

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF CHEMISTRY—BULLETIN No. 150.
H. W. WILEY, Chief of Bureau.

TECHNICAL DRUG STUDIES

BY THE

DIVISION OF DRUGS.

Examination of Hydrogen Dioxid Solutions.

By L. F. KEBLER, L. E. WARREN, and E. A. RUDDIMAN.

The Purity of Glycerin.

By L. F. KEBLER and H. C. FULLER.

Notes on Two Important Alkaloidal Reactions.

By H. C. FULLER.

The Separation and Identification of Small Quantities of Cocain.

By H. C. FULLER.

The Determination of Molybdic Trioxid.

By B. HERSTEIN.

A Method for Testing Ammonium Salts.

By B. HERSTEIN.

Character of Samples of Beeswax Submitted with Bids.

By L. F. KEBLER and F. M. BOYLES.



LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF CHEMISTRY,
Washington, D. C., April 4, 1910.

SIR: I have the honor to submit for your approval a series of technical studies made in the Division of Drugs of this Bureau. Three of these, dealing with hydrogen dioxid, glycerin, and beeswax, are investigations of the quality of these commodities as found on the market, the others are studies of methods of analysis presenting special difficulties, or yielding results which require the greatest degree of accuracy obtainable. I recommend that these papers be published as Bulletin No. 150 of the Bureau of Chemistry.

Respectfully,

H. W. WILEY,
Chief of Bureau.

Hon. JAMES WILSON,
Secretary of Agriculture.

CONTENTS.

	Page.
EXAMINATION OF HYDROGEN DIOXID SOLUTIONS. By L. F. Kebler, L. E. Warren, and E. A. Ruddiman.....	5
Historical note.....	5
Plan of the investigation.....	7
Investigation made in Washington.....	8
Determination of hydrogen dioxid.....	8
Preservatives.....	10
Analytical results.....	11
Investigation made in Nashville.....	11
Comments by manufacturers.....	11
Discussion of results.....	21
Hydrogen dioxid.....	21
Acetanilid.....	21
Acidity.....	22
Nonvolatile matter.....	23
THE PURITY OF GLYCERIN. By L. F. Kebler and H. C. Fuller.....	24
Scope of investigation.....	24
Discussion of methods and results.....	25
Analytical data.....	26
Comments by manufacturers.....	29
Conclusions.....	32
References.....	33
NOTES ON TWO IMPORTANT ALKALOIDAL REACTIONS. By H. C. Fuller.....	36
THE SEPARATION AND IDENTIFICATION OF SMALL QUANTITIES OF COCAIN. By H. C. Fuller.....	41
THE DETERMINATION OF MOLYBDIC TRIOXID. By B. Herstein.....	44
A METHOD FOR TESTING AMMONIUM SALTS. By B. Herstein.....	47
CHARACTER OF SAMPLES OF BEESWAX SUBMITTED WITH BIDS. By L. F. Kebler and F. M. Boyles.....	49
Introduction.....	49
Methods of analysis.....	49
Tabulated results of examination.....	51

Digitized by the Internet Archive
in 2007 with funding from
Microsoft Corporation

TECHNICAL DRUG STUDIES.

EXAMINATION OF HYDROGEN DIOXID SOLUTIONS.

By L. F. KEBLER, L. E. WARREN, and E. A. RUDDIMAN.

HISTORICAL NOTE.

Hydrogen peroxid was discovered by P. Thenard in 1818 by the action of dilute acids on barium peroxid in the presence of water. It occurs in minute quantities in the atmosphere and is formed by the oxidation of many substances in the presence of water, for example, phosphorus, zinc, cadmium, tin, bismuth, copper, turpentine, and certain essential oils. It is also generated in appreciable quantities in the metabolic processes of chlorophyll-bearing plants. Hydrogen peroxid was considered a chemical curiosity for many years after its discovery, but was finally introduced as a medicinal agent by B. W. Richardson in 1856. It was believed for a long time by some to be a specific in the treatment of diphtheria, but this is now known to be a fallacy. Hydrogen dioxid is, however, known to be a most valuable germicide and antiseptic and is probably used more generally by the public and the several professions handling medicinal agents than any other single germicide. Numerous investigations have been made to devise methods that would yield a suitable product without the use of preservatives, but the results have not been entirely satisfactory. The experiments undertaken to find a preservative which would minimize the rate of deterioration were apparently more successful.

Numerous reports have been made on the quality and stability of the various brands on the market. The results obtained often were not very favorable, to the regret not only of the manufacturers but the members of the medical profession as well. Some of the early unfavorable results may, however, have been due to the use of new and untried analytical methods. In 1884 Carpenter and Nicholson^a carefully studied the action occurring between hydrogen peroxid and potassium permanganate in the presence of sulphuric acid. The samples examined by these two workers were represented as containing from 10 to 20 volumes of hydrogen peroxid. The exact amounts of hydrogen peroxid present in the various samples examined

^a Analyst, 1884, 9: 36.

were not calculated, but it is plainly evident from the data obtained that there was a great difference between the amount of hydrogen peroxid claimed and the amount actually present.

Leffmann and Beam ^a in 1892 published the results of an examination of original packages of a number of brands and their report reflected credit on the material then on the market. The acidity of 50 per cent of the samples, however, was excessive. The number of volumes varied from 9.02 to 15.6. It appears that the potassium permanganate method at the time this investigation was made was fairly well established, as is indicated by the following statement made by Leffmann and Beam: "The proportion of hydrogen dioxid is expressed, as is customary, in volumes of oxygen determined by the standard method with potassium permanganate." Two years later Leffmann ^b examined 21 original packages, in which the amount of available oxygen varied from 1.1 to 11.1 volumes. After making the first determination of available oxygen, the packages were set aside for several weeks at a temperature of 20° C., and then reexamined, the results showing that but little change had taken place. In a number of cases the amount of available oxygen had increased, which is not an uncommon observation, and is due to the fact that the water is more volatile than the hydrogen peroxid. In 1895 ^c Leffmann reported on the quality of hydrogen peroxid used in filling prescriptions and as supplied to the dental profession. Prescriptions calling for 1 ounce were filled by druggists in various sections of the city and samples were also obtained from several dental-supply offices. Leffmann notes particularly the inferior character of the goods supplied to the dental profession.

The most comprehensive examination of hydrogen peroxid made hitherto was reported by Smith and Oerte ^d in 1892, including 50 samples, representing all of the available brands at that time on the market. One-ounce samples in glass-stoppered bottles were purchased in New York City, and in New Haven, Hartford, and Bridgeport, Conn. The first examination was made within 24 hours after the sample was purchased, and the amount of available oxygen found varied from none to 8.86 volumes. These investigators made the following observations on their findings:

Reviewing the results, it is seen that 56 per cent of the samples contained from 2 to 2.5 grams of the dioxid in 100 cc, or this percentage yielded from 7 to 9 volumes of oxygen. Solutions of this strength, therefore, may be taken as representing the better class of preparations with which we have gained our therapeutic knowledge. That 8 per cent of the samples contained no hydrogen dioxid, and that 36 per cent more must be regarded as deficient, inasmuch as they contained less than 2 per cent of hydrogen dioxid, shows very clearly that more care is needed in dispensing this agent.

^a Medical News, 1892, 60: 404.

^b Medical News, 1894, 64: 288.

^c Intern. Dental J., 1895, 16: 78.

^d New York Med. J., 1892, 56: 147.

Tests were also made for boric acid, an agent which at one time was largely exploited as an ideal preservative for hydrogen peroxid.

Dr. E. R. Squibb,^a in 1892, made an examination of nine samples of prominent brands then on the market. All bore labels claiming 15 volumes strength. The findings, however, show that the actual amount of hydrogen peroxid varied from one-half to two-thirds of that claimed.

The same year Dr. S. S. Wallian^b published observations on nine brands, determining the amount of available oxygen at intervals. For example, the samples were examined when first received, then reexamined three weeks later and again at the end of six months. The amount of deterioration was marked in several cases, although in most instances the loss in six months was comparatively small. For example, one sample when originally tested showed an oxygen volume of 15, while at the end of six months the amount present was 11.5 volumes. On the contrary, another sample contained when first analyzed 8.25 volumes and at the end of six months only 0.5 volume. The number of volumes stated to be present in the several packages varied from 10 to 15.

R. L. Lloyd^c reported on five samples of medicinal hydrogen peroxid, which were all represented to be chemically pure and of 15 volumes strength. The examination showed that the amount of available oxygen varied from 10.5 to 13.5, and all of them contained the usual impurities.

H. Endemann^d in 1894 examined 14 different brands and found the amount of available oxygen to vary from 0.5 to 16.55 volumes. One sample was found to contain 27.35 volumes, but this brand is represented and sold as containing a much higher volume of available oxygen, and for this reason can not properly be classed with the usual hydrogen peroxid sold to the public.

PLAN OF THE INVESTIGATION.

The results obtained by the investigators quoted clearly show that the quality and character of the various brands of hydrogen peroxid were not satisfactory, but during the past 10 years marked improvements have been made in the manufacture of this commodity. It is, however, a common experience that hydrogen peroxid is prone to decompose, and for this reason it was deemed desirable to make a full and exhaustive investigation, with a view, first, to determine the keeping qualities of the various brands of hydrogen peroxid available on the market; second, to ascertain the nature of the preservatives used, if any; third, to establish an age or time limit; and fourth, if

^a N. Y. Med. J., 1892, 56: 149.

^b N. Y. Med. J., 1892, 56: 599.

^c Amer. J. Pharm., 1893, (4) 65: 276.

^d Times and Register, 1894, 28: 372.

possible, to approximate the maximum per cent of variation below the standard prescribed by the Pharmacopœia.

In order to secure fresh material, the samples were purchased through certain wholesalers, and the results obtained by the first analyses show that they were satisfactory in this respect. In order to eliminate certain personal and climatic factors, it was considered advisable to have examinations made by two observers in separate localities, and Washington, D. C., and Nashville, Tenn., were selected. One hundred and fifteen different samples, representing 36 brands, were examined, the samples including all of the leading makes at present available in the United States. As soon as received they were placed in a cool, partially darkened room, simulating as nearly as possible the conditions usually found in drug stores and other storage places. The temperature in the Washington storeroom varied from 30° C. in the summer to 0° C. in the winter. The samples in the Nashville laboratory were kept under similar conditions, except that the variation in temperature was less marked, ranging from 15° C. in winter to 27° C. in summer.

A list of the brands examined will be found in the table embodying the analytical results (p. 12). Some of the packages bore a guaranty serial number in accordance with section 9 of the food and drugs act and regulation 9 for its enforcement.

As before stated, hydrogen peroxid was once considered a remedy for diphtheria, but it is now known to be virtually worthless for this purpose, yet direct and indirect statements are made to the effect that hydrogen peroxid is a preventative and cure for this disease. It is also represented that the acetanilid is added because of its antiseptic properties. This statement certainly needs confirmation.

INVESTIGATION MADE IN WASHINGTON.

DETERMINATION OF HYDROGEN DIOXID.

The work was begun in December, 1907, some of the initial examinations having been made early in January of 1908. Unless otherwise stated, the methods prescribed by the United States Pharmacopœia, eighth revision, for testing the quality and purity of hydrogen dioxid solutions were employed. In view of the fact that the value of a hydrogen dioxid solution is largely judged by the actual amount of hydrogen dioxid present, the various products were analyzed with particular reference to this point as rapidly as possible after receiving same. The pharmacopœial method was used, excepting that the measured samples were weighed and the percentage computed on this basis. The results obtained will be found in column headed "U. S. P. Method." The results clearly show that a large percentage of the samples examined by this method contain about 3 per cent of

hydrogen dioxid. In order to check the permanganate-sulphuric acid method for determining hydrogen peroxid and compare it with other standard methods, it was decided to analyze the samples by three additional methods, namely, the iodine method and the gasometric methods, using sulphuric acid and potassium permanganate in one case and manganese dioxid and sulphuric acid in the other. In each case the hydrogen dioxid solution was measured out and weighed as before stated and aliquots used for the determinations. The iodine method proposed by Rupp^a was carried out as follows:

Iodine method.—Place 1 gram of potassium iodide in a 250 cc Erlenmeyer flask, add 10 cc of 10 per cent sulphuric acid, and as soon as the salt is dissolved run in 10 cc of the diluted peroxid solution, 1:10, by means of a burette. Cover the flask with a watch glass and allow it to stand for 30 minutes. Then add about 200 cc of distilled water and titrate the liberated iodine with tenth-normal sodium thiosulphate solution, using starch solution as indicator.

This procedure proved somewhat less satisfactory than the pharmacopœial method, being less rapid and giving less concordant results. Each assay was made in duplicate and the mean result is given in the accompanying table in the column headed "Iodine method."

This determination was next made by measuring the volumes of oxygen liberated by means of manganese dioxid and potassium permanganate, respectively, in the presence of sulphuric acid. It was found that Lunge's nitrometer, with a two-way stopcock did not give satisfactory results when the reaction took place inside of the instrument. After making a number of experiments, the following apparatus and procedure were adopted:

Manganese dioxid method.—The apparatus consists of a 50 cc side-arm distilling flask closed with a perforated rubber stopper, through which the delivery stem of a glass-stoppered burette has previously been passed. The side arm of the flask is connected to the nitrometer by means of tightly fitting rubber tubing of any convenient length and securely wired at each end to prevent leakage. The burette is fastened loosely in a Bunsen clamp in such a manner that the burette and flask can be shaken freely in one plane. The nitrometer is filled with water, the level adjusted, and the determination made as follows: Place about 1 gram of finely powdered manganese dioxid in the side-arm flask and add 10 cc of 10 per cent sulphuric acid. Dilute 10 cc of the hydrogen peroxid solution to be tested to 100 cc and place a portion in the burette. After sufficient of the solution is run out to fill the delivery stem of the burette fit the stopper (with attached burette) snugly into the neck of the generating flask, and adjust the level of the water in the nitrometer so as to equalize the pressure within the system. Allow 10 cc of the diluted dioxid solution to run slowly into the generator through the burette. After shaking the flask to liberate the dissolved oxygen as completely as possible again adjust the level and note the temperature and pressure. A correction of 10 cc (the volume of solution run into the generator) is subtracted from the reading, and the remainder reduced to 760 mm pressure and 20° C. temperature.

^a Archiv. Pharm., 1900, 238: 156.

The results obtained by this procedure will be found in the column headed "Gasometric analysis, volume of oxygen evolved by MnO_2 ." The potassium permanganate method was carried out in the manner just described, except that the dilute sulphuric acid and dilute dioxid solutions were placed in a generating flask and sufficient half-normal potassium permanganate solution was added from a burette to give a pink color to the solution. The figures obtained by this procedure will be found in column marked "Gasometric analysis, volume of oxygen evolved by K_2MnO_4 ," and were made between January 14 and February 12, 1908. The results obtained by the two gasometric methods are fairly concordant, but in general are less reliable than those given by the iodine and official methods, being too dependent on slight variations in temperature, pressure, leakage, and other factors.

In order to determine the rate of decomposition, the samples were reexamined for percentage of hydrogen dioxid by the pharmacopœial method at the expiration of 3, 6, 10, and 12 months after the initial analysis. These results are also recorded in the accompanying table. After determining the percentage of hydrogen dioxid in the various brands by the methods outlined, they were examined for preservatives, acidity, nonvolatile matter, fluorids, arsenic, barium, etc.

PRESERVATIVES.

The principal labels on the packages, as well as the analytical results obtained, show that a large proportion of the hydrogen dioxid solutions contained small quantities of acetanilid. The acetanilid was determined by shaking a 50 cc sample of hydrogen peroxid twice with ether and once with chloroform, combining the several extracts in a tared beaker and drying at $75^\circ C$.

