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The Determination of Total Alkaloids, Sugar, and Oily Substances in Opium.

BY JITENDRA NATH RAKSHIT.

(Read at the Meeting, May 18, 1926.)

THE valuation of opium is at present mainly based on its morphine contents, the amount of which forms nearly one-third of the total active principles actually present. The quantities of important alkaloids in opium given in the tables in Pictet's *Vegetable Alkaloids* (English Translation, First Edition, p. 265) and *Allen's Commercial Organic Analysis* (Vol. VI., p. 354) might be far below those actually present. The total alkaloids in opium, according to the above-mentioned tables, are only 15.8 per cent., but the figures obtained by the following process are very nearly double this. The substances obtained as total alkaloids by the method here described may not be quite as pure as those of previous authors by whom the alkaloids have been isolated separately and determined quantitatively. The defects in the methods of isolation and determination of alkaloids for the above-mentioned tables will form the subject of a subsequent communication. Although the total alkaloids obtained by the present process are not absolutely free from impurities, the results obtained from the same sample are fairly uniform, and a manufacturer of opium alkaloids would know how much he might expect, should he try to start a process of recovery from the residual bases.

DETERMINATION OF TOTAL ALKALOIDS.—The method of determining total alkaloids consists essentially of three processes:—(1) The preparation of a solution containing all the alkaloids present in the sample; (2) precipitation of some of them by a suitable precipitant; and (3) recovery of the bases left unprecipitated in the mother liquor.

The bases which ordinarily occur in an aqueous extract of opium, did not offer much difficulty, but numerous test experiments were made to find out a

suitable process for the determination of bases left in admixture with the opium wax (Rakshit, *ANALYST*, 1918, **43**, 321) insoluble in water. Extraction by immiscible solvents was, as a rule, interfered with by the formation of the most obstinate emulsions which did not separate even after keeping for days, except in the case of ether.

Precipitation of all the alkaloids from dilute acid extracts of opium was tried with several bases, and ultimately sodium carbonate was found to be the most suitable precipitant. To determine the amount of alkaloids remaining unprecipitated by sodium carbonate, the mother liquor left after precipitation and filtration of the bases from 10 grms. of opium by the process described below was extracted three times with chloroform, 50 c.c. being used each time. The chloroform extract was dried over anhydrous potassium carbonate, filtered, evaporated, and the residue weighed. The residues thus obtained are given in Column 2 in the subjoined table.

The mother liquor, after extraction with chloroform, was evaporated to dryness on a steam bath, the residue powdered, extracted beneath a reflux condenser with chloroform, and the extract evaporated, dried, and weighed. The results are recorded in Column 3 in the following table.

The powdered residue from these successive extractions, when dissolved in dilute hydrochloric acid, gave only a slight precipitate with Mayer's reagent, and was discarded.

1	2	3
Opium samples.	Residue from chloroform extract of mother liquor. Grm.	Residue from chloroform extract of evaporated mother liquor. Grm.
Benares	0.340	1.062
Benares	0.350	1.060
Benares	0.373	1.058
Ghazipur	0.364	1.049
Ghazipur	0.341	1.044
Ghazipur	0.336	1.052
Ghazipur	0.335	1.050
Indore	0.335	1.040
Indore	0.368	1.020
Indore	0.340	1.030
Average	0.3503	1.0465

The total alkaloids in a large number of samples of opium were determined by the following method, and no practical difficulty was experienced:—Ten grms. of opium were triturated in a mortar with 50 c.c. of water for 30 minutes or more, and the liquid filtered in a Büchner funnel, with the aid of a filter pump. The residue was carefully transferred to a mortar, the filter paper being repeatedly washed into the mortar with 50 c.c. of 4 per cent. hydrochloric acid, and ground well for 15 minutes. It was again filtered with the aid of the pump, the residue transferred to a conical flask, shaken with 200 c.c. of ether, the extract

filtered with the aid of the pump, and the residue was extracted twice more with ether, 100 c.c. being used each time. The united ethereal extracts were repeatedly shaken in a separator with 50 c.c. of the above dilute acid till the acid aqueous extract ceased to give any precipitate with an excess of sodium carbonate solution, or produced merely an opalescence with Mayer's reagent; generally, three such extractions were required. The residue from the ethereal extract and all the filter papers with adhering opium residues were rubbed well in a mortar with 25 c.c. of the above dilute acid, and the mixture filtered with the aid of the filter pump, such extractions being repeated till the extract gave no precipitate with sodium carbonate on keeping for some time, and only a faint opalescence with Mayer's reagent.

All the aqueous and acid extracts were put together in a conical flask, treated with 25 grms. or more of anhydrous sodium carbonate, added only in very small quantities at a time, and set aside overnight, after which the precipitate was filtered off in the same way as the precipitate of morphine obtained in its determination in opium by the British Pharmacopoeia process, on counterpoised double filter papers, washed with water previously saturated with total alkaloids similarly obtained, dried, and weighed.

The alkaline filtrate, after removal of the alkaloidal precipitate, was evaporated to dryness on the water bath, finely powdered, transferred to a conical flask, extracted repeatedly with a boiling mixture of equal volumes of chloroform and absolute alcohol (50 c.c. being used each time, till the extracts were practically colourless, and did not give any appreciable residue on evaporation). The results thus obtained with a few typical samples are given below, expressed as percentages on the dried material.

Samples.	Morphine by B.P. process. Per Cent.	Alkaloids precipitated by sodium carbonate. Per Cent.	Alkaloids extracted by chloroform alcohol mixture. Per Cent.	Total alkaloids present in opium. Per Cent.
Chinese opium	12.0	22.5	13.0	35.5
Chinese chandu:				
Monkey brand on tin	7.5	24.5	23.5	48.0
Deer brand on tin	9.0	18.7	26.3	45.0
Plain, without mark on tin	7.0	20.4	28.2	48.6
Hill opium from Kohat	11.4	21.0	14.0	35.0
Afghan opium from N.W.F.	12.1	21.7	17.5	39.2
Persian opium from Karmausa	7.3	16.8	23.5	40.3
Ghazipur opium	9.8	24.6	15.0	39.6
Lucknow opium	10.0	26.3	14.6	40.9
Gwalior opium	9.2	23.0	12.4	35.4

DETERMINATION OF SUGAR IN OPIUM.—The presence of sugar in opium has a retarding effect on the precipitation of morphine for its determination in opium. Consequently, its determination is sometimes required. Natural opium contains a certain quantity of organic matter which reduces Fehling's solution, but its isolation by precipitation, by extraction, or by conversion into its derivatives of

osazone, semicarbazone or phenylhydrazine has not been found quite suitable. For the determination of sugar in opium, titration with Fehling's solution, after removal of the bulk of the alkaloids, seemed to be the only practicable method. After numerous trial experiments it has been found that the following method gives fairly concordant results:

Ten grms. of opium in any condition are heated for one hour or more under a reflux condenser with 100 c.c. of water, cooled, and the liquid filtered on a Büchner funnel with the aid of a filter pump. Five grms., or an excess, of anhydrous sodium carbonate are added for the precipitation of alkaloids, and the mixture similarly filtered again, and the filtrate titrated with Fehling's solution, 4 c.c. being taken for the determination of sugar before inversion, and a freshly prepared solution of potassium ferrocyanide in acetic acid being used as indicator. Fifty c.c. of the alkaline filtrate are acidified with hydrochloric acid, boiled for ten minutes, neutralised with sodium carbonate, made up to 50 c.c. again, and similarly titrated with Fehling's solution. A few typical figures are given below.

Sample.	Reducing substances expressed as sucrose.	
	Before inversion.	After inversion.
	Per Cent.	Per Cent.
Opium.		
Ghazipur	2.9	3.1
Azamgarh	3.0	3.0
Lucknow	2.8	3.0
Indore	3.1	3.3
Gwalior	2.5	2.7

DETERMINATION OF "ADDED OIL" OR WAX IN OPIUM.—Opium cultivators in Central India are in the habit of mixing oil with the opium. It is often difficult to ascertain the presence of this oil by ordinary methods of analysis, and as the cultivators are unwilling to give up the habit, it became necessary to devise suitable methods for the detection and determination of oil and wax with reasonable accuracy.

The author has shown that opium wax (ANALYST, 1918, 43, 321) has a saponification value of 114.5, whilst the saponification values of the common adulterants (sesame oil, poppy oil, or linseed oil) range from 188 to 195. Sometimes beeswax forms a most deceptive adulterant, as its saponification value is 88 to 98. Determination of the saponification value of the opium wax would, however, give an indication of admixture with an oil or wax when the adulterant was a pure substance or a mixture with a saponification value differing from that of the opium wax.

The method of determining the saponification value of opium wax has already been described (*loc. cit.*), and, in order to ascertain the amount of oil added, from the deviation from the normal saponification value, it is necessary to know the quantity of wax naturally present in opium. Wax in opium was conveniently determined by extracting 10 grms. of dry opium powder with benzene for at least eighteen hours in a Soxhlet's apparatus. The benzene extract was repeatedly shaken with 1 per cent. hydrochloric acid, 50 c.c. at a time, till the acid

aqueous extract ceased to give any precipitate with Mayer's reagent. Practically pure wax was thus obtained, and could be weighed after drying the benzene extract with anhydrous sodium carbonate and evaporation on a steam oven. When, however, there was much emulsification while the benzene extract was being shaken with the dilute acid, the emulsion was always separated from the two layers, and all such portions were united and shaken with an equal bulk of ether; the emulsion was thus broken up into two layers, the acid aqueous layer was removed, and the benzene-ether layer was twice washed with water (50 c.c. each time), dried over anhydrous sodium sulphate, and added to the original benzene extracts. A few results are given below.

Samples.	Percentage of wax in dried opium.			
	1.	2.	3.	4.
Gwalior	6.3	6.4	6.0	6.5
Indore	6.5	6.2	6.1	6.3
Ghazipur	12.3	12.0	13.4	13.0
Benares	12.8	12.8	12.6	12.9
Azamgarh	10.0	11.8	13.6	13.0
Kohat Hill	10.9	—	—	—
Afghan	9.3	—	—	—
Persian	8.6	—	—	—
Chinese	9.2	—	—	—

Added oil or wax in a sample of opium could be determined on the basis of these values by determining the saponification value, and, in the case of suspected beeswax, by determining the iodine value. But, as these methods take a long time, and as it is not possible to examine a large number of samples by such methods, a quick, rough and ready method was considered to be more useful for practical purposes.

It was found that a natural raw opium containing varying quantities of added oily substances showed a fairly sharp gradation in its change of appearance when heated on a porcelain plate over steam. And when the method was applied to the practical determination of added oil in opium results were obtained which agreed reasonably with those obtained by the other processes.

For the actual determination of added oil in unknown samples, genuine specimens of the drug were obtained from different opium-producing centres, and standard samples were prepared by adding from a burette 0.2 c.c., and its multiples, of oil of the kind usually used by the local cultivators, to each portion of a sufficient quantity of this raw opium containing 18 grms. of dry solid matter. The opium and oil were mixed thoroughly, dried on a porcelain plate heated on a steam table, finely powdered, and stored in sealed test tubes. The samples under examination were powdered, treated in the same way, put into test tubes and compared with the standard samples. The addition of oil made the powder look moist. Inferior and old opium, however, did not give equally satisfactory results.

Polarimetric Determination of Sucrose in Sweetened Condensed Milk.

By PAULA HONEGGER, Ph.D.

(*Read at the Meeting, May 18, 1926.*)

MOST of the polarimetric methods for determining cane sugar in condensed milk take less time than the gravimetric method, but are not so accurate, or, like the method of Revis and Payne (*ANALYST*, 1914, **39**, 476), are very complicated. Although this last-named method is, perhaps, one of the most precise, it is not always reliable. It will be proved later that the nature of the fresh milk was not taken into account.

For my analyses I used a Hilger saccharimeter, with electricity as the source of light. The method finally adopted was the following modification of that of Revis and Payne, and has been checked by comparison with gravimetric determinations:

MODIFICATION OF REVIS AND PAYNE'S METHOD.—Twenty-six grms. of sweetened condensed milk are weighed out and washed into a flask of 110 c.c. capacity with sufficient boiling water to bring the volume to about 90 c.c. The flask is then heated in boiling water for 3 minutes, and, after the milk solution has been cooled to 20° C., 3 c.c. of acid mercuric nitrate are added, after which the volume is made up to the 100 c.c. mark at 20° C., and an additional 4 c.c. of water at 20° C. are added. The whole is vigorously shaken for one minute, and filtered through a single folded filter (Schleicher and Schüll, 602 hard). As soon as sufficient filtrate at 20° C. for the direct reading is obtained, the polarimetric tube is filled and the reading taken at 20° C. (The time necessary from the beginning to the moment of reading was fixed at 24 to 25 minutes.)

The solution is inverted by heating it in boiling water for 7 minutes, then cooled immediately, filtered through a double folded filter (Schleicher and Schüll, No. 597), and the reading again taken at 20° C. (The time from the moment when the inversion was finished to the second reading must not exceed 5 minutes.)

The acid mercuric solution is made by dissolving pure mercury in twice its weight of nitric acid (sp. gr. 1.42), and diluting the solution to twice its volume with water.

Before Dr. A. Bakke and I finally adopted this method, we studied all the possible influences on the polarimetric results, such as the following:

(a) **THE KIND OF FILTER.**—Schleicher and Schüll, No. 602 hard, filters were found to give exceedingly clear solutions, and it was noticed that the results were lower than with the large-pored filters. Apparently the colloidal qualities of the milk have a distinct influence on the determination of sucrose in condensed milk.

(b) THE INFLUENCE OF MILK SUGAR ON THE POLARIMETRIC VALUES.—It is well known that milk sugar, owing to its muta-rotation, does not give constant values until five hours after the solution is made. Accordingly, some of the polarimetric methods for the determination of sugar in sweetened condensed milk, require the solution to be left for five hours or more before the polarimetric reading can be taken, and others recommend acceleration of the process by heating the milk solution for a few minutes over boiling water. Thus, for instance, the Revis and Payne method proposes 5 to 10 minutes without fixing definitely the exact length of the time.

To determine the minimum period necessary to stop the muta-rotation of the milk sugar, three solutions of lactose with boiling water were prepared, each containing 3 grms. of the sugar. The first solution was kept for one minute in boiling water, the second for two minutes, and the third for three minutes.

Time in boiling water.	Reading before the heating.	Reading after the heating.
1 minute	9.58	9.40
2 "	9.40	9.40
3 "	9.35	9.40

It will be seen that even after 2 minutes the milk sugar had attained a constant value before and after the heating. The reading 9.35 may therefore be accepted as correct, as it gives a reading within experimental error.

In an experiment with a solution of 3 grms. of milk sugar, in order to see if it changes further with the time, the following results were obtained:

Before the heating:		After the heating:	
First reading after 21 minutes.	Reading after 67 minutes.	First reading after 5 minutes.	Reading after 34 minutes.
9.40	9.35	9.40	9.35

The change of the milk sugar in relation to time is thus negligible.

Again, to make sure that the influence of the milk sugar would be the same in the presence of other milk constituents, experiments were made with unsweetened milk and with sterilised milk, the samples being kept in boiling water for 3 minutes. The following results show that the value for milk sugar remains constant before and after heating:

Samples of sterilised and condensed milk.	Before the heating.	After the heating.
No. 1 (unsweetened)	9.60	9.60
" 2 "	9.85	9.85
" 3 "	{ 10.27	{ 10.30
	{ 10.25	{ 10.25
" 4 (sterilised)	{ 4.05	{ 4.05
	{ 4.02	{ 4.00

(c) THE INFLUENCE OF SUCROSE ON THE POLARIMETRIC VALUES.—A solution of 26 grms. of sucrose, without acid mercuric nitrate, was prepared. One part (I.)

of this solution was polarised immediately; the other part (II.) was heated for 3 minutes in boiling water, with the following results:

	Direct reading.	Difference.
I.	99.85	+0.25
II.	100.10	

The sucrose reading had increased 0.25 after the 3 minutes in the boiling water without the addition of acid mercuric nitrate, which is not the case with sweetened condensed milk. Experiments made with sucrose solution prepared in the same way as the milk (*i.e.* by heating in the water bath for 3 minutes, and then adding acid mercuric nitrate after cooling) showed that during the 10 minutes required for the work to the moment of the polarisation a contrary effect was produced. The inversion began from the moment the acid was added. This diminution was about equal to the increase after heating in the water bath. Below are some results obtained to illustrate this point:

	Direct reading.
25 grms. pure sucrose (96.14 per cent.)	96.10 per cent.
13 " " " (50.00 per cent.)	49.98 per cent.

This proved that the principle of the method was correct.

In the earlier tests it was noticed that the reading increased notably every minute after the first 7 to 8 minutes following the inversion, and experiments showed that the preparation of the solution for the reading must not last more than 5 minutes after the inversion.

CALCULATION OF THE SUGAR.—The percentage of sugar was first calculated according to the formula of Revis and Payne (*loc. cit.*), with the introduction of our alterations:—

$$S = \frac{D - I}{R - \frac{T}{2}} (100 + C)$$

where S indicates the percentage of sucrose; R = 141.71; T = 20; and C is calculated according to the formula of the correction of the volume:

$$C = 10 - \frac{(F \times 1.11) + (P \times 0.82)}{100} \times 26.034 \text{ c.c.}$$

where F = fat, and P = protein.

