tans	50–100
Extracts.	
Oak wood, sp. gr. 1·2 or over	18
Chestnut (liquid)	14
,, (solid)	7
Quebracho (solid)	6
,, (liquid)	9–13
Mimosa D	10–12
Gambier (block)	12–14
,, (cube)	10
Mangrove (liquid)	9
,, (solid)	6–7
Cutch	6
Myrobalans (liquid)	16
Hemlock	10–14
Pine bark	16

117. **Procter's extractor,** referred to in par. 5 (Figs. 12, 13, p. 185, Lea. Ind. Lab. Book), consists of a beaker of suitable size for the quantity of material taken, which is placed in a water-bath. A thistle-head funnel, of which the stem is bent twice at right angles, is covered with muslin or silk gauze and placed head downwards in the beaker, and about 20 grm. of silver-sand (purified with HCl), and the weighed tanning material are added. After the necessary maceration (preferably over night), the liquid is sucked over, and the flow regulated by a a pinchcock. The glass and rubber siphon-tube is usually 9–10 inches long. As the liquid siphons, it is made up from time to time with water of the same temperature as the bath. The Koch extractor consists of a closed bottle, placed in the bath and supplied with water at pressure from an elevated reservoir. It is more automatic when working smoothly, but more difficult to fill, and liable to choke, which involves taking the apparatus to pieces, and it is not easy to get bottles which will stand the temperature without cracking. The sand filtration is similar to the Procter apparatus, but the gauze strainer is necessarily much smaller. The Teas extractor mentioned in par. 1 is on the Soxhlet principle. It is not recommended by the International Association; but is much used in America, and is the extractor referred to in the A.L.C.A. directions.

118. **Filtration.**—The Berkefeld candle is most generally convenient, but quebracho extracts require

patience to obtain real optical clearness, and for some hemlocks it is impossible to get it without the use of (carefully purified) kaolin. Errors of 10 per cent. may arise in infusions apparently clear to transmitted but not to reflected light.

119. **Washing the powder** is one of the most important manipulations, as it is desirable that it should be rapid as well as thorough, and with badly made powders it is very difficult to get the necessary freedom from dissolved organic matter. Occasional blank experiments are a great safeguard against errors from this cause.

Official Method of the American Leather Chemists' Association for Tannin Analysis.

120. I.—*Crude Materials.*

(1) **Moisture Determination.**—Upon receipt of the sample, grind promptly and dry 10 grm. in the manner and for the period specified for evaporation and drying in extract analysis.

(2) **Preparation of Sample for Extraction.**—Sample must be dried at a temperature not exceeding 60° C., and then ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(3) **Amount of Sample and Proportion of Water for Extraction.**—For fresh materials, the amount of

sample and proportion of water for extraction should be such as to give between 0·35–0·45 grm. tannin per 100 c.c. of solution. For spent materials, this should be approximated as closely as practicable.

(4) **Extraction of Sample.**—Extraction shall be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued until a portion tested with gelatin salt solution fails to give a precipitate. At least 500 c.c. of the first portions of extractive solution should be removed, and not subjected to further heating. A thin layer of cotton must be used, in order to prevent fine material passing over.

(4A) **Sumach and Kindred Materials.**—Put the material (the amount should be such as to give between 0·35–0·45 grm. tannin per 100 c.c. of solution) in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, cover it with water, and allow to soak one hour. Then extract by collecting 2000 c.c. of the extractive solution outside through lower tube, in from six to eight hours. Let the extractive solution stand over night, and analyse the following day by the Official Method for Extracts.

(5) **Analysis.**—After extraction and dilution, solutions must be heated to 80° C. and analysis conducted as per Official Method for Extracts. In case of weaker dilutions than the Official Method specifies, the amount

of hide-powder must be reduced in proportion to the reduction of tannin.

Ten grm. of the air-dried sample should be dried as in (1) to determine moisture content of the portion extracted, and the analysis calculated and reported upon a "dry" basis. The tannin in fresh materials should also be reported on the basis of the moisture content of the sample "as received."

121. II.—*Analysis of Extracts.*

(6) **Amount and Dilution for Analysis.**—Fluid extracts must be allowed to come to room temperature, and weighed in stoppered weighing bottle. Such quantity shall be taken as will give from 0·35–0·45 grm. tannin per 100 c.c. of solution. Dissolve in exactly 900 c.c. of distilled water at 80° C., and make up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not go below 20° C.

(7) **Total Solids.** — Thoroughly mix solution, pipette 100 c.c. into tared dish, evaporate and dry as directed under "Evaporation and Drying."

(8) **Soluble Solids.**—To 1 grm. of kaolin in a beaker add 75 c.c. of solution; stir and pour on a "590 S. & S." 15 cm. plaited filter-paper; return filtrate to paper for one hour, keeping filter full. At the end of an hour pour solution from filter or remove with pipette. Bring 800 c.c. of solution to 20° C.,

refill the filter with this solution, and begin to collect filtrate for evaporating and drying so soon as filtrate comes clear. Keep filter full. Evaporate and dry the first 100 c.c. of filtrate, as per "Evaporation and Drying."

(9) **Non-tannins.**—A quantity of hide-powder, sufficient for the number of analyses to be made, shall be prepared in the following manner: Digest with ten times its weight of water till thoroughly soaked. Add 3 per cent. of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours, and let stand over night. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press if necessary, so that the wet hide will contain between 70 and 75 per cent. of water. Use approximately 20 grm. of wet hide for moisture determination. Add to 200 c.c. of the original solution such quantity of the wet hide as re presents from 12 to 13 grm. dry hide. Shake for ten minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grm. kaolin to the filtrate, stir and filter through folded filter (No. 1F Swedish recommended) of size sufficient to hold entire filtrate returning until clear. Evaporate 100 c.c. of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide-powder.

Note.—In order to limit the amount of dried hide-

powder used, determine the moisture in the air-dried powder and calculate the quantity equal to 12½ grm. of actual dry hide-powder. Take any multiple of this quantity, according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70 to 75 per cent. water. Weigh the whole amount and divide by the multiple of the 12½ grm. of actual dry hide-powder taken to obtain the weight of wet hide-powder for 200 c.c. of solution.

The non-tannin filtrate must not give a precipitate with a 1 per cent. gelatin, 10 per cent. salt solution.

(10) **Tannin.**—The tannin content is shown by the difference between the soluble solids and the corrected non-tannin.

122. III. *Analysis of Liquors.*

(11) **Dilution.**—Liquors must be diluted for analysis, so as to give as nearly as possible 0·7 grm. solids per 100 c.c. of solution.

(12) **Total Solids.**—To be determined as in extract analysis.

(13) **Soluble Solids.**—To be determined as in extract analysis.

(14) **Non-tannins.**—To be determined by shaking 200 c.c. of solution with an amount of wet chromed hide-powder, containing 70 per cent. moisture, corre-

sponding to an amount of dry hide-powder shown in the following table.

Tannin Range per 100 c.c.	Dry Hide-Powder per 200 c.c.
0·35–·45 grm.	9–11 grm.
·25–·35 grm.	6·5–9 grm.
·15–·25 grm.	4–6·5 grm.
·00–·15 grm.	0–4 grm.

Solutions to be shaken for non-tannins as in extract analysis; 100 c.c. must be evaporated as in extract analysis.

123. IV. *Evaporation and Drying.*

(15) **Evaporation and Temperature.**—All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer," at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(16) **Dishes.**—The dishes used for evaporation and drying of all residues, shall be flat-bottomed glass dishes, of not less than $2\frac{3}{4}$ inches diameter nor greater than 3 inches in diameter.

124. V. *Determination of Total Acidity of Liquors.*

(17) (*a*) **Reagents.**—One per cent. solution of gelatin neutral to hematine. The addition of 25 c.c. of 95 per cent. alcohol per litre is recommended to prevent frothing. If the gelatin solution is alkaline,

neutralise with tenth normal acetic acid and if acid, neutralise with tenth normal sodium hydroxide.

(*b*) **Hematin.**—A solution made by digesting hematin in cold neutral 95 per cent. alcohol, in the proportion of ½ grm. of the former to 100 c.c. of the latter.

(*c*) Acid washed kaolin free from soluble matters.

(*d*) Tenth normal sodium hydroxide.

125. **Directions.**—To 25 c.c. of liquor in a cylinder that can be stoppered, add 50 c.c. of gelatin solution, dilute with water to 250 c.c., add 15 grm. of kaolin, and shake vigorously. Allow to settle for at least 15 minutes, remove 30 c.c. of the supernatant solution, dilute with 50 c.c. of water and titrate with tenth normal soda, using hematin solution as the indicator. Each c.c. tenth normal soda is equivalent to 0·2 per cent. acid as acetic.

On public analytical work by members of this Association, the fact that the Official Method has been used shall be so stated.

126. **The Löwenthal Method of Tannin Estimation** is a volumetric process, which, although not suitable as a standard method, gives relative results of considerable accuracy, and from its rapidity is often useful in the control of liquors, and, as compared with the hide-powder method, often gives interesting data as to the particular tannins present (see Chap. V.). It was invented by Löwenthal in 1860 * and improved by

* Jour. f. Prakt. Chem. 1860, iii. p. 150.

him in 1877,* and until the introduction of the hide-powder method was the standard process, and many of the older published analyses were made by it, often in its earlier and less accurate forms, and usually with much lower results than by hide-powder.

The process depends on the oxidation of the tannin substances in very dilute acid solution with permanganate in presence of considerable excess of sulph-indigotic acid, which serves not merely as an indicator, but as a regulator of the oxidation, which should only extend to substances more oxidisable than the sulph-indigotic acid. As, however, the oxidised products are capable of further oxidation by permanganate, a certain amount of secondary oxidation always takes place, due to local excess of permanganate over indigo, and this is greater, the less the excess of the indigo and the more slow and imperfect the mixture. In order, therefore, to get concordant results, it is essential that the titration should be carried out in a systematic and uniform manner.

For a few or occasional analyses the gravimetric method is less troublesome, and for systematic control work, or where a large number of analyses are to be made, it is worth while to fit up self-filling burettes for the permanganate and indigo solutions, and to provide an automatic stirrer driven by a small turbine or electric motor, as the stirring must be continuous and rapid throughout the operation. A very effective

* Zeit. f. anal. Chem. 1877, pp. 33, 201 ; 1881, p. 91.

stirrer consists of one of the common chimneys for incandescent gas pierced with round holes near the base. If this is suspended upside down in the beaker below the surface of the liquid by a copper wire attached to a vertical spindle which is rapidly rotated, the solution is centrifugally projected from the holes, and the liquid very thoroughly mixed. If mechanical stirring is not employed, the hand-stirring must be very thorough and rapid, and in place of a straight glass rod, one bent several times upon itself, or, still better, one with a perforated disc moved up and down in the liquid may be used. The addition of the permanganate must, as far as possible, be at a constant rate; but no advantage is gained by extreme slowness, and a useful method is to open the glass tap of the burette so as to allow it to *drop* at first as rapidly as the drops can be counted, and only close the tap when, from the change of colour, the reaction is seen to be nearly at an end; after which the solution is added a drop or two at a time, till the originally blue solution becomes pure yellow. Since this yellow does not subsequently change by the addition of more permanganate, it is essential not to overstep the end-point, and it is often useful to keep a beaker titrated only to a slightly greenish yellow alongside the beaker being titrated, as a standard. The titration is equally exact by day or good artificial light, but as the end-point is slightly different, any single determination must be completed by one or the other.

As the quantity of permanganate used depends somewhat on the method of titration, it is impossible for different workers to calculate tannin satisfactorily by any constant factor, and it is necessary to adopt as a standard some body which can actually be estimated by the method, so that constant errors are eliminated. For this purpose gallic acid is the most appropriate, as it is oxidised in the same way as the tannins, and, being crystalline, is easily obtained of a high degree of purity. The gallic acid values of many tannins as estimated by hide-powder are given on p. 107.

127. **Solutions Used.**—(1) Permanganate of potash, 0·5 grm. per litre, best made at frequent intervals by dilution of a 5 grm. solution, as very weak solutions do not keep well.

(2) Sulphindigotic acid, by dissolving 5 grm. of purest "indigo-carmine" per litre with 50 grm. of concentrated sulphuric acid; or 1 grm. "indigo pure B.A.S.F." in 25 c.c. of concentrated sulphuric acid, and making up to 1 litre with 25 c.c. more sulphuric acid. 25 c.c. of either of these solutions should require about 25–30 c.c. of permanganate to give a pure yellow on titration; or a larger measured volume of the indigo solution must be used.

(3) Gallic acid, 0·1 grm. pure air-dried, freshly made up to 100 c.c. (gallic acid loses a further eq. of water if dried at 100°).

128. **Titration.**—About $\frac{3}{4}$ litre of good tap water is placed in a large beaker on a white plate or tile, and

25 c.c. of the indigo solution is twice titrated. The average (25–30 c.c.) is taken as the *indigo value.*

The process is similarly repeated with further addition of 5 c.c. of the gallic acid solution, and the indigo value deducted from the average result gives the *gallic acid value* of the permanganate. This should be practically a constant.

The same process is repeated with 5 c.c. of the tannin solution to be tested in place of the gallic acid, and the indigo value deducted, and this result, divided by the gallic acid value of the permanganate, gives the gallic acid value of the liquor in grm. per litre. If the permanganate required exceeds 50 c.c., the titration must be repeated with a smaller quantity or more diluted liquor, and the result multiplied by the necessary factor, or otherwise the proportion of indigo present would be insufficient properly to regulate the oxidation.

129. **Detannisation.** — Unfortunately, the *gallic acid value* of the liquor found as above includes not only tannins, but all astringent matters; and in order to get a correct tannin value the process must be repeated with the detannised liquor, and the result (non-tannin astringents) deducted. Löwenthal employed gelatin solution as a detannising agent, and, used as is described in a later paragraph, its action is rapid and satisfactory. As, however, at the present time it is frequently desired to express the results in terms of the hide-powder method, it is usually more

satisfactory to employ chromed hide-powder, and as astringents only are estimated by the titration, the details of its use may be considerably simplified; and careful washing of the powder after chroming is quite needless. It is most convenient to employ the "lightly chromed" dry powder of Dr. Paessler, or even fresh air-dried chrome-leather shavings; but, of course, white hide-powder can be chromed in the usual way, and the dilution calculated as in gravimetric analysis. If, however, dry chromed powder be employed, it is sufficient to add about 7 grm. with a little kaolin to 100 c.c. of the liquor to be analysed, diluted as for the Löwenthal determination, and, after well mixing, to shake for 10–15 minutes on the machine, and then filter till clear through paper and titrate, neglecting the small amount of water of dilution which is introduced by the air-dried powder. In this case 5 c.c. may be twice titrated with 25 c.c. of indigo in the usual way; and the result simply deducted from a similar titration of the undetannised liquor, and divided by the gallic acid value of the permanganate, will give the tannin contents of the (diluted) liquor in terms of pure gallic acid, which can be calculated into its actual weight of the tannin in question, either by direct comparison with a gravimetric determination, or by the approximate factors given in the following table.

In many cases, however, and especially in that of the mixed liquors of a tannery, it will be found most satisfactory to determine a special factor by a direct

TABLE V.

—	Tannin Value of 1 grm. Gallic Acid	Gallic Acid Value of 1 grm. of Tannin.
Chestnut extract	1·65	0·604
Oakwood extract.	1·89	0·527
Myrobalans	1·73	0·577
Quebracho extracts	1·69	0·592
Larch bark, hemlock bark . . .	1·97	0·501
Hemlock extr. spruce bark . . .	2·28–2·53	0·437–0·395
Valonia, sumach	1·55	0·604
Oak bark	1·71	0·583
Mimosa bark	1·88	0·529
Mangrove bark	1·46	0·682
Gambier-cube	1·78	0·559
Pure gallotannic acid	1·34	0·742
Sulphite cellulose liq. av. . . .	8·72	0·119

gravimetric analysis. To do this, one or more liquors are analysed in the ordinary way, and at the same time the gallic acid values of the tannin of the original liquor and of the non-tannin solution are determined by titration; and that of the latter is deducted from the former, having due regard to dilutions. On now dividing the tanning matter found gravimetrically by the corresponding gallic acid value of the tannins, the value of 1 grm. of gallic acid in the actual tannins of the liquor is obtained.

130. **Detannisation with Gelatin.**—In place of using hide-powder for detannisation, the following modifications (Procter, Hunt) of Löwenthal's original

gelatin method will be found rapid and convenient for series of control analyses, though the results do not accurately agree with those of hide-powder, but, possibly by a compensation of errors, are approximately exact for actual mixtures of pure gallotannic and gallic acids. To 50 c.c. of the liquor, diluted if required as for titration, 25 c.c. of a freshly prepared solution of good gelatin, 25 c.c. of a saturated solution of salt containing 50 c.c. of sulphuric acid per litre, and about 2 grm. of kaolin are added. The mixture is well shaken, allowed to stand for 15 minutes, filtered through paper, and 10 c.c. (corresponding to 5 c.c. of the original or diluted liquor) is titrated, and the result deducted as "non-tannins."

131. **Calculation.**—As the calculation of Löwenthal analyses appears somewhat complicated, the following example is given, but neither the reckoning nor the operation itself will be found in practice so difficult as it appears on paper.

100 c.c. of a layer-liquor is diluted to 1 litre and well mixed by shaking, and 5 c.c. is titrated with indigo, consuming 47·3 c.c. of permanganate. A portion is detannised, and an equivalent quantity again titrated consumes only 33·5 c.c. The tannin of 5 c.c. of the diluted liquor is therefore oxidised by 47·3 − 33·5 = 13·8 c.c. of the permanganate, or that of 5 c.c. of the original liquor by 138 c.c.

25 c.c. of indigo alone require 26·3 c.c. of permanganate, and with 5 c.c. of 1 grm. per litre gallic

acid solution 45·2 c.c., or an excess of 18·9 c.c. Therefore—

$$18{\cdot}9 : 138 :: 1 : 7{\cdot}30$$

The gallic acid equivalent of the tannin in the liquor is 7·30 grm. per litre, and multiplying by 1·66 or $\frac{10}{6}$, the average factor of commercial tannins, we have 12·17 grm. tanning matter per litre.

For greater detail, the Laboratory Book, Sect. XIV., may be consulted, as well as a paper by Procter and Hirst, Jour. Soc. Ch. Ind. xxviii. (1909) p. 294.

Analysis of Liquors.