Experiments made with samples of hydrogen peroxid containing known quantities of acetanilid showed that this method removed about 95 per cent of the amount present. The acetanilid was identified by its physical and chemical properties, the iodine-phenol reaction proving to be the most satisfactory. Tests were also made for boric acid and borax with negative results.

A number of samples found to be free from acetanilid possessed a noticeable odor of aldehyde after being kept for some time. It was suspected that alcohol had been used as a preservative, but distillation from both acid and alkaline media failed to give a distillate in which alcohol could be detected by the iodoform test. By applying the method directly to the sample, however, good results were obtained. The distillate from these gave the general reactions for aldehyde with fuchsin and sulphurous acid and with Tollen's reagent. The presence of fluorids was indicated in several products, but the

results were not conclusive. Caffein was found in several packages of one brand.

ANALYTICAL RESULTS.

The analytical results obtained in this investigation are given in the table on pages 12 and 13, together with a statement of the loss in hydrogen dioxid in six months and in one year on each sample.

INVESTIGATION MADE IN NASHVILLE.

All of the samples were examined as to purity, quality, and strength, by the pharmacopœial methods. The investigation covered two series, one begun in October, 1907, and the other in December of the same year. The acetanilid was extracted by means of chloroform, it having been shown that less than one-fiftieth of a grain could be detected by the phenol-isocyanid reaction. The several samples were reexamined at the intervals of time indicated in the table on page 14.

COMMENTS BY MANUFACTURERS.

The results of the analyses of the several brands were referred to the respective manufacturers, with the following results: No replies were received from the Clarion Chemical Co., Eimer & Amend, Larkin & Scheffer, Lehn & Fink, Matz & Cohen, and Squibb & Sons. The following firms acknowledged receipt of results but offered no criticisms, and their replies are therefore not further considered: American Druggists' Syndicate, Otis Clapp & Son, Harvey Co., Mulford & Co., Norwich Pharmacal Co., H. K. Wampole, William R. Warner, Tilden Co., William S. Merrell, Meyer Bros., Towns & James, and Powers, Weightman, Rosengarten Co.

The comments of the manufacturers who responded are as follows:

ALBANY CHEMICAL CO.

We venture to say that our samples make a very good showing, in view of the fact that hydrogen peroxid loses strength rapidly during the first few months after it has been prepared. What is your experience in this direction?

Acidity . . . The quantity present, found by you, apparently coincides with the findings of our laboratory for several years back, that is to say, our H_2O_2 shows about 50 per cent better than the U. S. P. allows. The same is the case with the solids.

Comment by authors.—It is to be noted that the results show that the acidity is excessive.

BRUEN, RITCHEY & Co.

Your letter of the 16th to hand and in reply would say the hydrogen peroxid we supply conforms to the U. S. P., and the test as outlined by you bears this out with the exception of the test for solids, as the U. S. P. allows only 0.030, whereas you make it much over.

Analytical results obtained in the examination of commercial brands of hydrogen peroxid, Washington, D. C. (Warren).¹

Name of manufacturer.	Acetanilid.		Acidity (calculated as N/10 H ₂ SO ₄ for 25 cc).	Solids in 20 cc.	Gasometric analysis (volume of oxygen evolved at 20° C., 760 mm.) by—		Hydrogen dioxid.						Loss in 6 months.	Loss in 1 year.
	Amount declared (grains per ounce).	Amount found (grains per ounce).			MnO ₂ .	K ₂ MnO ₄ .	By United States Pharmacopoeial method.					Per cent.		
							Iodin method.	Initial examina-tion.	After 3 months.	After 6 months.	After 10 months.			
Albany Chemical Co.....		0.07	3.50	0.0102	9.85	9.80	Per cent.	2.83	2.70	2.69	Per cent.	+1.05	5.65	
American Druggists' Syndicate.....		.09	3.60	.0245	9.50	10.00	Per cent.	2.78	2.70	2.69	Per cent.	3.10	10.99	
American Peroxide & Chemical Co.....		.10	2.60	.0183	11.17	11.08	Per cent.	2.84	2.58	2.58	Per cent.	1.21	3.25	
Bene, John.....		.11	2.50	.0180	11.15	11.39	Per cent.	3.23	3.14	3.14	Per cent.	+ .62	2.18	
Bruen, Ritchy & Co.....		.11	2.00	.0158	10.59	10.67	Per cent.	3.08	3.03	2.99	Per cent.	+ .65	3.05	
Clarion Chemical Co.....		.14	2.30	.0496	10.79	10.81	Per cent.	3.07	3.02	2.97	Per cent.	+ .65	3.25	
Drevet Manufacturing Co.....		.13	2.40	.0413	10.69	10.45	Per cent.	3.07	3.02	2.92	Per cent.	+ .32	4.82	
Eimer & Amend.....		.07	2.70	.0373	10.40	10.40	Per cent.	2.98	2.96	2.92	Per cent.	2.01	10.05	
Hance Bros. & White.....		.08	2.80	.0404	10.45	10.45	Per cent.	2.98	2.98	2.92	Per cent.	.67	11.37	
Harvey Co., The G. F.....		.09	1.50	.0095	11.05	10.80	Per cent.	2.98	3.09	2.81	Per cent.	.64	9.50	
Hydrox Chemical Co.....		.10	1.45	.0085	10.75	10.51	Per cent.	3.11	3.12	3.09	Per cent.	.64	2.19	
Lehn & Fink.....		None	5.15	.0691	8.15	8.23	Per cent.	2.31	2.08	1.93	Per cent.	36.79	70.65	
McKesson and Robbins.....		None	4.95	.0133	8.17	8.07	Per cent.	2.37	2.11	1.53	Per cent.	35.75	60.44	
Mallinckrodt Chemical Works.....		None	2.80	.0324	10.70	10.82	Per cent.	3.03	3.00	2.99	Per cent.	1.96	7.21	
Marchand, Charles.....		None	2.60	.0378	11.04	10.56	Per cent.	3.06	2.99	2.99	Per cent.	2.44	2.44	
		None	2.48	.0392	10.67	10.58	Per cent.	3.02	2.99	2.97	Per cent.	1.98	10.03	
		None	2.90	.0374	10.67	10.67	Per cent.	3.02	3.02	2.85	Per cent.	2.31	21.40	
		None	2.40	.0153	10.65	10.73	Per cent.	3.05	3.02	3.09	Per cent.	3.41	3.41	
		None	3.60	.0169	10.82	10.38	Per cent.	3.08	3.09	3.08	Per cent.	3.08	3.08	
		None	3.15	.0171	10.92	10.57	Per cent.	3.03	3.02	2.96	Per cent.	.33	6.19	
		None	2.80	.0178	10.47	10.40	Per cent.	3.02	3.02	2.92	Per cent.	3.32	5.17	
		None	3.30	.0191	10.36	10.25	Per cent.	3.03	3.03	2.90	Per cent.	.32	4.67	
		None	2.60	.0126	10.33	10.34	Per cent.	3.01	2.99	2.91	Per cent.	.65	5.00	
		None	2.70	.0119	10.37	10.47	Per cent.	3.09	3.09	3.02	Per cent.	+ .32	3.15	
		None	3.00	.0404	10.19	10.21	Per cent.	3.01	3.03	3.03	Per cent.	4.31	3.41	
		None	3.35	.0182	10.58	10.58	Per cent.	3.09	3.07	2.96	Per cent.	6.15	6.15	
		None	2.15	.0120	10.36	10.33	Per cent.	3.07	3.07	2.92	Per cent.	2.28	8.26	
		None	2.50	.0234	10.34	10.10	Per cent.	3.02	2.96	2.91	Per cent.	2.56	9.54	
		None	2.80	.0233	10.72	10.66	Per cent.	3.18	2.24	2.70	Per cent.	29.56	82.62	
		None	2.45	.0238	10.22	10.68	Per cent.	3.03	3.02	1.52	Per cent.	1.98	69.26	
		None	5.50	.0181	13.45	13.45	Per cent.	3.04	3.03	.73	Per cent.	1.64	90.57	
		None	6.40	.0169	13.67	13.67	Per cent.	3.00	3.01	.43	Per cent.	27.00	84.45	
		None	6.20	.0164	13.92	13.83	Per cent.	3.99	3.78	2.57	Per cent.	18.79	38.70	
		None	6.90	.0165	13.80	13.77	Per cent.	3.27	3.27	2.67	Per cent.	16.79	38.51	
		None					Per cent.	4.05	4.05	2.51	Per cent.	20.74	38.01	
		None					Per cent.	3.27	3.27	2.50	Per cent.	18.45	37.60	

Marchand, Charles (Hydrozone).....	None.	10.70	.0165	24.60	24.71	7.04	7.05	6.55	5.78	4.82	4.73	18.01	32.78
Matz & Cohen.....	None.	3.85	.0200	24.45	24.74	7.06	7.12	6.73	5.91	4.96	4.61	16.99	35.36
	None.	3.85	.0173	9.93	9.91	2.89	2.89	2.89	2.87	2.88	2.69	.69	0.99
	None.	3.00	.0229	9.80	9.97	2.79	2.85	2.89	2.84	2.70	2.73	+	4.48
	None.	2.00	.0195	10.70	10.74	3.08	3.05	3.10	3.09	2.97	2.91	+	3.75
	None.	2.45	.0114	10.74	10.74	3.05	3.08	3.08	3.09	3.02	3.01	+	3.40
	None.	2.80	.0124	10.78	10.74	3.05	3.08	3.10	3.09	3.02	3.01	+	2.40
	None.	2.40	.0119	10.60	10.67	3.03	3.03	3.09	3.10	3.02	3.00	+	2.97
	Trace.	2.20	.0277	10.47	10.55	2.95	3.03	2.97	2.85	2.41	2.20	+	27.28
	Trace.	2.75	.0257	10.17	9.65	2.85	2.89	2.84	2.89	2.19	2.04	+	29.48
	Trace.	2.30	.0156	10.40	10.68	2.99	3.02	2.84	3.03	2.93	2.80	+	5.39
	Trace.	2.60	.0166	10.16	10.13	3.02	3.04	3.05	3.04	2.97	2.91	+	4.40
	Trace.	2.85	.0094	11.88	11.88	3.56	3.58	3.60	3.58	3.43	3.40	+	5.37
	Trace.	2.75	.0096	12.61	12.22	3.49	3.58	3.59	3.54	3.36	3.32	+	7.10
	Trace.	2.10	.0091	12.35	12.35	3.57	3.58	3.58	3.52	3.40	3.42	+	4.46
	Trace.	1.70	.0084	12.61	12.34	3.56	3.56	3.64	3.59	3.48	3.41	+	4.93
	Trace.	2.35	.0147	10.34	10.34	2.94	2.96	2.97	2.98	2.89	2.83	+	4.25
	Trace.	2.40	.0149	10.33	10.14	2.99	2.97	2.96	2.96	2.83	2.82	+	4.98
	Trace.	3.25	.0109	10.70	10.11	3.01	3.01	3.00	3.00	2.93	2.90	+	3.55
	Trace.	4.05	.0114	9.84	10.28	3.08	3.04	3.01	3.01	2.94	2.91	+	3.35
	Trace.	3.20	.0114	9.84	10.28	3.08	3.04	3.01	3.01	2.94	2.91	+	4.60
	Trace.	3.00	.0129	10.11	10.16	2.93	2.99	2.98	2.99	2.95	2.89	+	3.70
	Trace.	3.20	.0208	10.57	10.40	3.15	3.19	3.12	3.12	2.91	2.82	+	46.50
	Trace.	3.20	.0196	10.68	11.15	3.21	3.20	3.21	3.12	2.68	2.42	+	24.52
	Trace.	4.40	.0186	10.91	10.51	3.15	3.21	3.18	3.12	2.82	2.78	+	13.31
	Trace.	3.20	.0181	11.03	10.71	3.15	3.22	3.16	3.12	2.82	2.78	+	34.52
	Trace.	4.00	.1562	14.68	4.24	4.27	4.27	3.78	2.70	1.72	1.37	+	36.76
	Trace.	3.85	.0929	14.91	14.91	4.28	4.30	4.04	3.38	2.81	2.50	+	41.95
	Trace.	3.80	.0182	10.91	10.71	3.34	3.41	3.37	3.20	2.74	2.74	+	20.29
	Trace.	3.80	.0166	10.91	10.71	3.35	3.41	3.39	3.34	2.41	2.18	+	36.24
	Trace.	3.80	.0175	11.84	11.74	3.30	3.43	3.33	3.11	2.60	2.42	+	9.32
	Trace.	3.90	.0164	11.77	11.19	3.31	3.43	3.31	3.08	2.50	2.29	+	29.49
	Trace.	6.40	.1231	11.08	11.59	3.16	3.18	3.16	3.14	2.99	2.69	+	15.34
	Trace.	7.50	.1231	11.00	10.59	3.17	3.18	3.15	3.15	2.98	2.91	+	8.03
	Trace.	2.70	.0404	10.64	10.64	3.05	3.07	3.08	3.03	2.92	2.88	+	6.22
	Trace.	2.00	.0443	10.86	10.70	3.06	3.06	3.04	3.04	2.95	2.92	+	4.76
	Trace.	4.80	.0212	11.25	11.27	3.27	3.28	3.30	3.31	3.21	3.18	+	4.39
	Trace.	4.80	.0195	11.00	11.27	3.27	3.29	3.30	3.30	3.21	3.18	+	16.36
	Trace.	2.00	.0115	10.00	10.17	2.95	3.01	3.04	3.02	2.85	2.89	+	2.13
	Trace.	3.05	.0135	10.11	10.18	2.91	3.01	2.94	2.89	2.78	2.69	+	0.04
	Trace.	3.20	.0102	10.78	10.59	2.95	3.01	2.99	2.95	2.80	2.74	+	8.62
	Trace.	2.70	.0126	10.57	10.70	3.09	3.02	3.05	3.04	2.98	2.91	+	3.54

¹ The pharmacopoeial standard is as follows:
 * * * Should contain, when freshly prepared, about 3 per cent, by weight, of absolute hydrogen dioxide, corresponding to about 10 volumes of available oxygen."
 Twenty-five cubic centimeters should not contain more free acid than that equivalent to 2.5 cc of tenth-normal sulphuric acid; 20 cc should contain not more than 0.03 gram of solids. For other data see United States Pharmacopoeia, 8th revision, p. 55.
² Bottle exploded between March 31 and June 30.
³ No denomination given on label.
⁴ Maximum.
⁵ Per cent.

Analytical results obtained in the examination of commercial brands of hydrogen peroxid, Nashville, Tenn. (Ruddiman).