The saccharimeter of Hilger being standardised for 26 grms. at 20° C. (100 $\frac{7}{4}$ per cent.), and the entire volume being 104 c.c. (100 c.c. of solution + 4 c.c. of water), the formula of volume applicable to our method and for our apparatus became

$$C = 4 - \frac{(F \times 1.11) + (P \times 0.82)}{100} \times 26 \text{ c.c.}$$

With the interpolation in the Revis and Payne formula of the value for $\frac{7}{4}C$, we had:

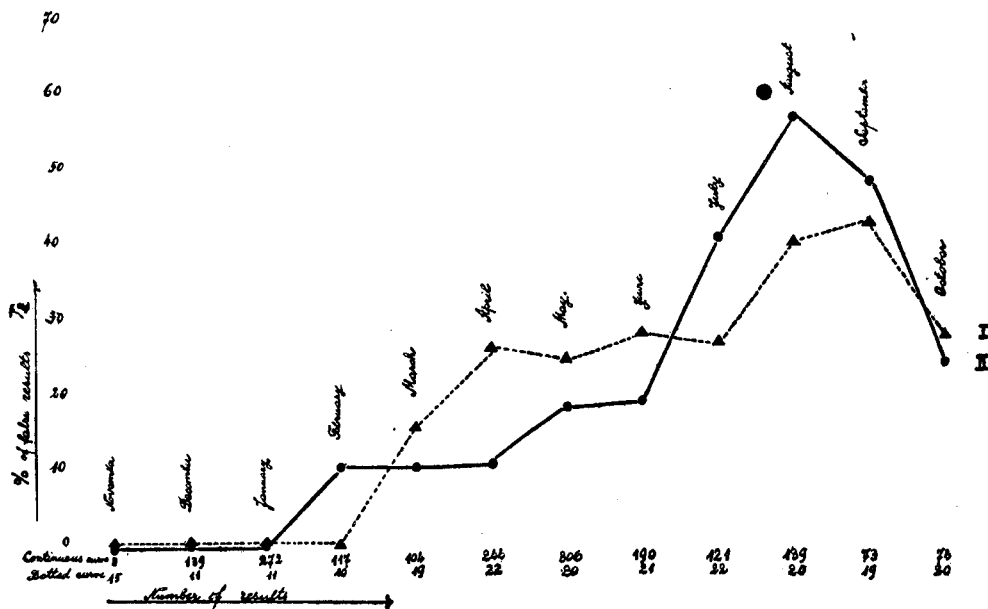
$$S = \frac{D - I}{141.71 - \frac{10}{10}} \times \left(100 + 4 - \frac{(F \times 1.11) + (P \times 0.82)}{100} \times 26 \right)$$

By the use of this formula we obtained lower results than by gravimetric analysis, but, by substituting the empirical factor $R = 141.40$ for the factor 141.71 in the formula of Revis and Payne, we finally obtained the formula:

$$S = \frac{D - I}{141.40 - 10} \times (100 + 4 - \frac{(F \times 1.11) + (P \times 0.82)}{100} \times 26).$$

In test analyses with the use of this formula the average difference between the gravimetric and polarimetric determinations was ± 0.10 per cent., and the greater deviations, which seldom occurred, did not exceed ± 0.20 per cent.

SEASONAL IRREGULARITIES.—When applying the method in our routine work, we observed that, though the method ordinarily gave results which agreed very well with those of the gravimetric method, it failed to do so at certain seasons of



the year. The polarimetric method was introduced at a season when the agreement was close (November, December). In the month of March, however, a difference between the polarimetric and gravimetric methods began to appear, and it increased in importance and frequency during the months of April to September, after which it decreased towards the winter months, until finally the results given by the two methods agreed again.

In the accompanying graph the abscissae represent the months of observation with the number of samples analysed, and the ordinates the percentage of false results.

The dotted Curve (I.) refers to the foreign milks, and the continuous Curve (II.) to the Swiss milks.

For the Curve No. I. we reckoned as correct those polarimetric results the difference of which from the gravimetric results did not exceed ± 0.20 per cent. for each result as controlled by the gravimetric result.

In the Curve II., however, where only a small part of the results was compared with the gravimetric results, and a greater part with the calculated sugar contents (a less exact figure), we have accepted as right the results which showed a difference not higher than ± 0.30 per cent.

For the Curve I. we had only about 20 results monthly; consequently one or two false results more would alter the curve considerably, whilst for the Curve II. we had in most cases more than 100 results monthly, and even over 200 in the months of January, April and May, which gives a more even curve. In spite of all this, it can be seen that the form of the two curves is similar.

After taking into consideration all possible influences which might cause these irregularities, such as, for instance, the heating and age of the milk, and the different methods of manufacturing the condensed milk, etc., we ultimately came to the conclusion that the cause was to be looked for in the variability of the volume of the elements of the condensed milk derived from the original fresh milk.

It very seldom happened that the polarimetric results were the lower; they were in most cases too high, and the difference reached as much as 0.60 per cent., and even more.

There are several causes which might influence the volume, or, more generally speaking, the nature of the lactic elements; such as *e.g.* the period of lactation, period of fresh grass, etc.

To determine this question one would have to study each constituent of the milk for a whole year, but even now one can say, with some degree of certainty, that it is mostly the fat and the colloidal substances which play an important part in this question.

To overcome this difficulty, it was found only necessary to modify the method so that quantities were made up to definite weights after dilution instead of being diluted to a known volume (previously the volume was made up to 104 c.c. after adding 3 c.c. acid mercuric nitrate, and, the average volume of 26 grms. sweetened condensed milk being 20 c.c. (sp. gr. 1.300) the volume of added water is 81 c.c.).

Therefore, this new modified method is arranged to give always 81 grms. of added water.

MODIFICATION IN WHICH VOLUME IS REPLACED BY MASS IN GRAMS.—In using the method as thus modified, the times of the various operations must be carefully observed:—Exactly 26 grms. of the sweetened condensed milk are weighed, with an accuracy of at least 10 mgrms., and then transferred, with boiling water, to a counterpoised dry 110 c.c. flask, so as to give a total volume of about 90 c.c. As

soon as the hot water is added a stop watch is started. The time for this stage is about 2 minutes. The flask is next placed in boiling water for 3 minutes, after which it is cooled under the tap, then for about $1\frac{1}{2}$ minutes in ice-water, and finally in water at 20° C. for five minutes. The time for the completion of this stage is 12 to 13 minutes.

The flask is now weighed, and any deficiency of contents from 107 grms. (26 grms. of condensed milk plus 81 grms. of water) is noted. This takes about 3 minutes. Three c.c. of the acid mercuric nitrate solution are added, and the flask shaken thoroughly, after which the volume of water at 20° C. required to make up the deficiency found before is added, and the flask again shaken vigorously for one minute, and its contents filtered through a Schleicher and Schüll No. 602 hard paper filter.

The filtrate is brought to 20° C. by cooling or warming, and the polarimeter tube is filled. The total time to the completion of this stage should be 27 to 28 minutes.

After polarising the filtrate is inverted by immersion in boiling water for 7 minutes, and is then cooled immediately in ice-water for $1\frac{1}{2}$ minutes, and filtered through a Schleicher and Schüll No. 597 paper filter, brought to 20° C., and again polarised. The total time from the beginning of inversion to polarising should be not more than 12 minutes.

CALCULATION.—The formula is as given above, but with the addition of a volume correction if the specific gravity of the condensed milk differs from the standard of 1.300.

$$S = \frac{D - I}{131.40} \times (100 + 4 - (1.11F + 0.82P) \times 0.26) \pm \text{Vol. Corr.}$$

The average value of the precipitate correction in 57 analyses of condensed milks was found to be 4.55 c.c., so that the formula can be simplified to:

$$S = \frac{D - I}{R - \frac{T}{2}} \times (100 + 4 - 4.55), \quad \text{or} \quad S = \frac{D - I}{141.30} \times 99.45.$$

A further simplification is to use a graph showing the percentage of sucrose for values of $(D - I)$.

A series of parallel determinations by the gravimetric, polarimetric (old way of preparation), and polarimetric (new way of preparation) methods, was made on 65 samples of condensed milk, the polarimetric results being calculated according to the accurate formula (*supra*).

These condensed milks were of the months of June, July, August, and September, when the differences between the gravimetric and original polarimetric method were greatest. In many instances the polarimetric method (both new and old mode of preparation), gave the same results, but there were others with

which one could not get an accurate result, except by the new way of preparation.

The following results are typical:

No.	Mode of preparation.	Sucrose, per cent.		Difference from gravimetric.	
		Polarimetric.	Gravimetric.	New method.	Old method.
1	New	41.37	41.33	+0.04	+0.04
	Old	41.37			
4	New	39.17	39.06	+0.11	+0.60
	Old	39.66			
11	New	39.08	39.08	0.00	+0.46
	Old	39.54			
33	New	40.02	40.04	-0.02	+0.54
	Old	40.58			
43	New	43.15	43.13	+0.01	+0.05
	Old	43.19			
65	New	39.74	39.61	+0.13	+0.47
	Old	40.08			

SKIMMED CONDENSED MILK.—When dealing with skimmed condensed milk with about 0.5 per cent. of fat and an average sp. gr. of 1.350, there was a far greater difference from the average figures; hence the full formula must be used for such milks. The following example gives the calculations of the sugar content in a skimmed condensed milk:

Direct reading	+55.58
Invert reading	- 2.10
Fat, per cent.	0.31
Proteins, per cent.	9.27
Sp. gr.	1.3392
Volume correction	- 0.59

$$S = \frac{55.58 + 2.10}{131.40} \times (100 + 4 - \frac{(0.31 \times 1.11) + (9.27 \times 0.82) \times 26}{100}) - 0.59.$$

$$S = 43.90 \times 101.93 - 0.59 = 44.75 - 0.59 = 44.16 \text{ per cent.}$$

The sugar content of this milk was, according to the polarimetric method 44.16 per cent., and according to the gravimetric method 44.12 per cent.

Thus, the method which has been established is accurate, easy to carry out, and applicable to all kinds of sweetened condensed milks, whether they be skimmed milks with 0.5 per cent. of fat or milks containing up to 10 per cent. of fat.

I wish to thank Dr. A. Bakke, Chief of the Laboratory, for his advice and practical help in this investigation.

CENTRAL LABORATORY,
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VEVEY.

DISCUSSION.

Mr. C. L. HINTON remarked that as the polarisation increased on standing—a fact which could be attributed to a lag in the muta-rotation of the dextrose—it might be desirable to take the reading after the lag had worked itself out. He had been doing some work with phosphotungstic acid, and thought it a more suitable precipitant than acid mercuric nitrate, in that it necessitated less H-ion concentration and gave a perfectly clear solution.

Mr. A. M. FERGUSON said that he had been using the method for a short time with some success. He pointed out that in the Fehling method the result depended on the weight of cuprous oxide obtained, a much smaller weight of milk was taken, and the volume of the resulting fat protein precipitate was negligible.

Mr. E. B. HUGHES, replying for the author, pointed out that the method under consideration was an empirical one and depended on closely following standard conditions.

The Determination of Very Small Quantities of Iron.

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(Read at the Meeting, May 18, 1926.)

THE determination of small quantities of iron can be readily carried out by the well-known colorimetric method involving the use of thiocyanates. If all proper precautions are taken, quantities of a few parts per 100,000 are determined with reasonable accuracy. If, however, the amount of iron is less than 10 parts per million several grms. of material must be used to obtain a colour which can be properly matched.

In the determination of very small quantities of iron two methods of attack may be considered: (1) To take large quantities of the substance under examination, and (2) to increase the sensitiveness of the reaction used to detect and determine the iron.

In this investigation the second method has had the greater consideration. Unless the substance under examination is very soluble, the first method necessitates either the use of a large volume of solution, or the separation of the iron from the bulk of substance in order to concentrate it into a small volume of solution. A large volume of solution has obvious disadvantages in testing for very small

quantities of iron; while the separation of the iron involves the use of reagents which may contain iron as an impurity in amount approaching or exceeding that in the material under examination. For these reasons one grm. has been considered as a desirable maximum of material to be examined when the quantity of iron present is not more than 5 parts per million.

Stokes and Cain (*J. Amer. Chem. Soc.*, 1907, **29**, 409) recommend the use of a mixture of amyl alcohol and ether in the proportion of 5:2 to dissolve the ferric thiocyanate. After the addition of the nitric acid and the thiocyanate, 5 c.c. of the alcohol-ether mixture are added, and the whole shaken and allowed to separate. The colour is concentrated in the alcohol-ether mixture instead of being diffused throughout 50 c.c., or more, of the aqueous solution. The colour is matched against a blank containing a known amount of iron. This modification has proved to be useful, small amounts of ferric thiocyanate, which cannot be determined and are difficult to detect in an aqueous solution, are readily observed and matched when concentrated in the small bulk of the alcohol-ether layer.

In the determination of very small quantities of iron more than usual care must be taken to avoid introducing iron by means of any reagents used in preparing the sample or in carrying out the test. Though a blank test is always carried out in which the same quantities of reagents are used, the introduction of iron in the blank makes it more difficult to match the colour. It is more difficult to distinguish between 0.006 and 0.007 mgrm. in the blank and test sample, respectively, than between 0.001 and 0.002 mgrm.

Every reagent used was tested for iron and purification was found necessary in almost every case.

PURIFICATION OF REAGENTS.—Considerable difficulty was experienced in obtaining the necessary reagents sufficiently free from iron for this work. The three essential reagents—nitric acid, potassium or ammonium thiocyanate, and the mixture of amyl alcohol and ether—when mixed, shaken and allowed to separate, should exhibit no colour in the alcohol-ether layer. This condition was not fulfilled when the test was carried out with the best commercially pure materials which could be obtained, and it became necessary to trace the impurity. The colour produced was typical of iron thiocyanate, the alcohol-ether layer being coloured distinctly pink. The nitric acid was suspected as the most probable source of the iron and was proved to contain a trace of iron. After purification of the nitric acid by careful distillation the colour still persisted, though to a less extent. The amyl alcohol and the ether were each distilled before mixing, but the colour was not lessened to any marked extent. As the colour still persisted, it appeared that the thiocyanate must contain iron, insufficient to show when used by adding it to a volume of 50 c.c. in a Nessler glass, but sufficient to give a definite colour when concentrated in the small alcohol-ether layer. A solution of neutral ammonium thiocyanate shaken out with a mixture of amyl alcohol and ether (5:2) yielded some colour in the alcohol-ether layer; the extraction was repeated until the alcohol-ether layer was not coloured. On mixing the test

reagents the colour was much less, but still, noticeable. Finally the solution was acidified with a few drops of nitric acid, and again extracted with the alcohol-ether mixture, when a further quantity of iron was extracted, as indicated by the development of more colour. The purified solution of thiocyanate with the recently distilled nitric acid showed only the faintest colour when shaken with the amy alcohol and ether and allowed to separate.

The following details describe the steps taken to procure the reagents sufficiently free from iron for the test:—

(1) *Nitric Acid*.—This was distilled from a glass retort shortly before it was required for use. No commercially pure acid was free from iron. The iron may have been taken up from the glass vessel in which the acid was stored. Even from selected white glass vessels the redistilled acid dissolved a little iron after some days. The acid should be colourless and free from oxides of nitrogen.

(2) *Thiocyanates*.—Iron was found in all samples of potassium and ammonium thiocyanates. To purify it a 5 per cent. solution was acidified with a few drops of nitric acid and extracted with amy alcohol and ether (5:2) before use.

(3) *Amyl Alcohol and Ether*.—These were separately redistilled and mixed at once.

The nitric acid was placed in an automatic pipette with a reservoir, the whole being of glass and in one piece, no cork or rubber being used. The other two reagents were placed in bottles fitted with automatic pipettes from which definite measured quantities could be delivered. A layer of amy alcohol and ether mixture was kept on the surface of the solution of the ammonium thiocyanate.

The blank prepared from the purified reagents showed only a very faint pink colour in the alcohol-ether layer, indicating the presence of considerably less than 0.0005 mgrm. of iron.

Water is used in all tests to make up the solution to the desired volume. With this no difficulty was experienced. The water was distilled from a tin-lined copper still, condensed by passing through a block tin condenser, and collected in a tin-lined receiver. With ordinary precautions against dust and accidental impurities it has given no trouble. In the laboratory it was kept in glass vessels.

GENERAL METHOD OF CARRYING OUT THE TEST.—The test is carried out in glass-stoppered tubes, all of the same diameter (about 1 inch), and each tube has a mark at 30 c.c. The material, being obtained in solution, is placed in the tube and water added to the 30 c.c. mark, 5 c.c. of nitric acid added, then 15 c.c. of a 5 per cent. solution of ammonium thiocyanate, and finally 5 c.c. of the alcohol-ether mixture, and the tube is shaken. A blank is prepared by mixing the same reagents in the same order, and the tube shaken. By adding known amounts of iron solution to the blank the colour can be matched.

After every care had been taken to ensure that the reagents were free from iron, no difficulty was found in determining 0.001 mgrm. of iron in 1 gm. of material. Smaller quantities can be detected.

In determining the iron in some substances some modification was found to be necessary. Details of these modifications in the case of silica and silicates, bismuth and zinc compounds are given below.

SILICA AND SILICATES.—The silica or silicate was treated with hydrofluoric acid and nitric acid, and evaporated to dryness. The residue was taken up with nitric acid, and the test carried out on this solution. It was found that the colour was of a different character from the blank prepared simply by the evaporation of the acids without silica. To overcome this difficulty some silica was used with the blank. Silica (1.5 gm.) was taken for the test, and silica (0.5 gm.) was used with the acids for the blank. Both were treated with a measured quantity (about 10 c.c.) of hydrofluoric acid and nitric acid and evaporated. The residue was taken up with nitric acid, diluted with water, and the test completed in the usual way.

With this modification there was no difficulty in matching the colours and in determining as little as 0.001 mgrm. of iron in one gm. of silica.

NOTE ON HYDROFLUORIC ACID.—The purest hydrofluoric acid obtainable contained about 0.007 mgrm. of iron in the measured quantity (about 10 c.c.) used in a determination of iron in silica. This gave so much colour that it was not possible to make determinations when the content of iron was about 0.001 to 0.003 mgrm. in one gm. of material. Distillation from a platinum still was resorted to, and the iron content of the hydrofluoric acid was halved after several distillations. It may be worth noting that it takes considerable time to remove iron from a new platinum still. Digestion in hydrochloric acid appears to be the best method. Finally the hydrofluoric acid was obtained with a negligible iron content. The hydrofluoric acid was distilled just before use. In order to avoid any chance of contamination with iron it was considered inadvisable to store it even for a day.

