JUNE, 1925. Vol. L., No. 591.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, 6th May, 1925. The President, Mr. G. Rudd Thompson, F.I.C., was in the chair.

A certificate was read for the first time in favour of Mr. Theodore Rendle.

Certificates were read for the second time in favour of:—Messrs. Lewis Eynon, B.Sc., F.I.C., Jack Rowan Heather, Frederick George Hitchman, and William David Rogers, B.Sc., A.R.C.S., F.I.C.

The following were elected members of the Society:—Messrs. George William Fraser Holroyd, M.A. (Oxon.), F.I.C., Cecil Eric Keeley, Andrew Francis Macculloch M.A., B.Sc. (Edin.), A.I.C., Frank Vegetus North Mitchell, Charles Henry Thomson, and Walter Peter Whitley, B.A. (Oxon).

The following papers were read:—"The Adulteration of Conserves, with Special Reference to Pectin and Agar-Agar," by John King, F.I.C.; "The Influence of Palm Kernel Meal on the Composition of Bacon Fat," by J. S. Willcox and H. T. Cranfield; "Points Arising from the Analytical Standardisation of British Chemical Standards," by C. H. Ridsdale, F.I.C., and N. D. Ridsdale; "A New Method for the Separation and Determination of Tin in Alloys," and "A New Colorimetric Method for the Determination of Cobalt in the Presence of Nickel," by B. S. Evans, M.C., M.B.E., Ph.D., B.Sc., F.I.C.; and "The Determination of Small Amounts of Iron by Colorimetric Methods," by W. B. Walker, B.Sc., A.I.C.

The Determination of Oxides of Nitrogen (except Nitrous Oxide) in Small Concentration in the Products of Combustion of Coal Gas and in Air.

By A. G. FRANCIS, B.Sc., F.I.C., AND A. T. PARSONS, B.Sc., A.I.C.

INTRODUCTION.—For the purpose of an investigation a method was needed to determine oxides of nitrogen both in the products of combustion of coal gas and in these products when largely diluted with air. The method, therefore, should combine delicacy with flexibility, since the proportions of oxides of nitrogen to be determined might vary from less than 1 part in a million to as much as 100 or 200 parts in 1,000,000. Methods depending on the precipitation of nitron nitrate and on the reduction of nitric acid to ammonia were clearly inadmissible unless very large quantities of the products of combustion could be worked up.

The process of Allison, Parker and Jones (*Technical Paper* 249, Bureau of Mines, Washington), was examined, as it appeared to be suitable for the purpose. This depends on absorbing the oxides of nitrogen in a closed bottle by 5 ml. of a 10 per cent. sodium hydroxide solution and 5 ml. of hydrogen peroxide (no strength stated) during 30 minutes, the resulting liquid being subsequently evaporated to dryness in a beaker over an electric hot plate. The dry solid is moistened with 2 ml. of a 50 per cent. solution of phenol-disulphonic acid in concentrated sulphuric acid, diluted to 10 ml. with distilled water, filtered, made ammoniacal with 15 ml. of concentrated ammonia solution diluted with water (1 : 1), and its volume made up to 100 ml. The colour is then compared in Nessler tubes with that developed by standard solutions of potassium nitrate. A blank determination on the reagents is made at the same time.

In the paper quoted no mention is made of the process having been tested upon mixtures of oxides of nitrogen and air. On making this comparison, results far below the truth were obtained, and it was also found that the alkaline solution of the absorbed oxides of nitrogen, after having been oxidised by hydrogen peroxide in several concentrations, still contained large quantities of nitrite when tested with the Griess-Ilosvay solution. Attention was consequently directed to:—(A) The absorption of oxides of nitrogen by hydrogen peroxide and by caustic alkali: (*a*) in a closed bottle; (*b*) by scrubbing. (B) The oxidation of sodium nitrite by means of hydrogen peroxide.

A. THE ABSORPTION OF OXIDES OF NITROGEN BY HYDROGEN PEROXIDE AND BY CAUSTIC ALKALI.

As it seemed from the preliminary experiments that nitric oxide in air escaped complete oxidation in alkaline hydrogen peroxide, further experiments were made to test the absorption of oxides of nitrogen by hydrogen peroxide and by

caustic alkali, respectively. Mixtures of known proportions of nitric oxide and air, namely from 7·5 to 36·7 thousands of a milligram of nitrogen per litre, were prepared by a modification of the method devised by Robertson and Napper (*J. Chem. Soc.*, 1907, **91**, 763), which depends on the measurement of the rates of velocity of the streams of nitric oxide and air.

The essential modification was in the mixing vessel. This was a round-bottomed flask of about 250 ml. capacity, fitted with a tight-fitting 3-holed rubber stopper, carrying the inlet tubes for air and nitric oxide and the outlet tube for the mixed gases. The inlet tube for the nitric oxide was of capillary tubing drawn down to a long (7·5 cm.) fine point and turned up at the end, the turned up end being placed at the middle of the flask. The air inlet of wide glass tubing passed to the bottom of the flask, and the outlet tube for the mixed gases passed just through the rubber stopper. By adjusting the rates of the two gases the desired mixtures of nitric oxide and air were obtained.

A (*a*). By Absorption in a Closed Bottle.—The following table gives the results of the absorption of mixtures of nitric oxide and air by acidified H_2O_2 and by 10 per cent. caustic soda contained in a closed bottle.

Table I.

Absorption of mixtures of nitric oxide and air in a closed bottle.

By acidified hydrogen peroxide. Thousandths of a milligram of N_2 per litre.							By 10 per cent. sodium hydroxide solution for 1 hour. Thousandths of a milligram of N_2 per litre.		
Found in			Taken.	Per cent. absorbed in			Found.	Taken.	Per cent. absorbed.
1 hr.	2 hrs.	3 hrs.		1 hr.	2 hrs.	3 hrs.			
5·8	6·8	—	7·3	80	93	—	5·9	7·2	82
5·5	7·1	—	7·6	73	94	—	8·4	7·9	106
6·0	—	8·3	7·4	81	—	112	13·4	13·5	99
—	—	7·5	8·4	—	—	90	15·3	15·8	97
9·1	10·1	10·1	10·7	85	94	94	15·4	16·2	95
19·5	—	20·7	21·9	89	—	95	17·6	18·0	97
—	—	22·5	22·7	—	—	99	21·8	23·0	95
—	—	25·5	24·1	—	—	106	25·0	23·0	108
33·0	34·5	36·5	36·7	90	94	99	25·3	27·0	94

The total nitrogen in the acidified hydrogen peroxide was determined colorimetrically by the phenoldisulphonic acid method after the solution had been made just alkaline with potassium hydroxide and evaporated to dryness as in the method to be described.