Name of manufacturer.	Acetamidid.		Acidity (calculated as H_2O_2 per 25 cc.).	Total solids in 20 cc.	Per cent of hydrogen dioxide present at the end of—								Per cent of loss in 9 months and in 1 year.			
	Declared.	Found.			Octo-ber.	No-ven-ber.	Janu-ary.	March.	May.	July.	Sep-tem-ber.	Octo-ber.		Per cent of loss in 5 months.		
															Grams per ounce.	
Investigation begun in December, 1907:																
Albany Chemical Co.	Grains	Grains	cc.	Grams.												
American Drug Syndicate	do.	Present.	3.9	0.0211	2.84	2.79	2.75	2.68	2.60	2.86	3.13				In 9 mos.	8.3
Johnson & Co.	do.	do.	2.7	0.016	3.32	3.28	3.26	3.24	3.23	3.13	1.80					2.0
American Peroxide & Chemical Co.	do.	do.	2.9	0.016	3.11	3.08	3.07	3.05	3.03	1.28	1.28					5.0
John Bene.	do.	do.	3.0	0.011	3.15	3.08	3.05	3.00	2.99	3.17	3.17					9.7
Bruen Ritchy & Co.	do.	do.	3.2	0.030	3.04	2.98	2.91	2.89	2.74	4.27	4.27					2.4
Clarion Chemical Co.	do.	do.	1.5	0.079	3.16	3.13	3.09	3.09	3.08	1.58	1.58					9.7
Drevet Manufacturing Co.	None.	do.	4.9	0.112	3.11	2.97	1.79	1.42	1.16	26.03	26.03					51.8
Elmer & Amend.	None.	Present.	3.1	0.084	3.11	3.05	3.01	2.97	2.95	3.21	3.21					5.4
Hance Brothers & White.	do.	do.	3.3	0.065	3.10	3.08	3.04	2.94	2.92	10.90	10.90					12.2
Harvey Co., The G. F.	1 0.0004	do.	2.9	0.092	3.18	3.13	3.11	3.09	3.08	2.20	2.20					3.3
Hydrox Chemical Co. (Hamlin's Peroxide of Hydrogen)	do.	do.	2.9	0.109	3.14	3.10	3.07	3.05	3.04	2.23	2.23					3.2
Lehn & Fink	0.12	do.	3.4	0.423	3.11	3.06	3.04	2.99	2.96	2.25	2.25					4.9
McKesson & Robbins	do.	do.	3.3	0.142	3.13	3.11	3.06	3.04	2.98	2.87	2.87					7.3
Marchand, Charles (hydrozone)	None.	do.	9.5	0.173	7.27	6.98	5.99	5.21	4.59	17.60	17.60					36.8
Marchand, Charles (glycozone) ²	None.	do.	0.00		0.00											
Matz & Cohen	None.	Present.	5.1	0.157	2.89	2.87	2.85	2.81	2.79	1.38	1.38					3.6
Mulford Co., The H. K.	do.	Trace.	2.1	0.060	2.88	2.76	2.66	2.43	2.21	8.68	8.68					23.1
Norwich Pharmaceutical Co.	do.	Present.	2.1	0.140	3.08	3.03	3.02	2.99	2.96	1.94	1.94					3.4
Otis, Chapp & Son	do.	do.	2.6	0.129	3.02	2.98	2.95	2.93	2.92	3.31	3.31					3.8
Smith, Kline & French	do.	do.	5.6	0.096	4.68	4.50	3.95	3.49	1.88	30.55	30.55					62.0
Frederick Stearns & Co.	do.	do.	7.0	1.188	3.22	3.19	3.15	3.08	2.98	2.47	2.47					7.8
Towns & James	do.	do.	3.3	0.080	3.11	3.09	3.02	2.98	2.92	2.60	2.60					6.2
H. K. Wampole Co.	do.	do.	4.0	0.164	3.45	3.42	3.38	3.35	3.32	2.93	2.93					3.7
Investigations begun in October, 1907:																
Hydrox Chemical Co.	do.	do.	2.5	0.101	3.06	3.01	2.99	2.95	2.87	2.86	2.86					7.2
Larkin & Scheffer	None.	do.	2.8	0.030	1.88	1.84	1.60	1.42	1.27	2.86	2.86					37.4
Mallinckrodt Chemical Works	None.	do.	2.6	0.100	2.94	2.89	2.82	2.63	2.57	17.34	17.34					56.9
Marchand, Charles.	None.	do.	6.6	0.042	0.05	0.04	0.02	0.01	0.01	0.00	0.00					98.6
Merck & Co.	None.	Present.	2.7	0.133	3.09	3.06	3.03	2.97	2.95	0.97	0.97					1.2
The W. M. S. Merrill Co.	do.	Small amount.	4.0	0.020	2.92	2.89	2.85	2.83	2.79	20.54	20.54					72.7
Meyer Brothers.	0.142	Present.	3.0	0.008	2.97	2.93	2.84	2.82	2.72	3.02	3.02					9.8
Oakland Chemical Co.	None.	do.	2.4	0.105	2.90	2.86	2.80	2.78	2.72	2.68	2.68					68.9
Parke Davis Co.	do.	Present.	2.8	0.162	2.75	2.69	2.68	2.62	2.55	2.47	2.47					10.1
Powers, Weightman & Rosengarten Co.	0.018	None.	1.3	0.268	2.45	2.35	1.75	1.21	0.76	19.60	19.60					75.7
Squibb & Sons.	None.	do.	7.8	0.136	2.51	2.47	2.10	1.86	1.65	10.93	10.93					38.5
The Tilden Co.	do.	Trace.	2.5	0.203	2.91	2.82	1.90	1.52	1.22	21.21	21.21					62.0
Warner & Co., Wm. R.	None.	None.	2.9	0.193	2.28	2.34	2.20	1.16	0.14	28.12	28.12					63.4

² Loss.³ Represented and believed to contain hydrogen dioxide, but in fact does not.¹ No denomination given.

We can account for this by your not using a desiccator, for if it is dried any other way it will take moisture from the air, thereby greatly increasing the residue.

We have never put out any peroxid which runs higher in residue than the U. S. P. allows.

Comment by authors.—All moisture determinations were made by cooling the dried material in a desiccator.

THE DREVET MANUFACTURING CO.

* * * We note the analyses of our various preparations made by your department, and are absolutely at a loss to understand the results obtained, unless perhaps the samples used were very old.

As you probably know, we were about the first to manufacture the medicinal peroxid of hydrogen, and we have jealously guarded the high standard of our preparations for more than 30 years and beg of you the privilege of submitting for your careful examination samples of our preparations taken from our present stock on hand, and at the same time we would kindly ask you to allow us to offer certificates of analyses made by well-known and prominent chemists of this city for your consideration.

We would be pleased to have your representative call and collect personally these samples from our stock if you wish, or we would be glad to forward such samples to you.

Trusting you will grant our request, and assuring you of our earnest desire and efforts to place our goods on the market in full conformity with or even superior to the U. S. P. standard, we beg to remain.

HANCE BROTHERS & WHITE.

We received yours of the 16th ultimo on the 28th. At the same date we inclosed it to Mr. John Bene, Brooklyn, N. Y., from whom we procure our supply of peroxid hydrogen. We have examined the articles several times and found it to comply so closely with the U. S. P. requirements, and in view of its perishable nature and its use almost entirely for external purposes, have issued it as being equal to other makes.

We are herewith inclosing Mr. Bene's reply, which rather confirms our estimate of his article and shows his faith in the declaration on his invoice of its conforming to the requirements of the Federal food and drugs act.

The letter of Mr. John Bene referred to reads as follows:

Your letter of the 28th instant to hand with inclosures, and in reply the hydrogen peroxid I supply you conforms strictly to the U. S. P., and the test as outlined by Dr. Wiley bears this out with the exception of the test for solids, as the U. S. P. allows only 0.030, whereas he makes it much over. I can account for this by his not having used a desiccator, for if it is dried any other way it will take moisture from the air, thereby greatly increasing the residue. I have never put out any peroxid which runs higher in residue than the U. S. P. allows.

HYDROX CHEMICAL CO.

We hasten to acknowledge receipt of your analyses of Hydrox peroxid of hydrogen, Hamlin's peroxid of hydrogen, and American peroxid of hydrogen, all of which products are manufactured by the chemists of the Hydrox Chemical Co.

We believe it is pretty well demonstrated that acetanilid, $\frac{3}{4}$ grain to the fluid ounce, acts as a preservative to this preparation (as is demonstrated by your analyses) so that the last drop in any container is full U. S. P. strength, making the preparation thoroughly dependable in the hands of the practitioner at all times.

We beg to state that in our investigations we have found that the breaking up or decomposition of acetanilid causes a slight increase in acidity of the product, this

change taking place probably three to six months after its manufacture, but not a sufficient increase to render the product harmful.

We have also observed that peroxid of hydrogen when not properly stored in an upright position decomposes, either with or without acetanilid, by contact with corks; foreign matter being taken up by the preparation.

We are pioneers in the manufacture of permanent peroxid and wish to make our product conform as closely as possible to governmental requirements; at the same time believe our present standard is so high as to permit of little change in formula.

MALLINCKRODT CHEMICAL WORKS.

Replying to yours of the 16th instant, I assume that the copy of analyses of our hydrogen peroxid refers to samples taken from a lot supplied by us in accordance with the requirements of your department—that it contain no acetanilid or other preservative. It is well known that hydrogen peroxid solution will not keep without the addition of some preservative, and we are not surprised that the samples should have lost so largely in the percentage of strength after being kept for a period of one year.

You are doubtless also aware that the acidity test of the United States Pharmacopœia is unreliable and shows larger amounts of acid when none is present, the amount being dependent on the manner of manipulation.

If you will examine our hydrogen peroxid as we supply it to the trade, with acetanilid as a preservative, I think you will find that if kept with ordinary precaution it will lose very little, if any, strength during the period of a year.

Comment by authors.—The samples examined in Washington did not contain any acetanilid, but the presence of caffein was established. The samples, furthermore, were not taken from the lot supplied, at the request of the department, free from acetanilid. The sample examined in Nashville was purchased through a local wholesaler. The point, therefore, raised relative to the absence of acetanilid as a preserving agent is not substantiated.

CHARLES MARCHAND.

* * * I have sold my interests in the Drevet Manufacturing Co. the beginning of January, 1909, and I have not manufactured "Marchand's Peroxide of Hydrogen," "U. S. P. Peroxide of Hydrogen," "Hydrozone," or "Glycozone" since that time.

Under these circumstances, I have nothing whatever to do with the goods manufactured and sold by the Drevet Manufacturing Co., although they are still labeled "Prepared only by Charles Marchand."

McKESSON & ROBBINS.

* * * We do not see that there is any comment for us to make upon your results, as the results speak for themselves. We might, however, add that we have recently adopted a time-limit label similar to the inclosed sample, which appears on all packages of peroxid sent out by us. While your results show that our peroxid will keep almost unchanged for a year, we place the time limit at six months, owing to the uncertainty surrounding the keeping properties of this preparation under the varying conditions met with in different parts of the country.

In our opinion six months would be a reasonable time limit for all manufacturers to adopt both for the protection of the public as well as for the reputation of the manufacturer and retailer. * * *

Comment by authors.—The time limit adopted by this firm is in accordance with the findings of this investigation.

MERCK & Co.

* * * We have looked over your tabulated results with interest. From the tabulation which you offered it appears that in the acidity test the method of the United States Pharmacopœia has been employed. But do you not think this method rather unreliable? This question was raised about three years ago by numerous investigators.

Replying to your favor of the 13th, asking us to advise you as to what we consider a reliable test for determining the amount of free acid in pharmacopœial hydrogen peroxid, we would say that we obtain the most accurate results by the use of methyl orange indicator instead of the phenolphthalein indicator prescribed by the United States Pharmacopœia.

Uniform and accurate results may also be obtained by simply titrating the original solution of dioxid with decinormal potassium hydroxid, using methyl orange and omitting all evaporation and heat.

Comment by authors.—The observations noted are in accordance with our findings.

OAKLAND CHEMICAL Co.

Replying to your letter of December 16, received yesterday, we beg to thank you for it. The plan that you are using of notifying manufacturers of the results of your investigations and the opportunity you are offering for comment on the report is very fair and commendable.

May we ask you to kindly give us the numbers which are stamped with a rubber stamp on the labels of the bottles which you have been using as samples? We ask this information so that we can check up your results with our records. We take it that this will not be unsatisfactory to you, and it will certainly be a matter of satisfaction to us to make the comparison. * * *

We beg to acknowledge receipt of your favor of the 5th instant. None of our records show anything that would compare with your report on this sample. The uniformity of the other four and the relative closeness of your statement with our results justify the assumption that the report on sample No. 5 can not be accepted as indicating either an exceptional case or a fair average of quality of our product; the not unreasonable possibility of something unusual having happened to this sample either before or after it reached your hands, the further possibility that it may not actually be our product, though apparently an original bottle bearing our label, are sufficiently important to warrant our request that this sample be either eliminated or a full opportunity be given us to make a rigid investigation that would allow us to trace its history completely. * * *

Your favor of March 1 was duly received. The statement that the label on the package of dioxigen, on which there is some question, contains the number 91, and which statement had previously been made in a department letter of January 13, has been carefully reviewed, and we beg to make you the following report.

The number referred to, which is placed on these bottles, is the key by which we can identify each lot of our product, its date of manufacture, and all the records which refer to it. These numbers run in series. The present series of numbers began in March, 1907, and No. 91 of this series was reached December 15, 1908. If the bottle bearing the mark received by your department from —— Co. was obtained in October, 1907, it could not have belonged to this series started in March, 1907, and must have belonged to a previous series.

The previous series began in November, 1904, and No. 91 of this series was reached August 13, 1906. In August, 1906, —— Co. received a shipment of goods bearing this number. Consequently this bottle, which your department has reported on, had

been in ——— Co.'s possession one year and two months before you received it. During the fall of 1906 and spring of 1907 we removed our manufacturing plant from Brooklyn, N. Y., to Richmond County, N. Y., and when our manufacturing operations began at the new plant we started a new series. It was during the confusion of this period that this lot, from which the bottle your department has examined came, was made.

Under these circumstances, we respectfully request you to eliminate this test from your published report. If it is the purpose of this report to supply information as to the quality and character of goods of the different manufacturers, then we respectfully point out that a bottle of a product of the character of peroxid of hydrogen, which is over a year old before the test is made, is not fairly illustrative of average conditions or quality. If other tests which you have made from time to time indicate that such a variation as this particular sample shows might be reasonably expected, we withdraw the request.

If in your judgment it is reasonable to expect that goods would be more than one year old before they reach the consumer's hands, as was this sample, then we withdraw the request.

If you in your experience with our product have found anything that would indicate that the result of this sample conveys a true estimate of the actual quality of dioxigen, we withdraw the request.

Comment by authors.—Considerable care was exercised to secure fresh samples. There was nothing on the package in this case to indicate possible deterioration from age. With justice to all, no one sample could be eliminated, but the explanation offered by the manufacturer is given in full.

PARKE DAVIS & Co.

* * * On the whole we feel very much pleased to note a statement from the Bureau of Chemistry which so nearly confirms our claim that we are marketing a high-grade hydrogen peroxid and one which is remarkably stable, considering the nature of the substance.

The amount of acetanilid reported is in each instance somewhat less than the quantity originally added to the solution of peroxid at the time of manufacture. Our formula calls for the addition of three-sixteenths grain of acetanilid per liquid ounce of the peroxid solution, this being equivalent to 0.41 gram per 100 cc. In each case the amount reported by you is less than this. It is entirely possible that in some cases a portion of the acetanilid has been destroyed by the action of the hydrogen peroxid, particularly in the old samples.

In examining the proportion of acid reported for the five different samples we note that this is in every instance high. We presume that the figures given are the direct statement of the acid in terms of cubic centimeters tenth-normal acid in 25 cc of the hydrogen peroxid, and are consequently not an indirect statement of the number of cubic centimeters of tenth-normal acid required to titrate back, as directed in the Pharmacopœia. If our first supposition is correct, we beg to say that the amount of acid reported by you is in every instance undoubtedly excessive in that you have estimated not only the amount of free acid present, but have also estimated as well the acid produced from the acetanilid which has decomposed by heating with alkali in carrying out the test as stipulated in the Pharmacopœia.

We have had occasion to refer in one or two previous instances to this error in estimating acid by the official method in hydrogen peroxid preserved by the use of acetanilid. Theoretically the acid in three-sixteenths grain of acetanilid will neu-

tralize or is equivalent to 0.75 cc of tenth-normal potassium hydroxid. In actual practice, however, we find by making numerous tests upon a given specimen of hydrogen peroxid, to a portion of which we add three-sixteenths grain acetanilid per ounce and to the second portion of which no acetanilid is added, that this three-sixteenths grain of preservative will increase the seeming content by about 1.3 cc of tenth-normal acid. We can not altogether account for this increase above theory, but presume that it is due to some acid body produced by the decomposition of the acetanilid, produced by the action of the hydrogen peroxid on the acetanilid in the presence of the alkali in carrying out the evaporation.