BISMUTH.—When bismuth oxide or nitrate, containing small amounts of iron, is dissolved in dilute nitric acid and a solution of ammonium or potassium thiocyanate is added a yellow colour is developed, and the characteristic red colour of ferric thiocyanate is not seen. Extraction of the ferric thiocyanate with a mixture of amyl alcohol and ether does not overcome this difficulty, since the alcohol-ether layer also becomes yellow.

Stokes and Cain (*loc. cit.*) use mercuric thiocyanate in their modification of the thiocyanate test with the view of preventing degradation of the colour of the ferric thiocyanate. This addition was tried, but, while the degradation of the colour was delayed, the delay was only for about 15 seconds, and this did not allow time for the accurate matching of the colour.

Experiments showed that if bismuth oxide was dissolved in hydrochloric acid, the characteristic red colour of ferric thiocyanate was obtained on the addition of a solution of a thiocyanate if any iron was present. If the iron was present in very small quantity, the solution was shaken with the amyl alcohol and ether mixture. When hydrochloric acid was substituted for nitric acid and no nitric

acid was present uniform and satisfactory results were obtained, the colour, whether in aqueous solution or in the alcohol-ether layer, being definite and as permanent as this colour is usually found to be.

NOTE ON HYDROCHLORIC ACID.—Ordinary pure hydrochloric acid was found to contain iron up to 0.04 mgrm. in 100 c.c. It was purified by distillation from a glass-stoppered flask, the joints between the flask and condenser being also of glass. No cork or rubber was used. As soon as the glass surfaces of the condenser had been freed from iron by the condensed acid, hydrochloric acid came over free from iron, and this distillate was used. The acid was kept in a stoppered bottle which had been used for hydrochloric acid for some time. After some weeks it was again tested and found free from iron.

ZINC OXIDE.—Commercial zinc oxide contains an appreciable quantity of iron, which can be readily detected in the ordinary course of analysis, if a sufficient amount of the oxide be taken.

When samples of commercial zinc oxide were tested by the ordinary method of adding the solution of ammonium thiocyanate to a solution of zinc oxide in nitric acid or hydrochloric acid, the iron, as determined by the colour produced, was evidently less than that actually present. When the process was carried out by extracting the ferric thiocyanate with amyl alcohol and ether the colour indicated a still smaller proportion of iron.

In view of the fact that iron in presence of zinc does not give the full colour with thiocyanate solution, it is interesting to note that the British Pharmacopoeia prescribes that "Zinc oxide should give no characteristic colour for iron."

Increasing the quantity of thiocyanate solution over the usual quantity does not give an appreciable increase in the colour produced; the lack of colour, therefore, cannot be attributed to the use of an insufficient quantity of thiocyanate.

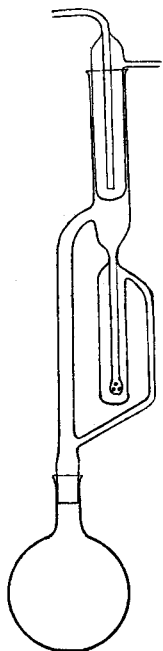
It was also found that the addition of known quantities of iron to the zinc solution did not produce so great an increase of colour as that given with the same quantity of iron free from zinc as used in a blank test. This was so whether the solutions were shaken out with amyl alcohol and ether or not.

It is, therefore, evident that the presence of a relatively large quantity of zinc interferes with the formation of the red colour of ferric thiocyanate, and that this interference is more marked when the ferric thiocyanate is concentrated in the amyl alcohol and ether layer than when the test is carried out in an aqueous solution.

It became necessary, therefore, to devise some method of separating the iron from the zinc before making the determination. Ordinary methods of precipitating the iron involving large quantities of reagents and the use of filter papers were considered impracticable when dealing with small quantities of iron.

The use of ether for the extraction of ferric chloride is well known, and a preliminary experiment carried out in a separating funnel showed that very little zinc was extracted by the ether.

An apparatus was designed which obviated the use of corks, allowed a comparatively small amount of ether to be used, and ensured that the extraction was carried out without exposure to the open air, so as to avoid contamination from dust, etc. As will be seen from the accompanying sketch, the apparatus is a modified Soxhlet extractor. The ether enters at the bottom of the extraction chamber, bubbles through the solution to be extracted and flows out at the top of the chamber back to the flask.



In order to ensure that the apparatus was free from iron which might be dissolved in the hydrochloric acid and extracted by the ether, it was first cleaned with hydrochloric acid and distilled water and then rinsed with a little alcohol and ether. Next, 5 c.c. of hydrochloric acid of about 20 per cent. strength were placed in the extraction chamber and 50 c.c. of ether in the flask. The apparatus was then warmed to distil the ether into the chamber for some hours. On repeating this extraction several times it was found, on determining the iron in the ether, that an almost constant quantity of iron was present, *viz.* 0.002 to 0.003 mgrm. This iron was finally traced to the ether, which was proved to contain about one part of iron per 20,000,000. It was found possible to get rid of this iron by careful distillation of the ether from a glass-stoppered flask having all connections of glass, but, as the quantity of iron in the ether has been found to be very constant, it was more convenient to use a carefully measured volume, and to allow for the iron in it. Specimens

of zinc oxide from two different sources were tested by:

(1) The usual method by adding thiocyanate solution to a solution of zinc oxide in nitric acid in Nessler glasses.

(2) The ferric thiocyanate was extracted by the mixture of amyl alcohol and ether, and the colour of the alcohol-ether layer matched.

(3) Zinc oxide, from 0.25 gm. to 1 gm., was dissolved in 5 c.c. of hydrochloric acid and extracted with ether in the special apparatus. The residue, after the evaporation of the ether, was taken up with nitric acid and tested in the usual way by matching the colour in Nessler glasses.

The results are given in the following table; the inaccurate results obtained, if the iron is not extracted from the zinc, are evident.

	Parts per Million.		
	Method 1.	Method 2.	Method 3.
Sample A.	about 20, colour bad, difficult to match	less than 1	30
Sample B	80	20	180-185

For quantities of iron such as have been found in these specimens there is no advantage in extracting the ferric thiocyanate with amyl alcohol and ether in the final determination, but for small quantities, *e.g.* about 10 parts per million, greater accuracy is to be obtained by the extraction and for quantities of 5 parts or less per million it is essential.

In the course of the work it was noticed that the aqueous layer in the extraction vessel sometimes increased considerably in volume, and also that a little zinc was extracted. The quantity of zinc extracted was greater in those experiments where the increase of volume of the aqueous layer had been noticed. It was found that in these experiments some alcohol was formed by the interaction of the acid and ether. This action does not take place noticeably if the strength of acid does not exceed 20 per cent. This strength of hydrochloric acid was adopted for the work.

As the presence of zinc has been shown to interfere with the formation of the colour due to ferric thiocyanate, it is obviously desirable to reduce the amount of the zinc extracted to a minimum.

As the result of a number of experiments it was found that the use of a mixture of 80 parts of ether and 20 parts of petroleum spirit (b.pt. 40°–60°C.) had less solvent action on the zinc than ether alone, but that the iron was not completely extracted. Further experiments showed that the addition of sufficient ammonium chloride to form zinc ammonium chloride facilitated the extraction of the iron, and did not increase the amount of zinc extracted.

The ammonium chloride was readily freed from all traces of iron by one crystallisation from dilute hydrochloric acid.

The following experiments with a sample of iron-free zinc oxide, with known amounts of iron added, indicate the degree of accuracy possible by this method. The final determination of the iron was done in stoppered tubes, amyl alcohol and ether (5:2) being used to extract the ferric thiocyanate, the colour being matched in the alcohol-ether layer. The mixture of ether and petroleum spirit was used in each case:

1. One grm. of iron-free zinc oxide with 5 c.c. hydrochloric acid. Iron found, none.
2. The same oxide and acid with 0.005 mgrm. iron. Iron found, 0.003 mgrm.
3. The same oxide, acid and iron with 0.7 grm. iron-free ammonium chloride. Iron found, 0.004 mgrm.

Nos. 2 and 3 were repeated, but with interchange of the extraction apparatus to ensure that the difference in the amount of iron was not due to the apparatus.

Experiments with ammonium chloride now gave 0.005 mgrm. iron. Without ammonium chloride the iron obtained was 0.003 mgrm.

For this extraction of iron from zinc solutions the zinc need not be in the form of chloride if sufficient hydrochloric acid be added. The iron in zinc sulphate may be extracted if a slight excess of hydrochloric acid be added.

These results show that in order to determine iron in zinc compounds by means of the colour produced on adding a solution of ammonium thiocyanate, the iron must be separated from the zinc as completely as possible. Ether or, better, a mixture of ether and petroleum spirit is a suitable solvent in the presence of hydrochloric acid.

The method of extracting the ferric thiocyanate with a mixture of amyl alcohol and ether and matching the colour of the alcohol-ether layer is applicable to the determination of very small quantities of iron in zinc, if the iron is separated from the zinc by the method described. The degree of accuracy obtainable is within 2 parts per million.

This work was carried out in the laboratories of the British Scientific Instrument Research Association. The authors desire to thank the Council of the Association and Sir Herbert Jackson, K.B.E., F.R.S., the Director of Research, for permission to publish the results of the investigation.

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

LIME SEED OIL AND OIL CAKE.

IN view of the fact that Messrs. Marshall and Salamon have been unable to discover any published data on lime seed oil (*cf.* ANALYST, 1926, 237), it has occurred to me that some account of the work done in this laboratory on lime seed* oil may be of general interest.

In 1922 a sample of oil expressed from the seeds was sent to the Imperial Institute, and their report was published in the *Imp. Inst. Bull.* (1922, 20, 465). It has been found here that there is no difficulty in obtaining a yield of about 70 per cent. of the oil present in the seeds, by expression after a preliminary heating of the crushed meal at 120° F. The ground seed, when extracted with ether, yielded 39.83 per cent. of oil, and, by expression, about 30 per cent. The expressed oil is a somewhat turbid greenish-yellow to light brown, liquid, which, when filtered, gives a clear brownish yellow oil.

The following values were obtained with a sample of the clarified oil:

Sp. gr. at 27°/15.5° C.	Solidif. Pt. °C.	n_D^{28}	Acid value.	Sapon. value.	Iodine value (Hübl).	Sol. in alcohol Per Cent.	Unsap. matter Per Cent.
0.9138	-3	1.4740	11.2	193.5	109.7	0.18	0.72

Lime seed oil extracted by pressure, like the oil extracted by a volatile solvent, has an unpleasant bitter taste, which can be removed, however, by treatment with alcohol, the resulting product being a bland tasteless oil which, like arachis

* The pips are termed seeds in the British West Indies.

oil, could be utilised as a salad oil. It belongs to the class of semi-drying oils, and is readily saponified, even at the ordinary temperature.

The manurial and feeding values of lime seeds from Dominica are shown by the following results, in which the first column gives the values for the untreated crushed seeds (freed from pulp by washing), and the second column the corresponding values for the press cake, on the assumption of a 30 per cent. expression of oil.

	I.	II.
	Per Cent.	Per Cent.
Nitrogen	3.43	4.9
Potash	0.48	0.68
Phosphoric anhydride ..	0.74	1.05

Analyses of seed from Antigua and Montserrat have also given percentages of nitrogen exceeding 3 per cent.

The following analytical figures indicate the value of the unextracted seeds and the press residue as cattle food:

	Moisture.	Ash.	Oil.	Crude	Crude	Carbo-
	Per Cent.	Per Cent.	Per Cent.	proteins.	fibre.	hydrates.
				Per Cent.	Per Cent.	Per Cent.
I.	10.54	2.22	39.87	21.37	14.10	11.90
II.	15.08	3.17	14.20	30.50	20.05	17.00

It will be seen that lime seed oil cake compares favourably as a feeding stuff with similar cotton seed products, being slightly lower in carbohydrates but richer in crude proteins.

Cattle eat raw and crushed lime pulp with avidity, and so do pigs. Both appear to thrive on these products, and the local milk from cattle in Dominica, which are systematically fed with them, is usually very rich, and much above the minimal limits adopted under the Food and Drugs Ordinance (*viz.* Fat, 3.0; solids-not-fat, 8.5 per cent.).

An admixture with molasses should overcome any repugnance of cattle to the slightly bitter taste of the seed meal. In feeding experiments, made for this department on a small scale, it was found that horses, mules and cattle either readily consumed the mixture or could easily be educated to do so. Pigs, however, contrary to expectation, appeared indifferent to, or were repelled by the material.

The importance of disposing profitably of this waste product of the citrus industry is obvious from the fact that in the island of Dominica alone the average lime crop is about 400,000 barrels, each barrel containing the equivalent of 32 lbs. of wet, or 3 lbs. of dry seeds. In other words, about 535 tons of dry lime seeds are produced annually as a waste product in that presidency alone.

A. E. COLLENS

(Government Chemist for the Leeward Islands).

GOVERNMENT LABORATORY FOR THE
LEEWARD ISLANDS, ANTIGUA.

THE COLORIMETRIC DETERMINATION OF IRON BY THE FERRO-CYANIDE METHOD.

SAMPLES of commercial casein, when examined for iron content by Walker's modification of the ferrocyanide method (ANALYST, 1925, 50, 279) gave low results.

On investigation, these were found to be due to the use of nitric acid for the extraction of iron from the ash.

Hydrochloric acid was substituted, 5 c.c. of concentrated acid mixed with 2 c.c. of distilled water, which gives a volume sufficient for two extractions of the ash. The acid extract was then evaporated to dryness, the residue dissolved in 3 c.c. of concentrated nitric acid, and the process continued as described by Walker, except that filtration was not resorted to under any circumstances.

The use of filter paper for eliminating turbidity of the acidified extract, when the quantity of wash water is limited, is a possible source of error through iron adsorption; the method of compensation suggested by Dovey (*ANALYST*, 1918, 43, 31) is to be preferred.

A number of determinations were carried out on various materials to ascertain the relative efficiency of the two acids, and the only instance in which the nitric acid was found to extract the total iron was that of the ash of tea.

It should be noted that in the first determination of casein the nitric acid extracted 44 parts per million of iron, and that the remainder (12 parts) was recovered by the use of hydrochloric acid.

	Ash extracted with HNO ₃ .	Ash extracted with HCl.
	Parts per million.	
Commercial casein, 1 ..	44	56
" 2 ..	7	22
" 3 ..	3	18
Dried milk (roller process) \ ..	38	76
Condensed milk ..	2	2.5
Milk chocolate ..	10	15
Cocoa ..	100	177
Coffee and chicory (ground) ..	80	120
Tea ..	116	116

W. R. MUMMERY.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE SECOND QUARTER, 1926.

THE total number of samples examined during the quarter was 1349, of which 1192 were taken under the Food and Drugs Acts.

FERTILISERS.—Eleven samples were examined for the Agricultural and Small Holdings Committee, and 7 of the vendors were cautioned. There is still a good deal of ignorance or carelessness in relation to the guarantees of the percentages of nitrogen, phosphate and potash required by the Fertilisers and Feeding Stuffs Act. In several cases no guarantees were given. A sample of kainit contained

10.1 per cent. of potash, whilst 12.4 per cent. was guaranteed. A general fertiliser containing 2.7 per cent. of nitrogen gave the amount of ammonia, but not the required percentage of nitrogen. In a garden fertiliser the percentage of phosphates was somewhat in excess of the amount guaranteed.

FOOD AND DRUGS.—Of the 1192 samples, 1161 were bought informally (35 adulterated), and 31 were bought formally (7 adulterated). Three samples of margarine were not labelled in accordance with the Act.

MILK.—Of the 658 samples analysed, 33 were adulterated. Twenty-seven of 445 samples taken from 16 different farmers were adulterated. In several cases a sample which was deficient in fat was accompanied by one or more samples containing a fair amount of fat, which suggests either carelessness in mixing the milk or that the deficiency was due to very unequal intervals of milking.

In view of the great increase in the quantity of milk brought by motor lorry, attempts were made to take samples systematically at the depots, and during the quarter 297 such samples were examined. It is more difficult, however, to follow up samples thus taken than those taken on a railway station. When milk is sampled informally at a depot the farm may have early intimation of the sampling, whereas this is very unusual when the milk is sampled at a railway station.

In one instance milk sampled at a depot contained 34 per cent. of added water, but the two following samples were of good quality, as were also samples taken at the farm. In three instances it appeared probable that the depot was not the place of delivery, and information was given to the County Authorities in whose district the farm was situated, so that they could follow up the case. There was no great difference in the samples obtained at railway stations and at the depots.

BORIC ACID IN CAKES.—Twenty-three informal samples of *sponge cake* were free from boric acid; one sample contained 13 grains per lb., but a subsequent formal sample contained none. Six informal samples of *cake* were either free from boric acid or contained only small amounts, but a sample of Genoa cake contained 6 grains, and a sample of plain cake from the same vendor, 17 grains per lb.

GROUND GINGER.—Twelve informal samples were genuine, but one sample contained about 3 per cent., and another about 2 per cent. of chalk and sand.

SEIDLITZ POWDERS.—Eleven of the 15 samples were of the correct composition and fairly uniform weights. One sample had been carelessly weighed, only 1.6 and 1.7 grms. of tartaric acid being present. Two samples were sold as Seidlitz powders, but approximated in composition to the "extra strength," one of them was marked "E.S." but this gave no indication to the purchaser that he was receiving a stronger drug.

Another contained an excess of 2.4 grms. of Rochelle salt, and also 0.8 gm. of sodium bicarbonate, and the resulting draught, instead of being practically neutral, would be alkaline. Three of the vendors were cautioned.

One sample of "Extra Strong" Seidlitz powders was of the correct composition, another was marked "Sweetened," and contained saccharin. The single sample of "Double Strength" was of correct composition.

J. F. LIVERSEGE.

METROPOLITAN BOROUGH OF STEPNEY.

ANNUAL REPORT OF THE BOROUGH ANALYST FOR 1925.

Of the 1414 samples analysed during the year, 1378 were purchased by inspectors under the Food and Drugs Acts, and comprised 886 formal and 492 informal samples.

MILK.—Twenty-four of the 825 samples examined were adulterated. In the case of one sample containing 19·4 per cent. of added water the vendor stated, at the time of purchase, that the milk was sour and was to be used for cheese-making. The milk was perfectly fresh, however, and this was mentioned on the certificate. A fine of £4 was imposed.