The total nitrogen in the sodium hydroxide solution was determined colorimetrically by the phenoldisulphonic acid method after oxidation of the nitrite to nitrate by hydrogen peroxide in acid solution, as in the method to be described.

In view of the difficulty of preparing such very dilute mixtures of nitric oxide and air, and having regard to the limit of accuracy in making colour comparisons,

we think that these figures may be taken to indicate complete absorption by acidified hydrogen peroxide in three hours, and by 10 per cent. sodium hydroxide in one hour.

A (*b*). By Scrubbing.—In order to see if, by the simpler process of scrubbing, complete absorption of the oxides of nitrogen could be obtained, the following scrubber was devised. A conical flask of 200 ml. capacity was fitted with a 2-holed rubber stopper carrying an inlet and an outlet tube. All rubber stoppers and connections were invariably first boiled with sodium hydroxide solution for some hours and then thoroughly washed with water. The inlet tube to the flask was of ordinary quill glass tubing, and passed just through the stopper of the flask. The outlet tube projecting from the 200 ml. flask formed the scrubber proper, the lower portion being of quill tubing about 15 cm. long, the upper widening into a tube 2·5 cm. in diameter and 35 cm. long. At the junction of the narrow and wide tube a perforated platinum cone was inserted, the wide upper portion being filled to within 2·5 cm. of the top with solid glass beads 0·5 cm. in diameter. An appropriate quantity of the absorbing solution was poured through the outlet tube into the flask to wet the beads; a total volume of 13 ml. was found convenient for a rate of aspiration of 3 cb. ft. of gas mixture an hour. The lower end of the outlet tube was now adjusted by sliding it through the rubber stopper of the flask so as to dip into the absorbing solution to such a depth that when suction was applied to the apparatus the bulk of the absorbent was drawn up into the outlet tube or scrubber to within a short distance of the top of the glass beads, where it remained so long as suction was applied.

Mixtures of nitric oxide and air were drawn at the rate of about 6 litres an hour through 3 such scrubbers in series each containing, in experiment (1) 5 ml. of 6 per cent. hydrogen peroxide made acid with 0·1 ml. 2 *N* sulphuric acid and diluted to 15 ml. with water; in experiment (2) 5 ml. of 6 per cent. hydrogen peroxide, 5 ml. 10 per cent. sodium hydroxide solution and 5 ml. of water; and in experiment (3) 5 ml. of 6 per cent. neutral hydrogen peroxide diluted to 15 ml. with water.

The results in thousandths of a mgrm. of nitrogen are given in the following table:—

Acid H_2O_2.			Neutral H_2O_2.			Alkaline H_2O_2.		
Taken.	Found.	Per cent. absorbed.	Taken.	Found.	Per cent. absorbed.	Taken.	Found.	Per cent. absorbed.
560	160	28	650	116	18	630	150	24

To see if caustic alkali alone would absorb oxides of nitrogen completely when bubbled through it, a 50 per cent. solution of potassium hydroxide was used, and mixtures of nitric oxide and air were scrubbed at the rate of 12 litres an hour, with the result that 27 per cent. of the nitric oxide was absorbed, and at the rate of 6 litres per hour, when 60 per cent. of the nitric oxide was absorbed.

It was thus clear that scrubbing failed to absorb the oxides of nitrogen completely, and in the further work absorption was always conducted in a confined space.

B. The Oxidation of Sodium Nitrite by Hydrogen Peroxide.

When nitrogen peroxide is absorbed by solutions of caustic alkali part of the nitrogen is found in the solution as alkaline nitrite. Since the colorimetric method of determination of the oxides of nitrogen takes account only of the nitrogen present as nitrate, the oxidation of sodium nitrite solutions by hydrogen peroxide was investigated under various conditions.

B (*a*).—The following table gives the results obtained when solutions of sodium nitrite were oxidised by hydrogen peroxide (1) in acid solution according to the method to be described; (2) in neutral solution; and (3) in alkaline solution according to the method of Allison, Parker and Jones. In all cases the nitrate was determined colorimetrically by the phenol disulphonic acid method.

Table II.

Oxidation of sodium nitrite by H_2O_2 in acid, neutral and alkaline solution.

	Taken. Thousandths of a mgrm. of nitrogen.	Found. Thousandths of a mgrm. of nitrogen.	
			Oxidation in acid solution.
(1)	9	8·5	,,
	18	18·5	,,
	18	18·0	,,
	27	26·4	,,
	36	37·0	,,
	36	37·0	,,
	45	45·0	,,
			Oxidation in neutral solution.
(2)	9	9·0	,,
	18	16·5	,,
	27	23·5	,,
	36	30·7	,,
	36	28·8	,,
	36	31·3	,,
	36	36·5	,, double oxidation
	45	35·9	,,
	45	32·5	,,
	45	37·0	,,
	45	42·0	,, double oxidation
			Alkaline oxidation.
(3)	9	0·0	,,
	9	0·5	,,
	18	1·0	,,
	18	1·0	,,
	27	1·0	,,
	27	1·5	,,
	36	1·5	,,
	36	2·0	,,

Thus complete oxidation of sodium nitrite by hydrogen peroxide takes place only in acid solution.