Turning now to the five samples reported, if we make a correction in each instance for the amount of acetanilid reported by you, the equivalents would be as follows:

	cc N/10 KOH.
Sample No. 1.....	0.6
No. 2.....	0.7
No. 3.....	0.5
No. 4.....	0.45
No. 5.....

Subtracting the above quantities of tenth-normal acid from the quantities you report, the free acid would appear as follows:

	cc.
Sample No. 1.....	2.65
No. 2.....	3.35
No. 3.....	2.7
No. 4.....	2.55
No. 5.....

· Making the theoretical correction, each of these samples would fall below the requirements of the U. S. P. for the content of free acid with the exception of No. 3.

We do not regard this matter of slight excess of free acid as being of very great consequence, but think it best to call your attention to this error, inasmuch as we presume you will go into this matter of hydrogen peroxid very thoroughly, and the evidence which we offer is the result of a very great deal of experience. There is really no reason for resorting to the indirect method as outlined in the Pharmacopœia. Equally good results and (in the case of hydrogen peroxid containing acetanilid) more correct results are obtained by direct titration. It is only necessary to add to 25 cc of the hydrogen peroxid about 5 or 6 minims of phenolphthalein test solution (U. S. P.) and titrate directly with tenth-normal alkali to the development of a light-pink color. Under the conditions this method is accurate to 0.1 to 0.2 cc. For practical purposes the test in the Pharmacopœia should be stated as follows:

If to 25 cc of the solution of hydrogen peroxid 5 or 6 minims of phenolphthalein test solution are added, not more than 2.5 cc tenth-normal KOH should be required to produce a pink color (limit of free acid).

Comment by authors.—It is probably true that the presence of acetanilid will increase the acidity of hydrogen peroxid, particularly when determined according to the prescribed method, but the manufacturer is aware of the facts and should, therefore, make due provisions. If he desires to add acetanilid, and it is known to him that the addition of this chemical will increase the acidity of the product, he should make ample allowance to come within the maximum limit of the prescribed acidity. The subject of direct titration, using phenolphthalein as indicator, is discussed on page 22.

SMITH, KLINE & FRENCH CO.

We beg to acknowledge receipt of your letter of the 16th with analysis of our hydrogen peroxid.

First of all we note that samples 1 and 3, judging from their strength, must be our 15-volume peroxid. Therefore, so far as acidity and solids are concerned, they would have to be judged from a different standpoint than the 10 volume, for it must be remembered that 15-volume peroxid, being one-half stronger, the acidity and the solids would necessarily increase in the same proportion.

This peroxid is plainly branded 15 volumes, and is therefore distinguished from the 10-volume product.

We are surprised to note that only sample No. 3 contains acetanilid, because we have been putting acetanilid in our peroxid for almost two years, and this would indicate that samples 1 and 2 are very old. If you could let us know the numbers on the packages we could in turn let you know the age of the peroxid, which might be of interest. * * *

We beg to acknowledge receipt of your letter of January 7 giving us the serial numbers of packages of peroxid, the test of which you have reported under date of December 16.

We find that the No. 4926 was put up on October 31, 1907, and No. 4935 on November 11, 1907. The packages, therefore, were two years old last October and November. It is therefore fair to presume that they were a year old before the tests were begun.

Since that time peroxid in general, and our peroxid in particular, have been much improved. We think it would be only fair, when the tests are published, to give the date of manufacture and the date of the beginning of the test, because otherwise it would be rather unfair to, for instance, say 15-volume peroxid, and then give the strength found, unless the interval between the manufacture of the goods and the date of the first test was given. We leave this, of course, entirely to your own good judgment.

Comment by authors.—It will be observed that the investigation was begun in October, 1907, and the samples, examined were, therefore, comparatively fresh.

FREDERICK STEARNS & CO.

We are very much surprised to learn that you have found any of our product to run high in solids and so very high in acidity. We test very carefully every batch of this preparation and aim to have it comply with pharmacopœial requirements, except in so far as we, like many other manufacturers of this article, add acetanilid as a preservative, as is stated on every label. This would increase the amount of total solids by the amount of acetanilid so added. In addition to this, the acetanilid also has the effect of increasing the apparent percentage of acid because in the U. S. P. method of assay, the peroxid solution is boiled with the tenth-normal KOH which saponifies the acetanilid, some of the alkali combining with the acetic acid. On a 25 cc sample, basing calculation upon the amount of acetanilid you found (26.5 mg=average), we ought to deduct 0.5 cc tenth-normal KOH from the total number of cubic centimeters required to neutralize the acid, because this amount (0.5 cc) is equivalent to the 26.5 mg acetanilid present in a 25 cc sample of peroxid.

We understand, of course, that this does not explain the high results you obtained, but it occurred to us that this matter may not have been taken into consideration.

We have gone over our record of tests for the entire year of 1909 and find that we had but four batches that yielded as much as 30 mg of residue, the next highest was 26 mg the average for the year being 20.73 mg. Likewise the average acidity for

all of the hydrogen peroxid manufactured during the entire year is 2.31 cc tenth-normal KOH, tested according to the U. S. P.

We always make our determinations before the addition of the acetanilid.

Comment by authors.—Manufacturers are aware that the Pharmacopœia prescribes a maximum for solids, and therefore if a preservative is added it should be only in such amounts as to keep well within the limits.

DISCUSSION OF RESULTS.

HYDROGEN DIOXID.

As before stated, the value of a solution of hydrogen peroxid is largely judged from the percentage of hydrogen dioxid present. The investigations were begun in October, 1907, and continued over approximately one year. The results obtained on hydrogen dioxid by the gasometric methods and the iodine method do not materially vary from those by the pharmacopœial method, and for that reason the latter will be made the basis of comment. The Pharmacopœia states that hydrogen peroxid solution should contain, when fresh, about 3 per cent by weight of absolute hydrogen dioxid, corresponding to about 10 volumes of available oxygen.

A review of the results obtained by the first examination shows that 21 of the samples fall below the 3 per cent basis and 8 fall below a 2.75 per cent basis. The results obtained five and six months after the first examination show that 24 of the samples examined had lost 10 per cent and over of the original content of hydrogen dioxid, while on a 15 per cent basis, 21 were found defective, which is only 3 less than on the 10 per cent basis. The point may be raised that this commodity is less stable in warm than in cold weather, but this generally accepted idea is not supported by the data. The degree of deterioration taking place between 5 and 6 months and 9 and 10 months, respectively, which covers the summer period, does not differ materially from that noted over similar periods of time in cooler weather. It should, moreover, be noted that these observations were made after the samples were at least five or six months old and deterioration had set in, a condition favorable for decomposition.

Knowledge of trade conditions leads to the belief that it is not necessary to keep hydrogen peroxid solutions on hand longer than five or six months, the latter being the maximum limit.

ACETANILID.

The results of this work undoubtedly show that acetanilid retards the deterioration of hydrogen peroxid solutions. The inhibition, however, is not uniform. For example, of two samples of hydrogen

peroxid, made by the same firm and both containing acetanilid, one will deteriorate rapidly, while the other is fairly stable. The cause of such apparent abnormalities has not yet been determined. There are probably numerous contributing factors, but one undoubtedly is the difference in the methods of manufacture. Furthermore, the absence of acetanilid from a number of brands and their slow rate of deterioration shows that acetanilid is not necessary to prevent or retard decomposition. Hydrogen peroxid solutions containing acetanilid sooner or later develop a yellowish or brownish tint and an odor resembling nitrobenzol. To what extent the presence of nitrobenzol and similar agents are objectionable has not been established.

The Pharmacopœia neither recognizes nor prohibits the use of acetanilid as a preservative or antiseptic or otherwise, yet many packages bear labels declaring the presence of acetanilid and at the same time designate the article to be the pharmacopœial product, an obvious inconsistency. The acetanilid is not added because of its antiseptic property, as is indicated on some labels, but because of its apparent inhibiting influence on deterioration. The presence of acetanilid was declared in 72 samples, and found in 70.

ACIDITY.

The results on acidity show that a large majority of the products are excessively acid. This may be interpreted that the standard equivalent of 2.5 cc of tenth-normal sulphuric acid for 25 cc of the solution is too exacting. By placing the upper limit at 3 cc of tenth-normal sulphuric acid for 25 cc, 51 samples would still be excessively acid, and by placing the standard at 4 cc, 22 would remain above the limit.

A certain amount of the acidity may be due to the oxidation of the acetanilid present. This is a point, however, which should be provided for by the manufacturer who uses the chemical. The maximum acidity prescribed by the United States Pharmacopœia does not appear to be too exacting, particularly when it is remembered that hydrogen peroxid solutions are largely used as mouth washes. If this product should contain an excessive amount of free acid, it would of necessity exert a deleterious influence upon the teeth.

Numerous experiments have been made on the determination of the acidity of hydrogen peroxid solutions by the pharmacopœial and other methods, and it has been found that methyl orange could be substituted with advantage for phenolphthalein if the present pharmacopœial method is retained. Experience and experiments furthermore show that the free acidity can readily be determined by direct titration, using phenolphthalein as indicator, and there seems to be no good reason for continuing the use of the present pharmacopœial method.

NONVOLATILE MATTER.

The results show that a comparatively small number of samples contain an excessive amount of solids. There should be little difficulty in properly adjusting this matter, particularly in view of the fact that the majority of those containing excessive amounts of solid material come from the same factory. One manufacturer states definitely that the amount of nonvolatile matter is in excess of that prescribed by the Pharmacopœia. The solid material on examination was found to contain one or more of the following: Chlorids, phosphates, sulphates, and acetanilid. In no case was the presence of fluorids established, but in several instances a trace of metals was noted. Tests made on the solid material show that the acetanilid was neither completely decomposed nor volatilized at 120° C.

Notwithstanding the fact that hydrogen peroxid solutions are known to be more or less unstable, some manufacturers place such statements as the following upon the labels: "Permanent," "Guaranteed unsurpassed in keeping qualities," "A permanent * * * preparation," "Unsurpassed in strength and keeping qualities," "Full 10 volumes strength," etc. The analysis showed that the sample bearing the latter label was less than two-thirds of the standard strength. Why such statements should be made in connection with products of this character is difficult to understand, since it is well known that they are liable to deterioration. It should be noted, however, that this investigation shows the quality of medicinal hydrogen peroxid available on the market to be, on the whole, very satisfactory.

THE PURITY OF GLYCERIN.

By L. F. KEBLER and H. C. FULLER.

SCOPE OF INVESTIGATION.

The question of the purity of glycerin has assumed great importance during recent years because of the extensive use of this product in the preparation of medicinal agents. This has been impressed on the manufacturers to such an extent that the quality of glycerin on the market has been greatly improved and the best grades may now be procured without difficulty.

The claim has often been advanced that the present glycerin standard is too rigid and in certain respects can rarely be attained; hence the Pharmacopœia should be so modified that it will be consistent with conditions which actually exist. To confirm or refute this statement it was necessary to investigate the quality of the glycerin on the market in the United States, and to determine exactly to what extent samples from different sources conformed to the tests prescribed in the Pharmacopœia. Another purpose was to learn whether there were any glycerins which would not reduce Fehling's solution, the claim that no such article was obtainable being of importance owing to the use of glycerin in the preparation of Haines's solution, an alkaline copper liquid which has been recommended for detecting sugar in urine and whose value as a testing reagent would naturally be impaired if reduction occurred when no sugar was present.

Letters were sent to manufacturers in different parts of the country requesting samples, the scope of the inquiry being outlined sufficiently to give them every opportunity to submit glycerin of as high quality as possible, together with any comments and suggestions deemed desirable. When the examination had been completed, the several dealers who had responded were sent analyses of their own makes of glycerin, with a request for further criticisms before the publication of the results. Samples were received from the following 11 firms in the United States, two additional samples of foreign manufacture having been purchased on the open market:

- Armour Soap Works, Chicago (two samples).
- Colgate & Co., New York.
- Harshaw, Fuller & Goodwin Co., Cleveland, Ohio.
- Wm. A. Jobbins, Aurora, Ill.
- Jas. S. Kirk & Co., Chicago.
- Larkin Co., Buffalo, N. Y. (two samples).
- Marx & Rawolle, New York.
- Peet Bros. Manufacturing Co., Kansas City, Kans.

Powers, Weightman, Rosengarten Co., Philadelphia.

Procter & Gamble Co., Cincinnati, Ohio.

M. Werk Co., Cincinnati, Ohio.

E. Schering, Berlin, Germany.

Price's Patent Candle Co., London, England.

DISCUSSION OF METHODS AND RESULTS.

The samples were examined first according to the methods prescribed in the Pharmacopœia. A rigid examination was made for arsenic in order to determine whether even traces of this substance were left in the glycerin; special tests were made to note the action on Fehling's solution, and a sample of Haines's solution was made up with each product. The physical appearance was good in every instance. The samples were all neutral to litmus paper. The specific gravities at 25° C. varied from 1.248 to 1.258, in most cases being above 1.250, with an average of 1.254. In this respect they were all above the standard requirement of 1.246 at 25° C.

The pharmacopœial test for sugar gave negative results, as would be expected. Experiments were then conducted, noting the action on Fehling's solution, using concentrated and diluted glycerin and without previously heating with acid as in performing the sugar test. Two samples which reduced Fehling's solution in the undiluted state gave no reduction on dilution; two reduced the solution on diluting, but did not in the concentrated condition; three showed no reduction either diluted or undiluted; while the remainder reduced Fehling's solution under any condition. Several of the samples which reduced Fehling's solution in the undiluted condition had reduced ammoniacal silver nitrate in the Hager test.^a Haines's solution, when made according to directions given in works on urinalysis^b was reduced in every instance, thereby substantiating the claims which had already been advanced in this connection.^c

Most of the samples were well within the requirements as to the color imparted by concentrated sulphuric acid, various shades of yellow occurring. One sample was dark brown and fluorescent, while another turned brown and gave off a strong fatty odor. In fact, the odor varied more than the color, some samples having the fatty odor just mentioned, while others had an unmistakably pleasant aromatic smell; four had a characteristic hydrocarbon odor, and in one instance the product was practically without color or odor, but evolved a quantity of minute gas bubbles. When the samples were treated with alcohol and sulphuric acid and warmed on the steam bath ethereal odors were noted in all cases, the unpleasant butyric ester predominating, although with two samples an agreeable fatty

^a Handbuch der Pharm. Praxis, 4th ed., 1905, 1: 1221.

^b Purdy, R. G., Practical urinalysis and urinary diagnosis. 1895, p. 103.

^c Mayer, J. L., The reducing action of glycerin, Merck's Report, 1905, 14: 165.

odor was noticed. In certain instances this test ran parallel with the former one, in that samples which gave scarcely any color or odor with sulphuric acid gave but a slight ethereal odor, but for the most part the tests were entirely at variance, as will be noted on examining the table on page 27. When simply heated on the steam bath marked differences in odor were noted, four samples gave off a slight odor of no particular character, two an aromatic odor, and the remainder a fatty odor of varying intensity.

A reaction was obtained showing a slight trace of sulphates in five products, a trace of chlorids in two, and a reduction of silver nitrate in five, this being very marked with one specimen; oxalates were indicated in two samples from the same manufacturer; heavy metals were shown in three cases, while six gave no reactions for metals or acids.

Only one sample showed the presence of objectionable amounts of arsenic, and this was of foreign make and labeled "arsenic free." The Marsh test was rigidly applied to every glycerin in order to determine how completely the arsenic had been eliminated; six specimens gave no mirror, and the others, with the exception of the one above mentioned, contained less than one part in a million. It is of interest to note that of two samples submitted by one manufacturer one contained arsenic and the other did not.