132. **Tannin Estimation** may be made either by the gravimetric or by the Löwenthal method; the latter is the more convenient for regular control. In using the gravimetric method the liquors must be diluted till they do not contain *more* than 3·5–4·5 grm. of tannin per litre, but if they contain *less* need not be concentrated. The same quantity of hide-powder is used in the I.A.L.T.C. as for an ordinary analysis; for the A.L.C.A. method see par. 122.

133. **Non-Tannins** consist largely of decomposed tannin products and gummy matters which cannot be separately estimated; sugars are rarely present in quantities.

134. **Mineral ash** mainly consists of lime and

potash salts, and the bases which have been in combination with organic acids remain as carbonates and can be titrated with N/10 HCl and methyl orange. It is best to add the acid in slight excess to dissolve $CaCO_3$ and titrate back with N/10 NaOH. Ca may be estimated separately by precipitation of the HCl solution with ammonium carbonate and a little oxalate after rendering alkaline with ammonia, and after gentle ignition either weighing or redissolving in N/10 HCl and titrating back. Any excess in the original ash after calculating the bases found by titration as carbonates may be put down as salts of mineral acids, or examined separately by ordinary methods.

135. **Acidity.**—Any titration with indicators is dependent on the "weakness" of the acid to which the special indicator is sensitive. Phenolphthalein indicates all acids and some phenolic bodies; violet hæmatin paper is slightly less sensitive, and congo red and methyl orange are, roughly, only affected by acids strong enough to have some plumping effect on hide. As liquors are too dark for the use of internal indicators, the latter should be used as papers, best previously wet and laid on a white tile, and the liquor spotted on to them with a glass rod. Previous de-detannisation is unnecessary and apt to cause loss of acid. The acidity of the tannins is very slight, and of the indicators named only affects phenolphthalein.

Procter's lime-water method gives direct information as to the lime that the liquors are capable of

neutralising without precipitation, which in practice is often important. The liquor is filtered till optically clear, and lime-water is added from a burette to 10 c.c. in a beaker with constant stirring, until slight cloudiness remains (blurring a printed sheet seen through the liquid). The results are best stated merely as c.c. of saturated lime-water, or as N/10 acid, as the nature of the acid estimated is unknown. In the case of tannins which do not give a decided precipitate a few drops of gallotanic acid solution, or some other lime-precipitated tanning liquor, may be added, the amount of lime-water required for its precipitation being deducted from the result. Oxalates may be removed by addition of calcium chloride solution and filtration, an aliquot quantity of the diluted liquor being titrated.

The separation of organic acids is beyond the scope of this work, but volatile acids may be separated by distillation, with repeated additions of water, titrating each distillate with N/10 NaOH in presence of phenolphthalein till acid can no longer be detected. If the liquid be acidulated with sulphuric or oxalic acid before distillation, all weaker volatile acids will be estimated, whether free or combined with bases.

Estimation of Colour.

136. The estimation of colour in extracts is frequently demanded, though it is mostly valuable as a numerical basis of contract, and gives little information

as to the colour to be expected in tanning, unless the extracts are of the same make and character.

137. **Tintometer.**—The analytical solution containing 3·5–4·5 grm. of tannin per litre is matched in a 1 cm. cell by the coloured glasses of the instrument, and the results are calculated from the analysed strength to a 5 grm. per litre solution of tanning matter by simple rule-of-three. The results are not theoretically correct, nor in accordance with the I.A.L.T.C. prescription, which demands the use of an accurate 0·5 per cent. solution; but it is found that colour-changes rapidly occur in keeping the liquors, and the method of calculation had been so generally adopted before its error was discovered that it is not easy to alter it. An alternative colorimetric method introduced by Procter has been recommended provisionally by the I.A.L.T.C., and may very probably be made compulsory at the next conference.

138. **Procter's Colorimetric Method.***—Depends, like the tintometer, on comparison with Lovibond's standard graduated colour-glasses, but instead of determining the glasses to match a standard strength of liquor, the strength of liquor is determined which will match a definite colour-standard in glasses. This has the advantage that strengths are directly proportionate, while colours are not; an extract of double the actual colour of another allowing accurately half the strength, while the tintometer readings are much less

* Journ. Soc. Chem. Ind. 1910, 663; Colleg. 1910, 292, 459.

than twice as great. The tints red and yellow are also much more easily understood as percentages of a total standard than as varying indeterminate amounts, and the measurement, as it does not in the first instance depend on analysis, can be made at once on the analytical liquor, and with a suitable instrument is much more rapid and exact.

Probably the best instrument for the purpose is the small Schmidt and Haensch colorimeter with Lummer-Brodhun prism ;* but any accurate colorimeter with variable depth of liquid will serve, and the author has constructed a cheap form with mirrors which answers well, and will probably be put on the market shortly. As a standard colour the sum of 10 Lovibond units of red or yellow is adopted, and should be matched to tenths, though for rough work units only may be used, with a great economy of glasses. The colorimeter (with water in the cylinder) is first carefully adjusted so that the two fields are absolutely equal in light. If necessary, colourless glasses may be added to one side or the other, but the last adjustment is best made by shifting the source of light (preferably an incandescent gas-burner, about 6 inches from the opal glass reflector of the colorimeter) slightly to one side or the other. The solution to be measured is now substituted for water in the cylinder, and colour glasses (say, 7·5 yellow and 2·5 red) placed on

* The Figs. 2 and 3, in Collegium are misplaced in reverse order.

the opposite side and compensated with four colourless glasses added above the liquid, the depth of which is varied till the nearest match is attained. If the standard is, for instance, too red, red units are removed and an equal number of yellow added, and the process repeated till a perfect match results. The depth of liquid to make this match is measured repeatedly, and preferably by more than one observer, and the average is taken. The depth in cm., multiplied by the strength of solution in grm. per litre, will give the extract or tannin in grm. per litre required to give the standard colour in a 1 cm. cell. The standard may be stated as 7·5 yellow and 2·5 red, or whatever is used. If, as is sometimes needed, a small value of blue on one side or the other is required for a perfect match, it is stated as + blue if added to the glasses, indicating a duller-coloured extract, and if to the extract as − blue, showing the colour of the extract to be brighter than the glasses.

139. **Tanning Tests.**—As has been stated, colour-measurement by optical means is principally useful as a numerical basis for contracts, or a means of control of colour in different deliveries of *the same extract;* and for the comparison of different tanning materials a direct tanning test is of more practical value, though even then the results of rapid tannage under laboratory conditions may differ from those of the tannery, and it is not possible at present to express either numerically.

The material generally used for this purpose is

calf or sheep grain, obtained from the tanner after splitting in the limed state, which, after "scudding" and thorough washing with distilled water, is soaked for some hours, with frequent stirring, in a solution of 2 per cent. boric acid and 1 per cent. pure crystallised phenol to remove lime; again, "slicked" on a glass plate with a smooth-edged slate or brass slicker, and preserved in a fresh portion of the boric phenol solution (in which it will keep for some months if occasionally stirred) until required for use. Probably, the Seymour-Jones preservative process might also be advantageously used, the grains, after cleansing from lime and dirt, being soaked for twenty-four hours in a solution of 2 or 3 grm. of 90 per cent. formic acid and 0·5 grm. mercuric chloride per litre, and then in saturated solution of common salt, after which they may be kept in a moist state as long as required, but must be well washed before use.

The actual tannage is best done in a rotating drum or bottle similar to that used in hide-powder analysis, but preferably larger, a tannage of two hours, beginning with a solution of $\frac{1}{4}$ per cent. and rising to $\frac{1}{2}$ per cent. of tanning matter, being sufficient for thin grains; but the liquor can be raised to much greater strengths with little darkening of colour. Similar results may be obtained, but in considerably longer time, by suspension in a jar, with occasional shaking. The leather is generally rinsed in water, slicked out, or passed through a rubber wringing machine, pinned

on a board, slightly oiled with cod oil, and dried in the dark.

Since it is impossible to obtain skin which at all times is perfectly regular and identical in the colour which it takes, and as its preservation is somewhat troublesome, H. C. Reed * and G. A. Kerr † have proposed the use of white woollen broadcloth for the purpose, while Dr. A. Gansser ‡ uses a close cotton fabric, "animalised" by first passing it through a 40 per cent. formaldehyde solution, and then repeatedly through a hot 6 per cent. gelatin solution, and drying. The colours produced by tanning solutions are even and regular, but not quite identical with those obtained on leather. For details, the original papers must be consulted.

* Jour. Am. Lea. Ch. Assoc., 1908, 382.
† Ibid., 1910, 94.
‡ Colleg., 1909, 37.

CHAPTER VIII.

MATERIALS USED IN MINERAL TANNAGES.

140. **Alumina Salts.**—In most cases the determination of alumina, the detection or determination of iron, and the basicity of the alumina salt will be found sufficient.

Alumina is determined gravimetrically, the dilute solution, containing 0·5 – 1 grm. of the salt, being heated in a porcelain (or platinum) basin, ammonium chloride added, and the boiling solution precipitated with ammonia, which is added in slight excess. The heating is continued until the solution but faintly smells of ammonia, the precipitate allowed to settle and washed several times by decantation and then thoroughly on the filter with boiling water. The precipitate after carefully drying is transferred with it paper to a platinum or porcelain crucible and ignited, using first a small flame and a cover to avoid loss by spurting, and finally heating very slowly over the blow-pipe. This strong ignition must be continued for five to ten minutes in case of sulphates having been present. The weight of the precipitate (grm.

Al_2O_3) can be expressed in per cent. Al_2O_3 or in per cent. Al.

141. **Iron salts** are determined colorimetrically or volumetrically, a sufficient quantity of the substance being weighed out, dissolved in water, and precipitated with ammonia. The precipitate need not be washed carefully, but merely collected on the filter, then redissolved in dilute hydrochloric acid.

For colorimetric estimation of traces of iron see par. 27. Larger amounts of iron are determined either by the iodometric method or with permanganate. The iodometric method demands absence of chromium and nitric acid. The solution is oxidised with bromine water to wholly convert the iron into ferric salts, and all free bromine expelled by subsequent boiling. An aliquot portion of the solution, containing as nearly as possible 0·1 grm. of Fe, is placed in a bottle with a well-fitting stopper and 30 c.c. of a 10 per cent. solution of potassium iodide is added. After twenty minutes standing the liberated iodine is titrated with N/10 thiosulphate.

$$2FeCl_3 + 2KI = 2FeCl_2 + 2KCl + 2I$$

$$2I + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

$1Na_2S_2O_3$ indicates 1Fe

Each c.c. N/10 thiosulphate corresponds to 0·0056 grm. of Fe or 0·008 grm. Fe_2O_3.

For the permanganate method a measured quantity

of the solution, which should not contain more than about 0·1 or 0·2 grm. of iron, is strongly acidified with pure sulphuric acid in a flask, the neck of which is closed with a cork, through which passes a short tube drawn to a capillary opening to permit escape of the hydrogen evolved; or preferably with two tubes, through one of which a slow current of coal-gas is passed into the flask to expel oxygen. The solution is warmed, and fragments of zinc (free from iron) are dropped in together with a small piece of platinum foil (or a few drops of platinum chloride) until the solution becomes colourless. The heating is continued till the zinc is entirely dissolved, and the solution is titrated with N/10 potassium permanganate (3·16 grm. per litre) till a faint pink coloration is produced.

$$10FeSO_4 + 8H_2SO_4 + 2KMnO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

$2KMnO_4$ (or $1K_2Mn_2O_8$) indicate $10Fe$

Each c.c. N/10 permanganate corresponds to 0·0056 grm. of Fe or 0·008 grm. of Fe_2O_3.

A strong (N/1) solution of permanganate should be kept, and may be diluted as required, as dilute permanganate solution does not keep well. A glass-tapped burette must be used. The standardisation of N/1 permanganate solution is done with pure ammonium-ferrous-sulphate $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$ (0·7 grm. of this salt containing 0·1 grm. Fe). The

salt is powdered, dried between blotting-paper, and dissolved in dilute sulphuric acid.

As to the basicity of the aluminium salt solution, see Lab. Book, p. 254.

142. **Chromium Compounds.**—The determination of chrome can be done gravimetrically or volumetrically. The gravimetric estimation consists of precipitating the solution of trivalent chromium (chromium salt) with ammonia and weighing the precipitate after filtering, washing and igniting. If the original substance or solution only contains trivalent chromium, the method can be applied at once, but if hexavalent chromium (chromic acid, chromates or bichromates) be present, the solution must first be reduced to chromic salts. This is either done by heating the solution with hydrochloric acid and alcohol, whilst covering the beaker with a watch-glass to avoid spurting and driving off aldehyde and excess of alcohol, or, in the cold, by adding hydrochloric acid and sodium-bisulphite (or a similar reducing agent) to the solution.

A measured quantity of the chrome compound solution (containing 0·1 to 0·2 grm. chromium) is heated in a porcelain basin (after eventually being reduced to chromic salts, as stated above), and ammonia added in slight excess. The liquid is then boiled to remove the excess of ammonia, the precipitate washed several times by decantation, filtered and thoroughly washed on the filter with boiling water. The precipitate is thoroughly dried, transferred with

its paper to a platinum or porcelain crucible, where it must be ignited at first very cautiously, with the cover, to avoid loss by spurting, and then very strongly over the blowpipe (grm. Cr_2O_3)

The volumetric method supposes the presence of hexavalent chromium only, or anticipates the conversion of trivalent chromium into the hexavalent form. This oxidation process can be carried out (*a*) with the dry substance, or (*b*) with the aqueous solution.

(*a*) *Oxidation of the Dry Substance.*—A weighed quantity of the chrome compound (containing 0·2 to 0·3 grm. chromium) is mixed with about an equal weight of the fusion mixture in a platinum crucible. (The fusion mixture consists of equal parts of dry sodium carbonate and magnesium oxide.) The whole mixture is heated gently at first, with the cover, and if it coheres to a solid mass must be turned out of the crucible and powdered with a little more magnesium oxide. The igniting is continued over a Teclu-burner for 20 minutes, stirring frequently with a platinum wire, till the mass is pure yellow.

$$Cr_2(SO_4)_3 + 5Na_2CO_3 + 3O = 2Na_2CrO_4 + 3Na_2SO_4 + 5CO_2.$$

The crucible, after allowing to cool, is placed in a beaker, covered with water, and hydrochloric acid gradually added (loss by spurting being avoided by covering the beaker with a watch glass, which finally is washed into the beaker). The solution must be clear,

and any insoluble green particle is due to unoxidised chrome oxide, which must be filtered, fused again, and its solution in hydrochloric acid added to the first.

The solution is transferred into a 250 c.c. graduated flask and made up to the mark with water. Aliquot portions are placed in a stoppered bottle, about 10 c.c. of 10 per cent. potassium iodide solution and some more hydrochloric acid added, and the liberated iodine titrated with N/10 sodium thiosulphate, starch being added when the colour of iodine has nearly disappeared.

$$2Na_2CrO_4 + 4HCl = H_2Cr_2O_7 + 4NaCl + H_2O.$$

$$H_2Cr_2O_7 + 6KI + 12HCl = 6I + 2CrCl_3 + 6KCl + 7H_2O.$$

$$6I + 6Na_2S_2O_3 = 6NaI + 2Na_2S_4O_6$$

$$6Na_2S_2O_3 \rightarrow 6I \rightarrow H_2Cr_2O_7 \rightarrow 2Cr$$

Each c.c. N/10 $Na_2S_2O_3$ corresponds to 0·00173 grm. Cr or 0·00253 grm. Cr_2O_3.

This method is also useful for the estimation of chromium in solutions, after evaporating them and drying the residues.

(*b*) *Oxidation of the Aqueous Solution.* A measured quantity of the solution (containing 0·2 to 0·3 grm. chromium) is diluted to about 100 c.c. with distilled water, in a conical flask. The flask is covered with a small funnel and 2 to 3 grm. of sodium peroxide added in portions to the cold solution. After each

addition the funnel should be rapidly replaced and the solution gently shaken. The liquor, which will now have assumed a reddish-yellow colour, is heated over a bunsen flame, and kept boiling until the whole of the sodium peroxide is decomposed, and there is no sign of effervescence in the liquid, large bubbles only being formed.

$$Cr_2(SO_4)_3 + 5Na_2O_2 = 2Na_2CrO_4 + 3Na_2SO_4 + O_2.$$

$$\text{Excess of } Na_2O_2 + H_2O = 2NaOH + O.$$

The volumetric estimation of Cr in this solution is done as described above.

Another method of oxidising the aqueous solution is as follows:—

A measured quantity of the solution (containing 0·1 to 0·2 grm. chromium) is rendered decidedly alkaline with sodium hydrate and raised to a boil, and N/1 potassium permanganate is added till the supernatant liquor remains pink after boiling for two or three minutes. A drop or two of alcohol is now added, and the boiling continued till the pink disappears, when the solution is cooled, made up to 250 c.c. and filtered, and the chromic acid is determined in 50 c.c. with potassium iodide and thiosulphate as before.

143. **Analysis of One-bath Chrome Liquors.**—The estimation of chromium is done according to par. 142.

The estimation of alumina is carried out in the oxidised solution, where all chromium is present in

form of chromates. An aliquot part of this solution is precipitated with ammonia in a porcelain basin (according to par. 142), and the precipitate (which must be of pure white colour) washed, dried, ignited and weighed as Al_2O_3; or aluminium and chromium are determined together in an aliquot portion of the liquor by the gravimetric method (precipitating the original solution with ammonia, etc.), and deducting the chromium found volumetrically from this liquor.

Of great interest for the practical chrome tanner is the degree of basicity of the chrome salt present. The estimation is done in the following way :—

A measured quantity of the liquor (containing 0·2 to 0·3 grm. chromium) is diluted to about 200 c.c. in a porcelain basin, 3 to 4 c.c. of 1 per cent. phenolphthalein added, and the boiling solution titrated with N/2 NaOH, stirring constantly. When nearing the end-point the bunsen should be removed and the titration completed. The end-point is seen by a greyish violet tint of the well-stirred liquid, or by a distinct pink colour seen on the side of the basin, after allowing the precipitate to settle.

Each c.c. N/2 NaOH corresponds to 0·024 grm. SO_4 (or 0·017 grm. Cl) combined with the trivalent chromium (or alumina).

The basicity of the liquor is expressed in grm. SO_4, combined with 52 grm. chromium. If, for example, the analysis of 25 c.c. of the liquor gave 0·2185 grm. Cr and 0·378 grm. SO_4, the proportion

would be $\frac{0{\cdot}2185}{0{\cdot}378} = \frac{52}{x}$ and $x = 90$. In presence of alumina the aluminium is calculated as chromium, and thus allowed for in the determination of the basicity of the liquor.