The vendor of another sample, showing a deficiency of 20 per cent. of fat, stated that there was a continuous sale of milk to customers while the cows were being milked. Samples of evening and morning milk taken from this cow showed 5·20 and 1·60 per cent. of fat, respectively, whilst the mixed morning milk from the rest of the herd showed 2·68 per cent. of fat. It is of interest to note that these samples were obtained from one of the cowsheds in the Borough. The cows are kept in these sheds for about 10 months, and are then disposed of.

DRUGS.—Six of the 83 samples examined were adulterated. Two (informal) samples of grey powder were deficient in mercury to the extent of 38·1 and 85·3 per cent., respectively.

Sal Volatile.—An informal sample contained 1·5 per cent. of chloroform, and was 8·2 per cent. deficient in alcohol (sp. gr. at 15° C.=0·924). The formal sample contained 2·5 per cent. of chloroform and was 10·1 per cent. deficient in alcohol (sp. gr. 0·930). The vendor was fined £5, with £4 5s. costs. It is possible that spirit of chloroform had been used instead of alcohol (90 per cent.).

CANNED FISH.—Five samples, examined for the Public Health Department, were unsatisfactory. The interior of the tins showed considerable corrosion, and all contained excessive quantities of tin, *viz.* 5·3, 2·5, 4·2, 4·0, and 4·2 grains per lb., respectively.

DOUGLAS HENVILLE.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

NON-ALCOHOLIC MEAT AND MALT WINE.

ON August 25th a confectioner was summoned at Salford for selling "Meat and Malt Wine" not of the nature, substance and quality demanded, and a Manchester drug company was summoned for aiding and abetting.

Mr. W. H. Robinson, for the Salford Health Department, said that the inspector had bought a bottle of meat and malt wine for which he had paid 4s. 6d.

The certificate of the City Analyst was to the effect that the sample contained 81·2 per cent. of water, 16·4 per cent. of total sugars, and 2·4 per cent. of other extractive matter. The "other extractive matter" contained 0·06 per cent. of phosphoric anhydride, indicating the possible presence of not more than 2 per cent. of a mixture of meat and malt extracts. This opinion was based on the fact that equal parts of meat and malt extracts contained about 3 per cent. of phosphoric anhydride. A genuine meat and malt wine should contain at least 5 per cent. of a mixture of equal parts of meat and malt extract with a wine basis. The sample was therefore deficient of 60 per cent. of the minimum amount of meat and malt extracts and was entirely deficient of wine—there was not a trace of alcohol in it.

While the prosecution did not attempt to maintain that there was a definite legal standard for meat and malt wine, the Public Analyst, said Mr. Robinson, would show authority for laying down a standard.

The inspector said that he estimated the value of the bottle and its contents purchased at less than 6d. In cross-examination, he admitted that the label on the bottle described the contents as "non-alcoholic," but he would not admit that a non-alcoholic wine was a wine at all. He would not use the words "temperance wines," used by Dr. Hancock in his report to the Ministry of Health.

Mr. H. H. Bagnall, the City Analyst, agreed that "wine" was the fermented juice of the grape, and said that the sample was merely a flavoured cordial. In cross-examination, he agreed that there was no legal standard for meat and malt wine.

Mr. G. D. Elsdon, the Lancashire County Analyst, gave evidence in support of Mr. Bagnall's statements.

Dr. Ramsbottom, Assistant Medical Officer for Salford, said that a wine was not a wine unless it contained alcohol. The food and tonic value of the sample was practically negligible.

Mr. Wingate Saul, K.C., for the defence, said that the defendants were charged with selling to the prejudice of the customer, because the label described the article as "an extract of meat and malt wine." It was urged that because the liquid contained no alcohol it could not properly be described as a wine. This, he submitted, was quite a wrong attitude for the prosecution to take, for it had no foundation. The label made it quite clear that the person buying the contents of that bottle was buying something that was non-alcoholic. There was the word "wine" and the word "non-alcoholic" on the bottle; in other words, they had the exact words used by the Minister of Health in his Preservatives Order; they were the words used throughout by Dr. Hancock in his report, and also by the Government Chemist, who gave tables of non-alcoholic wines.

Lastly, Mr. Saul submitted that the prosecution had not established their case, as there was no legal standard for meat and malt wine, as the prosecution had admitted. In the case of *Davidson v. Macleod* it was held that, although a cream was of an inferior type, it was still cream; but there was no standard for cream, neither was there a standard for meat and malt wine.

The Stipendiary Magistrate (Mr. P. W. Atkin) said that, on the legal points raised by Mr. Saul, the summons would be dismissed, but he was sorry that people should be imposed upon in this way.

CHICKEN AND HAM ROLL.

On September 1, a tradesman was summoned at Salford for selling a chicken and ham roll which was not of the nature, substance and quality demanded.

The certificate of the City Analyst, Mr. H. H. Bagnall, stated that the sample contained: Beef protein, 8.5; beef fat, 13.3; starch and crude cellulose, 13.3; mineral matter, 2.2; and water, 62.7 per cent. The "mineral matter" included 0.3 per cent. of boron preservative, and the analysis corresponded approximately with the composition: Beef, 42; starchy filler, 26; and excess water, 32 per cent. The Analyst added: "It is not a chicken and ham roll; the meat contained in it consists of beef."

A solicitor representing the manufacturers pleaded guilty to a technical offence, and said that there was no chicken in the roll, which was made of beef. The description was a trade term. "Savoury ducks" were often heard of, but they did not contain duck. He submitted that no one could possibly be deceived.

The defendant, in cross-examination, said that he had followed other traders in not calling the product "beef roll."

A fine of £10, with two guineas costs was imposed.

Another tradesman was summoned on the same occasion for having sold chicken roll which contained no chicken.

The City Analyst's certificate showed that the sample contained:—Pork protein, 16.1; pork fat, 15.8; starch and crude cellulose, 11.7; mineral matter, 3.1; and water, 53.3 per cent. This would correspond approximately to: Pork, 75; and starch filler, 25 per cent. In this case the article had been supplied by a wholesale firm who had given notice that they relied upon a warranty from the manufacturers; they were accordingly dismissed from the case.

The defendant stated that the goods were invoiced to him as chicken roll; the tins were also marked chicken roll, and he sold it for what it was sold to him.

The inspector said that he had first bought an informal sample, and had subsequently seen a member of the manufacturing firm. Five weeks later the article was still being sold as chicken roll in the defendant's shop, and so a formal sample was bought. The following day he had received a letter from the manufacturers enclosing a specimen of a label they had sent out. This read, "Delicious roll. Chicken and ham flavoured," and witness would not have taken exception to it, but he told the manufacturers that he could not possibly accept it then.

The Stipendiary Magistrate ruled that, as the manufacturers had sold to the intermediate wholesale firm, they could not be held to have aided and abetted the defendant. The summons against them would therefore be dismissed, and the defendant would be fined 5s. The Magistrate added that this amount did not indicate the seriousness of the case. He regarded it as a fraud and would have convicted the manufacturers if he could.

ADULTERATION AND MISBRANDING OF ICE CREAM.

U.S.A. *v.* ARCTIC DAIRY PRODUCTS CO.*

ON April 25, 1925, the United States Attorney for the W. District of Missouri, acting upon a report by the Secretary of Agriculture, filed in the District Court of the United States an information against the defendants, alleging shipment, in violation of the Food and Drugs Acts, in two consignments, of quantities of ice cream which was adulterated and misbranded.

Adulteration was alleged for the reason that a substance, to wit, coconut oil had been mixed and packed therewith so as to lower and reduce and injuriously affect its quality and strength, and had been substituted in part for ice cream, which the article purported to be. Adulteration was alleged for the further reason that a valuable constituent of the article, to wit, milk fat, had been in part abstracted.

Misbranding was alleged for the reason that the article was a product composed in part of coconut oil, prepared in imitation of ice cream, and was offered for sale and sold under the distinctive name of another article, to wit, ice cream.

On November 9, 1925, a plea of guilty to the information was entered on behalf of the defendant company, and the Court imposed a fine of \$40.

* U.S. Department of Agriculture, Bureau of Chemistry. Supplement 212. June, 1926. No. 14083.

Report of the Government Chemist upon the Work of the Government Laboratory.

FOR THE YEAR ENDING MARCH 31ST 1926.*

THE Government Laboratory carried out the chemical work for the same departments as in the previous year (*ANALYST*, 1925, 50, 504), except that the Office of Woods and Forests is now the Forestry Commission. The total number of samples examined was 445,606, a decrease of 2500 on those of the previous year; 10,152 fewer wine samples and 18,631 fewer tea samples are recorded, but 4755 more offal tobaccos and 2590 more export tobacco and snuffs, and a large number of imported beer, cocoa, imported spirits, etc., were examined. The new duties on silk and artificial silk necessitated the examination of over 12,000 samples, and work in connection with the Safeguarding of Industries Act nearly 10,000 samples.

MINISTRY OF AGRICULTURE AND FISHERIES.—*Butter*.—Six out of 855 samples, and also 8 out of 353 margarine samples, contained more than 16 per cent. of water.

Cheese.—The proportion of fat on dry matter varied from 19 to 68·2 per cent., and 57 per cent. of the samples are regarded as prepared from whole milk, 21 from milk containing three-quarters to the whole of its fat, 4 from milk with half to three-quarters, and the remainder from milk with one-third to one-half the fat. The "cheese" material of an imported cheese biscuit consisted of about one-third cheese and two-thirds milk powder and coconut fat.

Cream.—Three out of 29 samples of preserved cream were at fault over labels, and 4 contained sucrate of lime as a thickening substance, whilst the fat content varied from 45 to 59 per cent. With the exception of one sample containing 50 per cent. of fat, the 61 unpreserved creams contained 20 to 30 per cent. fat.

Condensed Milk.—A large decrease in samples contravening the regulations is reported: 19 are reported against, of which 3 contained less than the minimum percentage of fat, and one was deficient in milk solids.

Sheep Dips.—Twenty-two samples out of 101 were reported as defective.

FERTILISERS AND FEEDING STUFFS ACT.—Of 8 samples of fertilisers and 20 of feeding stuffs, 3 of basic slag were deficient in citric-soluble phosphates; more than half the guaranteed quantity of lime in a proprietary fertiliser was derived from the phosphate present; five samples of barley meal contained from 6 to 30 per cent. of tapioca meal with wheat offals up to 15 per cent., or rice husks; 2 samples of barley meal contained 35 per cent. of wheat offals; 2 samples of sharps contained rice husks, and 5 samples 15 to 50 per cent. of tapioca meal; a sample of meat meal had 25 per cent. of cereal matter, and one of Sussex ground oats 30 per cent. of ground barley. Convictions were obtained in the last case, and for barley meal containing tapioca. There was only 1 case of disagreement with the previously obtained results of the agricultural analyst.

MERCHANDISE MARKS ACT.—Of 34 samples of barley meal and of offal obtained as a bye-product in the preparation of pearl barley, 6 contained appreciable quantities of the more husky barley offal; 2 consisted entirely of it; 7 contained 5 to 15 per cent. of oat husk; 2 contained 25 to 30 per cent. of ground oats; 1 contained 30 per cent. of tapioca and 15 per cent. of wheat offal, and one 15 per cent. of tapioca and 15 per cent. of palm kernel meal. A sample sold as rice husk meal contained 60 per cent. of added mineral matter.

* Obtainable at Adastral House, Kingsway, W.C.2. Price 1s. 6d. net.

AIR MINISTRY.—In addition to 767 samples examined, an investigation was made of the determination of helium in natural gas.

CUSTOMS AND EXCISE.—*Beer and Brewing Materials.*—In all, 55,527 samples were examined, an increase of 1129 on the previous year. Of these, 164 were of malt, corn, brewing sugars and spent grain, and 231 were yeast foods and miscellaneous substances; 7332 samples were examined as a check on assessment of beer duty; 1988 were sour and unsaleable beers; of 3908 samples of beer as retailed, 196 showed evidence of dilution. In 1 sample out of 7 of non-alcoholic beer for exemption from duty, the proof spirit exceeded 2 per cent., and of 48 other such samples, 5 contained from 2 to 5 per cent. of proof spirit. Of 1365 samples of beer and brewing materials tested for arsenic, 94 contained it in slight excess of the limit (1/100th of a grain arsenious oxide per lb. or gal.).

Cocoa and Chocolate.—Analyses of 13,100 samples were made for duty valuations, and 2730 chocolate confectionery samples contained spirit.

Silk.—In connection with duty 12,237 samples were examined, 10,313 of which were from imports.

Duty-free Spirits.—Of exported spirituous preparations, 17,327 were examined, and of imported 13,106.

Sugar, Glucose and Saccharin.—There are fixed rates of duty for many of the sugar-containing preparations, but, in addition, such substances as egg yolk, glue, soap, pills, printers' paper, etc., have to be specially examined, and the total number of sugars and such articles tested in the year was 59,094; glucose was determined in 1909 samples, and saccharin searched for in 349 samples, whilst 1590 samples were examined in connection with the subsidy on home-grown beet sugar.

Tea.—Out of a total of 39,391 samples 524 were reported against.

Tobacco.—Moisture (limited to 32 per cent.) was determined in 9840 samples of manufactured tobacco for home consumption, and oil (limited to 4 per cent.) in 1737 samples. Of tobaccos for export, 2833 more were examined than in the previous year, and of offal samples, 29,016 tobacco stalks samples were examined for drawback, 8477 for uniformity of condition, and 6993 offal snuffs, shorts and smalls for condition, together with 703 miscellaneous samples.

HOME OFFICE.—Out of 346 samples examined one was a wall paper containing 0.007 grain of arsenic per sq. yard, and one a vermin killer containing strychnine.

BOARD OF TRADE.—The quantity of lime and lemon juice approved under the Merchandise Shipping Act for foreign-going ships was 27,392 gals.; and one sample out of 94 of fortified juice was rejected. Crystallisation of accumulated sodium salts was found to have occurred in pipes where a boiler explosion had taken place at a point where overheating was alleged.

TREASURY.—Some inked impressions were examined for permanency for record purposes, and recovery of radium from disused luminous compass dials, gunsights, etc., was continued.

CORPORATION OF TRINITY HOUSE.—A specimen of defective cable link was analysed, and some deposits from oil vaporisers were examined for lead.

SALE OF FOOD AND DRUGS ACT.—In proceedings under this Act 34 milk, 4 butter, 2 sponge cake, 1 jam, and 1 lemon cheese samples were examined, and in 37 cases the results were in agreement with those put forward by the prosecution. Of the six cases of disagreement, one sample of milk alleged to contain added

colouring matter did not afford evidence of its presence in the decomposed sample; another sample alleged to be deficient in fat contained 6.43 per cent. of fat; and a third sample alleged to be deficient in fat and non-fatty solids was found to be deficient in fat, but to contain 8.55 per cent. of non-fatty solids. Two samples of butter, alleged to contain excess of water, contained 14.9 per cent. and 15.5 per cent., respectively, and two samples of butter alleged to contain foreign fat did not afford evidence of the presence of foreign fat.

D. G. H.

Dominion of Canada.

REPORT OF THE DOMINION CHEMIST FOR THE YEAR ENDING MARCH 31ST, 1925.

THE report of Dr. F. T. Shutt, the Dominion Chemist, states that, during the year 7872 samples were examined for various Government Departments. These included 201 soils, 89 fertilisers, 4292 feeding stuffs, 166 waters, 2502 samples from the Meat and Canned Foods Division, and 632 miscellaneous samples.

SOILS.—Many of the samples were submitted by farmers for information as to liming, special deficiencies, etc. Investigational work on Canadian soils has also been continued, and details are given in the Report of the physical and chemical characteristics of Prince Edward Island and British Columbian soils.

WORK ON FERTILISERS.—Ten formulae for fertilisers for potatoes have been devised, and tested upon potato crops, and are supplied to farmers to suit the requirements of the individual soils. Other experimental work has been done to determine the influence of manuring and crop rotation on potato yields.

Malagash Salt, mined in Cumberland County, N.S., consists essentially of common salt, but contains small and varying amounts of potash, seldom exceeding 1 per cent. Practical tests with this salt as a fertiliser have shown that the results are little different from what might be anticipated from a dressing of common salt.

CORN (MAIZE): RELATION OF PROTEIN CONTENT TO SPECIFIC GRAVITY.—The data obtained with high and low protein corn do not support the contention that there is any direct relationship between the specific gravity as determined by the potassium carbonate method and the protein content. The work also indicates that specific gravity cannot be relied upon for the selection of kernels as to protein content—high or low; further that the protein content of the parent does not determine the protein of the progeny; evidently, as has been shown with wheat, the protein content may be profoundly influenced by the conditions of environment.

COUMARIN CONTENT AND NUTRITIVE VALUE OF SWEET CLOVER.—It is generally considered that the young crop of sweet clover (*Melilotus alba* and *officinalis*) contains less coumarin than the more mature herbage, and is therefore less bitter and more palatable to stock. Cured as hay, it is stated to be less bitter, owing to the volatilisation of part of the coumarin in drying. The long series of analyses given in the Report show that there is a slight tendency towards a higher coumarin content in the leaves of the second cutting, this trend being more marked for the stalks than for the leaves. There is a correlation between protein and fibre, high protein being associated with low fibre, both in the leaf and stalk. The data collected have not shown that the coumarin content is an inherited transmitted quality.

CONDENSED AND EVAPORATED MILKS.—Of the 1404 samples examined, 62 of the condensed milk were found to have “sugar down,” *i.e.* a deposit of milk sugar at the bottom of the can. One can of evaporated milk had undergone gaseous fermentation. The percentage of condensed milks under weight was rather high (32 per cent.).

CANNED AND PRESERVED FRUITS.—Under this heading are included jams and marmalades (home-made and imported). Seven of the 236 samples examined contained preservatives (benzoate in 6, salicylic acid in 1); two samples contained small amounts of formic acid. Thirty samples of jam were examined for added fruit juice, and 4 were considered to contain it in excess of the quantity allowed by the regulations. Apple pulp was detected in 6 samples of jam.