Satisfactory results seemed impossible with the pharmacopœial test using ammoniacal silver nitrate; reduction took place in every instance, and it was apparent that no significant conclusions could be drawn from its use. Accordingly it was abandoned for the test described by Hager,^a with which better comparative results were obtained. Five cubic centimeters of the sample were mixed with 5 cc of 26 per cent ammonia water and 5 drops of silver nitrate added; the mixture was allowed to stand at the ordinary temperature in the dark for 15 minutes and its appearance noted. There was no reduction of the silver nitrate in six cases, and a marked reduction in two, the other samples being slightly colored.

ANALYTICAL DATA.

The investigation showed that glycerin could be produced which would answer all of the pharmacopœial requirements with the exception of the ammoniacal silver nitrate test. It also showed that although some glycerins gave off a fruity odor when treated with alcohol and sulphuric acid, they were otherwise of good quality; therefore the wording of this test should be modified in order to include the disagreeable butyric odor as it now discriminates only against a "fruity odor."

^a Loc. cit.

Glycerin analyses.

Manufacturer and serial number.	Odor on heating.	Odor with alcohol and sulphuric acid.	Color and odor with sulphuric acid.	Action with silver nitrate and ammonium hydroxid (Hager's test).	Metals and acids.	Arsenic (parts per million).	Haines's solution (cuprous oxid formed).	Undiluted and treated with Fehling's solution.	Diluted (1-1) and treated with Fehling's solution.	Diluted (1-3) and treated with Fehling's solution.	Specific gravity at 25° C.
Armour, 2129...	Fatty....	Umpleasant ethereal.	Slight yellow; fatty.	Colorless.....	None.....	None.	In one week.	No reduction hot or cold.	No reduction hot or cold.	No reduction hot or cold.	1.258
Armour, 2130...do.....do.....	Dark yellow; fatty.do.....do.....	None.	In three hours.	No reduction on heating.do.....do.....
Colgate, 2134....	Slightly aromatic.	Ethereal.....	Yellow; slight fatty.	Slight coloration.do.....	0.17	A little overnight.	Slight reduction.	In half an hour cold; no reduction hot.do.....	1.253
Hashaw, Fuller, & Goodwin, 2132.	Strong fatty.	Ethereal with butyric compound dominating.	Light yellow; aromatic.	Very slight color.	Trace of sulphate.	0.25	Overnight	No reduction hot or cold.	In half an hour cold; no reduction hot.	Slight reduction none hot.	1.255
Jobbins, 2137...	Slight fatty.	Umpleasant ethereal.	Very little.....	Colorless.....	Slight trace of sulphate.	0.2	A little overnight.	Slight reduction.	Slight reduction cold; none hot.	No reduction hot or cold	1.256
Kirk, 2138.....	Very little.	Fatty ethereal.	Darkens; odor of machine oil.	Reduces considerably.	Slight trace of sulphate and chlorid.	None.	At once...	Reduces at once hot; reduces in one-half hour cold.	Reduction in 15 minutes both hot and cold.do.....	1.254
Larkin, 2139....	Slight; not fatty.	Fatty ethereal (turns dark).	Brown - fluorescence; oily.	Slight color....	Slight oxalate; reduces with silver nitrate.	0.4do.....	No reduction hot or cold.	No reduction hot or cold.do.....	1.255
Larkin, 2140....	Considerable.	Fatty ethereal (turns dark).	Yellow; oily...	Yellow.....	Slight oxalate; reduces with silver nitrate; slight color with figs.	None.do.....	Turns green cold; no action hot.do.....do.....	1.248
Marx & Ruwolle, 2136.	Slightly fatty.	Slightly ethereal.	Little color; air bubbles.	Colorless.....	None.....	0.4	Overnight	No reduction hot or cold.do.....do.....	1.255
Powers-Weigman - Rosengarten, 2131.	Strong aromatic.	Umpleasant ethereal.	Dark yellow; fatty.	Very slight color.do.....	0.75do.....	Little on heating.	Considerable cuprous oxid comes out overnight.do.....
Procter & Gamble, 2135.	Slightly fatty.do.....	Little color; slight fatty odor.	Colorless.....	Trace of sulphate and chloride.	None.do.....	No reduction hot or cold.	No reduction hot or cold.do.....	1.250

Glycerin analyses—Continued.

Manufacturer and serial number.	Odor on heating.	Odor with alcohol and sulphuric acid.	Color and odor with sulphuric acid.	Action with silver nitrate and ammonium hydroxid (Hager's test).	Metals and acids.	Arsenic (parts per million).	Haines's solution (cuprous oxid formed).	Undiluted and treated with Fehling's solution.	Diluted (1-1) and treated with Fehling's solution.	Diluted (1-3) and treated with Fehling's solution.	Specific gravity at 25° C.
Werk, 2133.....	Fatty.....	Ethereal with butyric compound predominating. Slight fatty ethereal.	Slight yellow; fatty.	Very slight color.	None.....	None.	Little cuprous oxid overnight. Reduction overnight.	Reduces on heating; none cold.	Cuprous oxid in one-half hour cold; no reduction on heating. Reduction hot and cold.	No reduction hot or cold.	1.254
Scherling, 2192....	Slight.....	Slight fatty ethereal.	Slight yellow; slight fatty.	Considerable reduction.	Slight reduction with silver nitrate; slight iron.	0.4	Reduction overnight.	Reduction hot and cold.	Reduction hot and cold.	Reduction hot and cold.	1.257
Price, 2193.....	Strong fatty.	Strong fatty ethereal.	Yellow brown; considerable fatty.	Little color.....	Much reduction with silver nitrate; slight iron.	3.75	Considerable reduction overnight.do.....do.....do.....	1.256
Peet Bros., 2818.	Slight.....	Slightly fruity; not disagreeable.	Yellow; slight hydrocarbon, oily.	Colorless.....	Trace of sulphate reduces with silver nitrate.	Slight.	Slight reduction hot; none cold.	No reduction hot or cold.	No reduction hot or cold.	1.2522

COMMENTS BY MANUFACTURERS.

Replies were received from all of the manufacturers whose goods were examined. The following excerpts from these letters are of interest. This investigation shows that the glycerin available on the American market is of excellent quality, the one sample which was materially defective being of foreign origin.

COLGATE & Co.

We would call attention to the fact that the directions for Fehling's test as given by the U. S. P. are not explicit enough, as it is not stated whether the mixture is to stand for six hours at ordinary temperature or on the water bath. The test is entirely uncalled for, as any C. P. glycerin should leave but a very slight residue seldom over 0.01 per cent on being allowed to burn off spontaneously, and if any sugar were present it, as well as other nonvolatile impurities, would show in the amount of residue. Silver tests, and ammoniacal silver tests, are unreliable, as it is easy to get results ranging from no coloration to a heavy mirror of silver on the same glycerin by slight variations in the method of testing. The test is no criterion for the presence of acrolein, as it is easy to work the test so as to give a heavy silver mirror with any glycerin made, although acrolein may be entirely absent. I will add that the sample of glycerin we sent you gave no appreciable reduction when we tested it with ammoniacal silver nitrate U. S. P.

The mixing of glycerin with an equal volume of concentrated sulphuric acid is another test which is apt to give very erratic results.

In reference to specific gravity it should be mentioned that the specific gravity given in the U. S. P. as corresponding to 95 per cent glycerin is not correct within 1 per cent of glycerin, but was calculated from old, inaccurate tables. Of the published tables, that of Nicol at $\frac{20^{\circ}\text{C.}}{20^{\circ}\text{C.}}$ is most accurate, being very nearly correct.

Now that the U. S. P. has become the legal standard, it is desirable that the tests should be rational in every particular, and that they should be so rigid as to exclude inferior goods, and on the other hand should require no unnecessary tests and no tests apt to give erratic results.

Comments by the authors.—The application of the designation "C. P." to the available glycerin misrepresents the facts and should therefore be discontinued.

THE HARSHAW, FULLER & GOODWIN Co.

Under date of May 18, 1907, we forwarded to you a sample of our glycerin, which represented the average run of goods we were at that time turning out. This, however, was nearly two years ago, and since that time we have been constantly endeavoring to improve our product. We have succeeded so far as sulphate is concerned. Your analysis of the sample referred to states that it showed a trace of sulphate. An analysis of our present product would not show this.

With reference to butyric acid, it seems impossible to entirely eliminate this. In operating our glycerin refinery, we must purchase our crude material from a great number of producers located in France, Italy, Spain, Germany, South America, and elsewhere. No two of them make exactly the same product. There are certain producers who make such an excellent quality of crude that it is possible for us to produce from it a refined glycerin without any objectionable features. The quantity of this material, however, is comparatively small, and while we could send you a sample

made from it, which would test as above, yet it would not fairly represent an average product.

WILLIAM F. JOBBINS, (INC.).

Definite, fixed limits of impurities should be prescribed and taste and odor tests eliminated, as two different individuals almost invariably have a widely different sense of taste or smell. One chemist will sometimes be of opinion there is a foreign taste or smell, while another can detect neither.

As the glycerin industry throughout the world has been revolutionized by our patented processes and machinery, which have gradually been adopted during the last past 15 years, and are now almost exclusively used by glycerin producers, we submit we speak as recognized authorities on the subject, and beg to suggest that the Pharmacopœia requirements be changed, as follows:

Specific gravity not less than 1.258 at 15° C. (60° F.), the specific gravity to be ascertained by means of a Westphal specific gravity balance, all materials being at the temperature of the room, the value found being reduced to the value at 15° C. by adding a product represented by $(\text{temperature} - 15) \times 0.000581$.

Carbonaceous residue, including mineral and readily carbonizable impurities, not to exceed 0.009 per cent. Test: Weigh 50 grams of glycerin in a tared platinum dish, heat cautiously until it inflames, then remove the source of heat (preferably Bunsen burner) and allow the glycerin to burn away in a place free from draft; transfer the dish to a desiccator and when cool weigh.

Ash, including chlorids, not to exceed 0.005 per cent. Test: Ignite the carbonaceous residue at a red heat till it ceases to lose weight; then transfer to a desiccator and when cold weigh.

Chlorids, not to exceed 0.001 per cent, figured as NaCl. Test: Put the ash in 100 cc distilled water, make slightly acid with HNO_3 , add two or three drops of a cold, saturated solution of neutral chromate of potassium as indicator, then run in from accurately calibrated burette one-tenth normal silver nitrate volumetric solution till tinge of permanent red color appears. The cubic centimeter of one-tenth normal silver nitrate volumetric solution used multiplied by 0.005806 for each cubic centimeter, and then by 2, giving the percentage of chlorin as sodium chlorids.

Total acid equivalent, in terms of NaOH, not to exceed 0.02 per cent. Test: Weigh 100 grams of the glycerin, add 100 cc of distilled water and a few drops of phenolphthalein solution as indicator. Run in an excess of one-tenth normal NaOH solution (3.976 grams of NaOH to 1 liter) from a burette, boil for three minutes over Bunsen burner, then titrate with tenth normal H_2SO_4 solution (4.8675 grams per liter) run in from a burette, until pink color just disappears. The NaOH solution used, less the H_2SO_4 solution used, must not exceed 5 cc to neutralize.

In addition to the foregoing tests an aqueous solution (1 cc of glycerin to 10 cc of distilled water) with 5 cc of tenth-normal silver nitrate volumetric solution, the mixture shaken and placed in a dark place for 10 minutes, may assume a slight pink or gray tinge, but must not turn red nor black, nor give a precipitate. The glycerin shall then be considered chemically pure and free from chlorids, acids, or other impurities.

These tests cover all possible impurities to be found in C. P. glycerin, and being set forth with definiteness leave no latitude for controversy between chemists, and insure a glycerin of such purity as is applicable in the use of medicines, foods, or drugs, and are requirements which no honest refiner of glycerin can possibly make objection to, and are, in fact, the tests by which the leading glycerin refiners are governed.

American glycerin is equal to any foreign glycerin. Regarding test with Fehling's solution, we have to say that same is no longer employed. If adulterated with sugar it would increase the carbonaceous residue beyond the recognized limit, so sugar adulteration is provided against by the carbonaceous residue test.

J. C. LARKIN Co.

In looking back over our tests we find one made on the batch of glycerin from which the sample forwarded you was taken. We find that this test indicates the glycerin to be very much better quality than your tests show. Of course, the matter of odor, darkness of color when mixed with sulphuric acid, etc., is largely a matter of judgment, and the tests are not specific enough to enable two independent operators to check exactly their results. For instance, what you might consider a strong odor, or a dark color, might not be so considered by our chemist, etc.

We note, however, that you state that this glycerin reduces ammoniacal silver nitrate when tested by the U. S. P. method. We never turned out a glycerin, as far as we are aware, that responded to this test. We are making tests of our glycerin continually as we produce it, and looking back over our files we can not find a single test which shows a quality as poor as your tests would indicate. We would call your attention to the fact that, as far as we can learn, the sample of the glycerin which you have tested is almost two years old. We can not tell what happened to it during the interval after it left our hands and was tested by you.

PEET BROS. MANUFACTURING Co.

It is barely possible that our C. P. glycerin contains a trace of sodium chlorid, but it is almost inconceivable that it should contain a trace of sulphate, as we use muriatic acid exclusively in its preparation, with the resultant conversion of any sulphate which might be present into chlorids.

Also notice you mention a slight trace of arsenic. We would like to ask what test was used in arriving at this conclusion?

POWERS, WEIGHTMAN, ROSENGARTEN Co.

Referring to your favor of the 10th instant, regarding the report of examination by the Department of Agriculture on our sample of glycerin, we would advise that some of our tests agree with those made by the department, but vary in others as follows:

Test 3: D. A.—Strong aromatic odor on heating at temperature of water bath. P. W. R.—Slight odor of volatile fat acids on heating at water bath temperature.

Test 4: D. A.—Unpleasant ethereal odor on warming with alcohol and sulphuric acid. P. W. R.—Pleasant ethereal odor on warming with alcohol and sulphuric acid.

Test 5: D. A.—Dark yellow color with strong odor when mixed with equal volume of sulphuric acid in the cold. P. W. R.—Dark yellow color and mild odor when mixed with equal volume of sulphuric acid without heating (the mixture becomes hot when mixed). Pale yellow and faint odor when mixture is kept cold with water.

Test 6: D. A.—Reduces ammoniacal silver nitrate U. S. P. test. P. W. R.—This test is doubtful. No reaction reported in two tests out of three.

Test 7: D. A.—Slight color with ammoniacal silver nitrate, Hager's directions. P. W. R.—No reaction. Hager's directions rather vague; there may be a reaction under some conditions of applying the test.

Test 10: D. A.—Reduces Fehling's solution in the cold on standing, no reduction on heating. P. W. R.—No reduction, either hot or cold.

Test 11: D. A.—Reduces Fehling's solution made according to Haine; sugar none. P. W. R.—Does not reduce Fehling's solution made according to Haine.

Of course the same sample was not used in both instances, which doubtless accounts for some of the differences shown above. However, both tests seem to agree that the glycerin contains the merest trace of a fat acid, which most likely is butyric.

PRICE'S PATENT CANDLE Co. (LTD.).

We may say at once that the results differ so widely from those obtained from the examination of our current make, all of which is carefully tested before issue, that we are quite at a loss to understand the divergence.

SCHERING & GLATZ.

* * * We had lengthy correspondence with Messrs. Schering in 1905 and 1907, relative to their glycerin, and they reported that their product complies with every test of the U. S. Pharmacopœia, save that for fatty acids. This test they consider extravagant and impossible to comply with, therefore labeling their product, as per specimen inclosed: "Schering's glycerin, thrice distilled, complies with every test of the U. S. Pharmacopœia, excepting the one for volatile fatty acid, which is not made by the pharmacopœia of any other country. While this test may show the presence of minute quantities of fatty acids, these are so infinitesimal that they are wholly without significance. No glycerin, so far as we know, responds to this test."