144. **Analysis of Two-bath Chrome Liquors.**—Solutions containing hexavalent chromium, together with more or less mineral acid, may be composed of monochromates, bichromates, bichromic acid, or of mixtures of bichromates with monochromates or bichromic acid, as well as of bichromic acid with mineral acid.

The qualitative and quantitative estimation of any of these possible cases requires the determination of hexavalent chromium (see par. 142), and of the amount of alkali necessary to redden phenolphthalein used as indicator. The colour of the solution turns first from orange to yellow, and then sharply from a bright yellow to the well-known red of alkaline phenolphthalein. The alkali first neutralises any mineral acid present, then converts bichromic acid and bichromates into monochromates, and finally reddens the phenolphthalein.

$$HCl + NaOH = NaCl + H_2O$$

$$H_2Cr_2O_7 + 4NaOH = 2Na_2CrO_4 + 3H_2O$$

$$Na_2Cr_2O_7 + 2NaOH = 2Na_2CrO_4 + H_2O.$$

The proportion of c.c. NaOH and of thiosulphate used for the respective titrations is characteristic of the

composition of the solution, as can be seen by the table on next page.

Monochromates do not react with alkali, and solutions of monochromates are slightly alkaline to phenolphthalein. Hence no alkali is needed for their titration ($b = 0$).

Bichromates react with alkalis according to the above equation, each c.c. N/10 NaOH corresponding to 0·0147 grm. $K_2Cr_2O_7$.

In the case of free chromic acid (see above equation) each c.c. N/10 NaOH corresponds to 0·005 grm. CrO_3.

As regards the iodometric figures found for chromates, bichromates, and for chromic acid, they all behave identically so far that 2Cr corresponds to $6Na_2S_2O_3$ (see par. 142). Calculating the 2Cr as potassium chromate, bichromate or chromic acid, we come to the following relations which are used in the table: 1 c.c. N/10 $Na_2S_2O_3$ is equal to 0·0065 grm. K_2CrO_4, or to 0·0049 grm. $K_2Cr_2O_7$, or to 0·005 grm. CrO_3.

The proportion of a (c.c. N/10 thiosulphate) to b (c.c. N/10 NaOH), as given in the table, follows from the above equations, according to which 1 mol. of bichromate corresponds to 2 mol. of NaOH and to 6 mol. of thiosulphate (hence $a = 3b$); and 2 mol. of CrO_3 correspond to 4 mol. of NaOH and 6 mol. of thiosulphate $\left(\text{hence } a = \frac{3b}{2}\right)$.

The solution contains:	Proportion of $\frac{a \text{ c.c. } \frac{N}{10} \text{ Hypo}}{b \text{ c.c. } \frac{N}{10} \text{ NaOH}}$	Calculation of results
Monochromates only . .	$b = 0$	a . 0·0065 grm. K_2CrO_4
Bichromates only.	$a = 3b$	a . 0·0049 = b . 0·0147 } grm. $K_2Cr_2O_7$
Chromic acid only . . .	$a = \frac{3b}{2}$	a . 0·0033 = b . 0·005 } grm. CrO_3
Mixtures of Chromates and bichromates	$a > 3b$	$(a - 3b)$. 0·0065 grm. K_2CrO_4 b . 0·0147 grm. $K_2Cr_2O_7$
Bichromates and chromic acid	$\frac{3b}{2} < a < 3b$	$(2a - 3b)$ 0·0049 grm. $K_2Cr_2O_7$ $(3b - a)$ 0·0033 grm. CrO_3
Chromic acid and HCl . .	$a < \frac{3b}{2}$	a . 0·0033 grm. CrO_3 $\left(b - \frac{2a}{3}\right)$ 0·00365 grm. HCl

In mixtures the ratio of a to b will necessarily be between these ratios found for the single components.

The only part of the table which thus remains to be explained is the calculation in the case of mixtures, and a mixture of potassium bichromate and bichromic acid may be taken as an example for such calculations.

Let a be the number of c.c. N/10 thiosulphate necessary for the titration of a given volume of the mixture, and b the number of c.c. N/10 NaOH for the titration of the same volume of this mixture, and consider a to be composed of a' : a'', when a' is the thiosulphate necessary for the potassium bichromate only, and a'' the thiosulphate necessary for the bichromic acid only, so that $a' + a'' = a$. Consider further that b is composed of b' and b'', when b' is the alkali necessary for the potassium bichromate only, and b'' the alkali necessary for the bichromic acid only, so that $b' + b'' = b$. From the relation between a and b, explained above for bichromate and chromic acid, we come to the equations $a' = 3\,b'$ and $a'' = \frac{3\,b''}{2}$, and we are in the position now to calculate a' and a''

$$b' = \frac{a'}{3}$$

$$b'' = \frac{2\,a''}{3}$$

$$b' + b'' = b$$

$$a' + a'' = a$$

$$\frac{a'}{3} + \frac{2\,a''}{3} = b$$

$$a' + 2\,a'' = 3\,b$$

$$(a - a'') + 2\,a'' = 3\,b$$

$$a'' = 3\,b - a$$

$$a' = a - a'' = 2\,a - 3\,b.$$

Remembering that a' is the number of c.c. N/10 thiosulphate required for the bichromate only, and that each c.c. N/10 thiosulphate corresponds to 0·0049 grm. $K_2Cr_2O_7$, and that further a'' is the number of c.c. N/10 thiosulphate wanted for the chromic acid only, each c.c. N/10 thiosulphate corresponding to $0{\cdot}00\dot{3}\dot{3}$ grm. CrO_3, we come to the formulæ given in the table, viz.—

$(2\,a - 3\,b)$ 0·0049 grm. $K_2Cr_2O_7$ and

$(3b - a)$ $0{\cdot}00\dot{3}\dot{3}$ grm. CrO_3.

The calculation for the other mixtures is similar, but in the case of monochromates and bichromates it is simpler, because b' (number of c.c. N/10 NaOH for monochromates) is 0; and in the case of chromic acid and hydrochloric acid the calculation is simplified since a'' (c.c. N/10 thiosulphate for hydrochloric acid) is 0.

CHAPTER IX.

ANALYSIS OF FORMALDEHYDE.

NUMEROUS methods have been suggested for the analysis of formaldehyde, but only two of them may be described here in detail.

145. **Method of O. Blank and H. Finkenbeiner.**—3 grm. of the formaldehyde solution are weighed in a weighing bottle and introduced into 25 c.c. of 2N sodium hydroxide contained in a tall Erlenmeyer flask. Immediately afterwards 50 c.c. of pure 2·5–3·0 per cent. hydrogen peroxide are added slowly (in about three minutes) through a funnel to prevent splashing. (The hydrogen peroxide must be tested for acidity, for which an allowance must be made in the calculation.) After remaining for about half-an-hour the funnel is rinsed with water (from which, in accurate estimations, the carbon dioxide has been completely expelled by boiling), and the excess of sodium hydroxide is titrated with 2N sulphuric acid. The indicator is a tincture of litmus. (When the tincture is being prepared, the reddish-violet colouring matter must be extracted by alcohol, since otherwise the end-point is not sharp.)

Two reactions take place, viz. :—

$$2HCHO + 2NaOH + H_2O_2 = 2HCOONa + H_2 + 2H_2O$$

and to a minor extent :—

$$HCHO + NaOH + H_2O_2 = HCOONa + 2H_2O.$$

The percentage of formaldehyde is obtained directly by multiplying the number of c.c. of sodium hydroxide used by 2.

$$\frac{n \times 2 \times 0{\cdot}03 \times 100}{3} = 2n.$$

146. **Method of Romijn.**—25 c.c. of the dry formaldehyde solution are weighed accurately in a tared weighing bottle with a well-ground stopper, and washed without loss in a 500 c.c. flask. The solution is made up to the mark, and 5 c.c. are accurately measured into a bottle with a well-ground stopper. 30 c.c. of about N/1 NaOH, which need only be measured in a graduated cylinder, are rapidly added. About 50 c.c. of N/5 iodine are immediately run in from a burette, with frequent shaking, until the liquid is deep yellow. The bottle is stoppered, well shaken for half a minute, and the contents acidified with 40 c.c. of N/1 sulphuric acid (measured in a graduated cylinder), and after a short time, during which

the bottle is kept stoppered, the excess of iodine is titrated with N/10 thiosulphate.

$$HCHO + 2I + 2H_2O = HCOOH + 2HI.$$

Each c.c. N/5 I equals 0·003 grm. HCHO.

For other methods of determining formaldehyde see Lunge, "Technical Methods of Chemical Analysis," Vol. II., Part II., p. 898–911.

Where formaldehyde cannot be estimated or detected in the original mixture in which it exists, it may be separated by distillation, preferably with a little dilute sulphuric acid to decompose proteid compounds. The cooling must be good and the distillation carried nearly to dryness, if the results are to be at all quantitative, though a good deal of the formaldehyde comes over in the early stages. Formaldehyde leathers should be digested for 1–3 hours with 1 c.c. of N/10 sulphuric acid, and 20 c.c. of water on the water-bath, either in a closed flask or connected with the condenser.

As a qualitative test for formaldehyde which is useful for deciding if a leather has been tanned with formaldehyde, a drop of fuchsin sulphurous acid (colourless solution) is placed on the leather and turns red in presence of formaldehyde. The reaction is based on the combination of formaldehyde with sodium sulphite liberating the fuchsin.

147. **Common Salt.**—This being such a cheap

article it is rarely adulterated, but may contain natural impurities.

Moisture.—This may be estimated by drying a small quantity over a small flame, taking care that no loss occurs by decrepitation.

Insoluble Matter.—About 10 grm. of the salt are dissolved in water and filtered through a tared quantitative filter-paper, dried and weighed. The filter-paper is then ashed and the residue weighed as insoluble inorganic matter. If the residue is brown or yellow it should be tested colorimetrically for traces of iron. (See par. 27.)

Salt occasionally contains calcium and magnesium chloride as impurities, and these have a tendency to absorb moisture. They are best determined gravimetrically in about 10 grm. of the salt dissolved in 100 c.c. of water. For details of this determination see ordinary chemical text-books.

CHAPTER X.

ANALYSIS OF SOAPS.

148. **Constituents.**—Soaps are in principle salts of soda and potash with fatty and resin acids, but contain much water, and frequently excess of base, as hydrate or carbonate, and sometimes as silicate or borate, as well as inert substances (clay, etc.) added merely as weighting materials.

149. **Sampling.**—Sampling demands great care, as soaps dry rapidly, and the outer part of a bar has generally lost much water before it reaches the chemist. The inside of a bar, or in soft soap the centre of a barrel best represents the original. If desired, analyses can be calculated to dry substance, and contracts made on a guaranteed moisture.

150. **Cold Saponification.**—Many soaps are easily produced on a small scale by cold saponification. 10 lb. of good caustic soda or 14 lb. of potash are dissolved in 4 gallons of water. 75 lb. of oil or fat are warmed to 25° C., or till just liquid, and the alkaline solution is slowly added in a thin stream with vigorous stirring, which is continued till the mass becomes too stiff. It is then covered up in a warm place and left for 12

hours at least. If absolute freedom from free alkali is essential, it may be re-melted and a few lb. of oleic acid added, which will render it superfatted. Such soaps are very useful for fat liquors. Oleic acid (candlemakers' oleine) can be saponified even by carbonates, and a small addition to neutral oils renders their emulsion or saponification much easier.

151. **Water Determination.**—(*a*) 2 or 3 grm. of soap are rapidly cut into fine shavings and weighed in a porcelain basin tared with a glass rod, and are first dried in a draught of warm air, at a temperature insufficient to melt the soap, and finally in the water-oven at 100° C.; the glass rod being used to break up the flakes. (*b*) For a more rapid determination (applicable also to soft soaps) the soap in shavings is added to a known weight of dry oil (olive, neatsfoot or tallow) in a crucible, and heated over a small flame as described, par. 155. 5 grm. soap may also be dissolved in 25 c.c. alcohol, and dried in a basin with a glass rod for stirring, and say 25 grm. of dry sand, first on the water-bath and afterwards till constant in air- or water-oven. Often it is sufficient to estimate from loss after adding other constituents (see p. 137).

152. **Determination of Fatty Matter and Alkali.** (*a*) *Aqueous solution.* 10 grm. soap, dissolved in 100 c.c. water with frequent stirring on water-bath, are decomposed, after adding a few drops of methyl-orange, with 50 c.c. N/1 HCl (or more if needed to fully redden the indicator); and the heating is continued till

the fatty acids collect in a clear oily layer on the surface. The stirring rod is rinsed into the beaker with boiling water, and the fatty layer allowed to cool and solidify. If solid the cake can be carefully detached with a thin spatula, and the acid liquid poured into another beaker and the cake is rinsed with two or three portions of cold distilled water, which is added to the acid liquid. The cake is now carefully dried, first with blotting paper, and then in a tared basin in a cold desiccator for some hours over sulphuric acid or dry $CaCl_2$ and weighed. If the fatty acids are liquid, a weighed quantity of beeswax or paraffin wax may be added and deducted from the final weight. For more accurate separation, see fatty acids, par. 165. The fatty acids of palmnut and cocoanut oils are appreciably soluble in the acid liquid. The fatty layer may contain unsaponifiable oils (see par. 163).

The acid liquid if turbid is filtered through a tared filter paper, which is washed, dried and weighed. The gain of weight of the paper is "filling," such as silica or china clay, insoluble in HCl. The acid liquid (with any wash water used) is titrated to orange with N/1 NaOH, and the difference between this and the acid originally added gives the total alkali present, not only as actual soap, but as hydrate, carbonate, borate, and salts of other weak acids, including calcium carbonate if present. It is, however, usual to calculate as sodium hydrate in hard, and potassium hydrate in soft soaps.

A rapid method is to pour the acid liquor and fat into a tap-burette, running the aqueous part off through the tap into a beaker, and finally to wash the fat with hot water, and measure it, heated to boiling point by plunging the burette into a deep beaker, or cylinder filled with steam. The volume of fat in c.c. multiplied by the average gravity, 0·85 gives the weight in grm. The titration is done as above.

(*b*) *Alcoholic Solution.* 4–5 grm. of the soap, previously dried if very moist, are dissolved in 50 c.c. of absolute alcohol, and filtered through a tared filter into a flask (narrow-necked to lessen carbonation), and the filter washed with alcohol. The residue dried at 100° C. is mineral and organic "fillings" including alkaline carbonates, silicates, borates and sulphates. The organic matter and water of crystallisation are driven off by ignition and estimated by loss, and the bases by titration with NaOH and methyl orange, after adding a known quantity of HCl in excess.

The alcoholic soap solution is titrated with N/1 HCl and phenolphthalein exactly as in saponification-value, par. 162, and the result calculated as caustic alkali. The alcohol is now distilled off; and the residue, freely diluted with water, is again titrated with N/1 HCl and methyl orange to distinct redness, and the result calculated as alkali present as soap.

In calculating the total weight of soap from its constituents, it must not be forgotten that in the combination of each mol. of acid, with alkali or glycerin

1 mol. of H_2O is eliminated. If this is overlooked the results will add to considerably over 100 per cent.

The nature of the fatty acids may to some extent be inferred from melting point, gravity, and especially from saponification (or acid), and iodine values. Resin acids are common constituents of hard soaps. They may often be recognised by taste and smell, and estimated by Twitchell's method (Lab. Book, p. 316). Sulphated oils are often present in fat liquors and sometimes in soaps. Ammonia is detected by warming with addition of NaOH.

CHAPTER XI.

OILS AND FATS.

153. THE true oils and fats are compounds of three molecules of a so-called "fatty acid" with one of glycerine. In waxes, wool-fat and certain oils such as sperm, the place of the glycerin is taken by monovalent high-carbon alcohols, solid waxy bodies, which are set free on saponification and form natural "unsaponifiables." "Paraffin" wax, and mineral and rosin oils are hydro-carbons without acid properties and are also "unsaponifiable" (see par. 163).

Oils are liquid, fats solid at ordinary temperatures, the only difference being that of melting point.

The qualities of individual oils and fats depend on the particular fatty acids they contain. The "saturated," or "acetic" series consist of straight or branched chains of CH_2 terminated at one end by H, and at the other by a CO.OH, or acid-forming group, all four valencies of each carbon atom being thus saturated or satisfied. Of these acids, stearic $C_{17}H_{35}CO.OH$ and palmitic $C_{15}H_{31}CO.OH$ are the most important, and both the free acids and their glycerides are of the

nature of hard fats.* The "unsaturated" acids differ from these in having one or more pairs of carbon atoms in the chain combined by "double bonds" CH = CH with the elimination of two atoms of H; oleic acid, $C_{17}H_{33}CO.OH$, and other acids of that series have only one such double linking. Their glycerides are liquid "non-drying" oils, the principal constituents of olive and neatsfoot oils. Lard, tallows, and other animal fats, are mostly natural mixtures of these fats with those of the saturated acids, and their hardness depends on the proportion of the latter which they contain. Drying oils and fish oils contain acids with two to four double linkings, and readily absorb oxygen from the air which replaces a link of the double bonds, forming gummy or solid compounds. The proportion of double bonds in an oil is measured by its "iodine value" (par. 167), one link of each double bond being broken, and replaced by two atoms of iodine (or bromine).

Fatty acids also exist, either naturally or as a result of oxidation, in which one or more of the H atoms attached to the carbon chain are replaced by OH. The most important natural oil of this type is castor, of which the acid is ricinolic or hydroxystearic. The degree of hydroxylation of an oil may be deter-

* The termination "in" (stearin, olein) is used to distinguish the neutral fats or glycerides of the fatty acids, while the words "stearine," "oleine" should be reserved for the commercial products, which often consist largely of the free acids.

mined by acetylation (Lab. Book, pp. 318–321). Castor oil is insoluble in petroleum ether; and in general the presence of OH makes itself felt by diminishing the

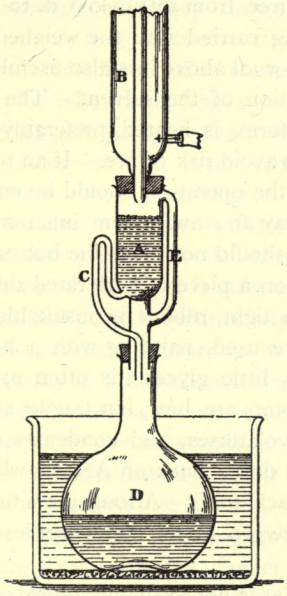

FIG. 2.

solubility in hydrocarbon solvents and increasing that in alcohol.