SAUSAGES AND PRESERVED MEATS.—All the eleven samples examined were free from benzoates or salicylates; 6 contained coal tar colours in the casings. Seven samples of lunch tongue were badly “blackened” on the surface. The discoloration was found to be due to iron sulphide. The agar-agar used in preparing the tongue contained more than the usual quantity of iron, and it was thought that this iron might have combined with the sulphur in the meat proteins.

ESTIMATION OF DEGREE OF RIPENESS OF FRUITS FROM DETERMINATIONS OF THEIR SPECIFIC GRAVITIES.—At the request of the Fruit Commissioner, Department of Agriculture, an investigation was carried out to ascertain if it is possible to estimate the degree of ripeness of fruits—plums, peaches and grapes—from determinations of specific gravity.

Eighty samples were received, covering ripening periods of from two to five weeks. It was found that for plums and grapes there was a gradual rise in specific gravity with ripening. In the case of peaches, there was found to be a gradual fall in specific gravity with ripening. The correlation of specific gravity and ripeness appeared to be more uniform for peaches and grapes than for plums.

CORRELATION BETWEEN SPECIFIC GRAVITY, TOTAL SOLIDS AND STARCH CONTENT OF POTATOES.—Requests have frequently been made for information as to the value of specific gravity determinations for indicating the starch content of potatoes. During the past year some preliminary work was carried out to see if any correlation could be found between specific gravity, total solids and starch content. Fifteen samples of “Irish Cobbler” and ten samples of “Dakota” potatoes were analysed, and the results show a close correlation between specific gravity, total solids and starch content of the fresh potatoes.

INFLUENCE OF FEEDING WITH COD LIVER OIL ON THE DEPOSITION OF LIME COMPOUNDS IN THE SHELL OF HENS' EGGS.—Owing to the part that some factor present in cod liver oil has been found to play in the metabolism of lime, it was thought that the feeding of laying hens with cod liver oil might have some influence in causing the deposition of lime compounds in the egg-shell. In co-operation with the Division of Poultry Husbandry an investigation was carried out with this end in view. Three hundred and twenty-five eggs were examined. The results of this enquiry gave no evidence in support of the view that feeding with cod liver oil tends to a heavier deposition of lime compounds in the shell.

THE NITROGEN COMPOUNDS IN RAIN AND SNOW.—The study of the character and amount of the nitrogen compounds in rain and snow has formed the subject of an enquiry by the Division of Chemistry of the Dominion Experimental Farm system during the past seventeen years. This investigation, which has determined the quantities of the several nitrogen compounds contributed, per acre, per annum to the soil by the rainfall and snowfall in the district of Ottawa, has now been brought to a close, and the results obtained are here given in summarised form.

During this period (1907-1924) every fall of rain and snow which yielded from the catchment area a sufficiency for the work, has been analysed, the determinations comprising nitrogen present as free ammonia, as albuminoid ammonia, and as nitrates and nitrites.

From the agricultural point of view this enquiry has been of very considerable interest in showing that the rain and snow supplied annually per acre, nitrogen in available forms equivalent approximately, to an application per acre, of 44 lbs. of commercial nitrate of soda.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Determination of Moisture in Meat Extract. C. Dedlow and D. T. Smith. (*Ind. Eng. Chem.*, 1926, 18, 858-860.)—The usual methods of determining water in meat extract yield results which are from 2 to 6 per cent. too high; this excess is due to decomposition of the extract at the high temperatures employed. A vacuum-distillation method in the presence of xylene is, therefore, recommended. A weighed quantity of the extract is placed in a flask with about three times its weight of xylene, and the mixture is distilled for two hours under 30 mm. pressure, the temperature required being about 50° C. The exit tube of the flask is attached to the side of a tapered measuring tube, the upper end of which is connected with a reflux condenser. Iced brine is passed through the jacket of the condenser during the distillation and the condensed water collected in the tube is measured at the end of the operation. It is proved, by means of calcium chloride tubes and sulphuric acid tubes attached to the top of the condenser, that there is no loss due to the escape of water or ammonia.

W. P. S.

Determination of Glucose in the Presence of Phosphate Buffers. M. B. Visscher. (*J. Biol. Chem.*, 1926, 69, 1-2.)—During the course of an enzyme study it was found that the copper equivalent of glucose in different buffer mixtures varied considerably; hence a series of experiments was made to determine the amount of cupric salt reduced by a standard amount of glucose in the presence of different proportions of di-acid and di-basic phosphates. The copper reduced was determined by the iodimetric method of Shaffer and Hartmann (*J. Biol. Chem.*, 1921, 45, 365) by thiosulphate titration of the excess of iodine used to re-oxidise the copper. A table shows the results. The larger quantities of potassium di-acid phosphate interfered with the reduction of copper by glucose. There is a 20 per cent. difference between the reducing power of glucose in the presence of the smallest and the largest amount of acid phosphate used in the experiments; this makes a 20 per cent. error. Therefore the presence of potassium acid phosphate in glucose solutions lowers the reducing power of the glucose for copper, and this fact must be taken into account whenever the sugar content of buffered solutions is determined.

P. H. P.

Oxidation of Methylated Glucoses. H. Sobotka. (*J. Biol. Chem.*, 1926, 69, 267-275.)—In order to characterise the possible oxidation products of sugars, a systematic comparison of their degree of oxidation must take into account two factors; (a) the virtual maximum of hydroxyl groups (ortho forms); (b) the scission of the C-C linkages by H-OH, introducing hydroxyl groups without oxidation. The amount of hydroxyl groups divided by the amount of C atoms, as listed below, serves for the desired comparison of molecules with chains of different lengths.

OXIDATION PRODUCTS OF SUGAR IN THE ORDER OF THEIR DEGREE OF OXIDATION.

Substance.	OH C
Carbohydrates, lactic acid, glyceric aldehyde, methyl glyoxal, acetic acid, formaldehyde	2
Hexonic acids	$2\frac{1}{6}$
Pentonic acids	$2\frac{1}{5}$
Tetronic acids; $\text{CH}_3\text{.CHOH.CO.COOH}$	$2\frac{1}{4}$
Glyceric, pyruvic, hexuronic, ketohexonic acids	$2\frac{1}{3}$
Penturonic acids	$2\frac{1}{5}$
Glycolic, saccharic, tetruronic acids	$2\frac{2}{5}$
CHO.CHOH.COOH ; $\text{CH}_2\text{OH.CO.COOH}$	$2\frac{3}{5}$
Trioxylglutaric acid	$2\frac{3}{5}$
Tartaric, oxalyl-acetic acid	$2\frac{3}{4}$
Tartronic, glyoxalic, formic acid	3
Dioxytartaric acid	$3\frac{1}{4}$
Mesoxalic acid	$3\frac{1}{5}$
Oxalic acid	$3\frac{1}{2}$
Carbonic acid	4

Some of these substances have actually been prepared by the oxidation of sugar. A comparison is given of oxidising reagents. One class is important in chemical sugar determination, viz., the alkaline solutions of certain heavy metal salts. The numerous copper and mercury methods differ from one another in the concentration of the dissolved salts and in the procedure of heating and boiling. Individual constant factors have been given which allow of the evaluation of the sugar content from the amount of metal salt reduced. These factors might be called "pseudostoichiometrical," and the following table gives a survey of the range of such factors, calculated as oxygen equivalents (1 equivalent = $\frac{1}{2}$ atom), reacting with 1 molecule of glucose.

PSEUDO-STOICHIOMETRICAL FACTORS.

Reagent and method.	Equivalents of oxygen $\frac{O}{2}$
HIO	2
Hg(CN)_2 alkaline (Liebig-Knapp's solution), HgI_2 (Sachs's solution)	6
Copper acetate (Barfoed's reagent)	$\angle 1$
Fehling's solution, Lehmann-Maquetten method	5-5.5
Bertrand's method	5-6
Fehling, Alihn's modification, and Pavy's method	6
Ost's bicarbonate solution	9-10
Ag ammoniacal	18-24
KMnO_4	18-24

From these factors the amount of sugar may be ascertained, and an approximate judgment formed as to the nature of those secondary reaction products which retain but a slight reducing power. The oxidation of the methyl ethers of sugar promised new evidence as to the mechanism of oxidation. A series of methylated glucoses was oxidised by the Bertrand and Lehmann-Maquet methods, and the results compared with those from equivalent amounts of unsubstituted glucose. The influence of methylation upon the reducing power of glucose is shown graphically. The reducing power of a substituted hexose depends not only upon the number of the substituting groups, but also upon their location. The reducing power is decreased by an increase of methyl groups as well as by the proximity of one of them to the reducing carbon atom (1). The progress of enolisation and thus of oxidation is blocked by that methoxy group which is nearest to carbon atom (1), despite the presence of free alcoholic hydroxyl groups in the lower part of the chain. Dimethyl glucose with one of the methoxy groups on carbon atom (2) approximates and surpasses fully substituted 2, 3, 4, 6-tetramethyl glucose, whilst 3, 5, 6-trimethyl glucose with a free hydroxyl in position (2) shows a stronger reducing power than either of the others. Both tetramethyl glucose and diacetone mannose reduce the theoretical amount of iodine and thus prove their aldehydic character.

P. H. P.

Grape Pectins and their Influence on Wines. L. Semichon and Flanzy.

(*Compt. rend.*, 1926, 183, 394–396.)—Pectins and gums may be precipitated from wine or must by alcohol in the presence of 1 per cent. of hydrochloric acid, the pectic acid being removed from a solution of the filtered precipitate by the calcium pectate method, and the gums precipitated in the filtrate by alcohol. Grape musts contain only pectins, and wines only gums or a mixture of pectins and gums. Pectins are present as a result of the splitting up of the cellulosic tissues, too great an acidity in the must preventing the transformation of pectose into soluble pectin. Gums have their origin in the yeast. The pectin content of a wine is an index of the degree to which the drying of the grapes in the sun has been effective, and, consequently, of the mellowness of the wine. It is also related to the bouquet, this being a result of the dissociation of the methyl pectic ether, which, with other organic and mineral compounds, constitutes the pectin precipitate. Dextran, which is produced by *Botrytis cinerea* on Sauterne grapes, differs in composition and properties from pectins. The following results show the influence of sun-drying on the pectins in grape must :

	Sugar per litre. Grms.	Acidity per litre. Grms.	Pectins per litre. Grms.	Pectose per kilo. of Marc. Grms.
Must from fresh grapes	360	3.25	1.54	2.53
Must from the same grapes, after 12 days' drying in the sun	502	3.30	5.25	3.80

J. G.

Determination of Starch in Pectin and Apple Juices by a Sedimetric Method. H. Eckart and A. Diem. (*Z. Unters. Lebensm.*, 1926, 51, 272-274.)—

A quick method for the determination of starch in commercial pectin and apple juices is described. Ten grms. of the sample are warmed on the water bath for ten minutes with 80 c.c. of a solution containing one part of calcium chloride in two parts of water, and previously neutralised to phenolphthalein with acetic acid. The whole is then washed into a 100 c.c. flask with the hot solution, cooled, made up to the mark, and filtered through a dry folded paper. The standard consists of 0.1 gm. of pure potato starch dissolved in a little calcium chloride solution on the water bath, and, together with the washings, made up to 100 c.c. with hot water. For the determination of 0.1 to 1.0 per cent. of starch, 10 c.c. of each solution are placed in a graduated sedimentation tube, excess of an iodine in potassium iodide solution is added, and the whole centrifuged after it has stood for half-an-hour. The ratio of the amount of precipitate produced from the sample to that from the standard, as shown by the calibrations on the tubes, gives the percentage of starch in the sample.

J. G.

Soft Pork Studies. II. Influence of the Ration upon the Composition of the Body Fat of Hogs. N. R. Ellis and H. S. Isbell. (*J. Biol. Chem.*, 1926, 69, 219-238.)—

The intimate relation between the firmness of the body fat of hogs and the quantity and character of the ingested fat has been an important field of study in investigations on soft pork. Rations low in fat produce firm body fats, whilst those high in unsaturated oils produce fats with the characteristics of the ingested fat. The animal body tends to deposit ingested fat in preference to synthesising new fat when there is a surplus of food materials and the ingested fat is not needed for energy requirements. The hog is suitable for a study of fat formation because of the rapid rate at which the process proceeds. The physical and chemical properties and the percentages of total saturated acids and various unsaturated acids were determined on lards obtained from hogs given various rations. The iodine values and refractive indices were an excellent measure of firmness of the adipose tissue. Other fat constants showed less correlation. The percentages of saturated acids, oleic acid and linolic acid in lard from hogs given peanuts and soya beans were similar to the content in arachis and soya bean oils. The linolic acid showed the most striking change, increasing from 1.9 per cent. in the hard fat from hogs fed with brewers' rice to 30.6 per cent. in oily fat from hogs fed with soya beans. Small amounts of arachidonic acid were found in lard samples representing all types of feeds. A decrease in the unsaturation of the fat results from a change in the ration from peanuts or soya beans, softening feeds, to corn and tankage, a ration which produces hard fat. Corn and soya bean oils produce greater softening of the fat than arachis and rice oils. Tables show the results of the experiments.

P. H. P.

Soft Pork Studies. III. Effect of Fat in Food upon Individual Fatty Acids in the Body Fat. N. R. Ellis and H. S. Isbell. (*J. Biol. Chem.*, 1926, 69, 239-248.)—A complete separation of the fatty acids was made on six samples of

fat obtained from as many lots of hogs. The hogs were well matured and fattened, and were fed on rations (1) very low in fat, (2) moderately low in fat, and (3) high in fat. The feeds used to obtain the desired results were from different sources and were, respectively, (a) brewers' rice and tankage, (b) corn and skim milk, (c) soya beans alone, and peanuts alone, both represented by two samples each. The procedures for the separation of the unsaturated and saturated acids are given in detail. The fatty acids occurring in all samples were oleic, linolic, arachidonic, myristic, palmitic, and stearic. Palmitic acid and stearic acid occurred in a ratio of 2:1, and, in fact, the proportions between the various saturated acids were much more constant for the six samples than between the unsaturated acids. The feeding with soya beans caused the deposition of small quantities of linolenic acid, whilst the feeding with peanuts led to the deposition of arachidic acid. The oils of these two feeds have a pronounced effect on the composition of the lard. A greater likeness was noted between peanut oil and "peanut lard" than between soya bean oil and "soya bean lard." The fat formed on a ration of brewers' rice and tankage which contained less than 1 per cent. of fat was very hard. The glycerides of oleic, palmitic and stearic acids composed over 97 per cent. of the fat.

P. H. P.

Colour of Compound Tincture of Cardamoms. R. R. Bennett and G. Middleton. (*Pharm. J.*, 1926, 117, 173-175.)—Tincture of cardamoms is very sensitive to changes in the P_H value, particularly in the region of 4 to 6, and the addition of a buffer giving a P_H value of 7 is recommended. The colour in tinctures from dark and silver grain cochineal after addition of sodium phosphate as buffer only differed by about 5 per cent. in favour of the silver grain. During percolation, contact with metallic iron or copper should be avoided, and the use of well tinned copper percolators is advisable. Storage under proper conditions does not affect the colour, but colour may be lost through being carried down by a basic precipitate in the mixture, whilst alkaline mixtures are decolorized by oxidation in air.

D. G. H.

Chemical Constituents of the Oleo Resin and Fatty Matter of Indian Valerian Root. K. Bullock. (*Pharm. J.*, 1926, 117, 152-157.)—An examination of the oil obtained by steam distillation of Indian valerian root from two different sets of bales showed the oil to consist chiefly of a sesquiterpene hydrocarbon and a small quantity of sesquiterpene alcohol. The combined acids found were valerianic and formic, and valerianic and the isomeric methyl ethyl acetic acids were present in the free state, together with some saturated acids (probably stearic and palmitic) and a small quantity of unsaturated acids of the oleic series. In addition to the above constituents, the petroleum spirit extract contained arachidic acid, hentriacontane and some linolic and linolenic acids, but no trace of terpenes or of borneol was found.

D. G. H.

Natural Occurrence of Aconitic Acid and its Isomers. O. A. Beath. (*J. Amer. Chem. Soc.*, 1926, 48, 2155-2158.)—Six species of native delphiniums, and two species of *Aconitium* (including the U.S.P. official drug), were extracted

with water, treated with basic lead acetate till the extract was clear, and extracted with ether. The ethereal extract was dissolved in a minimum quantity of pure hot acetone, and aconitic acid precipitated by an excess of chloroform. All the acids from the plants, and also a commercial sample, had m.pts. of 172° to 173° C., and the results of combustions and conductivity measurements were also the same for all the samples. The extracted acid may be recovered by hydrolysis from its ethyl ester, and is therefore comparatively stable. The variations in the m.pts. hitherto recorded for aconitic acid are due to mixtures of two or more forms of the acid, the product obtained from the plants being an isomeric form of the normal acid.

J. G.

Analysis and Composition of Commercial Glycerophosphates. G. J. W. Ferrey. (*Pharm. J.*, 1926, 117, 159-162.)—The glycerophosphates of the alkali and alkaline earth metals on the English market are mostly salts of definite composition, and differ with their source of manufacture chiefly in the proportion of water of crystallisation present, particularly in the case of the magnesium and 50 per cent. sodium salts. The acid and alkaline titration method is recommended for routine analysis, and, in conjunction with the ignition method and in the absence of appreciable amounts of inorganic phosphate, affords a means of detecting condensation products, such as the di-ester of Carré. In the case of sodium glycerophosphate most of the 50 per cent. solutions on the market do not appear to have been adjusted to a 50 per cent. by weight basis of anhydrous sodium glycerophosphate.