CONSIDERATION OF RESULTS.—The results of these experiments showed firstly [A (*b*)], that scrubbing by means of hydrogen peroxide and caustic alkali failed to remove the oxides of nitrogen from the products of combustion, and that when these were bubbled at the rate of 6 litres an hour through even 50 per cent. potassium hydroxide solution as much as 40 per cent. of the oxides of nitrogen remained unabsorbed. On the other hand, the oxides of nitrogen were completely absorbed when shaken in a bottle with acidified hydrogen peroxide for 3 hours [A (*a*)], and by 10 per cent. sodium hydroxide solution for 1 hour [A (*a*)]. As the simpler process of bubbling was unsatisfactory, it was necessary to conduct the absorption in a confined space. Secondly, the experiments [B (3)] showed that sodium nitrite in very dilute solution was not oxidised in the presence of alkali by means of hydrogen peroxide; oxidation of minute quantities of nitrite [B (2)] was complete in neutral solution when this was evaporated once on the steam bath with hydrogen peroxide; but with larger quantities, from 20 thousandths of a mgrm. of nitrogen upwards, oxidation was incomplete. As nitrous acid in acid solution was oxidised by hydrogen peroxide completely and almost instantaneously in the cold [B (1)], this reaction was used as a basis for our process. Under the same circumstances gaseous oxides of nitrogen were not immediately oxidised, and so a longer time for reaction must be allowed. Moreover, in the method of Allison, Parker and Jones the presence of so much alkali as they use is unnecessary and even disadvantageous, owing to the difficulty of ensuring complete nitration of the phenol-sulphonic acid in the presence of a large quantity of sodium sulphate. In addition, the tint developed in the solution is not exactly the same as that of the standard, even when the excess of alkali has been neutralised by dilute sulphuric acid. In the light of the above preliminary work the process as given by Allison, Parker and Jones was modified in the following manner.

PART I. METHOD OF DETERMINING NITRIC OXIDE PRESENT IN PROPORTION OVER ONE PART IN A MILLION.

SOLUTIONS REQUIRED.—**1.** Hydrogen peroxide 50 ml. $7\frac{1}{2}$ per cent. hydrogen peroxide (25 vols) and 1 ml. 2 *N* sulphuric acid were diluted to 100 ml.; 7 ml. of this mixture were used for each experiment. The hydrogen peroxide must contain no organic preservative and not more than minute traces of nitric acid, from which no specimens examined were entirely free. The best sample showed a "blank" equal to 1·0 ml. of standard nitrate solution (1 ml. = 0·001 mgrm. N_2) in the quantity required for each experiment.

2. Normal potassium hydroxide. Most samples (also of sodium hydroxide) contain traces of nitrite. Specimens free from this impurity must be chosen.

3. Phenol-disulphonic acid.

4. Standard potassium nitrate solution (1 ml. = 0·001 mgrm. N_2).

Solutions 3 and 4 are prepared as described in the *Standard Methods for Water Analysis*, American Public Health Association, New York, 1917, p. 23.

PROCEDURE.—A water pump was used to aspirate the products of combustion for some time through a clean, dry, empty bottle, of known capacity (about

1 litre). The bottle was fitted with inlet and outlet tubes passing through a well-fitting 2-holed rubber stopper that had previously been boiled with caustic alkali and well washed with water. The outlet tube was in the form of a tap funnel. After the sample bottle had been disconnected from the current of gases, 7 ml. of the hydrogen peroxide mixture were added to it through the tap funnel. The end of the inlet tube was then sealed with a cap of pressure tubing and glass rod, and the bottle rotated so that the inner surface of the bottle was thoroughly wetted by the liquid. The bottle was set aside and rotated frequently during 3 hours; after this, absorption of the oxides of nitrogen was complete. The preliminary experiments showed that sufficient time would thus be allowed for absorption and oxidation. The solution was then rinsed into a flat porcelain dish of 50 ml. capacity, where it was made just alkaline to litmus by 0·5 to 1·0 ml. N-KOH, and evaporated to dryness on an electrically heated water-bath. When dry the residue in the dish was allowed to cool, and was then moistened with 2 ml. of the phenol-disulphonic acid reagent. The acid liquid was now diluted, made ammoniacal with 15 ml. of ammonia solution (1 vol. NH_4OH solution, sp. gr. 0·880, to 1 vol. water) and brought up to 100 ml. This solution was then compared with the standard solution in Nessler tubes.

It was rarely necessary to filter the solution, as the quantity of alkali used is very small and the consequent action on the vessels negligible. Blank tests, run side by side with the experiments, showed quantities of nitrate varying from 1·0 to 1·5 ml. of standard solution, equivalent to 1·0 to 1·5 thousandths of a mgrm. of nitrogen, and the appropriate deduction was invariably made.

RESULTS.—The method when tested upon mixtures of nitric oxide and air, prepared as described above, gave the results shown in Table III.

TABLE III.

Mixtures of Nitric Oxide and Air.

Thousandths of a mgrm. of nitrogen per litre.

Found.	Taken.		Found.	Taken.
7·5	8·4		20·7	21·9
7·1	7·6		37·4	36·6
6·8	7·3		38·7	36·6
9·6	10·7	—	38·0	36·6
15·4	15·6		36·5	36·7
16·4	17·0		34·3	36·7
18·5	20·1		—	—

TABLE IV.

Comparison of results given by the two methods.

Thousandths of a mgrm. of nitrogen per litre found.

Method of Allison, Parker and Jones:—											
14·0	5·5	7·8	11·1	4·6	8·8	7·8	6·5	5·2	33·6	8·4	36·0	12·5
New method:—											
23·2	16·2	18·0	27·0	13·7	22·2	21·9	15·8	13·5	62·8	23·0	60·5	24·4

The figures in Table IV. show the results obtained by the two methods when applied to the products of combustion of coal gas diluted with air. The method of Allison, Parker and Jones gives results from 40 to 60 per cent. less than those obtained by the new method, which was checked against known mixtures of nitric oxide and air with satisfactory results as given in Table III.

PART II. Determination of Oxides of Nitrogen in Proportion less than 1 pt. in a Million.

By a slight modification in procedure an attempt has been made to determine the proportion of oxides of nitrogen in the air where the quantity present is of the order of a few parts in 100,000,000.