154. **Separation of Fatty Matters from Non-fats.** This is almost invariably done by the Soxhlet apparatus (Fig. 2). A weighed quantity of the material

to be extracted, preferably powdered or in shavings, is placed in the extraction vessel A, either in a filter-paper thimble, or if the powder is coarse, with a little cotton-wool (free from oil) below it, to prevent solid portions being carried into the weighed flask D. A tuft of cotton-wool above it is also useful to ensure the even distribution of the solvent. The flask D, best of spherical form, is heated, preferably by steam or electrically, to avoid risk of fire. If an ordinary water-bath is used, the operation should be conducted on a large metal tray and away from inflammable objects; and the flask should not touch the bottom of the bath, but may rest on a piece of perforated zinc. All joints must be quite tight, rubber is unsuitable, and if ordinary corks are used, painting with a hot solution of gelatin and a little glycerin is often useful. Ground or mercury joints are best, but fragile and expensive. The solvent volatilises, and condenses in reflux condenser B, and drops back on A, from which it siphons at intervals back to C. A long glass tube fitted with a cork into the top of the condenser lessens escape of vapour.

If a Soxhlet is not available, repeated washing with the solvent, first by decantation, and, finally on a filter, gives fair extraction. In either case the bulk of the solvent is recovered by distillation, and the remainder driven off by continued heating on the water-bath, the process being hastened by sucking or blowing dry air through the flask. The flask is then cooled and

weighed, and this is repeated till approximately constant, the gain of weight being fats. With drying or partially volatile oils, the heating must be as short as possible, and absolute constancy cannot be expected. With most materials ten or twelve siphonings in a two hours extraction suffice, but as a precaution a few siphonings may be taken with fresh solvent in a clean flask which should gain no appreciable weight.

Various solvents can be used, sometimes with slight differences in result according to the solubility of the fats. The most useful are petroleum ether carefully rectified so that the whole boils below 70° C., and carbon disulphide. The latter is safer and easier to handle as its boiling point is quite steady, and though very inflammable, the temperature of its flame is low and does not readily set fire to surroundings. It should be kept in the dark and occasionally distilled to free it from sulphur due to decomposition. In either case the operation is safer if a liberal amount of solvent is used so that the temperature is not too suddenly altered by the siphoning. Chloroform and carbon tetrachloride are free from the danger of fire, but powerful anæsthetics, and dissolve some matters such as lecithin (in egg yolk), not soluble in petroleum ether or carbon disulphide.

When the material is mainly fat, it is often sufficient to filter it through paper in the drying oven or other warm place. This at the same time removes any water present. If it is desired to estimate solid

non-fats, the (tared) filter paper may be soxhleted, or freely washed in the funnel with the solvent, dried and weighed. If, as is usual, the subsequent determinations are made on the filtered fat, the fact should be stated on the report.

155. **Determinations of Water in Oils and Fats.** If the oil or melted fat is quite clear and transparent, it seldom contains more than negligible quantities of water.

If not, two to three grams of the fat are heated over a small flame in an open crucible (platinum is best). If much water is present, the fat boils gently at first, but finally with slight crackling and tiny puffs of smoke, when the flame must be instantly withdrawn and the crucible weighed after cooling. Result should be exact to about 0·25 per cent. (Fahrion). Where little water is present the fat may simply be dried in a beaker, with a small stirring rod weighed in, in an air oven at 110–120° C. with frequent stirring, till weight (cooled) is constant.

156. **Determination of Ash.**—Heat 20 grm. in a shallow basin (preferably platinum) with a small flame at one side. The oil first boils and then burns off quietly, after which the heat is increased till carbon is burnt off. A yellowish ash usually indicates iron.

157. **Detection of Mineral Acids.**—Sulphuric acid is often present in acid-extracted fats, and is very injurious to leather. Boil 25 grm. with 200 c.c. water, transfer to separating funnel, and shake well

after partial cooling, allow fat to rise, separate aqueous layer, and titrate the whole or an aliquot part with N/10 sodium hydrate or carbonate and methyl-orange as indicator.

158. **Physical Constants of Oils and Fats.**—Specific gravity is often useful for purposes of identification (see pp. 167–169 for constants), but mineral oils are lighter and rosin oils heavier than any natural fats, so that by judicious mixture the gravity of any oil can be imitated, and adulteration must be detected by chemical means.

For oils liquid at ordinary temperature (15° C. or 60° F.) the determination is made with the specific gravity bottle by weighing say 10 c.c. in the usual way. Smaller quantities may be accurately weighed in the Sprengel tube (Fig. 3) which is filled by suction, a piece of india-rubber tube being slipped on the marked end, and the oil being finally adjusted to the mark by suitably sloping the tube and touching the point with blotting paper to remove, or with a drop of oil on a glass rod, to add oil. The gravity of solid fats is most conveniently taken at 100° C. (as compared to water at 15° C.), in a similar way, but suspending the gravity bottle or Sprengel tube by a wire sling in steam in a beaker or in the neck of a wide flask covered with a clock-glass, any fat which exudes being carefully removed with blotting-paper or a rag dipped in petroleum ether, and the instrument cooled before weighing. The gravity of minute

globules of oil or fat may be obtained by making a mixture of alcohol and water in which they neither float nor sink, and determining its gravity either by

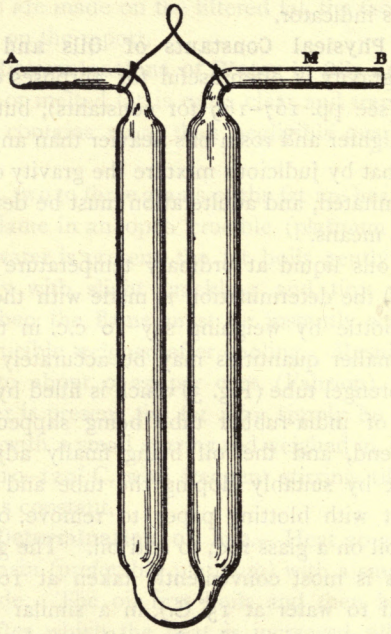

FIG. 3.

direct weighing, or volumetrically by alcohol tables. Oleometers (hydrometers) only give very rough results, but the Westphal balance is convenient and accurate where many determinations are required.

The melting-point of fats is subject to many errors which cannot be discussed here. It is most easily taken by placing a fragment of fat in a thin glass tube drawn to a capillary point, which is sealed. The tube is attached to a thermometer by a rubber band, and the whole is stirred in a large beaker of water gradually heated by a small flame, the temperatures at which the fat adheres as a drop to the glass, and at which it becomes clear and transparent ("incipient" and "clear" fusion) being both noted. The fat must be free from water and solid impurities, and must have been in the solid state for 24 hours before testing, as melted fats only slowly recover their proper solidity and specific gravity. Interesting information is given by the temperature-curves of solidification. (See Lab. Book, Sect. xx.)

159. **Refractive Index** gives nearly the same information as specific gravity, and is more rapidly taken if a refractometer is available. (For details and for the calculation of "refractive constant" from the gravity and refractive index, see Lab. Book, Sect. xx.)

160. **Physico-chemical Tests.**—The specific temperature reaction with sulphuric acid (Maumené, Thomson, Ballantyne) and that with Bromine (Hehner) (Lab. Book, pp. 299–301), give little information which cannot more satisfactorily be deduced from the iodine value (par. 167).

Colour-reactions with sulphuric and nitric acids were formerly much in vogue as oil-tests, but are of

little practical value. A drop of concentrated sulphuric acid gives reddish or bluish violet coloration with *all* liver oils.

161. **Acid-value.**—The *free* fatty acid in oils and fats is not a constant, but varies with the age and rancidity of the sample, and its mode of preparation ; but is sometimes important in judging suitability for various uses, and in detecting adulteration of tallow with distilled stearines which consist mainly of free acids. Oils with free acid corrode metals. As the particular acid present is generally unknown, it is not possible to determine accurate percentage, and no advantage is gained by calculating to stearic or oleic acid. It is therefore usual to state both this and the saponification value in terms of milligrammes of caustic potash required to neutralise the acids of 1 grm. of fat or oil. If the molecular weight of the acid is known, its percentage is easily calculated by dividing the acid or saponification value by 561 (the equivalent of KOH × 10), and multiplying by the molecular weight of the acid (stearic = 284, oleic = 282).

50 c.c. of good alcohol and 20 drops of 1 per cent. alcoholic phenolphthalein solution are placed in a 250–300 c.c. conical flask, and enough N/10 NaOH solution (1 to 2 drops) is added to render the liquid very faintly pink. The oil is weighed in a small beaker with a glass tube ; 3–5 grm. is transferred into the flask and the quantity taken is determined by re-weighing the beaker. The mixture is now titrated with aqueous

(or alcoholic) N/10 KOH till the faint pink colour is reached which the solution had before the fat was added, and no longer disappears at once on vigorous shaking; and the number of c.c. used multiplied by 5·61 and divided by the weight in grams of oil taken is the acid-value. In determining the acid-value of solid fats, the flask must be warmed as slightly as possible to liquify the fat.

162. **Saponification Value.**—This is the measure of the total fatty acid contained in the sample, both free and combined with glycerin. It depends on the fact that while aqueous or even alcoholic potash added only to neutrality does not saponify the neutral fats in the cold, alcoholic potash does so very rapidly at boiling temperature and especially when used in excess. The reaction for olein and potash is :—

$$\underset{\text{Triolein}}{C_3H_5(C_{17}H_{33}COO)_3} + \underset{\text{Potash}}{3KOH} = \underset{\text{Glycerin}}{C_3H_5(OH)_3} + \underset{\text{Potass. oleate}}{3C_{17}H_{33}CO.OK}$$

This value is approximately constant for any individual oil, but varies from about 250 for cocoanut and palm-nut oils to 176 for rape oil, while that of mineral oil is *nil*, so that it is a valuable characteristic for identification, and if very low, usually indicates adulteration with mineral or rosin oils. For approximate constants, see pp. 167–169.

The alcoholic potash must be made with suffi-

ciently pure and nearly absolute alcohol, or the solution darkens and becomes useless. If for reasons of cost methylated spirit must be used, it must be previously purified by adding 10 grm. per litre of metaphenylene diamine hydrochloride, allowing to stand two or three days with frequent shaking, and distilling nine-tenths with a fractionating column (Mann); or by shaking with finely powdered permanganate till the liquid is deep red, allowing to stand and settle, and after treating for a day or two with potassium carbonate or quicklime, distilling the clear liquid, rejecting the first and last portions for commoner uses. To make up the solution, 8 grm. of caustic potash, "pure by alcohol," is dissolved in 10 c.c. of water and made up to 250 c.c. with the nearly absolute alcohol. The solution is allowed to stand 24 hours to deposit undissolved carbonate, and is preserved in a dark and not too cool place in a bottle fitted with a 25 c.c. pipette, closed at the upper end with a piece of rubber tube and a pinchcock, and passed through a rubber cork.

For the determination, quantities of oil or fat not exceeding 2 grm. are transferred as before from the weighed beaker to conical flasks of Jena or other hard glass of 150–200 c.c. capacity, and 25 c.c. of the alcoholic potash are added, allowing in each case the same number of drops to fall from the pipette after the stream has ceased, to secure constancy of measurement. A similar quantity is run into an

empty flask as a control, as the standard of the solution varies slightly on boiling. The flasks are fitted with corks and vertical tubes, about 0·3 cm. diameter and 50 cm. long to act as reflux condensers, and are placed, resting on perforated zinc, in a shallow water-bath such as a "dripping tin," and simmered for half-an-hour, the flame being regulated to evaporate as little spirit as possible, and the flasks frequently shaken with a rotary motion. 1 c.c. of 1 per cent. phenolphthalein solution is now added to each flask, and the liquor accurately titrated with N/2 HCl till colourless, great care being taken not to overstep the point of decoloration. The difference between the HCl used with the oil and that for the empty control flask represents the potash used in saponifying the total fatty acids present. The saponification-value (i.e. the milligrammes of KOH combined with 1 gram of oil) $= \frac{\text{c.c. difference of acid} \times 56{\cdot}1}{\text{grm. of oil taken} \times 2}$. The difference between this and the acid-value is called the "ether-value," and is the potash used in saponifying the neutral fats. Waxes, wool-fat, and oils of the sperm type are not completely saponified by this process, and must be heated with 2N alcoholic potash in a pressure-flask, in a water- or brine-bath, at 100–110° C. 84–86 per cent. of the total acids of wool-fat are saponified by boiling with alcoholic potash in the usual way, and this proportion is fairly constant and will often serve for comparison.

163. **Unsaponifiables.**—These are of two classes, first the hydrocarbons (mineral and rosin oils and paraffin waxes) used as adulterants or mixtures; and second, the higher alcohols naturally present in solid or liquid waxes, among which we must reckon some of the constituents of wool-fat and of certain marine oils (sperm, dolphin, porpoise, shark, and dog-fish). As much simpler methods suffice for the former, which are also of the more common occurrence in the laboratory, it is desirable to deal with the two classes separately.

If the presence of ordinary hydrocarbon oils is considered probable, it is best to determine saponification values with about 5 grm. of the oil, and 50 c.c. (in place of 25 c.c.) of approximately half-normal alcoholic potash, and to use the soap solutions after titration for the estimation. Where the ordinary smaller quantities have been used for duplicates, it is possible by uniting them to obtain enough for a *single* determination of unsaponifiables.

To the soap solution of 5 grm. of fat or oil, 1 grm. of sodium bicarbonate (or, less satisfactorily, a few drops of the potash solution) are added, so as to make sure that no soap has been decomposed in titration, and the whole is made up to about 100 c.c. with distilled water, transferred to a 200–250 c.c. separating funnel, and shaken with a gentle rotary motion with 25 c.c. of petroleum ether (boiling below 70° C.) The ether is allowed to separate fully, the soap solution

is returned as completely as possible to the saponification flask, together with 5 c.c. of water which is used to slightly rinse the etherial layer, and the latter is run into a well-corked flask. The soap solution is now returned to the separating funnel and again washed with 25 c.c. of petroleum ether, which is treated as before and added to the first, and this washing is repeated four times in all, the later shakings being more vigorous than at first if the ether separates well and shows no emulsification: and the last time, great care must be taken that none of the etherial layer escapes with the soap solution. The whole of the etherial solution is now returned to the empty separating funnel and washed four times with 50 c.c. of distilled water, the shaking the first time being very gentle, but afterwards vigorous, and great care being taken not to lose any of the etherial layer. The wash-water may either be added to the soap solution or preserved separately, if the fatty acids are to be determined.

The etherial solution and a little clean petroleum ether used in rinsing the separating funnel is run into a dry well-corked flask, in which it is allowed to stand some hours to deposit suspended water, and is then transferred to a weighed flask, rinsing with a little petroleum ether, the ether distilled off and recovered, and the residue dried at 100° with occasional sucking of dry air through the flask, till after cooling and weighing, the weight remains practically constant.

This simple method is quite satisfactory for the determination of adulteration with hydrocarbons, as all ordinary oils and fats are completely saponified, and at least the results are accurately comparable with saponification values; but it has two defects, as applied to the liquid waxes or their mixtures:—the saponification is incomplete, and the high alcohols are imperfectly taken up by petroleum ether, in which they are not very soluble. Where waxes are suspected, the following methods may be adopted.

164. **Saponification of Waxes** (including sperm oil, wool-fat, etc.).—Complete saponification is obtained either by heating 5 grm. of fat or oil with 3 grm. of stick potash and 25 c.c. of good alcohol (or 25 c.c. 2N alcoholic potash) in a strong sealed bottle in the water-bath for 1 hour; or by boiling for an hour with 50 c.c. of absolute alcohol in a flask with a reflux condenser, gradually adding 2·5 grm. of metallic sodium in small pieces. A copper flask, with screwed cap and without soft-soldered joints, is the safest pressure bottle, as thick glass is apt to crack, and the pressure of alcohol vapour at 100° is considerable, but a small soda-water bottle with wired-in cork, or screw or lever top may be used. To avoid danger it should be wrapped up in canvas and heated very gradually in a water-bath, starting cold.

The resultant soap-solution must be boiled (distilled) till free from alcohol and syrupy, redissolved in sufficient boiling water to make it fully liquid, nearly

neutralised with HCl and phenolphthalein, 1 grm. sodium bicarbonate added, and shaken out with ethylic (not petroleum) ether as already described. As such materials frequently give rise to troublesome emulsions and intermediate layers, the following alternative method may be used. The saponified mixture is transferred to a shallow porcelain basin, rinsing the saponification-flask with alcohol, about half the alcohol is evaporated on the water-bath, 10 grm. of sodium carbonate and 25 grm. purified sand (par. 94) are added and well mixed with a glass rod, and the evaporation continued with frequent stirring to *complete* dryness. The mixture is then pulverised and placed in a Soxhlet in a paper thimble, the basin being rinsed with a portion of ethylic ether (previously dried by distillation off potassium carbonate), and the extraction continued with this solvent for 4–5 hours. The etherial extract is then washed with distilled water in a separating funnel, and treated as already described. The A.L.C.A. recommend a similar process for *general* determinations, but Soxhlet with petroleum instead of ethyl ether, which in absence of waxes, is satisfactory.

By any of these processes volatile and soluble unsaponifiables are of course lost.

165. **Fatty Acids.**—On acidifying the soap-solutions obtained in the preceding operations, the fatty acids are set free, and those which are insoluble in water (non-volatile) may be recovered for examination. The dissolved alcohol or ether is boiled off, care

being taken that it does not ignite. The solution is then rendered distinctly acid with HCl, and heated in a beaker till the acids separate as a fatty layer. If solid on cooling, the fat-cake may be cautiously pierced with a glass rod, the acid liquid poured off, and the fat washed repeatedly with boiling water. (If the washings of the etherial layer (prev. par.) have not been added to the soap-solution, they may be slightly acidified and used instead of water for a first washing). The washed cake may be carefully separated, dried on filter paper and weighed (see par. 152). If the acids are liquid they may be separated with the aid of a little petrol ether in the separating funnel or by washing on a tared wet filter paper. In drying unsaturated acids, their ready oxidation and consequent gain in weight must be remembered.

166. **The Acid-value of Fatty Acids** is often characteristic, and the "mean molecular weight" is obtained by dividing $56 \cdot 1 \times 100$ by it. The saponification value of free acids is ordinarily identical with the acid value, though in a few cases, they have a "permanent saponification value" due to lactones. The iodine value may be determined by the usual methods. The melting and solidification points are important characteristics. For the determination of the latter, see Lab. Book, p. 292.

167. **Iodine Value.**—As has been explained, this is the measure of the unsaturated bonds, and therefore

of the drying and oxidising properties of the oil, and where only one unsaturated acid is present (e.g. oleic in tallow) it affords a means for its estimation. Several methods have been proposed, by Hübl, Wijs and others, but that of Hanûs is simplest and most convenient, and quite satisfactory for all oils likely to be met with by a leather-chemist.