D. G. H.

Determination of Arsenic in Chemicals by the Electrolytic Method. N. Evers. (*Pharm. J.*, 1926, 117, 183-184.)—The apparatus described for the determination of arsenic by the electrolytic method only differs from that of Monier-Williams (*ANALYST*, 1923, 48, 112) in slight modifications making for more convenient working. These include a cathode made by rolling lead foil round a glass rod which passes through a rubber stopper and is connected with the negative terminal of the current source; the arrangement of the absorption tube so that the cotton wool may readily be removed for cleaning, and the abolition of the dropping funnel. The presence of organic matter does not adversely affect results, and a list of substances which require no preliminary treatment is given. If halogen is likely to be evolved, sodium thiosulphate (10 per cent. solution) should be used in the outer chamber instead of sulphuric acid containing cadmium; with hypophosphites and phosphites the material is warmed on a water bath with 2 grms. of potassium chlorate and 30 c.c. of 25 per cent. sulphuric acid containing cadmium, and after being heated until the disappearance of white fumes the solution is diluted to 30 c.c. and the ordinary method applied. Chlorates require warming with 30 c.c. of sulphuric acid containing cadmium, and this is also advisable with organic materials such as foodstuffs, and, if frothing tends to occur, a few c.c. of amyl alcohol should be run on to the surface. With the exception of the citrate scale preparations, iron and manganese salts are tested as usual with the addition of 2 grms. of citric acid to keep the electrode clean.

Bismuth salts require previous distillation; nitric acid must be removed from nitrates, and carbon dioxide from carbonates, by addition of 30 c.c. of sulphuric acid containing cadmium in the presence of a few drops of bromine water.

D. G. H.

Biochemical, Bacteriological, etc.

Relationship between Hydrogen Ion Concentration and Chemical Constitution in certain Local Anaesthetics. E. B. Vliet and R. Adams. (*J. Amer. Chem. Soc.*, 1926, 48, 2158–2162.)—The hydrogen ion concentrations of solutions of the hydrochlorides and of some other salts of compounds of the form $p.NH_2.C_6H_4.COO(CH_2)_x.N(RR')$ have been determined, where R and R' are alkyl or allyl groups, and x is a number greater than one. From these results the basicity constants were calculated. In general, there is a consistent relationship of hydrogen ion concentration to structure, the basicity decreasing and increasing with increase in size of the R and R' groups, and with increase in the value of x , respectively. But if the carbon atoms are added as side chains, the basicity decreases. Geometric isomers have the same hydrogen ion concentrations, although their physical and anaesthetic properties differ considerably. Cyclohexanol derivatives behave as if the nitrogen and oxygen atoms are connected by two straight chains of carbon atoms, the basicity being determined by the length of the shorter chain.

J. G.

Chamomile (Mayweed) and a Taint in Milk. F. Procter. (*J. Agric. Sci.*, 1926, 16, 443–450.)—The following species of chamomile were present in hay which had been given to cows producing tainted milk:—*Anthemis arvensis* (corn chamomile), *A. cotula* (stinking mayweed), *Matricaria chamomilla* (wild chamomile), and *M. inodora* (scentless mayweed). Separate tests with the different species showed that *Anthemis cotula* was much the most potent in producing taint in the milk of cows feeding on it, and the taint is regarded as due to a chemical substance or substances, which could be extracted by soaking the chamomile in petroleum spirit boiling at or below 44° C., filtering, distilling under reduced pressure, and allowing the remaining spirit to evaporate spontaneously in air. The golden coloured resinous extract thus prepared from 2 lbs. of mixed chamomile was found to taint the morning milk when suspended in water and given as a drench to a cow on the previous evening. Butter prepared from tainted milk was only slightly tainted, but the separated milk and butter milk were strongly and equally tainted.

D. G. H.

“ Apparent Ropiness ” (Thread Formation) in Milk due to Surface Influence. A. T. R. Mattick. (*J. Agric. Sci.*, 1926, 16, 459–465.)—A physical form of “ ropiness ” which may be induced in milk is similar to Ramsden's surface aggregates (*Proc. Roy. Soc.*, 1903, 72), and is due to the formation of thin films of casein, or lactalbumin, or both, at the milk-air surface. In order to render the aggregate visible it must be swept up more rapidly than it re-dissolves. This

condition may be found on ordinary farm coolers whenever rate of flow, temperature and acidity conditions are favourable. A model cooler made of horizontal parallel glass tubes is very suitable for demonstrating the condition in opaque fluids. The phenomenon is of importance in making dilutions of milk with water or normal saline solution for bacterial enumerations, and either blow out pipettes should be used, or apertures should be large enough to avoid surface aggregate formation as a result of slow delivery.

D. G. H.

Determination of Hippuric Acid and Elimination of Benzoic Acid as Hippuric Acid in Rabbits. W. H. Griffith. (*J. Biol. Chem.*, 1926, **69**, 197–208.)—A method for the determination of hippuric acid in the presence of benzoyl glycuronic acid is described which is carried out in a specially designed extraction apparatus. The whole determination is made in the same flask, and the working time required for the completion of an analysis is very little more than that necessary for a nitrogen determination. The method consists in the continuous extraction of the urine with ether for one hour, treatment with free bromine and sodium hypobromite of the ether residue in order to decompose the traces of urea (the only other nitrogenous substance extracted with the hippuric acid), and the determination of nitrogen by the ordinary Kjeldahl method. One to 5 c.c. of 1 per cent. sodium tungstate solution added to the urine in the extraction tube precipitated any traces of protein and did not interfere with the extraction. A study was made of the excretion of free benzoic acid, hippuric acid and total benzoic acid in the urine of normal adult rabbits after the administration of sodium benzoate (equivalent to 0.25 to 1.0 grm. of benzoic acid per kilo). The maximum rate of elimination of hippuric acid occurred after the administration of 0.5 grm. of benzoic acid per kilo. Hippuric acid constituted only 65 to 90 per cent. of the combined benzoic acid in the urine of the 6 and 24 hour periods after the ingestion of 1.0 grm. of benzoic acid per kilo. The administration of glycine with benzoate increased the output of hippuric acid and decreased that of benzoyl glycuronic acid. Although conjugation of benzoic acid with glycine predominates, nevertheless conjugation with glycuronic acid plays an important rôle in the rabbit. The extent to which this occurs in the rabbit has been under-estimated. P. H. P.

Comparison of the Electrometric and Colorimetric Methods for Determination of the P_H value of Gastric Contents. G. Kahn and J. Stokes, Junr. (*J. Biol. Chem.*, 1926, **69**, 75–84.)—The hydrogen ion concentration of gastric juice is important on account of its effect on the activity of the gastric enzymes, its effect on the bactericidal powers of gastric juice, and its effect on intestinal secretion and digestion. The electrometric determination of the P_H value is generally accepted as the most accurate method available, and there is strong evidence for its accuracy. Standardisation of the colorimetric method against the electrometric method was thought to be important, and every conceivable precaution was taken with this work. The colorimetric system used was that recommended by Clark (*The Determination of Hydrogen Ions*, Baltimore, 1920). An effort was made to obtain specimens of gastric contents covering the whole

range of gastric acidity from P_H 1 to 8. If large enough, the sample was divided into three fractions, one left unaltered, another centrifuged, and the last filtered, and the P_H value of each was determined by both methods. The colorimetric method is not sufficiently accurate for the determination of the P_H value of gastric contents which are less acid than $P_H=2.1$. Dilution did not make the colorimetric method consistently more accurate. Above $P_H=2.1$ dialysis of the specimen against normal salt solution and the colorimetric determination of the P_H value on the dialysate are essential for even moderate accuracy. The slight differences found between the colorimetric determination of dialysates and the electrometric determination of the corresponding undialysed specimens can be explained in part by (1) the dilution which occurs on dialysis, (2) the loss of carbon dioxide during dialysis, and (3) the Donnan equilibrium. The electrometric method should be used where any considerable accuracy is required, but loss of carbon dioxide must be guarded against whenever the P_H exceeds 5.5, as the loss causes the results to be too high.

P. H. P.

Colour Reactions of Vitamin A. T. Cocking and E. A. Price. (*Pharm. J.*, 1926, 117, 175-179.)—A solution of antimony trichloride, prepared by dissolving 30 grms. of the salt previously washed with chloroform in sufficient B.P. chloroform to produce 100 c.c., gives a blue coloration in the presence of vitamin A which is more permanent and intense than that produced by any other reagent tried. The oil to be tested is dissolved in B.P. chloroform to form a 20 per cent. solution, 0.2 c.c. of the solution is added to 2 c.c. of reagent, and the colour of the mixed liquids recorded in the tintometer. It was found that, on the average, the Newfoundland cod liver oils examined had greater vitamin activity than the Norwegian; that neither the colour of the oil nor the proportion of unsaponifiable matter present was a criterion of the vitamin content; and that, judged by the above test, the vitamin activity of cod liver oils may vary as much as 8:1. The paper contains an alphabetical list of previously recorded colour reactions for vitamins. The following results were obtained on applying the antimony chloride test to other kinds of animal oils, a larger quantity of the solution (corresponding to 0.2 c.c. of oil instead of the usual 0.04 c.c.) being required; hence, for comparison with cod liver oil, the figure should be divided by 5.

Oil.	Unsaponifiable matter. Per Cent.	Natural colour of oil $\frac{1}{2}$ in. cell.		Colour produced by 0.04 c.c. or 0.2 c.c. in test in 8 mm. cell.		
		Yellow.	Red.	Blue.	Yellow.	Red.
Cod liver, pale refined	1.3	1.2	0.1	2.1	0.3	nil
Do. do.	1.2	1.0	nil	3.0	nil	0.4
	(average)					
Sperm	4.0	3.5	0.9	2.5	1.0	0.5
Whale	2.5	3.5	1.2	4.1	2.8	0.9
Seal	1.0	5.0	1.0	8.5	10.5	7.0
Neatsfoot	0.4	0.7	nil	0.2	0.7	0.2
Lard oil	0.2	3.9	9.9	0.4	2.0	1.7

D. G. H.

Destruction of Vitamin A in Milk by Ultra-violet Light. R. W. Titus, J. S. Hughes, W. R. Hinshaw, and J. B. Fitch. (*Ind. Eng. Chem.*, 1926, 18, 843.)—Feeding experiments on chickens with milk which had been exposed to ultra-violet rays showed that the rays practically destroyed the nutritive value of the milk as regards its vitamin A content. W. P. S.

Vitamin Content of Tinct. Limonis Fort., B.P.C. S. G. Willimott and F. Wokes. (*Pharm. J.*, 1926, 117, 184–186.)—Alcoholic extracts of the same strength as Tinct. Limonis Fortis B.P.C. and containing as much extractive matter as the commercial tincture, were added to the diets of rats and guinea pigs, and the results showed that, whilst Tinct. Limonis Fortis, B.P.C. contains very little of vitamins A or C, it is nearly as rich in vitamin B as yeast, and has the advantage over yeast in being practically free from nitrogenous derivatives. D. G. H.

Stimulation of Bacterial Activity in Milk. C. Gorini. (*Compt. rend.*, 1926, 183, 250–251; *cf. id.*, 1926, 182, 946.)—The irregularities previously noted by the author in the coagulation of milk by bacteria (pathogenic streptococci) may be suppressed if media rich in nutritive substances are added to the milk. Sterile beef broth, peptone, Liebig's extract, yeast water and blood, though incapable of coagulating casein themselves, have been used successfully for this purpose. The effect of these additions appears to be to stimulate the coagulating and caseolytic properties of the bacteria, rather than to increase their number, or to endow them with properties of this kind. The cholera vibrio, however, is an exception in the last respect. J. G.

Use of Sulphur Bacteria as Indicators in the Investigation of Polluted Water. D. Ellis. (*British Assoc.; Pharm. J.*, 1926, 117, 308.)—Sulphur bacteria are valuable agents for the detection of sewage pollution in waters which, superficially, appear to be clean. In most instances *Beggiatoa alba* is the sulphur organism which is present in polluted waters, and it multiplies under conditions in which animal or vegetable matter is undergoing decomposition under water or in waters, otherwise pure, which have been polluted with sewage. If it appears in a water, either flowing or still, in which organic remains are not undergoing decomposition, sewage contamination is almost certainly indicated. As an instance of the application of the method, the investigation of the black sand in the Clyde estuary is cited. It has been assumed that this black coloration was caused by the sewage poured into the Clyde, but it was found that at the various points where *Beggiatoa alba* grew in abundance the cause for its appearance could be traced either to animal or vegetable remains undergoing decomposition or to local sewage pollution unconnected with the hypothetical polluted matter in the main body of the river. In no single case was *Beggiatoa alba* found in the neighbourhood of the black sand in which both of these factors were absent. The author concluded that sewage-polluted water was not the cause of the formation of the black sand and the true reason was found to be the formation of ferrous sulphide through the reaction of

ferruginous constituents of the sand and the hydrogen sulphide liberated by the bacteria which consume the animal and vegetable matter on the shore.

Investigation of Hydrogenase. J. Gruss. (*Woch. Brau.*, 1926, 43, 265-268; *J. Inst. Brewing*, 1926, 32, 370.)—Hydrogen is a fermentation product of various bacteria, including *B. amylocyanicus*, *B. levans*, *B. corticalis*, and *B. butyricus*. The best known case is that of *B. butyricus*, concerning which some chemical and morphological particulars are given. In studying these organisms the usual method of determining the hydrogen produced is to burn it with an excess of oxygen in a eudiometer, and to measure the resulting decrease in volume. A method which can be used for the qualitative detection of hydrogen in fermentation gases, and also for roughly quantitative purposes, has now been devised, and may, perhaps, be capable of development into an exact quantitative method. It consists in placing in the fermenting liquid a strip of palladium foil, which absorbs all the hydrogen produced. After fermentation is complete the foil is taken out, rinsed with water, and transferred to a stoppered cylinder containing a solution of violamin (tetramethyl-*p*-phenylene-diamine hydrochloride) in which the colour has been developed by oxidation with atmospheric oxygen. In course of time the hydrogen in the palladium effects a partial decolorisation of the solution, the extent of which depends on the amount of hydrogen present.

Toxicological and Forensic.

Proof of Fatal Dose of Strychnine. V. Mount. (*Pharm. J.*, 1926, 117, 304).—An account is given of an appeal to the Michigan Supreme Court from a conviction of murder by administering strychnine. The jury had found that strychnine was given in food at least two hours before death, and that, notwithstanding the evidence of eye witnesses, death was preceded by convulsions. The Supreme Court stated that a fatal dose of strychnine, if it did not cause immediate death, produced severe convulsions ending in death. If the poison found in the organs of the body was given about two hours before death, the medical evidence was to the effect that there must, of necessity, have been convulsions. A minimum fatal dose was about 0.5 grain, and might be slightly less. A fatal dose might cause death almost immediately or after an interval up to three hours; and if an analysis of one-half of the stomach of a dead body, one half of the liver, and one half of the kidneys, disclosed 0.26 grain of strychnine, there would be approximately the same amount in the other half of those organs; and, if those organs contained 0.52 grain of strychnine, it would, of necessity, have produced convulsions, and was sufficient to have caused death. Chemical evidence had proved that half of the organs mentioned of the victim showed those results. The Court therefore held that the medical and chemical evidence fully supported the finding of the jury, that death was caused by strychnine.

"Gulf Sickness" and the Arsenic Theory. A. Juckenack and A. Brüning. (*Chem. Zeit.*, 1926, 50, 513.)—The illness from which the fishermen of the inland gulf of Pillau suffered (the so-called "gulf sickness," *Haffkrankheit*)

was at first attributed by Lockemann (*Chem. Zeit.*, 1926, 313) to the presence of certain volatile arsenic compounds which were detected in several samples of the water and in the gulf algae in 1924. The following year, however, Lockemann was unable to detect any arsenic in samples of water from the same gulf, and concluded that the reagents used the previous year could not have been free from arsenic. The author now describes a series of experiments in which no arsenic mirrors were obtained with Berlin water, whereas mirrors of varying intensity were obtained with samples of water from different parts of the inland gulf. He concludes that in 1924 arsenic was present in the water, and that, owing to a change in biological conditions, it was no longer present in 1925. According to the unanimous reports of the gulf fishermen there was an exceptionally vigorous growth of algae in the gulf in the summer of 1924, and it is well known that certain algae can produce volatile arsenic compounds when growing in arsenical water. Lastly, when Lockemann made his second series of tests the discharge of arsenical trade effluents into the gulf had been discontinued for more than 6 months, but even in that year he found unusually large amounts of arsenic in the gulf algae.

Agricultural Analysis, etc.

Aluminium and Acid Soils. J. Line. (*J. Agric. Sci.*, 1926, 16, 335-364).—

A change in hydrogen ion concentration varying with the original buffer properties of the solution or soil will result on the addition of aluminium salts. The buffer properties will also change, but, given the same initial P_H value, a culture solution containing an aluminium salt will have a more constant hydrogen ion concentration than the ordinary solution during the period of plant growth. Soluble phosphates are precipitated as aluminium phosphate except where the solution is more acid than $P_H = 3.5$ to 4.0 , and this might cause phosphate deficiency in culture solutions, but would not affect soils. Aluminium is precipitated from solutions of its salts as hydroxide when the reaction approaches $P_H = 4.0$, as phosphate from $P_H = 3.0$ to 4.0 , and a very small amount remains as colloidal hydroxide, of which about 0.001 to 0.006 per cent. (on the dry weight of acid soil) may be extracted by water. Depression of growth in aluminium-containing culture solutions is regarded as due to precipitation of phosphate or to increased acidity, but only results where the hydrogen ion concentration harmful to the particular plant is reached and maintained. Addition of aluminium to acid soils results in most of it becoming insoluble, and in increase of soil acidity, which is least in the better buffered soil. The good effects of lime and phosphate dressings on naturally acid soil are not due to any precipitating action on aluminium, and calcium aluminate is not formed under any acid soil conditions. Aluminium was not found to exert any toxic effect on barley or other plants, nor was its amount found to be related to soil fertility.

D. G. H.

Colorimetric Determination of Phosphoric Acid in Soils. A. Nemeč. (*Compt. rend.*, 1926, 183, 314-316).—The method is based on the reduction of phosphomolybdic acid by hydroquinone in acid solution and the formation

of a blue colour by subsequent treatment with sodium sulphite in an alkaline solution. As little as 0.005 mgrm. of phosphorus gives a distinct blue coloration on in 100 c.c.