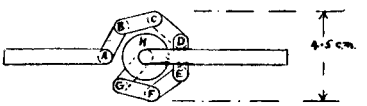
In the course of the investigation for which the method described above was used, the determination of carbon monoxide was also carried out by the iodine pentoxide method, liquid air being used to remove condensable gases. A blue solid, presumably N_2O_3, was frequently observed in the condensing tube, and this solid had a nitrous odour and reacted with potassium iodide and the Griess-Ilosvay solutions. It was therefore thought that the condensed products could be employed for determining the oxides of nitrogen, either as an alternative to the method described above, or for obtaining quantitative values when they were in extreme dilution.

Two condensing tubes for immersion in liquid air, one being a guard tube, are as shown in the sketch.

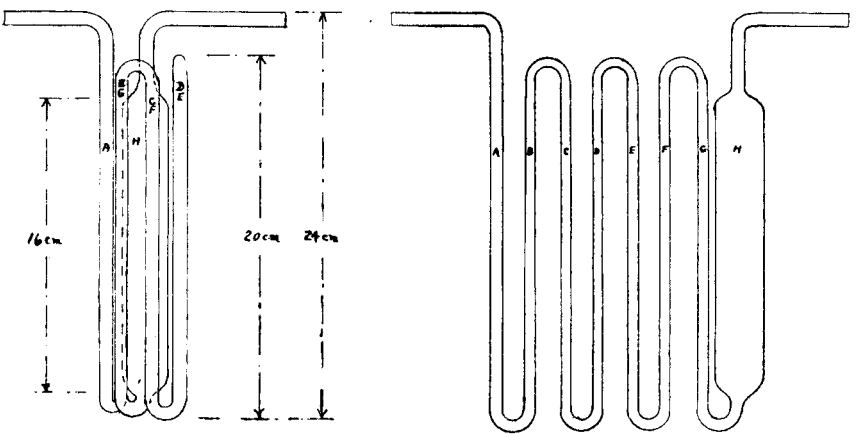
The procedure was as follows:—A drying system was provided consisting of a calcium chloride tower and a phosphoric anhydride U-tube. It was found advisable to evacuate and sweep out with air the tower containing the calcium chloride. After this the whole apparatus was swept free from any contamination due to the air of the room, by drawing through it a cubic foot of outside air which had passed through the drying system.

When the whole apparatus had been rinsed with air in this fashion the condensing tubes were immersed in liquid air, and from 5 to 20 cubic feet of air were drawn through the apparatus at a rate not exceeding 5 cubic feet an hour. If the drying of the air is efficient the tubes immersed in liquid air will not be blocked, as the loose white powder of carbon dioxide falls to the bottom of the wide tube. Meanwhile a bottle of such a capacity as would easily contain the carbon dioxide that would be evolved from the solid substance had been thoroughly cleansed, and 7 ml. of the hydrogen peroxide mixture run into it. The bottle was fitted with inlet and outlet tubes passing through a well-fitting 2-holed rubber stopper. The outside ends of the inlet and outlet tubes carried short lengths of pressure tubing that could be closed with screw clips. The bottle was now evacuated with a water-pump, whereupon the clip was screwed tight. When the desired quantity of air had passed through the apparatus the condensing and guard tubes were attached to their appropriate evacuated bottles before the tubes were removed from the liquid air. After the tubes had been removed from the liquid air they

were kept for some minutes until they came into equilibrium of pressure with their evacuated bottles, as shown by the disappearance of all the solid carbon dioxide. The clips on the inlet tubes of the bottles were now screwed tight, and the bottles disconnected from the condensing tubes and set aside for 3 hours or longer with gentle shaking at intervals. The determination was then completed as above described. The condensing and guard tubes were also treated with the hydrogen



Development Showing Tube Arrangement



peroxide mixture introduced through a fine pointed pipette. These tubes were then closed, and the contents subjected to the same process. The quantities of oxides of nitrogen found in the condensing tube, the guard tube and their respective bottles were added together after deduction of the appropriate blanks.

It should be stated that the calcium chloride used in the drying train had been previously treated with carbon dioxide, and that experiments were made to find out whether the drying train retained any oxides of nitrogen. In the first experiment the oxides of nitrogen in 10 litres of the products of combustion of coal gas containing 96·5 parts of nitric oxide per million were determined by the liquid air method. The result gave 103 parts of nitric oxide per million.

In the second experiment two simultaneous determinations on the air of the street by the liquid air method (1) without any drying train, (2) with the train, gave 2·3 and 2·5 parts of nitric oxide in 100,000,000 respectively. These experiments show that the drying train does not absorb oxides of nitrogen when present in air in concentrations varying from 100 parts in a million down to a few parts in 100,000,000.

Testing the Process.—The testing of this process presented a problem of some difficulty. A direct check against a mixture of nitric oxide and air containing

1 part of nitric oxide in 100,000,000 required air previously perfectly freed from oxides of nitrogen. The use of unpurified air was inadmissible, as it already contained a proportion of oxides of nitrogen probably comparable with that proposed to be added. Experiments in the course of this work had shown that any process of scrubbing was likely to fail in removing oxides of nitrogen completely from air, especially in such quantity as was needed for the test; and, even if such pure air could be obtained, it was scarcely possible to produce such a dilute mixture of nitric oxide and air as 1 or 2 parts in 100,000,000 by the method of mixing employed.

Indirect methods had therefore to be used to test the process, and as all the results were in agreement, a body of proof was obtained supporting the accuracy of the method. The indirect tests applied were:—

(1) The process was compared with the bottle method first described above with mixtures of nitric oxide and air at a concentration of about 100 parts of nitric oxide per million. In these cases the error due to the nitric oxide present in the air used for preparing the mixture was negligible. At this concentration the bottle method is exact. The results obtained by the two methods agreed well, and the air after passage through the tube immersed in liquid air was shown by the bottle method to be free from oxides of nitrogen.

(2) Similar experiments were carried out with mixtures of about 1 part of nitric oxide in a million of air. Here the error due to the nitric oxide in the air used for making such a mixture is 1 or 2 per cent., that is, not greater than the usual error in making colour comparisons. The two methods again gave similar results, but the probable error of reading with the bottle method when used for gas mixtures of this concentration was too great to enable an exact check to be based upon this concordance.