Reverting to your esteemed communication of the 10th ult., we would say that the Chemische Fabrik auf Action (vorm. E. Schering) in Berlin, beg to comment as follows on your findings relative to their glycerin:

"Slight odor on heating at temperature of water bath.—It is not stated that the odor noticed was an unpleasant one. Doubtless most products will show an odor upon warming, no matter how pure and how odorless in the cold state.

"Slight fatty ethereal odor on warming with alcohol and sulphuric acid.—Minimal traces of fatty acids are contained in every distilled glycerin. Our repeated request to send us any glycerin which is absolutely free from fatty acid, you have not been able to comply with.

"Yellow color with slight fatty odor when mixed with an equal volume of sulphuric acid in the cold.—A yellowish coloration on mixing glycerin with concentrated sulphuric acid is unavoidable and has been declared admissible by the U. S. Pharmacopœia.

"Traces of heavy metals.—It may be conceded that our glycerin contains traces of heavy metals. So long as vessels made of heavy metals are used, this will not be preventable. But the method of test of the U. S. Pharmacopœia is of such a nature that discoloration upon addition of hydrogen sulphid may also be due to the presence of organic substance, or the glycerin itself.

"Arsenic.—It has not been found possible in our analytical laboratory to demonstrate in unequivocal manner the presence of arsenic in our chemically pure glycerin. But if the finding of '0.4 part per million' is correct, the glycerin abundantly fulfils the revisions of the U. S. P. on this point.

"Reduces with ammoniacal silver nitrate, U. S. P. test and Hager's directions.—Regarding the behavior of ammoniacal silver solution to glycerin a great deal has been published, but the matter is still unclear. Inasmuch as refined glycerins, which are far less pure than distilled glycerins, do not reduce, the test is generally not considered of importance.

"Reduces with Fehling's solution.—It would be interesting to learn how this test was made. Inasmuch as Dr. Wiley's analysis showed no sugar and as we ourselves know that none is present, we do not understand the object of the test. That glycerin is a readily oxidizable body and therefore has a reducing action, must, of course, not be overlooked."

CONCLUSIONS.

It appears from this investigation that a high grade glycerin should meet the following requirements:

Its specific gravity should be about 1.250 at 25° C.

It should be neutral to litmus paper.

It should leave no ash on ignition.

It should give off but a slight odor when heated alone at the temperature of the water bath.

It should not give off an unpleasant ethereal odor nor a strong fruity odor when warmed with alcohol and sulphuric acid.

It should not develop more than a yellow color when mixed with an equal volume of sulphuric acid and no disagreeable odor should be evolved.

When treated with silver nitrate and ammonium hydroxid, according to Hager, no color, or at most only a yellow color, should develop.

It should give no reaction for sulphates, chlorids, oxalates, or metals.

It should give no reaction for sugars.

When diluted with an equal volume of water it should give no reduction with Fehling's solution.

It should not contain arsenic in excess of the limit prescribed in the Pharmacopœia.

REFERENCES.

GENERAL TESTS.

- ALLEN, A. H. Detection of glycerol. (*In his* Commercial organic analysis, 1905, Vol. II, pt. 1, p. 305.)
- BULLEHEIMER, FRIEDRICH. Ueber Kupfer-Alkali-Glycerinverbindungen. Ber. d. chem. Ges., 1898, **31** (2): 1453.
- CASPARI, CHAS. Glycerin—Satisfactory commercial conditions (abstract). Proc., Amer. Pharm. Assn., 1900, **48**: 777.
- GANE, E. H. Laboratory notes. American Druggist, 1900, **36**: 4.
- Glycerin—Examination of commercial samples (abstract). Proc., Amer. Pharm. Assn., 1900, **48**: 777.
- HENKEL, HUGO, and ROTH, A. W. Chemische und physikalische Methoden zur Analyse verdünnter rein wässriger Glycerinlösungen. Zts. angew. Chem., 1905, **18** (2): 1936.
- Chemical and physical methods for the analysis of pure and dilute aqueous solutions of glycerol. J. Chem. Soc. (Lond.) Abst., 1906, **90** (2): 129.
- JAFFÉ, B. Ueber die Vorschriften der neuen Pharmacopœe III für Glycerin. Chem. Ztg., 1890, **14** (2): 1493.
- LEWKOWITSCH, J. I. Qualitative tests. (*In his* Chemical technology and analysis of oils, fats, and waxes, 1898, p. 787.)
- REICHL, C. Tests for glycerin and also for woody fiber. J. Soc. Chem. Ind., 1883, **2**: 356.
- ROTH, A. W. See Henkel, Hugo.
- STRUVE, H. Notes on commercial glycerin. Analyst, 1900, **25**: 214.
- VAN DORSSEN, W. See Van Romburgh, Pieter.
- VAN ROMBURGH, PIETER, and VAN DORSSEN, W. Action of ammonia and amines on the formic esters of glycols and glycerol. J. Chem. Soc. (Lond.) Abst., 1906, **90** (1): 3.
- WELMANS, P. Zur Untersuchung des Glycerins. Pharm. Ztg., 1894, **39**: 774.
- Zur Prüfung des Glycerins. Pharm. Rund., 1895, **13**: 17.
- Test for glycerin (abstract). Proc., Amer. Pharm. Assn., 1895, **43**: 1068.
- WILL, H. Glycerin—The ammoniacal silver test (abstract). Proc., Amer. Pharm. Assn., 1892, **40**: 984.

ARSENIC IN GLYCERIN.

- BARTHE, L. Sur la présence de l'arsenic dans la glycérine officinale. *J. pharm. chim.*, 1902 (6), **16**: 52.
- BOUGAULT, J. De l'arsenic dans la glycérine (note). *J. pharm. chim.*, 1902 (6), **15**: 527.
- GALIMARD, J., and VERDIER, E. Note sur la présence de l'arsenic dans les glycérines "dites pures." *J. pharm. chim.*, 1906 (6), **23**: 183.
- Presence of arsenic in so-called "pure" glycerol (abstract). *J. Soc. Chem. Ind.*, 1906, **25** (1): 233.
- JAFFÉ, B. Ueber die Vorschriften der neuen Pharmacopœe III für Glycerin. *Chem. Ztg.*, 1890, **14** (2): 1493.
- Glycerin—Inefficiency of the test of the Phar. Germ. for arsenic (abstract). *Proc., Amer. Pharm. Assn.*, 1891, **39**: 570.
- LANGMUIR, A. C. The determination of arsenic in glycerin. *J. Amer. Chem. Soc.*, 1899, **21**: 133; *Analyst*, 1899, **24**: 131.
- Estimation of arsenic in glycerol. *J. Chem. Soc. (Lond.) Abst.*, 1899, **76** (2): 519.
- LEWKOWITSCH, J. I. Arsenical glycerin (abstract). *Proc., Amer. Pharm. Assn.*, 1893, **41**: 919.
- Glycerin—Conditions necessary to secure purity in its manufacture (abstract). *Proc., Amer. Pharm. Assn.*, 1891, **39**: 569.
- Qualitative tests. (*In his* Chemical technology and analysis of oils, fats, and waxes, 1898, p. 787.)
- PATCH, E. L. Arsenic in glycerin. *Merck's Report*, 1896, **5**: 403.
- Glycerin—Contamination with arsenic (abstract). *Proc., Amer. Pharm. Assn.*, 1897, **45**: 671.
- VERDIER, E. *See* Galimard, J.

IMPURITIES (OTHER THAN ARSENIC).

- BERGH, G. F. Ueber die im Glycerin vorkommenden organischen verunreinigungen. *Apoth.-Ztg.*, 1907, **22**: 741.
- COMANUCCI, EZIO. Über eine neue Reaktion der Ameisensäure. *Zts. anal. Chem.*, 1906, **45**: 535.
- DOWZARD, E. Iron in glycerin. *Chemist and Druggist*, 1903, **63**: 1061.
- Glycerin—Detection of iron (abstract). *Proc., Amer. Pharm. Assn.*, 1904, **52**: 901.
- FERRIER, C. Bestimmung der Alkalisulfide (Natriumsulfid), Hyposulfite und Sulfate im Glycerin der Seifenfabriken. *Chem. Ztg.*, 1892, **16** (2): 1840.
- HAUSSMANN, F. W. Iron in commercial glycerin. *Amer. J. Pharm.*, 1895, **67**: 84.
- HERZ, W., and KNOCH, M. Löslichkeit von Calciumhydroxyd in Glycerin-Wassergemengen. *Zts. anorg. Chem.*, 1905, **46**: 193.
- KAHN, S. K. Detection of small quantities of copper and iron in glycerin. *Amer. J. Pharm.*, 1906, **78**: 490.
- KNOCH, M. *See* Herz, W.
- LA WALL, C. H., and PURSEL, R. C. Glycerin. *Amer. J. Pharm.*, 1900, **72**: 377.
- LEWKOWITSCH, J. I. Qualitative tests. (*In his* Chemical technology and analysis of oils, fats, and waxes, 1898, p. 787.)
- SCHMITT, E. Nitrogenous impurities in glycerol and fats. *J. Chem. Soc. (Lond.) Abst.*, 1905, **88** (2): 769.
- TEGARDEN. La glycérine et ses impuretés. *J. pharm. chim.*, 1895 (6), **2**: 156.
- U. S. DISPENSATORY (Wood and Bache). Impurities and tests. 1907, p. 588.

REDUCTION OF FEHLING'S SOLUTION.

- BERTHELOT. Glycerin—Conversion into sugar (Abstract). Proc., Amer. Pharm. Assn., 1892, **40**:984.
- BERTRAND, GABRIEL. Étude biochimique de la bactérie du sorbose. Ann. chim. phys., 1904 (8), **3**:181.
- Sur le produit d'oxydation de la glycérine par la bactérie du sorbose. Compt. rend., 1898, **126** (1):842.
- Oxidation of glycerin by the bacteria of sorbose (Abstract). J. Soc. Chem. Ind., 1898, **17**:502.
- Product of the oxidation of glycerol by the sorbose bacterium. J. Chem. Soc. (Lond.) Abst., 1898, **74** (1):556.
- Sur une ancienne expérience de M. Berthelot, relative à la transformation de la glycérine en sucre par le tissu testiculaire. Bul. soc. chim. Par., 1902 (3), **27**:79.
- Über eine Beobachtung von Berthelot betreffend die Umwandlung von Glycerin in zucker durch das Hodengewebe. Chem. Centrbl., 1902, **73** (1):220.
- Transformation of glycerol into sugar by testicular tissues. J. Chem. Soc. (Lond.) Abst., 1902, **82** (2):159.
- BROWN, A. J. Action of B. Aceti on glycerol. J. Chem. Soc. (Lond.) Trans., 1887, **51**:639.
- DONATH, ED. Ueber invertirende Wirkungen des Glycerins. J. prakt. Chem., 1894, **49**:546.
- Inverting action of glycerol. J. Chem. Soc. (Lond.) Abst., 1894, **66** (1):436.
- EMMERLING, OSKAR. Neuer aus Glycerin-Buttersäure erzeugender Bacillus. Ber. d. chem. Ges., 1896, **29** (3):2726.
- A new bacillus which forms butyric acid from glycerol. J. Chem. Soc. (Lond.) Abst., 1897, **72** (2):113.
- FOX, J. J. See Frankland, P. F.
- FRANKLAND, P. F., and FOX, J. J. Fermentation of mannitol and glycerol. J. Chem. Soc. (Lond.) Abst., 1890, **58**:915.
- GRAHAM, W. R. See Pursel, R. C.
- MAYER, J. L. The reducing action of glycerin. Merck's Report, 1905, **14**:165.
- Reducing action on copper sulphate (Abstract). Proc., Amer. Pharm. Assn., 1905, **53**:788.
- PURDY, R. G. Haines's sugar test. (*In his* Practical urinalysis and urinary diagnosis, 1895, p. 103.)
- PURSEL, R. C., and GRAHAM, W. R. Glycerin. Amer. J. Pharm., 1901, **73**:556.
- Reduction of Fehling's solution on prolonged standing (Abstract). Proc., Amer. Pharm. Assn., 1902, **50**:1009.
- SEIFERT, W. Physiology and morphology of the acetic-acid bacteria. J. Chem. Soc. (Lond.) Abst., 1898, **74** (2):399.
- TRILLAT, ADRIAN, and TRILLAT, AUGUSTE. Acid glycerophosphates. J. Chem. Soc. (Lond.) Abst., 1898, **74** (1):550.
- VIGNA, A. Fermentation of glycerol with the bacteria from ammonium tartrate. J. Chem. Soc. (Lond.) Abst., 1884, **46**:170.

NOTES ON TWO IMPORTANT ALKALOIDAL REACTIONS.

By H. C. FULLER.

During the systematic analysis of a large number of pharmaceutical products it has been apparent from time to time that certain of the standard reactions employed as a means of identification of alkaloids can not be relied upon absolutely and in all circumstances. The tests in question are the Vitali color reaction given by atropin and the oxidation reaction of sulphuric acid and potassium bichromate on strychnin. When the ingredients of certain medicines were separated, and tests subsequently applied in order to establish the identity of the unknown substances, residues were found to give a purple color with alcoholic potash very characteristic of atropin, yet neither atropin nor belladonna extract had been added to the preparation, and in other instances on treating a residue with sulphuric acid and potassium bichromate a characteristic purple color was obtained, yet neither strychnin nor nux vomica was found. These facts become especially important in forensic work where, in many instances, the analyst has a comparatively small sample at his disposal, and often the proportion of alkaloidal substances is not large.

Allen ^a says in connection with Vitali's reaction:

The violet reaction is almost peculiar to atropin and its isomers. Out of some 60 alkaloids examined none others were found to give a violet coloration. Strychnin gives a red, brucin a greenish, and homatropin a yellow color when similarly treated, while Menegazzi ^b holds that strychnin acts similarly to atropin.

Beckmann ^c states that on evaporating veratrin with nitric acid a yellow residue is left which on the addition of alcoholic potash gives a violet color that quickly changes to a cherry red and gradually becomes brown.

Allen, commenting on the sulphuric-acid bichromate test, states that "colocynth resin gives a very similar reaction to strychnin, but is readily detected by agitating the acidulated solution with benzene or ether."

The similarity of the action of the alkaloids of gelsemium and of berberin has been mentioned in the literature from time to time.

In order to determine which of the drug extracts in common use yield substances responding to the reactions in question, a series of

^a Commercial organic analysis, 1907, vol. 3, pt. 2, p. 258.

^b Ber. d. chem. Ges., 1894, 27 (4):275.

^c Archiv. pharm., 1886, 224; :481.

experiments was conducted with some of the ordinary drug products employed in the manufacture of galenical preparations. It was deemed advisable to work with the drug itself and not with the purified alkaloid, as the former is generally used in the class of products under consideration. An alcoholic extract of the drug was evaporated cautiously until the alcohol had been driven off. The residue was then digested with normal sulphuric acid and filtered into a separator. To remove the basic constituents, ammonium hydroxid was added in excess and the solution shaken three times with Prolius mixture. The solvent was filtered and evaporated, and the residue dissolved in normal sulphuric acid. The solution was filtered into a separator and shaken out, first with chloroform and then with petroleum ether. Ammonia was then added in excess and the solution shaken out successively with three portions each of petroleum ether (boiling at 30° to 50° C.) and chloroform. The solvent solutions were washed with water and then filtered and evaporated. The residues thus obtained were practically free from any material other than that of an alkaloidal nature, and were virtually of the same character as those obtained in making a systematic analysis of a medicine. Portions of these residues were treated, according to the customary methods of analysis, with nitric acid and, after evaporation, with alcoholic potash; also with sulphuric acid and potassium bichromate.