W. R. S.

Determination of Biguanide. C. D. Garby. (*Ind. Eng. Chem.*, 1926, 18, 819.)—Biguanide may be precipitated and determined by precipitation as hydrated nickel biguanide provided the solution is rendered sufficiently alkaline with ammonia to dissolve any hydrated nickel guanyl-urea, should guanyl-urea have been present in the sample of cyanamide under examination. *In the absence of guanyl-urea.*—Thirty c.c. of a solution containing about 0.1 grm. of biguanide are treated, in a stoppered bottle, with 3 grms. of mannitol, 10 c.c. of concentrated ammonia and 5 drops of trinitrobenzene, and 25 per cent. potassium hydroxide solution is added, drop by drop, until the colour of the mixture changes from dark red to yellowish red. Three c.c. of nickel reagent (a mixture of crystallised nickel nitrate, 40 grms., 10 per cent. mannitol solution, 100 c.c., concentrated ammonia, 40 c.c., and 25 per cent. potassium hydroxide solution, 15 c.c.) are added, and, after three hours, the precipitate is collected, washed with 100 c.c. of 0.12 per cent. ammonia solution, dried at 125° C. for one hour, and weighed as nickel biguanide, $\text{Ni}(\text{C}_2\text{N}_5\text{H}_6)_2$. *In the presence of guanyl-urea.*—The 30 c.c. of biguanide solution are treated with 3 grms. of mannitol, 0.2 grm. of diammonium hydrogen phosphate, 0.1 grm. of ammonium nitrate (if ammonium salts are not present in the sample), 10 c.c. of concentrated ammonia, 5 drops of trinitrobenzene, and sufficient 25 per cent. potassium hydroxide solution to change the colour from cherry red to reddish yellow. Three c.c. of nickel reagent are then added, and the precipitate is collected as already described.

W. P. S.

Organic Analysis.

Acidimetric Titration and Composition of Commercial Lactic Acid.

R. Eder and F. Kutter. (*Helv. Chim. Acta*, 1926, 9, 557–578.)—Commercial lactic acid consists chiefly of free lactic and lactyl-lactic acids, with small amounts of lactide, and varying amounts of water. The action of alkalis under varying conditions of time, temperature, solvent and dilution, and the formation from the lactic acid by these means of lactide (which is subsequently split up into sodium lactyl lactate and eventually sodium lactate), have been investigated. Thence a method for the determination of these constituents has been evolved. Let a and a' be the volumes (in c.c.) of N sodium hydroxide required for direct titration of p grms. of the sample in water and alcohol solutions, respectively; and b and b' the corresponding volumes used up for the saponification of the acid as determined by back-titration. Then the percentages of lactic acid, lactyl-lactic acid, and lactide are given by the expressions $9.005(a' + b' - 2b)/p$, $16.208(2b - b')/p$, and $14.406(b' - b)/p$, respectively. The water is found by difference. The method depends on the fact that in aqueous solution half of the lactide is titratable, whilst in alcohol solution it is unattacked by alkali. Errors due principally to the presence of carbon dioxide and to the type of indicator used

are also discussed. The lactide produced in the above reactions, when separated and recrystallised from alcohol, was found to be a non-hygroscopic solid, m.p. 124° (corr.), and soluble in chloroform, benzene and acetone. J. G.

Typical Reactions of Phenols. K. Brauer. (*Chem. Ztg.*, 1926, 50, 553-554.)—The colour reactions suggested for the detection of resins (ANALYST, 1926, 51, 422), and attributed to the presence in them of the phenolic hydroxy group, are applied to phenols themselves. The phosphomolybdic acid reagent produces green colorations with pyrocatechol and pyrogallol, blue colours with hydroquinone and oxy-hydroquinone, but no colours with resorcinol and phloroglucinol. In all cases the subsequent addition of ammonia produces a blue colour. The combined reactions may therefore be used as a guide to the number and positions of the hydroxy groups in the molecule. The reaction given by resins with ammonium molybdate and concentrated sulphuric acid may also be used for phenols, but is masked by the action of the strong acid. J. G.

Determination of Unsaturated Compounds in Petroleum Products. A. W. Francis. (*Ind. Eng. Chem.*, 1926, 18, 821-822.)—A bromine absorption method is described in which the bromide-bromate solution used is rendered only slightly acid, so that the bromine is liberated slowly and absorbed by the olefines, thus avoiding substitution reactions. A slight excess of 0.5 *N* potassium bromide-bromate solution (preferably not more than 1 c.c. as determined by a trial titration) is placed in a flask, and from 3 to 50 c.c. of the petroleum, depending on its olefine content, are added. The mixture is acidified with 5 c.c. of 10 per cent. sulphuric acid and shaken for one minute. If the colour remains dark yellow in spite of vigorous shaking, too much bromate solution has been added, and the determination should be considered a trial only. In any case, to complete the liberation of the bromine, 15 c.c. more of the acid are added, and the shaking is continued for another minute; if the solution remains colourless, a further small quantity of the bromate solution is added. The final colour should be light yellow. Potassium iodide solution is then added, and the excess of bromine titrated with thiosulphate solution. The bromine value (grms. of bromine per gm. of sample) is calculated from the result of the titration. This value is useful for the comparison of different petroleums, but to determine the actual percentage of unsaturated compounds present, the mean molecular weight of the latter is required. For a narrow cut of a distillate the molecular weight can be determined from the mean boiling point, and is approximately 54 plus one half of the mean boiling point in degrees Centigrade. This relation is based on the boiling points of the pure normal olefines. From experiments with a highly unsaturated cracked petroleum, in which several cuts of 2.5 per cent. each were titrated and the olefines determined, the percentage of olefines was found to be given by the formula $U = MN/160$, where *N* is the bromine number and *M* the mean molecular weight. W. P. S.

Use of Carbon Tetrachloride as a Reagent for Phenols. G. E. Trease and H. Tingey. (*Pharm. J.*, 1926, 117, 151-152.)—Carbon tetrachloride presents no advantages over other solvents for the preparation of oleo resins, is unsuitable

for alkaloid extraction, and its solvent powers on iodine increase with rise of temperature. Characteristic colour reactions result with meta- and ortho-substituted phenols, but not with para-phenols (*vide infra*), and are probably due to the formation of aurin dyes. By modifying the B.P. Codex test for thymol and using iodoform or carbon tetrachloride pronounced colorations are obtained with various phenols. The reaction between phenol and carbon tetrachloride is very slow, but may be hastened by adding a little copper powder as catalyst. The test is applied by dissolving 0.1 grm. of the phenol in 1 ml. of potassium hydroxide solution (B.P.), adding 1 drop of chloroform, etc., and heating the mixture.

Phenol.	Colour with chloroform.	Colour with Iodoform.	Colour with carbon tetrachloride.
Phenol	Red	As with chloroform	Wine-red
<i>o</i> -Cresol	Red	do.	Wine-red
<i>m</i> -Cresol	Red	do.	Wine-red
<i>p</i> -Cresol	Orange-red	do.	No colour
Eugenol	Reddish-brown	do.	Not characteristic
Guaiacol	Purple-red	do.	Purple-red
Thymol	Crimson	do.	Purple-red
Resorcinol	Blood-red	do.	Purple-red
α -Naphthol	Blue	do.	Orange-red
β -Naphthol	Blue	do.	Not characteristic

D. G. H.

Flax Wax. W. Honneyman. (*Pharm. J.*, 1926, 117, 157-159.)—Samples of wax were prepared from flax grown in widely separated areas and upon which the three chief methods of retting had been used. The wax was dark green or brown according to the state of the chlorophyll present, slightly harder and more brittle than beeswax, capable of taking a very high polish, and more durable than carnauba wax, because more plastic.

Variety.	Specific gravity at 15° C.	M.pt. °C.	Acid value.	Saponification value.	Iodine value.
Irish	0.971	69.2	18.0	79.6	21.6
Courtrai	0.982	69.0	22.0	77.5	23.9
Dutch W.R.	0.983	69.5	18.0	82.0	28.8
Russian D.R.	0.985	69.8	19.5	81.4	21.8
Canadian D.R.	0.963	68.8	23.8	78.4	27.1
Dutch D.R.	0.980	67.3	17.5	83.7	23.3

D. G. H.

Contribution to the Study of the Constitution of Squalene (Spinacene). I. M. Heilbron, E. D. Kamm, and W. M. Owens. (*J. Chem. Soc.*, 1926, 1630-1644; *cf. id.*, 1917, 111, 56, and 1923, 123, 769.)—The authors consider that the hydrocarbons isolated independently by Chapman and Tsujimoto, and named by them spinacene and squalene respectively, are identical, and have the same molecular formula $C_{30}H_{50}$. This is supported by the close agreement between the physical and chemical properties of the two substances as recorded by different

workers, and by the fact that three isomeric hydrochlorides having different melting points but the same composition have been isolated from the unsaponifiable matter of the oils used. The presence of a terpene in the oil is supported by the ease with which it undergoes ring closure and regeneration from its hexahydrochloride, and by the succinic and laevulic acids obtained from its ozonide. The hydrocarbon is therefore an equilibrium mixture of isomerides, one form of which may be represented as $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot(\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2)_4\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CHMe}$. It may be separated from the fish-liver oil by saponification, or by distillation under reduced pressure, and the isomers isolated in the form of their hydrochlorides. Formic acid has been found to be the best catalyst for effecting ring closure, the isomerisation taking place in three stages according to the duration of the treatment, and representing the production of two, three, and four rings respectively. This is accompanied by an increase in density and viscosity.

J. G.

Inorganic Analysis.

Centrifuging in Volumetric Analysis. R. F. Le Guyon. (*Compt. rend.*, 1926, **183**, 361-363.)—This expedient is proposed for precipitation methods in which no colour indicator is available, *e.g.* the titration of phosphoric acid in presence of sodium acetate by means of silver nitrate solution. The liquid is titrated in a centrifugal tube, and centrifuged after each addition of standard solution until the supernatant liquid remains clear after addition of the precipitant. The procedure is more advantageous than gravimetric methods in micro-analysis.

W. R. S.

Qualitative Reaction for Copper. G. Denigès. (*Compt. rend.*, 1926, **183**, 289-291.)—A few drops of a solution of cupric salt are added to 4 c.c. of acetic acid containing one drop of 50 per cent. potassium bromide solution. The liquid assumes a strong green colour, and gives a characteristic absorption band in the red. If 8 drops (0.4 c.c. in all) of bromide solution are added, the coloration changes to sepia, then to reddish-violet. When the liquid is boiled the colour changes once more to green, but the violet colour is restored by cooling.

W. R. S.

Diphenylamine as an Internal Indicator for Iron. F. J. Dyer and W. B. Forbes. (*Pharm. J.*, 1926, **117**, 167-168.)—Diphenylamine was found to be superior to potassium ferricyanide as an internal indicator in the determination of iron in pharmaceutical iron preparations. For example, 0.5 grm. of saccharated iron carbonate is suspended in 2 ml. of water, and an equal quantity of concentrated sulphuric acid added, and to the solution 15 ml. of dilute sulphuric acid, 1 grm. of sodium sulphate and 50 ml. of water are added, the mixture cooled, treated with 1 ml. of diphenylamine solution (0.2 grm. dissolved in concentrated sulphuric acid and made up to 100 ml. with acid), and 0.1 N potassium dichromate run in. A violet blue colour, with no trace of green, indicates the end-point. Excess of phosphoric acid and a high temperature during titration are to be avoided.

D. G. H.

Colorimetric Determination of Nickel. A. P. Rollet. (*Compt. rend.*, 1926, 183, 212–213.)—Feigl's method for the determination of nickel (*Ber.*, 1924, 57, 758) involves a number of difficulties, in particular that of the effect of warmth. These are avoided by adding to the solution a small excess of bromine water. The excess is absorbed in ammonia, a few drops of an alcoholic solution of dimethylglyoxime added, and the resulting colour matched after 2 minutes. As little as 0.015 mgrm. of nickel in 100 c.c. of solution may be determined with a relative error of less than 5 per cent. for 0.001 to 0.01 mgrm. of nickel per c.c. In the presence of cobalt 0.01 mgrm. of nickel per gm. may be determined if the cobalt is obtained in the form of sodium cobalticyanide, the yellow colour of which may be compensated for in the standard. The method is satisfactory for nickel in organic compounds, and in steels, also, if the reagent is added before the ammonia, to avoid the entraining of the nickel by the precipitated ferric hydroxide.

J. G.

Reaction of "Aluminon" with Hydroxides of Beryllium, Rare Earths, Zirconium, and Thorium. A. R. Middleton. (*J. Amer. Chem. Soc.*, 1926, 48, 2125–2126.)—The "aluminon" reagent for aluminium (*ANALYST*, 1925, 50, 152) forms deep red lakes with the hydroxides or basic acetates of the above elements, that formed from cerous hydroxide being the darkest. The beryllium hydroxide lake alone is indistinguishable from the aluminium lake on account of its stability towards ammonium carbonate. The solubilities of the lakes are lower than those of the compounds from which they are made, and, in the absence of ammonia, the lakes are deeper in colour than when it is present. A reaction peculiar to lanthanum is the formation of a white flocculent precipitate on standing, which settles on top of the heavier red lake.

J. G.

Colorimetric Determination of Molybdenum. A. D. Funck. (*Z. anal. Chem.*, 1926, 68, 283–286.)—The method is based on the formation of brownish-red permolybdate by addition of hydrogen peroxide to the alkaline molybdate solution, the intensity of the coloration being proportional to the concentration of the molybdenum and hydrogen peroxide; the excess alkalinity is without influence. Hydrogen peroxide undergoes gradual catalytic decomposition, but this is too slow to affect the accuracy of the comparison of two solutions of approximately equal concentration in molybdenum and hydrogen peroxide. The sensitiveness of the reaction is 0.01 grm. of MoO_3 per litre. A small measured amount of solution (concentration about 1:1000) is mixed in a Nessler tube with with 2 c.c. of strong hydrogen peroxide, and matched against a sodium molybdate solution of known strength under identical conditions. The method can be used for the rapid approximate (within 0.5 per cent.) assay of commercial sodium or ammonium molybdate, molybdenite, and ferromolybdenum. Ammonium molybdate is boiled with sodium hydroxide until the ammonia is expelled. Molybdenite is roasted to constant weight, and the product dissolved in caustic soda. Ferromolybdenum is attacked with nitric acid, and the insoluble residue fused with sodium carbonate; the solution from the fusion is evaporated to dryness, together

with the nitrate solution, the residue treated with an excess of sodium hydroxide, again dried, and ignited for a few minutes. After cooling, the mass is dissolved in water, and an aliquot portion tested colorimetrically. Chromate and tungstate interfere.

W. R. S.

Constitution of Dissolved Molybdic Acid. A. Travers and Malaprade.

(*Compt. rend.*, 1926, **183**, 292-294.)—When anhydrous molybdenum trioxide is heated with water for several days at 100° C. in a pressure flask, the resulting pale-yellow solution contains 1.5 to 1.9 gm. of MoO_3 per litre, which, by evaporation, is recovered as crystallised anhydride. The solution, unlike that of true molybdic acid, oxidises ferrocyanide in the cold. A solution of molybdic acid, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, heated to 100° C., gives a copious white precipitate, the supernatant liquor being of a pale yellow colour and containing 1.9 gm. of MoO_3 per litre. The view is expressed that the solution contains a condensed tetramolybdic acid, $4\text{MoO}_3 \cdot \text{H}_2\text{O}$; the potentiometric determination of the neutralisation curve in the cold shows a break at the point corresponding to the addition of one-quarter of the alkali required for the normal molybdate K_2MoO_4 , and further neutralisation is actually a decomposition of the tetramolybdic complex. This is analogous to metatungstic acid, $4\text{WO}_3 \cdot \text{H}_2\text{O}$, which, however, is only changed into normal tungstate, K_2WO_4 , in a boiling solution. Phosphomolybdic acid may possibly correspond to the constitutional formula $\text{H}_3\text{PO}_4 \cdot 3(4\text{MoO}_3 \cdot \text{H}_2\text{O})$.

W. R. S.

Iodimetric Determination of the Halogens. P. L. Hibbard. (*Ind.*

Eng. Chem., 1926, **18**, 636-838.)—To determine iodine, bromine and chlorine in such substances as plant juices, etc., the organic matter is destroyed by ignition with sodium peroxide; higher oxides of the halogens are then reduced by means of sodium hydrogen sulphite, and the slightly alkaline solution is evaporated to a small volume. In this solution the iodine is first liberated by boiling with the addition of dilute sulphuric acid and nitric acid and ferric sulphate; the iodine is collected in potassium iodide solution and titrated. The residual solution is then treated with chromic anhydride, and the liberated bromine is removed by passing a current of air through the cold mixture; the bromine is collected in potassium iodide solution and titrated. The chlorine is then determined by distillation with potassium permanganate and sulphuric acid.

W. P. S.

Use of Glucose Syrup in the Titration of Borax. L. S. Weatherby and H. H. Chesny. (*Ind. Eng. Chem.*, 1926, **18**, 820-821.)—Dextrose, in the form of commercial "glucose," may be used in place of glycerol in the titration of boric acid; about 30 grms. of dextrose are required for each 1 gm. of anhydrous sodium tetraborate. Satisfactory results are also obtained when mannitol is used. (*Cf. Gilmour, ANALYST*, 1926, 404.)

W. P. S.

Physical Methods, Apparatus, etc.