(3) With gas mixtures of concentrations similar to that in (2) it was shown that when two tubes were immersed in liquid air the quantities absorbed in the two tubes were:—

Gas rate, cb. feet per hour.	Thousandths of a mgrm. of nitrogen. 1st tube.	2nd tube.
4	40·2	1·5

Thus from the largely diminished concentration of nitric oxide which reaches the second tube (about 4 parts in 100,000,000) nitrous gases can still be condensed. Further, it will be noticed that at a gas rate of 4 cb. feet per hour 25 times as much nitric oxide is condensed in the first tube as in the second. It is a reasonable inference from this that condensation is complete.

(4) In an experiment on the air from the street, the air after passing through the condensing tubes was scrubbed through 10 ml. of 5 per cent. sodium hydroxide solution. While the sodium hydroxide would not remove completely from the air any oxides of nitrogen remaining uncondensed by the liquid air tube, it would absorb a fraction of them, sufficient to be detected by the Griess-Ilosvay reagent and by the oxidation method. It was found, however, that the sodium hydroxide

contained, when tested by both methods, no more oxides of nitrogen than was shown by the blanks on the similar quantities of the reagents used.

These results show that

(1) At concentrations of nitric oxide and air down to 1 part in a million the process is satisfactory.

(2) Nitrous gases can be completely condensed by liquid air when present in air at a concentration of 1 part in a million.

(3) Condensation of the nitrous gases in the air of the street can be effected by means of liquid air.

To sum up, the accuracy of the second method is supported by evidence of a varied character. While it is not claimed that the method will determine accurately oxides of nitrogen when present in concentration so low as 1 part in 100,000,000, yet the cumulative effect of the results of all the experiments is sufficient, we think, to justify us in bringing it forward tentatively as being capable of determining oxides of nitrogen with some accuracy, even when present in concentration of a few parts in 100,000,000.

The following table shows the results obtained by the method on the air of this district (St. James' Square, Pall Mall, S.W.1) on various dates.

TABLE V.

Date 1923.		Oxides of nitrogen as NO_2 Parts per 100 million by volume.	Remarks.
July 2.		3·7	Motors about.
Sept. 4.		0·8	Dull wet day after heavy rain.
,, 5.		1·0	Bright sunny morning.
,, 10.	10 a.m.	2·0	No rain since Sept. 4. Fine dry day.
,, 10.	2 p.m.	1·8	
,, 11.		1·9	Fine dry day.
,, 13.		1·1	Fine dry day but windy.
,, 14.		1·1	Fine sunny day. No wind.
,, 15.		5·8	Fine day. Motors about.
,, 18.	11 a.m.	0·3	Showery morning after much rain.
,, 18.	2 p.m.	0·3	
,, 19.		1·0	Fine day. Motors about.
Nov. 26.	11 a.m.	16·8	Cold, foggy day.
,, 29.	2 p.m.	2·5	Dry dull day after rain in the night.
,, 30.	2 p.m.	2·2	Cold, bright day.
,, 30.	6 p.m.	10·7	Fog came up about 4 p.m.

It will be seen from Table V. that the proportion of nitric oxide falls to 0·3 part per 100 million after heavy rain, that normally the proportion lies between 1 and 2 parts per 100 millions, and that it rises to 15 or 16 parts per 100 millions on foggy days. As is the case with the high proportions of carbon monoxide found occasionally in the air of this district, a high figure on clear days may possibly be due to the exhaust gases from motor vehicles standing in the lane above the inlet tube through which the air is drawn into the apparatus.

SUMMARY.—(1) The method of Allison, Parker and Jones (*Technical Paper* 249, Bureau of Mines, Washington) has been examined, and found to give results as much as 50 per cent. below the truth.

(2) A modified procedure is described that has been tested against mixtures of nitric oxide and air and found to be satisfactory.

(3) The modified procedure has been extended to determine the very minute proportion of oxides of nitrogen present in the atmosphere.

In conclusion we wish to thank Sir Robert Robertson for constructive criticism and advice, and also for permission to publish the results given in this paper.

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A New Method for Determining Butter Fat.

BY G. VAN B. GILMOUR, B.Sc., A.R.C.Sc.I., A.I.C.

(*Read at the Meeting, March* 4, 1925.)

THIS method is put forward as a decided improvement on that of Kirschner. Like that method it gives a distillation number which is a measure of the butyric acid present in the fat, but the ease with which the new number can be obtained stands in marked contrast to the tedious operations involved in determining a Kirschner figure.

Essentially the process consists in first saponifying the fat with aqueous potassium hydroxide and glycerin, after which the fatty acids are liberated by the addition of excess of sulphuric acid. The solution is next filtered, and a portion of the butyric acid in the filtrate is distilled and titrated with standard alkali.

The success of the method is dependent on the fact that when the volume of the solution from which the fatty acids are liberated is kept small, these acids, with the exception of butyric acid, are almost entirely thrown out of solution.

In Table I. are shown some distillation figures for butter and coconut fats when the fatty acids were liberated from different concentrations of soap solution.

TABLE I.

	1	2	3	4	5	6
	5 grms. fat saponified and vol. made up to c.c.	Vol. filtered after adding 15 c.c. of 10 per cent. H_2SO_4 to (1). c.c.	Water added to filtrate (2). c.c.	Vol. distilled off from filtrate (2) made up to 150 c.c. c.c.	Vol. 0.1 *N* NaOH to neutralise distillate (4) for butter fat. c.c.	Vol. 0.1 *N* NaOH to neutralise distillate (4) for coconut fat. c.c.
(*a*)	150	150	Nil	100	23·8	1·9
(*b*)	100	100	50	100	21·6	1·4
(*c*)	50	50	100	100	17·45	0·8

As the concentration increases, the titration figure diminishes, but the rate of decrease for coconut fat is much greater than for butter fat.

It is interesting to note that under conditions (*a*) where the soap solution is made up to 150 c.c. the titration figures are of the same magnitude as the Kirschner numbers for these fats.