The Hanûs iodising solution is made by dissolving 6·6 grm. of iodine in 500 c.c. of warm (99·5 per cent.) glacial acetic acid, and adding 1·5 c.c. of bromine to the cooled solution. It keeps well if protected from light. A quantity of oil, varying from 0·1 grm. of a fish or drying oil to 0·4 grm. of neatsfoot or olive, is weighed into a well stoppered bottle, and dissolved in 10 c.c. of pure chloroform, and 25 c.c. of the Hanûs solution is accurately measured and run in from a burette, or pipette with safety tube, and the mixture shaken and allowed to stand one hour. 10 c.c. of 10 per cent. solution of potassium iodide (free from iodate) is then added, and the mixture rapidly titrated with fresh N/10 solution of sodium thiosulphate (24·8 grm. per litre) until pale yellow, when a few drops of a starch solution is added, and the titration completed with vigorous shaking to the disappearance of blue colour, no notice being taken of any reappearance on standing. A blank test is made at the same time without oil, and the difference of the two titrations gives the c.c. of thiosulphate equal to the iodine absorbed by

the fat. $\frac{\text{c.c. used} \times 1{\cdot}27}{\text{wt. of fat}}$ = the iodine value, or parts of iodine absorbed by 100 parts of oil. If oleic is the only unsaturated acid present, its percentage is given by multiplying the iodine value by $\frac{100}{90{\cdot}07}$ = 1·1601; the iodine value of pure oleic acid being 90·07.

If pure thiosulphate cannot be obtained, its exact normality may be determined against bichromate, p. 122. Potassium iodide contains iodate if its solution blues starch paste on the addition of a little pure concentrated hydrochloric acid.

In drawing conclusions as to the purity of an oil from the determinations described above, it must be remembered that the constants of genuine oils and fats are liable to vary to some extent, and the limit of this variation is not accurately known. Not only do animal fats and marine oils differ according to the part of the animal from which they are taken, but are affected by its food. Manufacture and age also affect constants to some extent, and especially the iodine value falls as the oil becomes oxidised; a point which is of special importance in the identification of fats extracted from leather. The following example of cod oil taken from actual practice may serve to illustrate the calculation and use of oil-values. One only of the duplicates actually made is given; but the greatest divergence was 0·6 in the saponification value.

Acid value	39·3
Saponification value	182·6
Unsaponifiables	0·6
Iodine value	161·5
Specific gravity	0·930
Refractive index	1·482

It may be observed that all these figures are approximately normal, and that there is no ground for reporting the sample as other than a somewhat rancid but genuine oil. If this were mixed with 20 per cent. of mineral oil (adjusted for gravity, and neglecting the small saponification and iodine values generally given by rosin oils), the results of analysis would be as follows:—

Acid value	= 31·7
Saponification value	= 146·1
Unsaponifiables	= 20·6
Iodine value	= 129·0

The gravity would be unaltered, but the refractive index would be materially increased.

168. **Dégras and Sod-Oil,** originally by-products of chamoising, are now frequently prepared by direct oxidation of oils. They consist of emulsions of more or less oxidised marine oils often mixed with tallow, wool-fat and mineral oils, which cannot always be considered as adulterants, since they may improve the dégras for use in currying.

Genuine dégras (möellon), and some sod-oils, are obtained by pressing the skins after soaking in warm water, but "Weissgerber-Dégras" and most sod-oils

are recovered by washing with alkaline solutions, which are afterwards decomposed with sulphuric acid; and may therefore contain soaps, free acid, or mineral sulphates according to circumstances. All natural dégras contains considerable water present as an emulsion, and is a thick yellow liquid or paste. "Evaporated" sod-oil has been freed from water by heating, and is more liquid and nearly black.

The following methods are mainly those of Fahrion * and will suffice for most requirements, but complete analysis will tax the ingenuity of the ablest chemist. Many variations have been proposed, for which, among others, the references given below may be consulted.† The most important determinations are of water, mineral ash, free fatty acids, total fatty acids, oxidised fatty acids, and unsaponifiables.

169. **Water and Mineral Ash.**—About 3 grm. of the dégras are weighed into an open platinum crucible or basin, and gently heated over a very small bunsen flame till foaming ceases, and slight cracking with possible puffs of smoke begins, when the heat is instantly withdrawn and the crucible cooled and weighed, the loss being reckoned as water. The difference between repeated determinations should not exceed 0·2 per cent.

* Collegium, 1911, p. 53.

† Collegium, 1906, p. 313; 1908, p. 21; 1909, pp. 24, 61; 1910, pp. 119, 144; 1911, pp. 53, 54; Leather Ind. Lab. Book, pp. 314, 338.

The heating is now continued and increased, the crucible being somewhat sloped, when the oil will ignite and burn quietly, heat being only given to maintain the combustion. After burning off the residual carbon at the lowest possible temperature the residue is "mineral ash." For unevaporated oils the water may vary in normal dégras from 15–20 per cent., and in sod-oil from 30–40 per cent., while the so-called "Weissgerber-Dégras" may reach 50 per cent. The mineral ash should not exceed 0·2–0·3 per cent., but in sod-oil recovered by alkali and acid treatment 1–2 per cent. is common. Traces of iron may be determined colorimetrically, but under 0·05 per cent. are not usually injurious. For exact ash determination considerably larger quantities of oil must be burnt in a platinum basin.

170. **Free Fatty Acids, Unsaponifiables, Total Acids and Oxidised Acids.**—About 3 grm. of dégras are weighed into a porcelain basin of 100 c.c. capacity, 20 c.c. of alcohol (not less than 95 per cent.) are added, with 1 c.c. of phenolphthalein solution, warmed, and titrated with N/1 or N/2 caustic alkali to distinct red. The solution used represents free acid and is generally calculated as oleic (mol. wt. 282).*

* In sod-oil recovered with acid, sulphuric acid may be present, either free or as sulphated fatty acid, which could be determined by adding a known excess of alkali, igniting, and titrating back, as in the Procter-Searle method (par. 203), which was first used by Allen for sulphuric acid in vinegar.

To the neutral solution after titration 3 c.c. of aqueous 50 per cent. potassium hydrate solution are added, and evaporated to dryness on the water-bath with frequent stirring.* The soap is dissolved in 50 c.c. of 50 per cent. alcohol, transferred quantitatively to a separating funnel, and shaken first with 25 c.c. of petroleum ether (completely volatile below 70° C.) and successively with two portions of 15 c.c. About 1 hour should be allowed for complete separation of each shaking. The petroleum ether solutions are now united in a second separating funnel and washed with 20 c.c. of 50 per cent. alcohol, which after complete separation is added to the soap solution. The residue from the petroleum ether solution after evaporation is the *unsaponifiable.* For details of manipulation cp. par. 163.

(Baldracco† prefers to saponify 15–20 grm. of dégras in a flask with 50 c.c. of ordinary alcohol and 5 grm. of caustic potash, boiling 2–2½ hours with a reflux condenser. The alcohol is then distilled off, the last traces being evaporated on the water-bath; 8 grm. of sodium bicarbonate and 50–60 grm. of purified quartz sand are added, and the mixture dried at 100° C. with frequent stirring, till when cool it can be powdered. It is now extracted in a paper "thimble"

* All glycerides will be completely saponified, but only about 85 per cent. of the total saponifiable of wool-fat if present, the remainder being estimated as "unsaponifiables."

† Collegium, 1904, p. 334.

in the Soxhlet apparatus, with petroleum ether volatile at 70° C., the etherial extract washed with hot water till the washings are neutral, and evaporated, and the residue weighed as above. The results are very concordant in themselves, but usually differ somewhat from those of wet extraction. The method may be recommended at least in cases where "shaking out" is difficult from the formation of persistent emulsions.)

In absence of mineral oils, wool-fat and liquid waxes such as sperm oil, the unsaponifiables by Fahrion's method should not usually exceed 1–2 per cent., or in presence of shark-liver oil about 5 per cent. (cp. par. 163).

171. **Fatty Acids.**—The soap solution is evaporated to dryness on the water-bath, dissolved in hot water, transferred to a separating funnel, and 10 c.c. 20 per cent. hydrochloric acid and 20 c.c. petroleum ether added, and the mixture well shaken and allowed to separate over-night. The etherial layer contains the fatty acids, and after washing with water may be evaporated, and the residue weighed.

172. **Oxidised Acids or "Dégras-former"** remain mostly adhering to the sides of the separating funnel. They are dissolved in alcohol, evaporated to dryness in a platinum dish, weighed, and the dish (including mineral ash) again weighed. The difference is oxidised acids. Traces remain in the acid solution, which can be recovered by evaporating to dryness, redissolving

in 10 c.c. of water with a little ammonia, acidifying, and again repeating the shaking-out process.

The water, ash, unsaponifiables, fatty acids and oxidised acids should amount to 95–96 per cent. of the total, the remainder being glycerine, volatile acids and loss. The oxidised acids should be from 6–10 per cent. Higher percentages are apt to make the dégras too viscous for satisfactory use. High iodine value of fatty acids (say over 100) indicates a tendency to "spue"; high acid value, if consisting of saturated acids, tends to the "sprouting" of crystallised fats on the surface of the leather.

173. **Egg-Yolk.**—Egg-yolk is principally valuable in leather manufacture for its oil, and its analysis may therefore be described here. The oil is chemically very similar to olive or neatsfoot. Most of the yolk used is preserved, generally with salt or boracic acid or borax and added water. Hence the important determinations are : water, egg oil, salt and ash.

174. **Water.**—10–20 grm. of the yolk are weighed and dried on sand, as described on par. 151, the basin and sand, including a short glass rod, being first accurately tared, and the sand and yolk frequently stirred as it dries. The final drying should be *in vacuo* at 100° C. or in an air-oven at 105° C. The loss is water.

175. **Fatty Matters (Oil).**—The residue is crushed as finely as possible with the glass rod or a small pestle and transferred to the paper thimble of a Soxhlet apparatus, and the basin and pestle rinsed

with petroleum ether, which is poured through the Soxhlet. The extraction is continued till the petroleum ether, which siphons, is colourless and free from fat. The ether is evaporated and the fatty residue is dried till constant, and weighed as in par. 154. The most rapid method is to distill off most of the ether, and finish the evaporation in an open beaker in the drying-oven. If the egg-yolk contains boric acid, a portion will be contained in the extracted oil, and may be detected by shaking 0·5 grm. of the latter with a few c.c. of warm *methyl* (not "methylated") alcohol, which will burn with a green flame. In this case the whole or a portion of the oil must be shaken out two or three times with distilled water, and the boric acid determined by titration (par. 16) and deducted, or the whole of the fat may be washed, with the precautions mentioned in par. 163, before drying and weighing. Foreign oils or fats may be added to preserved yolk, but their detection in most cases is very difficult, if not impossible.

176. **Ash (including Salt and Boric Acid).**—10 grm. of yolk are dried and carbonised at a low temperature in a platinum basin, and the mass washed with water to remove soluble matters, dried and ignited to a white ash, and the decanted washings returned, evaporated to dryness, and heated to 110–120° C. and weighed.

The ash is redissolved and the liquid made up to a definite volume, and salt is estimated in one portion

as in par. 26, and boric acid in another (par. 16). If a very accurate determination of boric acid is desired, it would be well to render the yolk alkaline with soda, and ignite as in the Procter-Searle method (par. 203).

Pure yolk of hens' eggs averages about 30 per cent. of oil, ducks' eggs being somewhat richer; preserved yolk should yield 20–24 per cent. The following references to original papers may be given:—

F. Jean, Congrès du Ch. appliq., 1900, p. 482.
,, Collegium, 1903, p. 71.
E. Carpiaux, "L'Oeuf de Poule," Bruxelles, 1903.
M. S. Bruère, Collegium, 1903, p. 45.
Kathreiner and Schorlemmer, Collegium, 1903, pp. 134, 137.
Vignon and Meunier, Collegium, 1904, pp. 325, 335.
Schorlemmer and Sichling, Collegium, 1906, p. 90.
I.A.L.T.C. Commission, Collegium, 1906, p. 242.
Paessler, Collegium, 1908, p. 56.
Parker and Paul, Collegium, 1910, p. 53.

177. TABLE OF CONSTANTS OF LIQUID OILS.

Name of Oil	Sp. Gr. 15° C.	Refract. Index, 15° C.	Solidifying Temp.	Saponification Value	Acid Value	Iodine Value	Unsaponifiable, per cent.
Blown rape	·967	1·481	..	200	..	63	..
Castor	·965	1·480	−18°	180	..	84	..
Raw linseed	·935	1·484	−18°	193	..	175	..
Cod liver— (Möller's)	·928	1·481	−10° or below	185	..	165	..
Brown cond.	·927	1·481	..	182	21·2	151	2·0
Av. of 9 spls.							
highest	·933	1·484	..	191	28·4	174	3·5
lowest	·924	1·479	..	178	6·5	132	0·8
"Coast cod" mixed livers	·930	1·482	..	185	..	172	..
Herring	·92–·94	1·478	..	..	..	145	..
Mixed fish (Eng.)	·929	1·480	..	184	..	140	..
Sardine (Japanese)	·916	1·479	20°	192	..	121	..
Whale	·931	1·476	−2°	193	..	118	..
Seal (pale)	·928	1·479	−2°	189	..	121–138	..
Shark liver	·913	1·476	−16°	168	..	102–120	..
Cotton seed	·923	1·475	..	193	..	107	..
Soja bean	·925	..	−8°	193	..	122	0·2
Sesame	·921	1·475	−5°	190	..	108	..
Olive	·917	1·472	−2°	193	..	83	..
Rape (colza)	·915	1·474	−2°	176	..	101	..
Neatsfoot	·915	1·474	"Tender"	193	..	70	..
Lard oil	·912	1·472	,,	193	..	79	..
Egg-yolk oil	..	1·466	20°–23°	190	..	50–70	..
Sperm	·884	1·468	deposits spermaceti	135	..	80–100	..
Mineral (for leather)	·85–·92	1·47	very low	nil	..	very low	..
Rosin oil (do.)	·96–·99	1·50	,,	resin acids	..	very low	..

178. TABLE OF CONSTANTS OF FATS.

Name of Fat	Sp. Gr. 98°–100° C.	Sp. Gr. 60° C.	Refract. Index 60° C.	Melting Temp.	Solidifying Temp.	Saponification Value	Iodine Value	Acid Value	Unsaponifiable
				deg.	deg.				
Purified wool-fat	·902	·885	1·465	..	..	102	27	..	..
Japan wax	·876	·907	1·450	52–56	45–50	221	5·8	7·33	1·63
"Oleo-stearine"	·875	·907	1·449	54	..	203	31	..	..
Mutton tallow	·859	·895	1·442	47–50	44–45	195	40	1·7–14	..
Beef tallow	·861	·901	1·442	43–45	36–38	196	42	3·5–50	..
Horse fat	·861	·894	1·455	34–39	20–30	197	79	2·44	..
Bone fat	..	·894	1·451	21–22	15–17	191	51	29·6–53	1·8
Lard	·861	·886	1·452	36–44	32–39	196	59	0·54–1·28	0·23
Palm oil	·859	·883	1·452	30–34	21–25	202	52	24–200	..
Coconut oil	·874	·897	1·442	23–28	14–20	255	8·7	5–50	..
Palmnut oil	·873	·896	1·443	23–28	20	247	13·5	8·36	..
Cacao butter	·858	·887	1·450	25–33	22–27	197	35	1·1–1·88	..
Carnaüba wax	·842	..	..	85	78	87	13·5	4–7	54·87
Distilled grease stearine	·836	..	1·445	48–57	45–53	Up to 195	..	..	..
Beeswax	·822	..	..	62–63	62–63	102	9·6	16·8–21·2	52·38
Vaseline	·832	·851	1·470	..	..	Nil	14–26	..	..
Paraffin wax	·752	·776	1·434	40–55	40–55	Nil	4	..	..

179. TABLE OF CONSTANTS OF FATTY ACIDS.

Name of Fatty Acid	Sp. Gr. 98°–100° C.	Sp. Gr. 60° C.	Refract. Index 60° C.	Melting Temp.	Solidifying Temp.	Saponification Value	Iodine Value
				deg.	deg.		
Stearic acid .	·850	·865*	1·433*	71	..	197·5	Trace
Palmitic acid .	·835	·862	1·432	62	..	219·1	Trace
Oleic acid. .	·847	·870	1·447	14	4	198·8	90
Mixed tallow acids	·845	·875	1·442	44	44–54	197	About 40
Mixed olive oil acids	·843	·873	1·446	26	17–23	..	..
Mixed cod oil acids	·858	·882	1·458	..	18	204	..
Do. Möller's	·876	·900	1·464	..	..	..	..

* 70° C.

The numbers given in the foregoing tables must be taken as approximate only, and representing the average character of a pure oil. Considerable divergence occurs between perfectly genuine samples of the same oil, and several of the constants are influenced by age and oxidation.

CHAPTER XII.

GLUCOSE DETECTION AND ESTIMATION.

180. As glucose or sugary matters are always present in tanning materials, and consequently in leather, a quantitative estimation is necessary to ascertain if the amount present is due to natural causes or added as an adulterant.

The methods employed are modifications of Fehling's methods.

Preparation of Solutions.

181. **Fehling's Solution.**—(1) 34·639 grm. of purest crystallised copper sulphate are dissolved in water, 10 c.c. of normal sulphuric acid is added, and the whole made up to 500 c.c.

(2) 173 grm. of pure crystallised potassium sodium tartrate (Rochelle salt) and 125 grm. of caustic potash, "pure by alcohol," are dissolved in distilled water and made to 500 c.c.

These solutions are best kept separated, being mixed when required.

182. **Basic Lead Acetate Solution.**—Rub together 300 grm. of pure lead acetate, 100 grm. of pure and finely powdered litharge and 50 c.c. of water, and digest on the water-bath until the mass becomes white, water being added as required to replace evaporation. Make the whole mass to 1 litre with distilled water, allow to settle, and filter.

183. **Sodium Sulphate Solution.**—A concentrated solution of sodium sulphate is made, and 10 c.c. of lead solution is titrated with it until no further precipitate is produced. This point may be ascertained by allowing the precipitate to settle and seeing if another drop of sulphate gives a further precipitate, if so, more will be required, or testing on a filter paper with sodium sulphide solution until no black spot is produced. 100 times the quantity of sodium sulphate required to precipitate the 10 c.c. of basic lead acetate is diluted to 1 litre.