Catalytic Activity of Dust Particles. F. O. Rice. (*J. Amer. Chem. Soc.*, 1926, **48**, 2099–2113.)—Reactions in closed vessels may be influenced by the catalytic action of finely divided dust particles, by the walls of the vessel, and by the action of small particles which become detached from the walls. Some reactions (*e.g.* the decomposition of hydrogen peroxide) are influenced principally by dust, and others (*e.g.* the oxidation of benzaldehyde) by the walls of the vessel. These influences may account for many anomalous results obtained, particularly in the case of the verification of Einstein's photochemical equivalent law. Negative catalysis may be due to dilution or to chemical inhibition of the reacting substances by the added catalyst, the latter being a case of heterogeneous catalysis and often due to suspended dust. The stability of hydrogen peroxide is increased, even at 60° C., if it is kept free from dust in vessels with smooth sides, the normal decomposition being due essentially to dust particles, these being poisoned, oxidised, or otherwise destroyed by any "preservative" or inhibitor added. The thermal oxidation of sodium sulphite is also a dust reaction. The same considerations hold for the photochemical decomposition of hydrogen peroxide, this being roughly proportional to the dust-content. Here, however, a substance unadsorbed by the dust may inhibit decomposition merely by absorbing the active rays. The Einstein law would probably hold in the total absence of dust. The substrate is assumed to be adsorbed in isolated aggregates, the size of which is a multiple of the quantum yield of the reaction; the aggregate is exploded by the absorption of one light quantum. The use of phosphorus pentoxide as a drying agent is a possible source of dust in gas reactions. Periodic reactions are due to competition for the surface of the vessel or suspended dust between the substrate and the inhibitor. The change of state of a liquid to a gas (evaporation) is not entirely governed by the amount of dust present, but is a catalytic action dependent on the presence of water, and probably also on the effect of the water on the catalytic activity of the dust.

J. G.

Method for Determining the Solubility of Sparingly Soluble Substances.

S. Mitchell. (*J. Chem. Soc.*, 1926, 1333–1336.)—Jamin's interferometer (*Ann. Chim. Phys.*, 1858, **52**, 171) is adapted to the determination of solubility, the movement of the interference bands, produced as a result of the difference in refractive index between pure water and the aqueous solution in question, being measured by means of a compensator. The instrument is calibrated by plotting the compensator reading against the percentage saturation of solutions of various strengths. Of the solutes used, benzene alone does not give a straight line. The method gives very accurate results, and may be used for solvents other than water, and for solubility determinations at all temperatures.

J. G.

New Type of End-point in Electrometric Titration and its Application to Iodimetry. C. W. Foulk and A. T. Bawden. (*J. Amer. Chem. Soc.*, 1926, **48**, 2045–2051; *cf. id.*, 1925, **47**, 9, 19.)—A "dead-stop" end-point in

electrometric titrations may be obtained by establishing, between two platinum wire electrodes placed in the solution, a difference of potential of the same order of magnitude as the counter electromotive force of polarisation. A reagent is then added, which, once the end-point is reached, depolarises the electrode, and produces a movement in the galvanometer. The method is thus available for titrations at the end-points of which sudden depolarisation of the polarised electrode (or of at least one electrode if both are polarised) is produced. One reagent must be an efficient depolarising agent, and one which does not produce depolarising reaction products, or else it must produce the required effect through a secondary reaction. The method is sensitive to a drop of 0.001 *N* solution in iodimetry, and is independent of the presence of coloured and suspended substances. It is affected less than the starch reaction by variations in the conditions, and the maximum recorded deviation for the same titration is 0.06 c.c. It is also applied to oxalate and thiosulphate titrations of permanganate. A simple method of producing the initial polarisation required is by means of a potassium chloride concentration-cell, the cathode in the weaker solution being depolarised by excess of iodine.

J. G.

The Eastman Universal Colorimeter. (*Nature*, 1926, 118, 30.)—The colour imparted to a field by the object to be tested is matched by means of a combination of three subtractive primary colour filters. These are coloured blue-green, magenta, and yellow, and are made in form of wedges of dyed gelatin, so that the thickness of the filters may be varied. The colours are permanent, so that the colour scale, though arbitrary, is constant, and may be calibrated against any known scale. Opaque or mounted objects may be measured, but difficulty may be experienced with dark colours.

J. G.

Use of Ultra-Violet Light in the Examination of Foods. Popp. (*Chem. Zeit.*, 1926, 50, 588.)—The quartz mercury vapour lamp can be used for preliminary tests of certain foods. Muscular fibre shows no luminescence, whereas sinews show an intense bluish light; this may enable a judgment to be formed as to the amount of sinew in sausages. Whole milk appears canary yellow, due to the fat, whilst whey is colourless. The amount of residual fat in machine-separated milk may thus be approximately estimated by the intensity of the yellowish luminescence. In the same way skimmed milk cheese may be distinguished from fresh whole milk cheese. It has been found, however, that with the ripening of the cheese the yellow luminescence of the milk fat disappears, so that the test is not applicable at a later period. Olive oil shows no luminescence, sesame oil a very faint one, and poppy oil a distinct blue, which enables it to be recognised in colza, linseed and marine animal oils. The luminescence is stronger after frequent exposure to ultra-violet light, and this must be taken into consideration. Mineral oils show pronounced luminescence or fluorescence, and may thus be readily recognised in fatty oils, such as linseed oil.

Meat extract appears yellowish-brown, whilst yeast extract appears grey. Formic acid appears yellowish-brown, and benzoic acid light brown, but the small

amounts used as preservatives cannot be detected in this way. Butter fat appears canary yellow, whilst margarine shows a faint bluish luminescence, due to coconut or palm kernel oil. A butter containing 25 per cent. of such margarine shows a distinct bluish light. Tallow and lard show no luminescence; cacao butter appears yellow. A thin layer of cacao butter adulterated with coconut oil does not appear yellow, but shows a faint luminescence.

Wheat and rye flours show a distinct bluish light, whilst barley meal appears dead white and potato flour grey-brown. An addition of 10 per cent. of barley meal to wheat or rye flour may thus be recognised. Pea flour gives a pink luminescence, and bean meal a greenish-blue. As little as 2 per cent. of bean meal may thus be detected in wheat flour. Water "noodles" show a bluish luminescence, whilst egg "noodles" containing about 2 egg yolks per pound of flour do not emit light.

Reviews.

RECENT ADVANCES IN PHYSICAL AND INORGANIC CHEMISTRY. A. W. STEWART.
Fifth Edition. Pp. 312. London: Longmans, Green & Co. 1926.
Price 18s. net.

Although earlier editions of this well known work have been noticed before in the pages of *THE ANALYST*, as this, the fifth edition, has only 5 out of its 21 chapters which have survived with alterations, it is almost a new work. There are a dozen new chapters dealing with subjects of absorbing interest at the present time, such as isotopes, hafnium, active hydrogen, intensive drying, and the new hydrides. Busy technical chemists will be grateful to the author for providing them with a readable (Prof. Stewart's style is very readable) account of all that is new and of fundamental importance in theoretical and inorganic chemistry. The book gives an account of all important advances in sufficient detail to make the development of the subject easily understandable, but is not overburdened with subsidiary matter or too numerous references. It goes a long way towards that co-ordination of new knowledge which is so desirable for a true conception of chemical philosophy; it is so difficult in these days when new discoveries in the sub-atomic field follow one another so quickly, to obtain a comprehensive view and grasp the bearing of one line of work upon another; Stewart distinctly helps us in this way.

When one turns to the detail there is found indisputable accuracy, a stimulating and lucid style and evidence of keen enthusiasm for the subject. Of course, we shall not all agree with some of the views put forward, and we analysts, if we have any tears left, will shed them over the demise of our beloved atoms; we love them and they served us well, yet Stewart says "they are . . . purely mathematical figments." "The case of the determiners of atomic weights . . . is one

of the most pathetic in the whole history of science." Surely not; is it not one of the most praiseworthy, for the care and accuracy bestowed on the work has been the means of revealing new elements, of developing technique, and forms the basis of all accurate quantitative work? Science goes round in circles: a corpuscular theory of light revived recently; transmutation of elements is an accomplished fact; Prout's hypothesis, once abandoned, is now coming into its own in a modified form; who knows whether Dalton's atoms will not one day resume their former glories?

All chemists, and particularly those whose labours lie in other fields than those here dealt with, should read the book and ponder; it makes one wonder what our science will be like in another generation.

H. E. Cox.

VOLUMETRIC IODATE METHODS. By GEORGE S. JAMIESON, Ph.D. Pp. 96.
New York: The Chemical Catalog Company, Inc. Price \$2.00 net.

This little book is a compilation of methods published from time to time in the form of papers by the author and other investigators. The text-matter deals with the determination of antimony, arsenic, copper, mercury, molybdenum, tin, zinc, hydrazine, hydrogen peroxide, peroxides, thiosulphate, tetrathionate, and sulphite.

The iodate method, based on the reaction $\text{KIO}_3 + 6\text{HCl} = 3\text{H}_2\text{O} + \text{KCl} + \text{ICl} + 2\text{Cl}_2$, possesses the features of an accurate volumetric method. The iodate is easily obtained in a state of purity and the standard solution is very stable; the results are stoichiometric, and the end-point is remarkably sharp, being marked by the final decoloration of a small quantity of immiscible solvent such as chloroform; the advantage claimed over the starch indicator is, that there is no return of the iodine colour. The volume should prove a handy laboratory companion to those intending to apply the iodate method to the determination of a variety of constituents.

The value for antimony given in the abridged atomic weight table, dated 1923, is 120.20, whereas the atomic weight was altered to 121.77 in 1925, *i.e.* prior to the publication of the present book. It is unfortunate that it was allowed to make its appearance without a reference to this, the most important change in atomic weights in recent years, and the bearing of the new value on the accuracy of the determination.

In the author's method for zinc, a precipitate of zinc mercuric thiocyanate (filter paper included) is titrated with iodate, after suction filtration and washing with a weak solution of mercuric thiocyanate which, apparently, is not displaced by another liquid prior to titration. The reviewer has no personal experience of this method, but he wonders what advantages, if any, it can have over the improved ferrocyanide process, in which a minute quantity of ferric salt is used as an internal indicator. The same may perhaps be said of the iodate titration of cuprous thiocyanate, as a competitor against Low's iodide method.

The text contains few and unimportant misprints, but all too often the temper of the lover of good English may be ruffled by changes from the passive to the active construction, such as "the method was tested by dissolving weighed quantities of . . ., *taking* precautions"; "another series of experiments was made, *using* weighed portion" (*cf.* ANALYST, 1925, 50, 47).

W. R. SCHOELLER.

APPLIED CHEMISTRY. By C. K. TINKLER, D.Sc., F.I.C., and HELEN MASTERS, B.Sc. Vol. II. (Foods). Pp. 276. London: Crosby, Lockwood & Son. Price 15s.

This volume, like its forerunner, Volume I., is written for students of household science and public health. It is described in the preface as dealing with "certain branches of the chemistry of food and with the interpretation of the analytical results obtained," but its scope is not so limited as this description might suggest, as is shown by the following list of contents:—Milk, 30 pages; Edible Oils and Fats, 33 pages; Carbohydrate Foods, 62 pages; Raising Agents, 27 pages; Meat, Meat Extracts, etc., 18 pages; Vinegar, Fruit Juices and Vegetable Acids, 17 pages; Beverages, 13 pages; Preservation of Food, Condiments, etc., 36 pages; The Calorific Value of Foods, 13 pages.

There can be no doubt that the book adequately fulfils its purpose, for it is obvious throughout that the authors have desired not only to present the necessary information, but also to ensure a thorough understanding of the chemical principles involved. This latter is such a feature of the book that, although it is written expressly for a special university course, it might well be read with profit by students who need a fuller knowledge of the chemistry of food. Excellent examples of the educational value of the book are the explanation of the iodine value of an oil or fat, pages 41 to 44; Chapter IV., on Raising Agents; Chapter VI., on Vinegar, etc.

The analytical methods given are those usually employed in routine analysis, and are well described. The necessary calculations are particularly carefully explained, though the extreme attention to detail in some of these suggests rather poor arithmetical ability on the part of the students. It is essential that methods given should be correct and complete in the important details, and also that standard methods, given as such, should not be subjected to alteration. There are a few exceptions in these respects, such as are included in the remarks below:

Page 6: Rose-Gottlieb Method. In this, after the addition of the ether, the student is instructed to mix the contents of the tube by inverting it three times, and told that if the mixture is shaken too vigorously an emulsion may be formed which separates very slowly. Actually, thorough mixing is a very important part of the process, and it is wise to specify vigorous shaking for one minute in order to ensure satisfactory results.

Pages 56 and 57. The method given for the Reichert-Meissl and Polenske values differs in some respects from that generally practised; moreover, no "blank" on the reagents is specified.

Page 180. The statement that the P_H value for distilled water = 7 requires amplification, as it is true only of distilled water specially prepared and stored.

On page 107 golden syrup is described as the mother liquor from which white granulated sugar has been separated. Golden syrup is not a by-product of this nature, but a substance of deliberate manufacture.

Page 217. With reference to the Marsh-Berzelius Test. "As little as 0.01 mgrm. of arsenious oxide giving a very distinct mirror." A well conducted test should show distinctly the presence of one-tenth of this amount of arsenic. As is usual, glucose is the standard example mentioned in connection with the arsenic test. Although it is true that glucose will often be found to contain arsenic, it would be only fair to mention that this product is manufactured with great care, and that the amount of arsenic present is generally well below 0.5 part per million.

Cocoa and Chocolate (pages 194 to 196) receive meagre treatment, and no analytical work is described.

A description of a method of determining the amount of stalk in tea might have been included as being of use to students of household science; also, a method for estimation of chicory in coffee mixtures might have been given.

The book is well printed and free from typographical errors, except for a very few in spelling which are of no real significance.

The volume bears evidence throughout of careful and considered compilation, and is of real educational value.

E. B. HUGHES.

INK MANUFACTURE. By S. LEHNER. Third Revised and Enlarged English Edition. Pp. 212+viii. London: Scott, Greenwood & Son. 1926. Price 7s. 6d. net.

The present is the third English edition which has been revised and compared with the seventh German edition by Mr. C. Ainsworth Mitchell. The book therefore has sold well, and it is manifest that a work on the subject of Ink Manufacture is needed. The reviewer is inclined to think, however, that the continued sale may not be due entirely to the value of the book, but to a hope on the part of ink manufacturers and others that what they see advertised may prove to be what they require, and possibly the buyers may be as disappointed as the reviewer.

The book is apparently intended as a practical guide to the ink manufacturer, but, despite its many editions, it has not yet grown out of the stage of the household book of recipes, and often contains just sufficient information to be misleading.

The two most serious faults are: First, a lack of uniformity in nomenclature; and, second, the insufficiency and vagueness of many of the formulae and directions.

given. Thus among the names applied to various ingredients are the following:— Acetic acid, vinegar and pyroligneous acid; alcohol, spirit and strong spirit; ammonia and dilute caustic ammonia; copperas, green vitriol and ferrous sulphate; copper sulphate and cupric sulphate. The vagueness referred to is exemplified by the recommendation to use hydrochloric acid, nitric acid and sulphuric acid, respectively, with frequently no indication of the strength required; also by the use of the terms alum, tartar, wax, fat, soap, and tin salt without any definition of what is meant. Again, the use of strong sulphuric acid may be most dangerous unless special precautions are taken to avoid accident, and the necessity for care is not mentioned; also the use of potassium or sodium silicate solution for preparing a safety ink might be disastrous if the commercial solution, which generally contains a large excess of strong alkali, were employed.

The directions for preparing such chemical reagents as ammonium sulphide, ferric sulphate, ferrous sulphate, lead iodide, potassium chromate, Prussian blue, and silver nitrate, are unnecessary, since all these substances may be purchased in any degree of purity required far better and cheaper than they can be made by the ink manufacturer, even though he may need them for experimental purposes, for which the small-scale preparation is specially recommended.

The restoration of faded writing is well described, but is altogether out of place in a book addressed to ink manufacturers, and such work, which is of a very delicate nature, can only be successfully undertaken by those who have made a special study of the subject and who have acquired the necessary experience.

The book would read better if the several lapses from the impersonal to the use of the third person plural (we) were avoided.

From what has been said it is evident that the book could be much improved, and it is hoped that this may be done in any future edition. As it is, however, it will be useful, and will more than repay its cost if it contains one new fact that will help or inspire the ink manufacturer towards the improvement of his ink or the cheapening of its production.

The author, of course, and not the translator, is responsible for the imperfections pointed out.

The size of the book, the type, the printing and the binding are all excellent.

A. LUCAS.

WATER STERILISATION BY GASEOUS CHLORINE. By the Paterson Engineering Co., Ltd., Kingsway, W.C. Pp. 70.

While frankly an advertisement, this is nevertheless a useful and informative little book, and very fairly makes out its case.

Of all the methods intended for the sterilisation of waters in use at the present time, the most efficient and, on a large scale, the cheapest, are based on the use of chlorine or chlorine compounds.

Subject to slight reservations, the technique of the process is fairly well understood, and accumulated experience has produced ingenious, reliable and compact apparatus for distributing and automatically regulating the quantity of the reagent required, though not to the extent of automatic adjustment to variations in the quality of the water supply.

Theoretically the addition to drinking water of such more or less noxious compounds is objectionable, but the minute proportions employed are probably quite harmless, and when the process has been properly carried out the reacting substance practically disappears.

As compared with bleaching powder and hypochlorites, gaseous chlorine has some very marked advantages. It is practically pure (*i.e.* 100 per cent.), is stable and contributes no solid matter to the treated water. As compared with caustic lime treatment, the economy of space and time is obvious.

The main objection to the use of chlorine, and this of course applies to the compounds of chlorine, is its liability to produce an unpleasant taste, due either to an actual excess of the reagent or to the action of the chlorine on the organic substances in the water. In the majority of cases more accurate control is the remedy.

The special claims on behalf of the Paterson installation are very clearly described and illustrated in the text. This specially designed and patented apparatus of British manufacture provides an automatic delivery of chlorine, the dosage being regulated by two different types of apparatus:—(1) The Pulser Chloronome, in which the gas is actually measured, intended for smaller plants up to one or two million gallons per day, and (2) the manometer type, for the largest installations, in which the gas is regulated, under constant pressure through an appropriate aperture, a scale on the manometer on the distal side of the diaphragm being read in pounds of chlorine per hour.

To avoid the corrosion of the metal parts of this apparatus the gas up to this stage must be dry, and, to ensure this, a "moisture seal" in the form of a layer of an inert liquid interposes a barrier between the control apparatus and the water to be treated. Having passed this, the gas is led into a glazed earthenware absorption tower in which a highly concentrated solution of chlorine is produced, which in turn is led into distributors to bring about uniform admixture with the main bulk of the water to be treated.

The details are very fully illustrated and described, including the chemical methods for controlling the strength of the chlorinated water.

CECIL H. CRIBB.