Conditions (*c*) were considered the most satisfactory for the new method, and the following are the details for carrying out a test:—Five grms. of fat and 7·5 grms. of glycerin are weighed into a small conical flask, and 2 c.c. of a solution of pure potassium hydroxide (1:1) are added. The flask is heated over a flame, with constant shaking, until the contents suddenly clear, and after cooling somewhat, about 20 c.c. of distilled water are added. When the soap is dissolved the solution and the rinsings of the vessel are transferred to a 50 c.c. measuring flask, the volume being made up to the mark with distilled water. The soap solution is shaken and then removed to a flask holding about 175 c.c., where the fatty acids are liberated by the addition of 15 c.c. of a solution of sulphuric acid (made either by dissolving 100 grms. of sulphuric acid of sp. gr. 1·825 in water and making up to 1 litre, or by diluting concentrated acid until 11 c.c. just neutralise 2 c.c. of the potassium hydroxide solution). Before the acid is added to the soap solution it is first used to rinse out the measuring flask. The flask containing the liberated acids is now corked and well shaken for about a minute, and the contents filtered through a folded filter paper. When filtering, the aqueous solution is run into the filter paper in such a way that the insoluble acids remain in the flask, which is then corked and shaken vigorously. In this way the acids are made to coalesce and more aqueous solution comes away; this is added to that already in the filter paper. Fifty c.c. of the filtrate are transferred to a 350 c.c. conical flask, and 100 c.c. of distilled water added. After the addition of 0·1 grm. of pumice powder the flask is connected with a condenser, and 100 c.c. distilled, the time of distillation being about 20 minutes. The distillate and washings of the containing vessel are removed to a flask and, after the addition of a few drops of phenolphthalein solution, the acid in the distillate is titrated with 0·1 *N* sodium hydroxide solution. The number of c.c. of alkali required gives the new distillation number of the fat.

Additional Details.—The fatty acids are liberated from the soap solution at the ordinary temperature (15 to 20° C.), and the filtrate from the acidified solution should be clear.

There is no difficulty in filtering 50 c.c. when butter or margarine is being examined, but occasionally, when working with pure coconut or palm kernel fat the liberated fatty acids when thrown out of solution, hold, emulsified with them, so much of the aqueous solution that 50 c.c. of the filtrate can only be obtained with difficulty. In such cases it is best to prepare the filtrate from a second 5 grms. of fat, and by adding sufficient of this to make the first filtrate up to the requisite volume.

The distilling flask and condenser need not be of specified dimensions. Any standard apparatus, such as the Reichert-Wollny or Polenske, with the usual

sources of heat, can be used. By varying the time of distillation from 20 to 35 minutes there was no appreciable effect on the distillation number.

A blank for the glycerin is determined, and this is subtracted from the distillation number. Only the 100 c.c. of the distillate are titrated, and the rinsing of the condenser is neglected. In the case of butters the acid in the condenser washings, after a distillation, is equivalent to only 0·1 c.c. sodium hydroxide solution. Eleven-twelfths of the fatty acids in the distilling flask come over with the 100 c.c. of distillate.

In the case of margarines, it has been found more convenient, when the sample of fat is not too small, to saponify 20 grms., instead of 5 grms., in a 350 c.c. flask, 8 c.c. of potassium hydroxide solution and 30 grms. of glycerin being used. The soap solution is now made up to 200 c.c., and 50 c.c. (equivalent to 5 grms. of fat) are used for determining the new distillation number. There is then left sufficient of the soap for repeating the determination, if necessary; also, 50 c.c. of the solution can be used for making a determination of the total volatile acid number by Blichfeldt's method. The use of this latter number in margarine analysis is referred to below.

RESULTS.—In Table II. are shown the new distillation numbers given by different fats:—

TABLE II.

Fat.	Typical New Distilation Number.	Range.
Butter	16·0	14–18
Coconut fat	0·8	0·7–0·9
Palm kernel fat ...	0·5	0·4–0·6
Other ordinary edible fats	0·15	0·1–0·2

Of butters so far examined, none has given a new distillation number below 14·4, and this number was from a butter which gave particularly low butyric figures by other methods. The highest number obtained was 17·5, the butter being of New Zealand origin. In routine analysis, therefore, a butter giving a new distillation number above 14 can be considered genuine.

In proportion as a butter is adulterated the new distillation number will be reduced.

The range between which the new distillation number for butters can lie permits of a sample originally giving a high number being considerably adulterated before the number is reduced below the lower limit. It is therefore necessary with samples giving low numbers, and still within the range, to apply other confirmatory tests. In such cases a microscopic examination is the best; the determination of the melting point of the insoluble volatile acids is also useful. (See Gilmour, ANALYST, 1921, **46**, 183.)

Several series of mixtures were made and the new distillation numbers determined. The results are given in Tables III.–VII. The calculated numbers are shown for comparison.

TABLE III.

Butter fat. Per Cent.	Sesame oil. Per Cent.	New Distillation number.	Calculated number.
100	0	17·45	—
75	25	12·7	13·1
50	50	8·2	8·7
25	75	4·0	4·4
0	100	0·1	—

TABLE IV.

Butter fat. Per Cent.	Coconut fat. Per Cent.	New Distillation number.	Calculated number.
100	0	17·45	—
75	25	12·75	13·3
50	50	8·5	9·1
25	75	4·5	4·9
0	100	0·8	—

TABLE V.

Butter fat. Per Cent.	Palm kernel fat. Per Cent.	New Distillation number.	Calculated number.
100	0	17·45	—
75	25	12·8	13·2
50	50	8·4	8·9
25	75	4·3	4·4
0	100	0·45	—

TABLE VI.

Butter fat. Per Cent.	Sesame oil. Per Cent.	New Distillation number.	Calculated number.
0	100	0·1	—
1	99	0·25	0·27
5	95	0·8	0·96
9	91	1·45	1·65
100	0	17·45	—

TABLE VII.

Butter fat. Per Cent.	Mixture.* Per Cent.	New Distillation number.	Calculated number.
0	100	0·4	—
1	99	0·55	0·57
3	97	0·8	0·91
5	95	1·15	1·25
7	93	1·35	1·59
9	91	1·6	1·93
100	0	17·45	—

* This mixture contained 30 per cent. of coconut fat, 30 per cent. of palm kernel fat and 40 per cent. of sesame oil.