In the case of the Vitali reaction, working with the portion removed by the petroleum ether, the addition of alcoholic potash to the dry residue gave a purple color in the case of extracts of belladonna, coca, nux vomica, and yohimbe. The material obtained from aconite, cinchona, colchicum, colocynth, conium, gelsemium, gentian, hydrastis, ipecac, opium, physostigma, pilocarpus, sanguinaria, and *Veratrum viride* gave no reaction of this character. The portion removed by the chloroform gave a purple color in the cases of belladonna and yohimbe, but not with nux vomica or coca. The color with nux vomica was very red. Colchicum, though the bulk of the alkaloid had been previously taken out of acid solution by chloroform, gave a residue which showed a faint purple tint, and cinchona a pale purplish pink.

In the case of sulphuric-acid bichromate reaction the petroleum ether residues from nux vomica, gelsemium, and yohimbe gave a purple color. The chloroform residues from the same drugs and from hydrastis acted similarly. Colocynth yielded a substance which developed a pinkish purple on standing, but it did not resemble the usual strychnin test. The reaction in the case of colocynth was obtained with a sample which had previously been shaken three times with chloroform in acid solution. The extract from sanguinaria gave a pale purple color visible in thin layers. The residue obtained from opium gave a slight purple color most prominent in thin layers. No

similar reactions were obtained with any of the other drugs mentioned.

These facts are, as previously stated, especially important when only small quantities of material are available, and further complications arise when mixtures are under examination. The similarity of the colors given by the coca and belladonna alkaloids is of special interest inasmuch as they are often found together. However, if cocain is present it will be at once apparent by the characteristic odor of ethyl benzoate, which is given off on the addition of the alcoholic potash, and, furthermore, the physiological effect on the tongue, together with the microscopic examination of its well-known salts, will substantiate its identity. The mydriatic effect of atropin can not be relied upon as an absolute proof of its presence in a mixture of this kind, because cocain has mydriatic properties, but atropin is much less soluble in petroleum ether than is cocain, and while two or three shakings with the solvent will usually remove the cocain and leave nothing in the coca extract giving Vitali's test to go into the chloroform solution, most of the atropin will be left in solution and when removed by the chloroform may be identified by this reaction, by its characteristic microscopic salts, and by other tests. It should be remarked that the purple color was obtained only when working with coca extract. The alkaloids cocain and tropacocain purchased on the market did not respond to this reaction, and in fact a very pure petroleum ether residue was found to give but a slight purple color.

In the case of nux vomica and belladonna the difference in the physiological properties of the alkaloids taken in conjunction with their characteristic microscopic salts would be sufficient to remove any doubt as to whether one or both of these drugs were present. In this connection it is of interest to note that pure strychnin was found to give the Vitali reaction the same as the extract from nux vomica.

If a mixture of coca, belladonna, and nux vomica is suspected, the identification of the atropin presents greater difficulties; or if one finds both cocain and strychnin in a product, it is not always an easy matter to state absolutely whether atropin is or is not present. Careful examination of the microscopic appearance of the precipitates given with the different alkaloidal reagents is necessary, together with further substantiation by the physiological action of the chloroform residue on the pupil of the eye, after it has been fully established that the cocain has previously been removed by petroleum ether.

When experimenting with a mixture of this description the atropin may be separated by obtaining a concentrated solution of the alkaloids in dilute sulphuric acid and precipitating the strychnin and cocain by platinic chlorid. Atropin is not thrown down, and by

filtering, adding ammonium hydroxid to the filtrate, and again filtering, the alkaloid may be obtained in a very pure condition, by shaking out with chloroform.

The writer was unable to confirm the reactions obtained by Beckmann with the alkaloids of *veratrum veride*.

The similarity in the reactions of yohimbin and strychnin are of interest, as the drug containing the former alkaloid has of late been exploited as a remedial agent for the same purposes for which strychnin has been used. It has been claimed to possess aphrodisiac properties, and might well be suspected in mixtures advertised for tonics and the like. When working with small quantities the two reactions of yohimbin were so much like those given by strychnin that one could not draw any conclusion as to which alkaloid was present. In the case of the oxidation reaction the play of colors was different, however, pure yohimbin giving first a purple, then a reddish shade changing to olive green, and if a large quantity was present the color was indigo blue, which soon changed to olive green. The reaction with ammonium vanadate was so nearly identical with that given by strychnin that no distinction could be drawn with any safety. With nitric acid and alcoholic potash a purple color appeared at once changing to a reddish shade, and with large quantities the purple changed to a chocolate which became black on warming.

Yohimbin forms very few salts which have any characteristic form under the microscope, while those given by strychnin are well defined and can be distinguished readily. Furthermore, yohimbin does not act the same as strychnin physiologically, neither does it possess the mydriatic properties of the belladonna alkaloids. It does not resemble the coca alkaloids further than by giving the purple color with alcoholic potash, for on evaporation of the solvent it is left as a solid mass, while the coca bases remain in a semiliquid condition for some time. It is further distinguished from cocain by not giving the ethyl benzoate test nor the characteristic crystalline picrate.

There is little danger of confusing strychnin with the principle of *colocynth* which gives the purple color with sulphuric acid and bichromate. With regard to the alkaloids of *hydrastis*, *gelsemium*, and *sanguinaria*, none of these give the Vitali reaction, and there are a number of well-defined reactions for these substances which have been fully described. (With ammonium vanadate *berberin* gives a red soon changing to plum color, and *gelsemium* a magenta changing to blue green.) In connection with the alkaloids of *gelsemium*, it might be noted that a mixture of the same with strychnin would, as far as the tests in question are concerned, give practically the same reaction as a mixture of *atropin* and strychnin, and as *gelsemium* has the property of dilating the pupil of the eye the physiological tests would not serve as final proof. Recourse must be had again to other

distinctive reactions of gelsemium and to the appearance of the precipitates under the microscope. These facts are of importance because combinations of belladonna and nux vomica and of gelsemium and nux vomica are on the market.

The purple test given by the opium alkaloids could hardly be mistaken for that given by strychnin, as the color is very lasting in the former case. Some of the free alkaloids obtained from opium were treated with sulphuric acid and bichromate, and it was found that narcein and papaverin gave a purple color, while no similar reaction was obtained with thebain, narcotin, codein, or morphin.

THE SEPARATION AND IDENTIFICATION OF SMALL QUANTITIES OF COCAIN.

By H. C. FULLER.

It is well known that the separation and positive identification of cocain is very difficult even when it is present in large quantities, and when there is only a small amount present the separation is often claimed to be practically impossible. The work here recorded, however, demonstrates that these claims are unfounded.

Contrary to the statements appearing from time to time in the literature of the subject, cocain has no characteristic color reactions on which any reliance may be placed, and if the amount present is sufficient to respond to certain reactions which have been described it could be more positively identified by its melting point and by other well-known properties; with a small quantity the color reactions are not given and in the presence of other alkaloids the tests would have little or no significance.

This paper deals entirely with the separation of small quantities of cocain, and the procedures described have been evolved after considerable experimentation with various methods recommended in the literature for the separation of alkaloids and with others as yet unpublished. The writer has been called upon to examine a number of medicinal products and medicated beverages supposed to contain cocain, and especially in the latter the amount of alkaloidal substance has been comparatively small. It has been interesting to note that many chemists have reported that no cocain was found in some of these products, even after claiming to have made a careful examination of the same, while subsequent testing proved beyond a doubt that marked quantities were present. It was clearly evident that these workers were not acquainted with the procedure for effecting a proper separation.

Cocain and the other alkaloids of the coca leaf are readily hydrolyzed on heating; consequently it is advisable to keep the solutions at room temperature during the manipulation, and if it is necessary to heat at any stage of the process the solutions or residues should be cooled again as soon as possible. If the substance under examination is a solid it should be dissolved in water, if possible, or in normal sulphuric acid: if it contains much drug material and is not readily dissolved in water an extraction with alcohol containing a small quantity of ammonium hydroxid should be resorted to, water added to the mixture, and the bulk of the alcohol subsequently evaporated. Liquid products, such as sirups, need no preliminary treatment unless they are very thick or in the form of emulsion; in the former

case they should be diluted to about the consistency of a 50 per cent sugar solution, and in the latter some method which will separate the gum and fatty material must be adopted.

Having obtained a clear solution of the substance in question the procedure is as follows:

Transfer the solution to a separator and add a slight excess of ammonium hydroxid. (If the product was originally alkaline it is best to acidify it and then add a slight excess of ammonia. If a precipitate is formed it should be separated by filtration and the filtrate used for analysis.) Shake out the solution with 50 cc of Prolius mixture (ether 4 parts, chloroform 1 part, and alcohol 1 part), and allow to stand; then collect the clear solvent in another separator and shake out the aqueous solution twice more with the Prolius mixture. Filter the combined solvent solutions through a creased paper into a beaker and evaporate the liquid over a steam bath, using a fan. Do not allow the residue to dry, but as soon as the last portions of alcohol are driven off remove the beaker from the steam. Add 25 cc of normal sulphuric acid in 10 cc portions, warm the mixture slightly and then filter into a separator after each portion of the dilute acid is added, and finally wash with a little water. Then shake out the solution five times with 15 cc portions of chloroform, preserving the chloroformic extracts in another separator. Wash the latter with 10 cc of distilled water, discard the chloroform, and add the wash water to the acid liquid which was shaken out with the chloroform. Then add 10 cc of petroleum ether (boiling at 40°-60° C.) and thoroughly shake the separator, separate the acid liquid, and discard the solvent. Add a slight excess of ammonium hydroxid, cool the mixture, and then shake out the solution with 15 cc of petroleum ether of the boiling point before specified and reserve the solvent solution in another separator. Shake twice again with the same quantity of solvent, then wash the combined petroleum ether solutions once with distilled water and filter into a small beaker, washing the separator and filter with 10 cc of petroleum ether. Evaporate the petroleum ether rapidly over a steam bath, using a fan, and if cocain was present in the original material it will be found in the residue.

By this method it is possible to obtain the cocain in a very pure condition; in fact, it will often crystallize in a few hours even though the amount present be very small. The identification tests are conducted as follows:

Dissolve the residue in petroleum ether and pour portions of the solvent into a beaker and a small evaporating dish, reserving the remainder for subsequent tests. After the solvent has evaporated dissolve the contents of the beaker in 5 cc of normal sulphuric acid, warming if necessary, and add potassium mercuric iodid test solution.

The formation of a precipitate indicates the presence of an alkaloid, but, of course, does not identify it as cocain; if no precipitate occurs further tests are unnecessary.

To identify the alkaloid treat the contents of the evaporating dish with 2 cc of concentrated nitric acid and evaporate the mixture to dryness over the steam bath. When there is no further odor of nitric acid remove the dish, cool, and add 5 to 10 drops of fifth-normal alcoholic potash solution, noting carefully the color and odor of the mixture while the dish is cool and then applying gentle heat and noting the odor again.

Minute traces of cocain will give off the odor of ethyl benzoate on treatment with nitric acid and alcoholic potash. The odor is very

marked in its character and can be readily distinguished, though until one is familiar with it a parallel test should always be run, using pure cocain.

The color reaction is also of interest and will prove valuable in detecting the presence of other alkaloids. A purple color would indicate that atropin, strychnin, or yohimbin were present, though it is well known that a residue obtained by the above method from the coca leaf will in some instances also give a purple color. Tropacocain, benzoylecgonin, and aconitin will also give the ethyl benzoate test, but the possibility of the presence of the first two can be eliminated by a subsequent microscopic test, and from the fact that the benzoylecgonin is not removed from the aqueous solution to any great extent by petroleum ether. The latter fact is also true of aconitin, but the presence of this very poisonous alkaloid would be readily apparent when performing the physiological test.

The portion of the material which had been reserved should be tested physiologically. The petroleum ether is evaporated, a part of the cool residue is placed on the tongue and rubbed gently with the finger for about one minute, when, if cocain is present, a sensation of numbness gradually develops, the tongue and often the lips which have been touched by the finger will have a smooth, ivory-like feeling, and the effect will be apparent for some time. This is another test which should be performed in conjunction with one on a known sample, unless the analyst is perfectly familiar with the sensation.

This residue may also be used for a microscopic test by removing a small portion, placing it on a microscope slide and noting, under the lens, the character of the crystals found with a drop or two of gold chlorid solution. Cocain forms a definite crystalline compound with gold chlorid, and the product obtained should be compared with that given by a solution of the pure alkaloid.

With a residue obtained originally as described, these tests will substantiate the presence of cocain even though it occur in a minute quantity, and the four reactions can be applied to very small residues, although if it is desired the first mentioned with potassium-mercuric iodid may be omitted.

Another reaction for cocain which is very characteristic when considered in conjunction with the ethyl benzoate test is obtained by transferring some of the residue to a pressure flask, adding a few crystals of salicylic acid and about 15 cc of dilute hydrochloric acid, and heating the flask, stoppered, for about an hour and a half over the steam bath. On opening the flask the odor of wintergreen will be very marked if cocain was originally present. Tropacocain does not respond to this reaction, though it might indicate the presence of cinnamyl cocain and the truxillins; all of the latter, however, are precluded if the mixture gives the ethyl benzoate test.

THE DETERMINATION OF MOLYBDIC TRIOXID.

By B. HERSTEIN.

The quantitative estimation of molybdenum and its compounds offers a number of difficulties. Of the titrimetric methods proposed for this purpose those based on the reduction with zinc and subsequent titration with permanganate solution ^a give persistently, though not consistently, too low results, while those based on iodometric methods ^b require great familiarity with the subject, scrupulous observations of empirical limitations, the concurrence of many favorable conditions, and the exclusion of all chance combinations which might interfere with the correctness of the results, which even then are not uniform. Of the gravimetric methods known, some are untrustworthy, as, for instance, precipitation as lead molybdate, while others require several repetitions of the operations to insure constant results. If a series of determinations is to be made, one must necessarily familiarize himself with the best conditions essential for the greatest degree of accuracy possible, but where molybdenum, or its compounds, is to be determined only occasionally, as is the case in most laboratories, a method is needed which, with ordinary skill and precaution, will give accurate results.

The method described in this paper is believed to meet this need. It involves the precipitation of molybdenum by means of thioacetic acid in a strongly acid solution, and the transformation of the precipitate so obtained into molybdic trioxid by mere ignition and weighing as such. Thioacetic acid under these conditions precipitates molybdenum quantitatively and within a short time, while hydrogen sulphid and similar reagents, as is well known, precipitate only partially and require several repetitions to complete the reaction. The precipitate formed by the thioacetic acid does not seem to be merely a combination of molybdenum with sulphur, as one would at first suppose, but apparently contains thioacetic acid within the molecule, since on ignition of the purified precipitate the penetrating odor of this acid is strong and unmistakable. The precipitate also seems to be less dense than the sulphid ordinarily obtained which greatly facilitates its transformation into molybdic acid when ignited.

Euler and Friedheim ^c in 1895 recommended that the molybdenum sulphid be transformed into molybdic trioxid and weighed as such. They, however, used paper filters which were incompletely ignited, and to separate the charred particles it was necessary to dissolve the

^a V. d. Pfordten. Ber. d. chem. Ges., 1882, 15: 1927.

^b Euler and Friedheim. Ber. d. chem. Ges., 1895 (2), 28: 2061; Gooch and Fairbanks. Amer. J. Sci., 1896 (4) 2: 156; and Gooch and Pulman. 1901 (4), 12: 449.