184. **Detannisation of Solutions.**—The tanning infusion or leather extract (pars. 114 and 195) should contain at least 1·5 grm. of solids per 100 c.c., and if the solutions employed for tannin analysis are used, they should be concentrated by evaporation. The solution should not contain more than 1 per cent. of sugar, but less quantities can be estimated.

To 200 c.c. of tannin solution add 20 c.c. of basic lead acetate, mix well, allow to stand 15 minutes, and then filter. The filtrate should be tested to ascertain if it gives any further precipitate with the lead acetate,

if so the quantity of the latter should be increased. To 110 c.c. of filtrate 10 c.c. of sodium sulphate are added, and after the lead sulphate has settled the solution is filtered through a dry filter paper. If it has been found necessary to increase the lead solution the sodium sulphate should be increased accordingly, and the fact noted in the calculation. According to the above quantities, 100 c.c. of the original solution has been diluted to 120, and therefore the results obtained with this solution must be multiplied by 1·2.

185. **Volumetric Method.**—This method, if carried out with care and attention to the details prescribed, will be found to give fairly approximate results.

The detannised sugar solution is placed in a burette. 5 c.c. of each of the Fehling's solutions is placed in a small beaker, 40 c.c. of water are added, and a few pieces of unglazed porcelain or pipe-stems to prevent bumping. The liquid is brought to the boil over a small flame, and the sugar solution is added 1 or 2 c.c. at a time, boiling after each addition. When the blue colour shows signs of disappearing the sugar solution may be added in smaller quantities; the titration should be continued until, on allowing the cuprous oxide to settle, the colour of the solution remains colourless or pale yellow.

When the quantity required to reduce the whole of the Fehling's solution has been approximately ascertained, a second titration is done, adding nearly

the whole of the solution at once, so that the boiling does not last more than two minutes.

Approximately 10 c.c. of a $\frac{1}{2}$ per cent. sugar solution will be required to complete the reduction of the Fehling's. If less is needed, the solution should be diluted accordingly ; if more, the quantity of the water in the beaker should be lessened proportionately.

Under the conditions given, 10 c.c. of mixed Fehling's solution will be reduced by the following approximate quantities :—

0·0500 grm. of glucose (dextrose, lævulose, or invert sugar).

0·0475 grm. of sucrose (cane sugar) previously inverted.

0·0678 grm. of lactose (milk sugar).

0·0807 grm. of maltose (malt sugar).

186. **Method of Calculation.**—Leather extract solution 25 grm. per 500 c.c.

Decolorised sugar solution required to reduce 10 c.c. mixed Fehling's = 15 c.c. As 15 c.c. sugar solution reduce 10 c.c. mixed Fehling's this quantity is therefore equivalent to 0·05 grm. of glucose.

$$\therefore \quad \frac{0{\cdot}05 \times 500 \times 100 \times 1{\cdot}2}{15 \times 25}$$

gives the percentage of dry glucose, 8 per cent.

As the above conditions are dependent on the exact conditions of titration, and slight differences are

caused by dilution and length of time of heating; it is advisable that the titrating should be compared with that of a pure sugar solution, using the same dilution and length of time for boiling. The standard sugar solution may be made by inverting cane sugar; dissolve 0·25 grm. of good lump sugar in 75 c.c. of water, add 2 c.c. of N/1 HCl, and heat in the boiling water-bath for 30 minutes. The acid is then neutralised with 2 c.c. of N/1 NaOH or Na_2CO_3, and made to 200 c.c. 10 c.c. of this solution should be equal to 0·05 grm. of glucose (and also to 5 c.c. of each Fehling's solution); if this is not found the case the factor should be ascertained.

187. **Von Schroeder's Gravimetric Method.**—This method is much more accurate than the Volumetric method; but the details must be rigidly adhered to, otherwise the results are of little value.

30 c.c. of each Fehling's solution and 60 c.c. of distilled water are put into a beaker of about 200-c.c. capacity and brought to a boil over a bunsen burner, and then placed in a boiling water-bath. 25 c.c. of the detannised solution (see par. 184) is added to each beaker and stirred well, and allowed to remain exactly half-an-hour in the boiling-bath. The liquid is allowed to settle and at once filtered through a weighed asbestos filter.

The filter tube is made by drawing out a piece of combustion tube about 10 cm. long and 1·5 cm. diameter, and drawn out at the lower end as shown

(Fig. 4), the upper portion being fitted with a small funnel. The tube is packed first with glass wool, then 2–3 c.m. of fibrous asbestos, the lower part of which should be fairly tightly packed and the upper part quite loose. The asbestos should be previously washed with 20 per cent. sodium hydrate, neutralised with acid, and finally with distilled water until all soluble matter is removed. It is advisable to make a blank experiment to ascertain if the weight of the packed tube remains constant. A Gooch crucible may be used in place of the glass tube and will be found even more convenient. No glass wool is needed for packing, and a larger surface is exposed on which to collect the cuprous oxide; the same precaution must be taken to see the asbestos is free from soluble matter. The tube or crucible is first dried in the air-oven, cooled in a desiccator, weighed, and the precipitated cuprous oxide is filtered off through the tube or crucible by the aid of the filter-pump. The asbestos

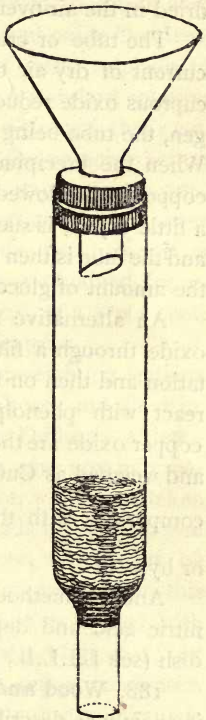

FIG. 4.

is washed free from alkali with hot water, then with alcohol and ether to quicken the drying, and finally dried in the air-oven for 15 minutes.

The tube or crucible is heated at first gently in a current of dry air to destroy organic matter, and the cuprous oxide reduced in a current of pure dry hydrogen, the tube being gently heated during the process. When the precipitate assumes the colour of metallic copper, it is allowed to cool in a current of hydrogen; a little dry air is sucked through to expel the hydrogen, and the tube is then weighed. From the gain in weight the amount of glucose is calculated from the tables.

An alternative method is to filter off the copper oxide through a filter paper, and wash first by decantation and then on the filter until the washings do not react with phenolphthalein. The filter paper and copper oxide are then transferred to a crucible, ignited, and weighed as CuO, which may be reduced to Cu for comparison with the tables by multiplying by $\frac{63{\cdot}6}{79{\cdot}6}$ or by 0·8.

Another method is to dissolve the copper oxide in nitric acid and deposit electrolytically in a platinum dish (see L.I.L.B., p. 274).

188. **Wood and Berry's Method.**—The procedure is exactly as described above up to the point of washing. The Gooch crucible containing the cuprous oxide is then transferred to a wide-mouthed stoppered bottle already filled with carbon-dioxide, and con-

taining 25 c.c. of 2½ per cent. ferric sulphate solution in 25 per cent. sulphuric acid, and the stopper put into the bottle. The bottle is allowed to stand, with occasional shaking, until all the cuprous oxide dissolves, reducing an equivalent amount of ferric sulphate to ferrous. This is then titrated with a standard solution of potassium permanganate of such a strength that 1 c.c. oxidises the ferrous salt formed by the reducing action of an amount of cuprous oxide containing 0·01 grm. metallic copper. The actual strength is just over 5 grm. of potassium permanganate per litre; it is standardised by weighing the copper obtained by reducing the cuprous oxide from 10 c.c. of a ½ per cent. glucose solution and titrating duplicates.

Commercial glucoses as used for weighting leathers usually contain a quantity of maltose and dextrin, and as these do not directly reduce Fehling's, a determination of glucose only, does not give any information as to the amount of adulteration which has taken place. When heated with dilute acids the dextrin and maltose are converted into glucose, which can be directly estimated by Fehling's solution. For this determination the detannised solution is heated with 10 per cent. by volume of hydrochloric acid sp. gr. 1·125 for two hours in a flask fitted with reflux condenser. The hydrochloric acid is neutralised with strong caustic soda, made to a definite volume, and the glucose estimated either volumetrically or gravimetrically. The excess of glucose obtained after inversion over that of

the amount found before inversion is calculated as glucose present as maltose or dextrin.

189. SUGARS NATURALLY CONTAINED IN TANNING MATERIALS. (*Von Schroeder.*)

—	Tanning Matter	Sugars	
		Per cent. on Material	Per cent. on Tanning Matter
Oak bark (average 118 samples) . .	10·5	2·7	25·2
,, inner flesh, tree 150 years old.	13·8	1·3	9·5
,, outer crust ,, ,,	7·6	0·7	9·2
,, young tree bark (Tharand) .	13·0	6·6	50·8
Oak wood. Trees over 100 years old (Mitrowitz) . . .	7·7	0·4	5·8
,, *Q. sessiliflora*. Young oak, 19 years; wood only . . .	2·2	1·2	53·7
Evergreen oak. *Q. ilex*, bark . .	17·7	3·6	20·3
Garouille. Root-bark, *Q. coccifera*, average	25·4	1·0	4·0
Pine bark, *Abies excelsa*, Lam., average .	11·6	3·5	33·5
Willow barks (Russian), average . .	13·4	4·5	33·6
Mimosa barks (Australian wattles), average	28·4	0·9	3·2
Aleppo pine ("Scorza rossa"), outer bark	20·6	2·0	9·9
Hemlock pine, *Abies canadensis*, old bark	12·3	7·1	5·8
Divi-divi pods, *Cæsalpinia coriaria* .	40·7	8·4	20·5
Algarobilla pods, *C. brevifolia*, average .	42·9	8·2	19·1
Myrobalans fruit of *Terminalia chebula*, average	30·8	5·4	17·4
Valonia, sugar very variable, average .	28·3	2·7	9·5
Sumach (Sicilian)	27·8	4·6	16·6
Canaigre, root of *Rumex hymenosepalum*.	30·1	4·3	14·3
Chestnut wood, without bark . .	8·3	0·3	2·9
Quebracho wood, *Loxopteryngium Lorenzii*	24·4	0·25	1·0
Cube Gambier, *Nauclea gambir* . .	47·2	1·9	3·9
Cutch, *Acacia catechu*, wood extract .	39·9	0·5	1·3

190. TABLE FOR THE DETERMINATION OF THE GLUCOSE IN TANNING MATERIALS FROM THE WEIGHT OF COPPER REDUCED, AFTER HEATING FEHLING'S SOLUTION WITH THE GLUCOSE SOLUTION FOR HALF AN HOUR. (*R. Koch and R. Ruhsam.*)

Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.
mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.
1	0·4	31	12·9	61	26·9	91	42·3
2	0·8	32	13·3	62	27·4	92	42·8
3	1·2	33	13·7	63	28·0	93	43·3
4	1·6	34	14·1	64	28·5	94	43·9
5	2·0	35	14·6	65	29·0	95	44·4
6	2·5	36	15·0	66	29·5	96	44·9
7	2·9	37	15·4	67	30·0	97	45·4
8	3·3	38	15 9	68	30·5	98	45·9
9	3·7	39	16·3	69	31·0	99	46·4
10	4·1	40	16·7	70	31·6	100	46·9
11	4·5	41	17·2	71	32·1	101	47·5
12	4·9	42	17·6	72	32·6	102	48·0
13	5·3	43	18·0	73	33·1	103	48·5
14	5·7	44	18·4	74	33·6	104	49·0
15	6·1	45	18·9	75	34·1	105	49·5
16	6·5	46	19·3	76	34·6	106	50·0
17	7·0	47	19·7	77	35·1	107	50·5
18	7·4	48	20·2	78	35·7	108	51·0
19	7·8	49	20·7	79	36·2	109	51·6
20	8·2	50	21·3	80	36·7	110	52·1
21	8·6	51	21·8	81	37·2	111	52·6
22	9·0	52	22·3	82	37·7	112	53·1
23	9·4	53	22·8	83	38·2	113	53·6
24	9·9	54	23·3	84	38·7	114	54·1
25	10·3	55	23·9	85	39·2	115	54·6
26	10·7	56	24·4	86	39·8	116	55·1
27	11·1	57	24·9	87	40·3	117	55·7
28	11·6	58	25·4	88	40·8	118	56·2
29	12·0	59	25·9	89	41·3	119	56·7
30	12·4	60	26·4	90	41·8	120	57·2

TABLE FOR THE DETERMINATION OF GLUCOSE—*continued.*

Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.
mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.
121	57·7	156	75·0	191	92·3	226	110·2
122	58·2	157	75·5	192	92·8	227	110·7
123	58·7	158	76·0	193	93·3	228	111·2
124	59·2	159	76·5	194	93·8	229	111·8
125	59·7	160	77·0	195	94·3	230	112·3
126	60·2	161	77·5	196	94·8	231	112·8
127	60·7	162	78·0	197	95·3	232	113·3
128	61·2	163	78·5	198	95·8	233	113·8
129	61·7	164	79·0	199	96·3	234	114·4
130	62·2	165	79·5	200	96·8	235	114·9
131	62·6	166	80·0	201	97·3	236	115·4
132	63·1	167	80·5	202	97·8	237	115·9
133	63·6	168	81·0	203	98·3	238	116·4
134	64·1	169	81·4	204	98·8	239	117·0
135	64·6	170	81·9	205	99·3	240	117·5
136	65·1	171	82·4	206	99·8	241	118·0
137	65·6	172	82·9	207	100·3	242	118·5
138	66·1	173	83·4	208	100·8	243	119·0
139	66·6	174	83·9	209	101·4	244	119·5
140	67·1	175	84·4	210	101·9	245	120·1
141	67·6	176	84·9	211	102·4	246	120·6
142	68·1	177	85·4	212	102·9	247	121·1
143	68·6	178	85·9	213	103·5	248	121·6
144	69·1	179	86·4	214	104·0	249	122·1
145	69·6	180	86·9	215	104·5	250	122·7
146	70·1	181	87·4	216	105·0	251	123·2
147	70·6	182	87·9	217	105·5	252	123·7
148	71·1	183	88·4	218	106·0	253	124·2
149	71·5	184	88·9	219	106·6	254	124·8
150	72·0	185	89·4	220	107·1	255	125·3
151	72·5	186	89·9	221	107·6	256	125·8
152	73·0	187	90·4	222	108·1	257	126·3
153	73·5	188	90·9	223	108·7	258	126·9
154	74·0	189	91·3	224	109·2	259	127·5
155	74·5	190	91·8	225	109·7	260	128·0

TABLE FOR THE DETERMINATION OF GLUCOSE—*continued.*

Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.
mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.
261	128·5	296	146·9	331	165·8	366	185·4
262	129·0	297	147·4	332	166·3	367	186·0
263	129·5	298	147·9	333	166·9	368	186·5
264	130·1	299	148·4	334	167·4	369	187·1
265	130·6	300	149·0	335	167·9	370	187·7
266	131·1	301	149·5	336	168·4	371	188·3
267	131·6	302	150·1	337	169·0	372	188·8
268	132·2	303	150·6	338	169·5	373	189·4
269	132·7	304	151·1	339	170·1	374	190·0
270	133·2	305	151·7	340	170·6	375	190·6
271	133·7	306	152·2	341	171·2	376	191·1
272	134·2	307	152·8	342	171·7	377	191·7
273	134·7	308	153·3	343	172·2	378	192·3
274	135·3	309	153·9	344	172·8	379	192·8
275	135·8	310	154·4	345	173·3	380	193·4
276	136·3	311	155·0	346	173·9	381	194·0
277	136·8	312	155·5	347	174·5	382	194·6
278	137·4	313	156·0	348	175·0	383	195·2
279	137·9	314	156·5	349	175·6	384	195·7
280	138·4	315	157·1	350	176·2	385	196·3
281	139·0	316	157·6	351	176·8	386	196·9
282	139·5	317	158·1	352	177·3	387	197·5
283	140·0	318	158·7	353	177·9	388	198·0
284	140·5	319	159·2	354	178·5	389	198·6
285	141·1	320	159·8	355	179·1	390	199·2
286	141·6	321	160·3	356	179·6	391	199·8
287	142·1	322	160·9	357	180·2	392	200·3
288	142·6	323	161·4	358	180·8	393	200·9
289	143·2	324	162·0	359	181·4	394	201·5
290	143·7	325	162·5	360	181·9	395	202·1
291	144·2	326	163·0	361	182·5	396	202·7
292	144·7	327	163·6	362	183·1	397	203·3
293	145·3	328	164·1	363	183·7	398	203·8
294	145·8	329	164·7	364	184·2	399	204·4
295	146·3	330	165·2	365	184·8	400	205·0

TABLE FOR THE DETERMINATION OF GLUCOSE—*continued.*

Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.
mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.
401	205·6	420	216·7	439	228·5	458	241·3
402	206·2	421	217·3	440	229·1	459	242·0
403	206·8	422	217·9	441	229·8	460	242·6
404	207·3	423	218·4	442	230·5	461	243·3
405	207·9	424	219·0	443	231·2	462	244·0
406	208·5	425	219·6	444	231·8	463	244·7
407	209·1	426	220·2	445	232·5	464	245·3
408	209·7	427	220·8	446	233·2	465	246·0
409	210·3	428	221·4	447	233·9	466	246·7
410	210·8	429	221·9	448	234·5	467	247·4
411	211·4	430	222·5	449	235·2	468	248·0
412	212·0	431	223·1	450	235·9	469	248·7
413	212·6	432	223·7	451	236·6	470	249·4
414	213·2	433	224·4	452	237·2	471	250·1
415	213·8	434	225·1	453	237·9	472	250·8
416	214·4	435	225·8	454	238·6	473	251·4
417	214·9	436	226·4	455	239·3	474	252·1
418	215·5	437	227·1	456	239·9	475	252·8
419	216·1	438	227·8	457	240·6	476	253·5

CHAPTER XIII.

ANALYSIS OF LEATHER.

191. In analysing a sample of leather the determinations which should be made depend entirely on the object of the analysis, whether it is required to detect:—

(*a*) If the leather has been weighted,
(*b*) „ „ „ undertanned,
(*c*) The method and materials used in manufacture,
(*d*) Or the errors in production.

It will be seen therefore that the scheme must vary according to the purpose in view and the class of leather to be dealt with.

192. **Preparation of Sample.**—The leather must be brought into a fine state of division before analysis can be commenced. Hard leathers, such as sole, should be cut into pieces of about an inch square and ground in a mill, similar to that used for tanning materials. The moisture should be taken before and after grinding. Some leathers can be shredded easily by fixing them in a vice and shaving with a plane.