From the tables it is clear that the method gives consistent figures. The distillation numbers are slightly lower than those calculated. It is considered that the method gives better results than those obtained by the Kirschner method, and the time required, which is about 45 minutes, is less than half that necessary for carrying through the latter process. In addition, the new method is much more economical.

The new process is particularly applicable to the determination of butter fat in margarines.

The Kirschner number for margarines containing butter is considerably influenced by the presence of a large percentage of fats of the coconut group; this is true, but to a less extent, in the case of the new distillation number.

Table VIII. gives the Kirschner and new distillation numbers for butter, coconut and palm kernel fats, also the calculated numbers for a margarine containing 5 per cent. of butter fat and 80 per cent. of coconut fat. The extent to which the butter and coconut fats in the margarine contribute to the numbers is shown.

TABLE VIII.

Fat.	Kirschner number.	New distillation number.
Butter	23·5	15·5
Coconut fat	1·8	0·8
Palm kernel fat	1·1	0·5
Margarine	2·61 { 1·17 contrib. by butter 1·44 ,, ,, coconut	1·41 { 0·77 contrib. by butter 0·64 ,, ,, coconut

EXAMINATION OF MARGARINES.—When determining butter fat in margarine allowance must be made for the effect of fats of the coconut group on the new distillation number. By combining the new distillation number and the number representing the total volatile acids by Blichfeldt's method (*J. Soc. Chem. Ind.*, **1919, 38**, 150T., or ANALYST, **1921, 41**, 183) the author has worked out the equations given below, which not only make a correction for this effect, but, in addition to giving the butter fat content of the margarine, give the percentages of fats of the coconut group determined either as coconut or palm kernel fat. If x represent the new distillation number, and y the total volatile acid number by Blichfeldt's method, then:—

(1) $7{\cdot}5x - 0{\cdot}21y =$ per cent. of butter fat $= B$.

(2) $4{\cdot}8y - 1{\cdot}43B =$ per cent. of coconut fat.

(3) $7{\cdot}8y - 2{\cdot}34B =$ per cent. of palm kernel fat.

These equations are for use in margarine analysis only.

Typical total volatile acid numbers by Blichfeldt's method for butter, coconut and palm kernel fats are 29, 20 and 13, respectively.

The following is an example in which the above equations are used:—A margarine mixture was made up of the composition 9·9 per cent. of butter fat, 60·9 per cent. of coconut fat, 9·4 per cent. of jus, and 19·8 per cent. of cottonseed oil. This mixture gave a new distillation number of 1·8(x) and a total volatile

acid number of $16{\cdot}2(y)$. On substituting the values of x and y in equation (1) and of y and B in equation (2), the percentages of butter and coconut fats are respectively 10·1 and 63·3.

Some workers, perhaps, will hesitate to use the Blichfeldt apparatus for determining the total volatile acid number. For them an alternative number is the sum of the Reichert-Meissl and Polenske numbers, obtained by the present standard apparatus in the following way:—

The 110 c.c. distilled are heated to about 50° C., and a known volume of 0·1 *N* sodium hydroxide solution added, together with a few drops of phenolphthalein solution; the alkali must be added in excess. After shaking and cooling, the excess of alkali is titrated with 0·1 *N* sulphuric acid. The condenser is then washed out with several lots of neutral alcohol, and the washings titrated with 0·1 *N* sodium hydroxide solution. The number of c.c. used to neutralise the washings is added to that required for the distillate, and the sum gives the total volatile acid number. The numbers obtained in this manner for typical samples of butter, coconut and palm kernel fats are 33, 25 and 16 respectively, figures somewhat greater than those given by the Blichfeldt method. When the total volatile acid number is determined in this way the equations given above are not applicable, and the following should be used instead:—If x represent the new distillation number and y the total volatile acid number (R.M.+P.) then:—

(1) $7{\cdot}6x - 0{\cdot}24y =$ per cent. of butter fat $=$ B.
(2) $4{\cdot}1y - 1{\cdot}27\text{B} =$ per cent. of coconut fat.
(3) $6{\cdot}7y - 2{\cdot}07\text{B} =$ per cent. of palm kernel fat.

In conclusion, it should be mentioned that the new distillation method has been tested over a considerable period of time with most gratifying results.

Discussion.

Mr. W. P. L. Hope said that he had found at the first attempt that the process could be carried through in just over an hour, which was a great improvement on the Kirschner test. He pointed out, however, that when potassium hydroxide was used instead of sodium hydroxide for the saponification the liquid would suddenly become clear, giving the impression that saponification was complete, whereas, on looking carefully, minute globules of oil could be discerned, so that care must be taken to make sure that saponification was complete. He had found no difficulty in filtering off the acid except when dealing with pure coconut oil. He compared some figures he had obtained for butter as follows:

Reichert-Meissl.	Polenske	Gilmour.
30·5	2·5	16·7
28·5	2·2	16·0
33·0	3·0	17·7

For coconut oil:—0·7 to 0·9.

For a sample of coconut oil not of edible quality he had obtained a duplicate result of 1 c.c. exactly.

In his opinion the Gilmour method had three advantages over recognised methods:—(1) It gave a low figure for coconut and palm kernel oils; (2) It was

rapid to carry out; and (3) Only one-third the quantity of glycerin was required and no silver sulphate. He regretted that the author did not multiply his results by 1·3 so as to get figures comparable with those obtained by other methods. He suggested that a figure, very similar to the Polenske figure, might be obtained from the insoluble acids which were left on the filter paper by the Gilmour method, and that this figure, together with the Gilmour figure, would furnish all the evidence necessary for the interpolation of the percentages of butter fat and fats of the coconut group.

Dr. H. E. Cox asked the author how the probable composition of the margarine was determined by his method, and particularly how the presence of coconut or palm-kernel oil was recognised. The old methods of Reichert-Wollny and Polenske gave more or less definite information on these points; did the new method give the same information. What would be the range of accuracy in duplicate determinations by the proposed method?