^c Loc. cit.

molybdenum compound with ammonium hydroxid, evaporate, and ignite again in order to obtain the molybdic trioxid in a pure condition. By using a Gooch crucible these complications and potential sources of error are eliminated. The procedure is as follows:

The solution containing not more than 0.5 gram (preferably between 0.2 and 0.3 gram of molybdic trioxid) is placed in a pressure flask or a thick-walled Erlenmeyer flask of about 200 cc capacity and acidified with 5 cc of concentrated hydrochloric acid. A freshly prepared aqueous solution of thioacetic acid containing 0.75 cc of the pure acid for each 0.1 gram of molybdenum trioxid is then added, the flask securely stoppered, the mixture digested on a water bath for from forty to sixty minutes,^a then cooled somewhat, filtered through a tared Gooch crucible covered with asbestos, and thoroughly washed with water containing about 2 per cent of hydrochloric acid. The use of too strong a vacuum is to be avoided. The particles which have crept up the sides of the crucible are washed down with a little alcohol, which at the same time replaces the water and facilitates the drying. The precipitate is dried at about 120° C. in the crucible, which is then set to half its depth in a close-fitting hole in a stout asbestos board and heated over a bunsen flame. The crucible is covered in such a way as to permit a little air to enter. The flame of the burner is to be kept very low at first until the thioacetic and sulphurous acids have disappeared, then it is gradually increased until the submerged part of the crucible shows dull redness and the heating is discontinued when the originally brown precipitate has assumed the yellow or slightly grayish color of molybdenum trioxid. The crucible is weighed after cooling in a desiccator. As a precaution the crucible may be reheated and reweighed.

Molybdic trioxid, as is well known, volatilizes in the open air at a bright red heat, but no loss need be apprehended if the directions given are followed. The protruding part of the crucible under these conditions remains sufficiently cool to condense any molybdic trioxid which might be vaporized. For the purpose of hastening the oxidation the cover may be removed after the volatile gases have ceased to come off, but it has been found that by allowing the oxidation to take its natural course a more uniform product is obtained.

The following figures, obtained on ammonium molybdate whose composition was carefully determined in various ways, show the availability of the method which, though not very rapid (requiring from 3 to 4 hours for a determination) has the advantage of giving reliable results:

Determinations of molybdic trioxid in known samples by proposed method.

Amount present.	Amount found.	Difference.	Amount present.	Amount found.	Difference.
<i>Gram.</i> 0.08156	<i>Gram.</i> 0.0815	<i>Gram.</i> -0.00006	<i>Gram.</i> 0.2039	<i>Gram.</i> ^b 0.2005	<i>Gram.</i> -0.0034
.2039	.2040	+ .0001	.4078	.4072	- .0006
.2039	.2038	- .0001	.4078	.4063	- .0015
.2039	.2043	+ .0004	.4078	.4082	+ .0004
.2039	.2038	- .0001			

^a Thioacetic acid dissolves in water to the extent of about 6 per cent, but such a solution deteriorates very rapidly and after standing about one week is worthless. It is, therefore, necessary to work with a freshly prepared solution only.

^b Owing to insufficient drying and the premature removal of the crucible cover some loss by decrepitation was sustained.

On account of the cost and rather unpleasant odor of thioacetic acid experiments were made substituting sodium thiosulphate for it, but although as much as 5 grams of the latter were used for 0.2 gram of molybdic trioxid and the heating under pressure was considerably prolonged the results were disappointing, the weight obtained in two instances being 0.0815 and 0.0977 gram instead of 0.2039 gram. Somewhat better, though by no means accurate, results were obtained when yellow ammonium sulphid was employed.

A METHOD FOR TESTING AMMONIUM SALTS.

By B. HERSTEIN.

While titrating acid solutions containing both formaldehyde and ammonium salts serious discrepancies in the results were noticed, and in 1909 an extended investigation of the phenomena was begun. It was soon found that formaldehyde acts upon ammonium salts in the same way as it does upon ammonium hydroxid, namely, by forming hexamethylentetramin. It was also found that in the presence of a sufficient quantity of formaldehyde the ammonium ion is liberated from the acid with which it has been combined, and the latter thus becomes titratable with a standard solution of sodium or potassium hydroxid, using phenolphthalein as indicator.

In a paper entitled, "Trennung von Amin- und Säurefunction in Lösungen von Aminsäuren mittelst Formaldehyd," Schiff^a reported the same reaction and later based thereon a method for determining formaldehyde.^b He also stated that this reaction may be utilized inversely, that is, for determining ammonium salts by means of formaldehyde, but no details are given. A. Ronchèse^c studied this reaction more carefully and recommends it as a method for determining ammonia. He uses, however, an unnecessarily large excess of formaldehyde which tends seriously to impair the results. In view of the fact that ammonium salts play a very important part in every chemical laboratory, an easy method for their quantitative determination is very desirable. The best method hitherto available was to add an excess of standard fixed alkali, heat until all the ammonia is expelled, and then titrate back the excess of alkali used by means of a standardized acid solution. This method has disadvantages, chief among which is the time required to drive off all ammonia. The following method requires a minimum amount of time and yet gives satisfactory results:

A weighed quantity, about 1 gram, of any ammonium salt is dissolved in approximately 50 cc of water, 3 or 4 cc of a perfectly neutral 40 per cent solution of formaldehyde, and a few drops of phenolphthalein are added, and titrated with a standard solution of a fixed alkali until the pink color remains permanent after the solution has been brought to boiling. The previous neutralization of formaldehyde is necessary, because it almost invariably contains some formic acid

^a Liebig's Annalen der chemie, 1901 ; 319 : 76.

^c J. chim. pharm., 1907 (6) 25 : 611.

^b Chem. Ztg., 1903, 27 (1) : 13

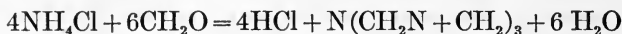
formed by spontaneous oxidation; of the many indicators tried phenolphthalein alone gave satisfactory results.

It can readily be seen that inasmuch as the formaldehyde eliminates the ammonium ion as a factor so far as the titration is concerned, the result obtained will always express the total acid present, either free or combined with ammonia. In the absence of organic acids an additional titration without formaldehyde, using methyl orange as indicator, will show whether, and to what extent, either the acid or the ammonia is in excess.

It is hardly necessary to point out that this method is applicable not only to relatively pure ammonium salts, but also to many mixtures containing such, provided they do not contain salts of metals precipitable by alkaline hydroxids. The method was tested on the following ammonium salts with satisfactory results: Ammonium chlorid, bromid, iodid, fluorid, sulphate, acetate, oxalate, citrate, thiocyanate, and molybdate.

The method was also tested by using known quantities of standardized acids, hydrochloric, sulphuric, nitric, and oxalic, neutralizing these either partly or completely, with an excess of ammonium hydroxid and then titrating as previously described in the presence of sufficient formaldehyde and a few drops of phenolphthalein with standard sodium hydroxid.

In the well-founded opinion of Schiff, formaldehyde in reacting upon ammonium salts forms hexamethylenetetramin according to the following equation:



During the reaction, especially in the case of weaker acids, much heat is evolved, and the avidity of the formaldehyde for the ammonium ion is so great that an aqueous solution of ammonium acetate, for instance (which ordinarily on heating gives off considerable ammonia) on boiling with formaldehyde in excess loses nearly all of its acetic acid, hexamethylenetetramin remaining.

CHARACTER OF SAMPLES OF BEESWAX SUBMITTED WITH BIDS.

By L. F. KEBLER and F. M. BOYLES

INTRODUCTION.

On account of the great variation in price, the uncertainty as to the quality of the samples, and the fact that if an award was made on an adulterated sample it would constitute the basis of purchase for a year, the departmental general supply committee referred 26 samples of beeswax, submitted with bids, to the Bureau of Chemistry for examination. The results given in the accompanying table clearly show that the price is not a reliable index as to quality. In fact, the sample of white beeswax for which the highest price was asked, namely, 60 cents a pound, was adulterated, not only with paraffin but with stearic acid as well. The prices quoted for yellow beeswax varied over 100 per cent, from 18 to 38 cents per pound, and for white beeswax the range is still greater, namely, 24 to 60 cents, yet some of the high-priced as well as some of the low-priced products were adulterated. Of the 26 samples examined, 53.8 per cent were adulterated. The more common adulterants were paraffin and ceresin; artificial coloring was detected in only one case. The examinations were made by the following methods:

METHODS OF ANALYSIS.

Specific gravity.—Drop the melted wax by means of a stirring rod onto a moist, cool, smooth porcelain surface in such manner as to obtain globules about one-eighth of an inch in diameter; allow to cool for from 2 to 24 hours, then place in a suitable glass cylinder of about 200 cc capacity and add a cooled mixture of alcohol and water having about the specific gravity of beeswax. If the globules sink, add water; if they rise to the surface, add alcohol. The water or alcohol is added with repeated agitation until the globules float indifferently in the mixture at the desired temperature. The specific gravity of the mixture is taken at this point with a pyknometer.

Melting temperature.—Thinly coat the bulb of a thermometer with wax and allow it to stand 24 hours. Place the bulb of the thermometer in a large test tube, holding it in place by a stopper grooved on the sides so as to allow free access of air. Immerse the test tube containing the thermometer in a beaker of water and raise the temperature very gradually (1 degree in from two to three minutes). The temperature at which a transparent drop forms on the end of the thermometer bulb is taken as the melting point.

Acid, ether, and saponification numbers.—Place 5 grams of the wax in a 200 cc Erlenmeyer flask with about 25 cc neutral alcohol and heat on the water bath until the mixture is entirely melted. Then add 1 cc of phenolphthalein solution and titrate the free acid quickly with seminormal alcoholic potash. Add 50 cc more of the

seminormal alcoholic potash and heat the mixture for at least three hours over a direct flame with a reflux condenser. The excess of potassium hydroxid is determined with seminormal hydrochloric acid. A blank with the alcoholic potash should be run.

Stearic acid.—Boil 1 gram of the wax for several minutes with 15 cc of 80 per cent alcohol, allow to cool to between 18° and 20° C., filter into a 200 cc cylinder, and dilute filtrate with water to about 200 cc. If stearic acid is present, it separates into flakes and collects at the surface. The test is sensitive to 1 per cent. If from 7 to 8 per cent are present, a thick, creamy mixture results.

Resin.—Method I: Keep at the boiling point for about one minute a mixture of 5 grams of the wax and 20 to 25 cc of nitric acid (specific gravity, 1.32 to 1.33), dilute with an equal volume of water and render slightly alkaline with ammonium hydroxid. The solution decanted from the separated wax in the absence of resin is of a yellowish color, while its presence produces a more or less intense reddish-brown coloration.

Method II: Heat 1 gram of wax for a few minutes with 25 cc of 50 per cent alcohol (alcohol of this strength will not extract stearic acid if present); cool and filter; evaporate the filtrate to dryness on a water bath and add 5 cc acetic anhydrid. Heat to boiling, cool, and then carefully allow sulphuric acid (specific gravity, 1.53), to flow into the solution. The presence of the minutest quantity of resin will develop a fine violet (fugitive) color.

Detection and estimation of paraffin.—The following method is the only one by which paraffin can be detected with certainty: Melt from 2 to 5 grams of the wax in a porcelain dish, then add an equal weight of finely powdered potassium hydroxid, continue heating for a few moments with thorough stirring. Cool and powder the hard mass, and mix the resulting powder with three times as much potash lime as wax used, then introduce this mixture into a thick-walled tube, immerse in an oil bath, and heat to about 250° C. for from three to four hours. After cooling, finally powder the tube with its contents, place the mass in a Soxhlet apparatus, and extract with petroleum ether for several hours. The petroleum ether is evaporated and the residue dried at 110° C. and weighed. By this treatment the esters are converted into alcohols, and these alcohols on heating with potash lime are in turn converted into their respective acids, while the hydrocarbons present are not affected and are extracted with petroleum ether. Pure beeswax contains naturally from 12.5 to 14 per cent of hydrocarbons, and any adulteration with paraffin or allied bodies will increase this percentage.

The Henriques^a cold saponification method.—This method was found very satisfactory. The wax is dissolved in high-boiling-point (100° to 150° C.) petroleum ether, alcoholic potassium hydroxid is added in excess, and the whole, after being warmed on the water bath, is allowed to stand twenty-four hours, when the excess of potassium hydroxid is titrated with seminormal hydrochloric acid, phenolphthalein being used as indicator.

The methods of the United States Pharmacopœia for testing beeswax are on the whole unsatisfactory. The carbonization of wax with sulphuric acid for detecting paraffin is unwieldy, disagreeable, and unreliable. Small amounts of paraffin can not be detected with any degree of certainty by this method. Again, the method for saponifying beeswax by heating on the water bath for one-half hour with alcoholic potassium hydroxid is uncertain.

^a Zts. angew. Chem., 1895, 81: 721; (Abst.) Analyst, 1896, 21: 192.

TABULATED RESULTS OF EXAMINATION.

In the following table are given the results of the tests made to determine the quality of the samples of beeswax, together with the prices quoted for the same:

Results of the examination of 26 samples of commercial beeswax submitted with bids.

Number and color.	Price quoted.	Melting point.	Specific gravity at 25° C.	Acid number.	Ether number.	Saponification number.	Ratio of acid number to ether number.	Adulterants.
Yellow:	<i>Cents.</i>	<i>° C.</i>						
1....	35.67	63.0	0.9588	20.40	69.40	89.80	3.40	Absent.
2....	34.75	63.5	.9562	18.94	72.74	91.68	3.84	Do.
3....	35.00	56.0	.9237	7.09	26.98	34.07	3.80	Paraffin.
4....	33.25	63.0	.9623	20.40	71.46	91.86	3.50	Absent.
5....	31.50	58.0	.9198	5.55	20.90	26.45	3.76	Paraffin and artificial color.
6....	30.00	55.0	.9286	28.21	18.16	46.37	.64	Paraffin and stearic acid.
7....	32.00	70.0	.9832	34.20	86.44	120.64	2.52	Resin.
8....	25.00	57.0	.9284	7.25	31.60	38.85	4.03	Paraffin.
9....	18.00	54.0	.9127	3.38	39.30	42.68	11.60	Do.
10....	34.24	63.0	.9564	17.65	73.18	90.83	4.14	Absent.
11....	34.24	63.0	.9599	18.21	74.91	93.12	4.11	Do.
12....	43.00	66.5	.9389	10.47	44.30	54.77	4.23	Ceresin.
13....	21.00	56.0	.9144	4.83	15.71	19.54	3.24	Paraffin.
14....	34.24	63.0	.9595	17.65	73.60	91.25	4.16	Absent.
15....	34.20	63.0	.9529	18.53	76.53	95.06	4.13	Do.
16....	32.00	63.5	.9609	18.37	73.30	91.67	3.99	Do.
17....	34.50	62.5	.9529	17.33	73.30	90.63	4.22	Do.
18....	28.00	52.5	.9126	3.62	11.42	15.04	3.15	Paraffin.
19....	38.00	64.0	.9483	12.48	62.04	74.52	4.97	Ceresin.
20....	24.00	52.5	.9132	4.03	12.43	16.46	3.08	Paraffin.
21....	45.00	62.5	.9583	18.00	72.74	90.74	4.04	Absent.
White:								
22....	45.00	63.0	.9603	17.83	74.52	92.35	4.17	Do.
23....	48.00	62.0	.9526	15.44	61.40	76.84	3.98	Ceresin.
24....	60.00	55.0	.9295	55.22	11.42	66.64	.21	Paraffin and stearic acid.
25....	24.00	56.0	.9124	4.43	12.43	16.86	2.80	Paraffin.
26....	46.00	63.0	.9632	20.90	73.02	93.92	3.49	Absent.





7 DAY USE

7 DAY USE RETURN TO

ED
AGRICULTURE LIBRARY
40 Giannini Hall - Tel. No. 642-4493
This publication is due on the **LAST DATE**
and **HOUR** stamped below
r

~~SEP 2 1974~~

~~SEP 17 1974~~

~~JUN 17 1975~~

APR 08 2001

received in
Natural Resources Library

OCT 12 1988

RB17-40m-8,'72
(Q4186810)4188-A-32

G
Unive.

LD 21-40m-2,'69
(J6057s10)476-A-32

General Library
University of California
Berkeley

received in
Natural Resources Library
MAR 11 1988