Curried leathers can only be satisfactorily cut with a knife, as grinding in a mill tends to cause clogging and loss of grease.

An analysis should consist generally of the following determinations :—

1. Water.
2. Fat.
3. Water solubles { Soluble tannins. / „ non-tans, including glucose, dextrin, etc.
4. Insoluble { Fixed tannin matters. / Hide substance.
5. Ash.

(The sum of the first four determinations should give 100 per cent.)

193. **Moisture.**—5 grm. of the powdered leather are weighed in a tared basin and dried, preferably in the vacuum-oven, until constant. In the absence of a vacuum-oven an air-oven may be used at 105° C. ; but no great accuracy can be expected, nor should the drying be too prolonged, owing to the great tendency of oils contained in the leather to oxidise. Occasionally the moisture is obtained by difference by deducting the sum of the fat, soluble, and insoluble matters, from 100 per cent. Where exact determinations are required the leather should be heated in a current of inert gas and the water collected in a drying tube and weighed.

194. **Fat.**—25 grm. of leather is placed in a Soxhlet apparatus, having a piece of fat-free cotton-wool placed in the bottom; a weighed flask is fitted to the Soxhlet and the whole apparatus attached to a reflux condenser. The extraction is made with either carbon disulphide, or petroleum ether (B.P. 40–60°), until no fat is left; this will take about 3 hours, with some leathers even longer. It is safer to replace the first flask by a second weighed flask and continue the extraction; any further quantity extracted should be added to that of the first, and the percentage calculated on the total. The solvent is distilled off and the residue dried in the vacuum-oven, and the percentage of fat calculated.

For further investigation of fat, see Chapter XI.

195. **Water-Soluble Matter.**—The extracted leather is removed from the Soxhlet to a glass mortar, and, after the solvent has evaporated off, is covered with cold water, bruised occasionally with a pestle and allowed to stand overnight. The leather is transferred to a Procter's extractor (omitting the sand), and extracted at a temperature of 45° C., in exactly the same way as for tanning materials. If necessary, the last washings should be concentrated by boiling so as to bring the whole into 1 litre. The time required for the extraction should occupy from two to three hours and should be commenced at the temperature named, and on no consideration exceed it.

196. **Total Soluble.**—The solution is filtered through a candle filter and 50 c.c. of optically clear solution is

evaporated in a weighed basin, dried in the vacuum-oven, cooled and weighed, and the increase of weight calculated as "total soluble" matter. The ignition of the soluble residue will give the amount of soluble mineral ash.

197. **Non-tans.**—In another portion of the water soluble matter, the non-tannins are estimated in exactly the same manner as described for tannin analysis (p. 84), the difference between the non-tans and the soluble matter being returned as uncombined tannin.

Where it is desired to identify the vegetable materials used in tanning, the soluble matter may be tested as specified for tannin extracts (Chapter V.).

Leathers which contain no added fat, sole leather, rough leathers, etc.—may be extracted with water without previous fat extraction.

198. **Glucose and Dextrin.**—400 c.c. of the water soluble matter are evaporated to 200 c.c. and the glucose estimated volumetrically or gravimetrically as described in Chapter XII. As many adulterated leathers contain cane-sugar, which does not directly reduce Fehling's solution, it is necessary to invert the detannised solution with hydrochloric acid, and do a further determination of glucose (see par. 188). It is generally assumed that leathers containing up to 2 per cent. of glucose are free from adulteration, over this amount being looked upon with suspicion. It must be borne in mind that glucose as estimated by

the methods described in Chapter XII. gives results in terms of dry glucose ; it is therefore necessary to increase the amount found by the same percentage of moisture as found in the leather.

199. **Insoluble Residue.**—The extracted leather should be removed from the extractor, placed on a piece of filter-paper, covered with a piece of muslin, and dried in a current of air. When air-dry the residue should be placed in a weighed basin and dried in the vacuum-oven till constant, and may be finally ashed to determine insoluble mineral matter, or a portion may be Kjeldahled (par. 41) to determine the actual hide fibre present. It is often more convenient to determine hide substance on the original leather.

200. **Hide Substance.**—0·6–0·7 grm. of the original leather is weighed into a Jena flask of 700 c.c. capacity, and 15 c.c. of pure concentrated sulphuric acid are added and boiled over a very small flame until the substance is dissolved. The contents of the flask are allowed to cool and 10 grm. of dried and powdered pure potassium sulphate are added, and the boiling continued till the solution is perfectly clear and colourless. On cooling, the solution is diluted with about 200 c.c. of distilled water and distilled in the same way as described in par. 41, and the amount of hide substance calculated in percentage.

201. **Total Ash.**—About 5 grm. of the leather are carefully ashed in a platinum crucible (the absence of

lead and tin must be first ascertained) by heating the empty crucible and adding the leather in small portions at a time, allowing time for swelling and carbonising between each addition. As a rule there will be very little fusible matter, but where soluble salts have been used it is necessary to powder the charred mass, wash out the soluble salts with hot water and filter off the insoluble residue through a quantitative filter-paper. The residue is ignited, and when thoroughly ashed the soluble portion is added to the crucible, evaporated to dryness and gently ignited and weighed. This is specially necessary where sulphates are present, as the latter are reduced to sulphide when ignited in presence of carbonaceous matter. A muffle furnace is to be recommended, but if this is not available a Teclu burner may be used; but the temperature of the crucible should never be above a dull-red heat.

The ash should be dissolved and made to a definite volume and a portion submitted to qualitative examination, and if necessary a quantitative analysis made. For details, see L.I.L.B., p. 363, *et seq.* It should be borne in mind that leathers containing mineral salts with large quantities of water of crystallisation lose the water on ignition, and the ash therefore in these cases only accounts for about half the amount of actual added salt, and should therefore be calculated to theoretical quantities. It is usual to infer that leathers containing less than 2 per cent. mineral ash are not adulterated (except in the case stated above).

For details of the analysis of chrome leathers, see pars. 207–214.

202. **Fahrion's Test of Resistance to Boiling Water.***—1 grm. of the leather in a very finely ground or shaved condition is placed in a 100 c.c. flask (Jena glass), with 70–80 c.c. distilled water. The flask is placed in a boiling-water bath for 10 hours, with frequent shaking, and evaporation is made up with more water. The solution is allowed to cool to 75–80° C., made up with water at room temperature, cooled, made up to mark, shaken, and filtered through linen (filter-paper clogs) into a dry beaker. 50 c.c. of the clear filtrate is evaporated to dryness in a platinum basin on the water-bath, and the residue is dried in an oven at a temperature of 105–110° C. or in the vacuum-oven, and weighed till constant. After cooling in the desiccator, the weighing must be immediate, as in tanning analysis; the residue is hygroscopic. After weighing, the residue is ashed, and again weighed, and the difference when multiplied by 200 gives the percentage of water-soluble organic matter. In the two operations the solubility and ash of the material are determined.

203. **Free Mineral Acids in Leather.**—The several methods in use for this determination are not wholly satisfactory, but perhaps the most rapid oxidation method is that of *Procter and Searle.* This method

* See Collegium, 1908, p. 495.

in careful hands gives fair satisfaction, tending rather to too low than too high results, but will be found quite accurate enough for most purposes. In all oxidation methods, an allowance should be made for the sulphur naturally present in hide (see L.I.L.B., p. 368). Organic sulphur compounds are estimated as acid.

2–3 grm. of the leather are moistened with 25 c.c. N/10 Na_2CO_3 and evaporated to dryness on the water-bath. The mass is gently charred, pulverised with a glass rod, and washed out with boiling water, the soluble portion being filtered through a quantitative filter-paper into a conical flask. The insoluble portion in the filter-paper is returned to the basin, ignited thoroughly, the ash taken up with 25 c.c. N/10 HCl and added to the portion previously washed out. The solution is titrated back with N/10 alkali, using methyl red or methyl orange as indicator, and the amount calculated to mineral acid, generally sulphuric. If the solution is alkaline no further titration is necessary.

204. **Jean's Method.**—This method depends on the fact that whereas sulphuric acid is soluble in alcohol, sulphates are undissolved. The leather is extracted with absolute alcohol in a Soxhlet, a little sodium carbonate being placed in the extraction flask. The alcohol is distilled off, and the free acid remaining as sulphate is estimated as barium sulphate.

205. **Balland and Maljean.**—A small portion of leather is first carefully ashed with necessary precaution, and sulphates estimated in the ash. A further portion

is moistened with excess of sodium carbonate, dried, ashed, and sulphates again estimated. The excess of the second sulphates over that of the first is calculated as free mineral acid.

206. **Wuensch.**—This method is the most accurate at present known. It consists in adding 5 grm. of the finely shredded leather piece by piece to 50 c.c. of fuming nitric acid (sp. gr. 1·52). The solution may be heated toward the end of the process if sulphuric acid only is needed; if hydrochloric acid is to be estimated, the process must be carried out in the cold, requiring about 24 hours. When only sulphuric acid is to be estimated, the solution is evaporated with barium chloride and hydrochloric acid to drive off the nitric acid, filtered, the residue washed with hydrochloric acid and weighed as barium sulphate. To the filtrate sulphuric acid is added to precipitate the excess of barium chloride and convert all bases into sulphates. The solution is filtered, evaporated to dryness, ignited, and smoked off with ammonium carbonate to decompose bisulphates, and after acidifying with hydrochloric acid the sulphates are estimated with barium chloride, and represent the total sulphuric acid which the bases are capable of neutralising. The first estimation, less the second, gives the amount of free sulphuric acid; if the second estimation is greater than the first no free acid can be present.

If it is desired to estimate chlorides as well as sulphates, silver nitrate and barium nitrate are added to

the solution before evaporation, and the residue is washed with hot water. The precipitate containing barium sulphate and silver chloride is treated with ammonia to dissolve out the latter, and the barium sulphate is ignited and weighed. The silver chloride is estimated in the ammoniacal solution by boiling off excess of ammonia and precipitating by neutralising with acetic acid. The total bases are determined as sulphates in the filtrate, after precipitating the silver and baryta with hydrochloric and sulphuric acids, and a proportion reckoned into chlorides corresponding to the chlorides found.

207. **Chrome Leather Analysis.**—If only fat, ash and chromium have to be determined, the following method will prove satisfactory.

15–20 grm. of the leather which has been reduced to very small slices is weighed out exactly, and dried for 2–3 hours at 100–105° C., to facilitate the subsequent fat extraction. In presence of sulphur (two-bath tannage, or combination chrome-sulphur tannage), the extraction is carried out with CS_2, while in absence of sulphur petrol-ether may be used. The dried leather is placed in a Soxhlet and the extraction carried out on a water-bath for 3–4 hours, a weighed conical flask being used for the solvent. The main part of the solvent is saved by distilling on the water-bath, the last portion of it being evaporated on the water-bath and the flask finally dried in the drying-oven at 100–105° C. until no smell of the solvent is observed.

The increase in the weight of the flask gives the fat (together with sulphur).

For the determination of ash and chromium about 5 grm. of the original leather shavings are gradually brought into the platinum crucible, a new portion not being added before the former is totally ignited. The ignition is commenced at a rather low temperature, and, after carbonising, the temperature is raised; the operation is finally completed with the blow-pipe. The ash after weighing is fused with a mixture of equal parts of MgO and Na_2CO_3. It is necessary to mix the ash intimately with about 3–4 times its weight of this mixture, and to stir frequently with a platinum wire during heating with a Teclu burner. Twenty minutes heating is usually sufficient for complete oxidising of the chrome oxide to sodium chromate.

$$2\ Cr_2O_3 + 4\ Na_2CO_3 + 3\ O_2 = 4\ Na_2CrO_4 + 4\ CO_2$$

After cooling, the crucible containing the fused ash is placed in a beaker with enough water to cover it, and dilute HCl is gradually added, covering the beaker with a watch-glass to prevent loss by spitting. The solution, which should be filtered (a green residue indicates insufficient fusing, and demands re-igniting, fusing and dissolving of the insoluble portion), is then made up to a definite volume, aliquot parts of which are taken for the iodometric chrome estimation (see par. 142).

208. While in frequent cases the determination of fat, ash, and chromium will prove sufficient (a comparison of the figures for ash and for Cr_2O_3 gives some idea of the amount of other mineral substances present), yet a more complete analysis will often be desired, and the above scheme will have to be enlarged according to the further determinations required. The following scheme is intended to give as complete information as possible, but in most cases only a part of the described estimations will be found necessary. This scheme includes the estimation of water, fat, sulphur, ash, chromium, alumina, sulphates, chlorides, barium, alkaline salts, vegetable tannin, sugar, and hide substance.

209. For the estimation of water and ash, weigh about 5 grm. of the leather, cut into small slices in a weighing glass, and dry at 100–105° C. until constant weight. The loss of weight expressed in per cent. on the original leather weight gives the per cent. H_2O (see also par. 193).

For the estimation of ash this dried leather can be taken and gradually ignited as described in par. 201. The ash is used for the determination of chromium and alumina. After fusing (see par. 207) and dissolving the fused ash in HCl, the solution, which should be filtered (from $BaSO_4$ and other insoluble salts), is made up to 250 c.c. and aliquot portions taken for the iodometric estimation of chromium (see par. 142, p. 122) and for the determination of alumina. The latter

is best carried out indirectly—viz. by reducing the chromates with hydrochloric acid and alcohol, and precipitating both chromic salts and alumina salts with ammonia; this is done in a porcelain basin (or in beakers of Jena glass), and the excess of ammonia boiled off until only a faint smell is perceptible. After decanting and washing with hot water, the precipitate is collected on a filter and the washing continued until no chlorine reaction is given by the wash water. The ignited residue gives $Cr_2O_3 + Al_2O_3$, the alumina being found by deducting the volumetric figure for Cr_2O_3.

210. Another portion of about 20 grm. of the leather shavings is taken for estimating fat, sulphur, water soluble matters, and barium sulphate.

After drying this portion for 3–4 hours at 100–105° C., to remove most of the moisture, the leather is extracted in a Soxhlet with carbon bisulphide (freshly distilled), and fat and sulphur determined as described in par. 207. The dry fatty residue is then treated with fuming nitric acid (free from H_2SO_4, sp. gr. = 1·52), and allowed to stand over-night, when the contents of the flask are poured into a porcelain basin and evaporated. The washings of the flask are then added (but not until complete evaporation) and again evaporated to dryness to remove most of the nitric acid. The residue is now dissolved in hot water, filtered, acidified with HCl, and the sulphuric acid obtained by the oxidation of the sulphur determined in the usual way

with $BaCl_2$. The weight of $BaSO_4$ thus obtained, multiplied by $\frac{32}{233} = 0{\cdot}137$, gives the amount of sulphur present in the leather, and after deducting from the (fat + sulphur) gives the percentage of fat.

If a qualitative analysis of the fat is desired, a rather larger portion of the leather must be extracted, and from the mixture of fat + sulphur the former is separated as completely as possible by dissolving in ether, filtering, and evaporating the ether. The investigation of the fat is then done according to the information given in Chapter XI.

211. The leather shavings, after being dried and extracted with CS_2, are exposed to the air, until most of the CS_2 is evaporated, and finally dried at 100–105° C., until no trace of CS_2 is perceptible. The leather is then extracted with hot water (in the way described in par. 195, but using nearly boiling water) and the solution made up to 250 or 500 c.c. Aliquot parts are first taken for qualitative tests for vegetable tannins (+ gelatin and with iron alum) sugar (Fehling's solution, after removing the tannins with basic lead acetate, see par. 184), sulphates, chlorides or barium and lead salts.

The quantitative estimation of vegetable tannins is carried out in an aliquot portion of the solution as described in pars. 196–197; the quantitative sugar determination is done according to pars. 185–188. Soluble chlorides or sulphates, or, in the absence of

the latter, soluble barium and lead acetate, are determined in the ordinary gravimetric or volumetric ways.

212. The leather after extraction with water is then wetted through with a 10 per cent. soda solution in a platinum basin, then evaporated, dried at 105–110° C., ashed and fused. The fused ash is repeatedly extracted with boiling water, filtered and the filtrate used for determination of sodium sulphate (precipitating with $BaCl_2$, etc.). The water-insoluble part of the fused ash is gently heated with dilute hydrochloric acid, and the solution (which must be filtered) used for the estimation of barium and lead, originally present as sulphates. By adding H_2SO_4, both $BaSO_4$ and $PbSO_4$ are precipitated, which, after filtering, washing, drying, and igniting, are weighed together; then the $PbSO_4$ is removed by repeated extracting with ammonium acetate solution, and the remaining $BaSO_4$ washed, dried, ignited and weighed again, the $PbSO_4$ being found by difference.

213. For the estimation of alkaline salts another 10–15 grm. of the leather are taken, dried and extracted with CS_2 as described in pars. 194, 207; and the extracted leather exposed to the air, and finally brought in the drying stove at 100–105° C. to remove all traces of CS_2. This leather is now added in small portions to 50–100 c.c. fuming nitric acid (free from H_2SO_4, sp. gr. 1·52), in a conical flask, care being taken that too violent reaction does not take place (keeping the flask cool). After allowing to stand over-night, the contents

of the flask are poured into a porcelain basin and evaporated. The washings of the flask are then added (but not until complete evaporation) and evaporated again to dryness, and the residue dissolved in hot water, filtered and made up to 250 c.c. The estimation of total soluble sulphates can be made with an aliquot part (100 c.c.) of this solution by precipitating the solution, after slightly acidifying with HCl, by means of $BaCl_2$ in the ordinary way. The $BaSO_4$ figure thus obtained need not be corrected for sulphur present in the hide substance itself, because most of this sulphur is oxidised (with HNO_3) to methyl sulphonic acid, which is not precipitated by barium chloride.

214. Another aliquot part (100 c.c.) is taken for the estimation of alkaline salts and evaporated, dried slightly, ignited to remove organic matters, extracted with very dilute HCl, filtered, and the filtrate boiled down to a small volume before adding NH_3 to remove traces of chromium which were not rendered insoluble by the igniting operation. After diluting and filtering, a few drops of H_2SO_4 are added to the filtrate, the whole being then evaporated in a weighed porcelain or platinum basin, slightly ignited and weighed (alkali sulphates).

A nitrogen determination by Kjeldahl's method, as described in par. 41, can be made with a separate sample of the leather, which gives the percentage of hide substance in the leather.

CHAPTER XIV.

THE USE OF THE MICROSCOPE.

215. In recent years the microscope has become a very necessary instrument in the leather chemist's laboratory; by its use much information can be obtained which is impossible by other means.

The minute structure of hides and skins can only be studied by its aid, and it has proved invaluable for identifying defects such as weak grain and various bacterial damages, the presence of adulterants in tanning materials, examination of the fibre of broken and burnt leathers, etc.

216. **Microscope.**—A good microscope will be usually found the cheapest in the end, and where bacteriological work has to be undertaken a sum of £15 to £20 will have to be expended for an efficient instrument; this sum will include an oil immersion objective. Where it is not intended to study bacteriology a less expensive instrument, fitted with 1-inch and $\frac{1}{6}$-inch objective, will in most cases suffice.

For full description of the working parts of a microscope, the reader is referred to text-books on

Practical Microscopy, also Leather Industries' Laboratory Book, Section XXIV.

217. **Objectives.**—The 1-inch and $\frac{1}{6}$-inch objectives will be found the most useful, and the latter will answer quite well for identification of most bacteria, although for the detailed study of the latter $\frac{1}{12}$-inch oil immersion is essential.

218. **Preparation and Mounting of Objects.**—Objects for examination are usually placed on a glass slide and covered with a thin cover glass. The slides and cover glasses should be carefully cleaned before use with alcohol, or if very greasy, with a solution of potassium hydrate, and finally with distilled water, and dried with a clean cloth. Immediately before use the slides and cover glasses should be polished with a chamois leather to free them from dust.

The grain of leather may be examined by cutting a small piece and placing on a slide and examining by reflected light. A section of the leather may be examined in the same way. The pieces should be as thin and even as possible, so that all parts are brought into focus at the same time. Much information may be obtained in this way, especially where such things as baryta and other weighting materials have been used, as they may he found lying in the interstices of the leather. Tanning materials in a ground state, if dusted on to a slide and examined in comparison with a genuine material, may often be identified. Permanent slides of leather and such like opaque

objects may be mounted as permanent preparations by affixing a zinc or ebonite ring to the slide by means of gold size or asphaltum, fixing the object inside the ring with gum arabic, and when dry covering the ring with a cover glass, fastened down with gold size. Thin sections of bark may also be mounted as just described, and can be cut by means of a plane blade.

Starches, powders, fibres, and pasty materials may be examined by placing a small portion of the mixture on the slide; staining with various materials such as iodine, coal-tar colours, etc., often assists in identification.

219. **Section Cutting.**—For the minute examination of the hide fibres, it is necessary first to obtain very thin sections. With practice a section may be cut by holding the hide between the thumb and finger and with a sharp razor, flooded with alcohol and resting on the tip of the forefinger, a thin shaving taken off the top of the strip, with either a drawing or pushing cut, as is most convenient. It is of great assistance in cutting if the hide has previously been dehydrated in alcohol for several days, as this hardens the tissue and a better section results.

The thin sections are examined, the poor ones rejected, and the best ones retained for mounting.

It will be found far more satisfactory to use the microtome for section cutting, as this gives much more even sections than can be obtained by hand.

For permanent slides it is necessary to stain the section (picrocarmine, logwood), dehydrating by passing through increasing strengths of alcohol, and finally absolute alcohol. They are then transferred to benzene, placed on a glass slide flooded with benzene, a small quantity of canada balsam in benzene is placed over the section, and the cover glass placed on and set aside until dry and hard, which requires two or three weeks.

The examination of the fibre of broken leather will often give information as to whether or not the leather has been burnt. The fibre of burnt leather will be seen very short and brittle, whereas a leather which has been actually torn will have a very much longer and less brittle fibre.

Under-tanned leather can often be detected by cutting a rather thin piece of leather and soaking it in a solution of equal parts glacial acetic acid, glycerin, and water for about one hour. On comparing this with a similar piece of leather which has not been treated, it will be seen that an under-tanned leather will have its fibres considerably swollen, but a fully tanned sample will not swell. Weak grain, unremoved epidermis, lime blast, etc., may after a little practice be easily detected.

220. **Sumach Adulterants.**—Perhaps the subject on which most work has been done is that of the detection of adulterants in sumach. Much information on this subject has been given by Andreasch, Lamb

and Harrison, and Priestman. The method suggested by Priestman is as follows:—About 2 grm. of the powdered sumach are placed in a boiling tube, and about 20 c.c. of concentrated nitric acid are added and heated in a water bath to 65–70° C for about 10 mins. with frequent stirring. The tube is removed from the bath, filled to the brim with distilled water, and allowed to stand until the fragments rise to the surface, when they are skimmed off and neutralised with ammonia in a porcelain basin. An alternative method is to remove the particles from the nitric acid and transfer them directly to ammonia.

Slides are prepared from the treated sumach and examined with the microscope, and compared either with a known specimen or with photographs.

221. A method suggested by Dr. Hellon for separation of the cuticles is as follows:—

1. A decigram of the sample is boiled for half a minute with, say, 7 c.c. 5 per cent. H_2SO_4, and the clear liquid poured away.

2. The residue is then boiled for half a minute with 7 c.c. 5 per cent. NaHO solution, and the liquid poured away.

3. The residue is boiled for half a minute with 7 c.c. HNO_3, sp. gr. 1·2, and the clear liquid poured away.

4. The residue is boiled as before with another portion of HNO_3, and during the boiling a centigram of $KClO_3$ is added from time to time until the substance is absolutely white. The clear liquid is poured

away and the residue washed free from acid with warm water, transferred to the microscope slide, covered and examined.

222. The following table summarises the effect of heating various of the more common sumach substitutes and adulterants :—

—	Cuticles separate at	Totally dissolved at
	deg. min.	deg. min.
Rhus coriaria leaves .	60–65 in 10	98 in 15 from cold
,, ,, stems .	75 ,, 10	95–98 ,, 15 ,, ,,
Tamarix stems . .	80 ,, 10	90 ,, 15 ,, ,,
Pistacia lentiscus . .	65 ,, 10	98 ,, 20 ,, ,,
Coriaria myrtifolia .	75 ,, 10	98 ,, 20 ,, ,,
Rhus metopium . .	70 ,, 15	98 ,, 25 ,, ,,
Rhus glabra . . .	75 ,, 15	Insol. Insol.
Colpoon compressa .	80 ,, 15	98 ,, 25 ,, ,,
Ailanthus glandulosa	75 ,, 15	Insol. Insol.

For photographs of cuticles of pure sumach and adulterants, see plates in L. I. L. B. page 408 *et seq.*

Rhus coriaria cuticles are very thin and transparent; they possess hairs on both the upper and the lower cuticles which are unlike those of any adulterant.

Pistacia lentiscus cuticles are very much stronger than *Rhus coriaria*, and are dyed an intense yellow with nitric acid. The cell structure is very characteristic; the lower cuticle possesses stomata, but hairs are entirely absent. This used to be the principal adulterant, but its use as such is now much diminished.

CHAPTER XV.

BACTERIOLOGY AND MYCOLOGY.

223. As bacteriology is so intimately connected with so many processes in the leather trade, a few remarks on the subject may be of use here; but the student is referred for more complete details to text-books of Bacteriology. For works more particularly related to the leather trade, the student is referred to the papers published by Mr. J. T. Wood in the J.S.C.I.; also J. T. Wood's "Puering, Bateing and Drenching" (E. & F. N. Spon, Ltd.); G. Abt, "Le rôle des Microbes dans la Putrefaction des peaux en Poils et en Tripe et dans les confits" (Bull. Mens. du Synd. Gen. de Cuirs et Peaux de France, Nov.–Dec. 1908, p. 416); Andreasch, "Gahrungserscheinungen in Gerbbruhen," (Vienna, "Der Gerber," 1895–7), and various publications in Collegium.

Micro-organisms may be divided into three groups, viz. :—

(*a*) Moulds,
(*b*) Yeasts,
(*c*) Bacteria,

all of which are of vital importance in the leather trade.

224. **Moulds** are the most complicated of the three groups; they grow to great size and in bulk are visible to the naked eye, although a microscope is necessary for examination. The moulds consist of a network of *mycelia*, which put forth *hyphæ* on the end of which *spores* are produced for the reproduction of the species. The mould does not attain its characteristic colour until the spores have been produced.

The moulds most frequently met with in the tan-yard are three in number:

1. *Mucor mucedo*, white mould.
2. *Penicillium* (many varieties, but chiefly) *glaucum*, green mould.
3. *Aspergillus* (many varieties, but chiefly) *niger*, black mould.

The production of the spores of these three moulds is typical for each family; for further particulars see L.I.L.B., p. 438 *et seq.*, and text-books on fermentation.

The presence of moulds in tan liquors has a destructive effect on the tannin present.

225. **Yeasts.**—*Saccharomycetes*. The yeast cells vary very much in size, and are usually of a round or elongated shape. The reproduction is by means of *budding* or *gemmation*. This consists of a small outgrowth forming on the parent cell, gradually

increasing in size. The new cell may separate from the mother cell or remain connected with it; in either case large colonies of buds are formed. The yeasts belong to a class which is capable of fermenting sugars with the production of alcohol and carbon dioxide, although this can also be brought about by certain bacteria. The thick felt often observed on old tan liquors is a yeast, *Saccharomycetes mycoderma.*

226. **Bacteria** consist of one cell only, which multiplies by division or *fission*, hence their name *Schizomycetes*, or Fission fungi. The division usually takes place at right angles to their general direction. Some bacteria secrete mucilaginous or gelatinous substances, which often enclose adjacent bacteria forming a *capsule* or *zooglœa.* Probably the microbes in soaks, puers, and drenches form zooglœa.

227. **Classification.**—For general purposes, classification is usually based on shape.

There are three forms :—

1. Cocci or micrococci, round.
2. Bacilli, rod-shaped.
3. Spirilla, twisted.

This first group may occur as small single spheres, *cocci*; in pairs, *diplococci*; like a string of beads, *streptococci*; in clusters like a bunch of grapes, *staphylococci*; in fours (division of spheres in two directions, but in one plane), *tetracocci*; or in packets or cubes (division of sphere in three directions), *sarcina.*

The second group may occur as rod-shaped, with square or rounded ends called *bacilli*; or intermediate between cocci and bacilli called *coccobacilli*; or in long chains called *leptothrix*; or special cases of leptothrix, where chains have more than one branch, *streptothrix* (able to reduce sulphates to sulphur).

The third group may occur as short simple curves similar to a comma, *microspira* or *vibrio*; or as long twisted threads bent in various directions, *spirochætæ*.

228. **Spore Formation.**—Some bacteria, chiefly bacilli and spirilla, produce spores. Under unfavourable conditions, such as defective nutrition, excess or too little oxygen, or the accumulation of the products of the organism's vitality, multiplication by fission is checked and formation of spores commences. These appear as minute and highly refractive granules, which run together to form a spore in each bacillus. The spores are formed either at the end or in the middle of the bacterium; the surrounding portion decays, leaving the spore to germinate when brought on to a favourable medium. Spores are very difficult to destroy, being very resistant to heat, chemicals, etc.; they can remain in soil for six months, or even after 2–3 years have been known to germinate under favourable conditions.

Some bacteria are motile, moving by means of whip-like appendages called *flagella*. Bacteria may be either *aerobic* or *anaerobic*—that is, the former require an atmosphere containing oxygen, and the

latter can only continue to grow in the absence of oxygen.

229. **Size.**—The *micron* μ is the unit of measure, and is $\frac{1}{1000}$ of mm., or $\frac{1}{25000}$ of an inch. The measurement is made by means of an eye-piece micrometer and a stage micrometer. The average size is :—

$$\text{cocci} = 0{\cdot}2 - 0{\cdot}4\ \mu$$
$$\text{bacilli} = 0{\cdot}5 \times 1{\cdot}5\ \mu \text{ or } 0{\cdot}6 \times 3{\cdot}0\ \mu$$

230. **Sterilisation.**—All apparatus used in connection with bacteriological work should be sterilised.

231. **Dry Heat.**—Test tubes, flasks, Petri-dishes and all glass apparatus should be sterilised in an air-oven at 150° C. The mouths of the flasks, etc., should be previously plugged with cotton-wool, and the temperature should be such as only to brown, but not to burn the wool, as this would give tar products which would act as antiseptics. Petri-dishes and apparatus of that kind should be wrapped in paper.

232. **Wet Heat.**—The autoclave is quite indispensable in a bacteriological laboratory. It consists of a boiler so arranged that pressure may be applied, thus raising the boiling-point. This apparatus is exceedingly useful for liquids which are not harmed at high temperatures, as its use only involves once heating, killing both bacteria and spores at the same time, whereas liquids sterilised at the temperature of boiling water must be heated on three successive days to

ensure complete sterilisation. An ordinary potato-steamer will be found useful for sterilisation at 100° C.

233. **Filtration.**—Solutions which cannot be heated may be sterilised by filtering through a Berkefeld or Chamberland candle.

234. **Culture Media.**—The same medium is not suitable for every class of bacteria, and the one most fitted for the organism it is desired to grow must be found by trial. Liquid media usually give a more rapid growth than solid, though the latter is necessary where it is desired to isolate the bacteria from mixed cultures. Beef broth is perhaps the most useful medium, and there are few cases, if any, where a growth cannot be obtained with it. Beef extract, such as Liebig's, Bovril, etc., may be substituted for meat when it can be guaranteed to be free from preservatives.

235. **Beef Broth.**—To 500 grm. of finely-cut beef, free from fat, add 1000 c.c. of water, and leave 12 hours in summer and 24 hours in winter. Filter through linen, boil for about 3 minutes to coagulate the albumens, and filter through wet filter-paper. To the filtrate add 5 grm. of sodium chloride and 10 grm. of Witte's peptone, and neutralise to faint alkalinity to litmus paper.

Heat the broth to 115–120° C. for 15 minutes in an autoclave, filter whilst hot, and fill into test-tubes with about 10 c.c. in each, and sterilise 15 minutes at 115° C. The second sterilisation should not be

higher than the first, or phosphates will be precipitated.

236. **Beef-Broth Gelatin.**—Dissolve 10 grm. (in summer 12 grm.) of gelatin in every 100 c.c. of beef broth in the autoclave, then neutralise to distinct pink to phenolphthalein, and then add 1 per cent. of N/1 hydrochloric acid. Cool to 50–55° C., add the white of an egg well broken and diluted with water, heat the mixture in the autoclave until all the albumen is coagulated, and filter through "Chardin" filter-paper or absorbent cotton-wool. Distribute into sterilised tubes plugged with cotton-wool, about 7–8 c.c. in each, and sterilise for 1 hour at 100° C. for three successive days. After the last sterilisation allow some of the tubes to solidify in an inclined position and the others to remain upright.

237. **Beef-Broth Agar.**—Proceed as for gelatin media, using 1·5 per cent. agar-agar in place of the gelatin. The addition of 2 per cent. gelatin along with the agar prevents the material from stripping from the tube, to which agar, when alone, is subject. Fill tubes, and sterilise for ¼ hour at 115° C., and allow the greater number of the tubes to set in an inclined position.

238. **Inoculation.**—For inoculation use pipettes or platinum wires. The former should have the end plugged with cotton-wool and be wrapped in paper, and sterilised in the air-oven. The platinum wires should be heated in a bunsen flame, care being taken

that they are sufficiently cool before taking the culture. The platinum wires usually consist of: (1) A thin straight needle, for stab cultures. (2) Bent into a loop "*öse*" for liquid media, when requiring less than from a pipette. (3) In the form of a spatula, i.e. stronger wire flattened at the end; this is useful to inoculate from solid culture to liquid, as a platinum wire is not quite strong enough.

Stab cultures in solid medium should be made with the tube inverted; a thick wire usually tends to split the gelatin. Inoculations with the "*öse*" into a liquid should be placed on the top of the solution, smearing the sides of the tube. All inoculations should be done in a sterile chamber, similar to a balance case, to prevent contamination from bacteria in the air.

239. **Incubators** should be used for cultivation, the cultures on agar being kept at 37° C., and those on gelatin at 22° C.

240. **Examination of Microbes.**—This may be done by means of the microscope in (1) a drop of the culture on a slide covered with a cover glass, (2) by killing and staining. If the culture is on solid medium, a little should be taken in sterile water and a drop of this examined. The staining method shows the shape of bacteria much plainer than when unstained.

241. **Staining.**—A drop of the culture is diluted in sterile water and a small quantity placed on a slide and

allowed to dry. When dry, pass the slide three times through the flame to fix the bacteria. The staining is usually done with alcoholic solutions of basic aniline dyes, the time of dyeing varying with the strength of colour given by the dye. Gentian violet, Fuchsin, Methylene blue, and Thionine are the usual dyes employed. For further details on bacteria, spore and flagella staining, see text-books.

242. **The hanging drop** is used to watch the multiplication, formation of spores and mobility of bacteria. A drop of the culture is placed on a cover slip over a hollow slide and examined from time to time.

243. **Isolation.**—Under natural conditions we get mixtures of several microbes; it is necessary to separate these and obtain pure cultures before we can expect to identify them. For this purpose a melted gelatin tube (about 40° C.) is inoculated with a drop of the solution containing the mixed bacteria, rolled between the hands, avoiding air bubbles, and poured into a sterile Petri-dish; the gelatin should spread evenly over the plate and cool as quickly as possible. For good isolation not more than 6–8 colonies should grow in one dish; if a larger quantity appear further dilution is necessary. When the colonies have grown for about 48 hours, their shape and general characteristics should be observed, and each separate colony inoculated with platinum wire on to a gelatin or agar slope tube.

A method often used, and of great value where the

quantity of bacteria present is unknown, is to melt about 6 tubes of gelatin, inoculate the first tube with 2 or 4 drops of the solution containing the bacteria, mix and pour into a plate, leaving about 1 c.c. in the tube. The solution left in the tube is then poured into the second tube, mixed, poured into a plate, and about 1 c.c. again is left behind. This is continued through the whole six tubes, when it will be found that one at least of the six plates will have the colonies well isolated.

244. In the examination of water, the sample should be collected in a sterile bottle and examined immediately. It is usual to examine qualitatively for the presence of pathogenic bacteria, but the quantitative determination can easily be done. Inoculations are made into sterile water as follows :—

1 c.c. of water under examination into 10 c.c. sterile water,
1 c.c. of water under examination into 100 c.c. sterile water,
1 c.c. of water under examination into 1000 c.c. sterile water,

or such dilutions as will give about 6–8 colonies on each plate. 1 c.c. from each of the above dilutions is taken into several gelatin plates and allowed to grow. The colonies are counted and calculations made as to the number of microbes present per c.c.

From what has been said it will be found possible, with the assistance of a good text-book, to isolate many of the bacteria which play such an important rôle in the leather trade. Wherever it is possible "selective" media should be used—that is, a preparation from the material on which the particular bacteria are known to thrive, and if this is not possible the nearest approach to this should be aimed at.

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