Mr. E. R. Bolton discussed the relationship between Mr. Gilmour's proposed test and the Kirschner value, and thought that it was a pity that the author had not devised his method in such a way that the figure obtained would be rather more comparable with the latter. In his opinion, it would help to make the test popular if chemists were able to draw a better comparison with data already recorded as Kirschner values.

Mr. C. E. Sage said that, in his opinion, it was necessary to take into consideration not only the margarine obtainable in England, but also Australian and Continental margarine, which were of quite different composition. For products containing cotton-seed oil and coconut oil, and for certain kinds of margarine of fairly uniform composition, the method should give good results, but he was not sure whether, in the case of abnormal samples, the figures would be of the same value as those given by other methods.

Mr. A. E. Parkes asked whether the author, before filtering the solution, cooled it to any definite temperature. He considered that when dealing with these partly-soluble fatty acids it was important that the solution should be cooled as much as practicable. If the solution were cooled to a definite temperature the variations in the figures might be considerably decreased, and this might lead to greater accuracy in the method. He pointed out that Bolton and Revis recommended that before the Reichert-Meissl, Polenske-Kirschner distillate was filtered it should be cooled down to some definite point. This made a considerable difference in the figure obtainable on titration afterwards (Analyst, 1911, 36, 333).

Mr. G. Rudd Thompson enquired whether the author did or did not use an alcoholic solution of alkali for saponification.

Mr. Gilmour, in his reply, referred to Mr. Hope's idea of using a factor for converting into butyric acid, and said that the same thought had occurred to him at first, but he had later discarded it, because any such factor would add nothing to the value of the method. He said that those who, like Mr. Bolton, preferred a distillation number of the same magnitude as that of Kirschner might use the alternative procedure pointed out in the paper, but that he, after trying both, considered the one adopted the more satisfactory. He did not think that it would often happen that the available amount of material would be small, and if it did, one could always make an admixture with a fat such as lard, and calculate the number from that of the mixture. It was unnecessary to know which of the two fats, coconut or palm kernel fat was present, for the purpose of calculating the percentage of butter fat. The equations shown giving the percentage of coconut or palm kernel fat were only for use after the presence of one or other of these fats has been ascertained by a method such as the determination of the melting point of the insoluble volatile acids. With regard to the closeness of

duplicate results given by the method, he had found that titration figures usually agreed to 0·1 c.c. In reply to Mr. Bolton, he pointed out that it was not contended that the number could be called a "Kirschner" number, but there was no doubt that it was a measure of the same acids that the Kirschner process gave. The rate of distilling, from aqueous solution, of the acids that gave rise to the new distillation number, was sufficient evidence that these acids consisted mainly of butyric acid. Actually the proportion of butyric acid to other soluble volatile acids was greater than that in the case of the Kirschner acids. He had not examined babasu oil by the method; it would most likely give a number intermediate between coconut and palm kernel fats. Cotton seed oil gave a small number, about 0·2. Referring to the accuracy of the method, he considered that it was inevitable to have different figures for different butters.

The temperature to which the acids were cooled before filtration was the ordinary temperature of 15° C. Lower temperatures did not give better results, and higher temperatures than 20° C. were inadvisable. He used aqueous potassium hydroxide with glycerin for the saponification.

The Determination of Small Amounts of Iron by Colorimetric Methods.

By WILLIAM B. WALKER, B.Sc., A.I.C.

(*Read at the Meeting, May* 6, 1925).

Thiocyanate Method.

Several methods for the detection and determination of small amounts of iron in inorganic and organic materials have, from time to time, been outlined. The best known method is, without doubt, the thiocyanate one, which is based on the fact that ferric iron and an alkali thiocyanate in an acid solution give a red colour, the intensity of which is proportional to the quantity of iron present. This colour is due to the formation of the compound $Fe(CNS)_3.9KCNS.4H_20$. Different investigators have used different modifications of this thiocyanate method. Some carry out the test in hydrochloric acid solution, some in sulphuric acid solution, and others in nitric acid solution. When hydrochloric or sulphuric acid is used it is necessary to employ potassium permanganate as well, to oxidise any ferrous iron to the ferric condition, and so, from this point of view, nitric acid is more advantageous, and is more commonly used.

Unfortunately, ordinary nitric acid gives a red colour with thiocyanate, which, although of a different tint from that given by a ferric salt, is so similar, that unless great care is taken to ensure that the same amount of nitric acid is contained in the control as in the actual liquid tested, erroneous results will be obtained.

The examination of the conditions leading to the production of the red colour caused by the addition of nitric acid to ammonium thiocyanate revealed the fact that the red colour was produced, not by the nitric acid, but by the nitrous acid

it contained. On using nitric acid from which all nitrous acid had been removed by passing air through it, only a very slight coloration was obtained due to traces of iron in the acid. Redistilled nitric acid free from nitrous acid gave not the slightest coloration with ammonium thiocyanate.

As stated before, the use of nitric acid in preference to any other mineral acid is usually based on the supposition that nitric acid will by itself oxidise any ferrous iron present to the ferric state. Investigations showed, however, that nitric acid in strong solution, when free from nitrous acid, does not at all readily oxidise a ferrous salt at ordinary temperatures, whilst in dilute solution it does not readily oxidise even at the boiling temperature. On the other hand, if free nitrous acid be present, oxidation is quickly effected at ordinary temperatures.

Under these circumstances it seemed desirable to modify the method so as to permit of the use of nitric acid containing nitrous acid as the oxidising agent, and then subsequently to endeavour to remove the nitrous acid before adding the thiocyanate solution. There are various ways in which nitrous acid can be completely removed from a solution, but the simplest appears to be to add a small quantity of hydrogen peroxide which immediately oxidises nitrous acid to nitric at ordinary temperatures.

With these modifications iron is obtained in the ferric state with the greatest possible ease, and in the test a coloration due entirely to ferric thiocyanate is given. The method is as follows:—

Solutions Required.—(1) *Standard Fe'' Solution.*—Dissolve 0·7022 grm. of ferrous ammonium sulphate in 100 c.c. of water, and add 5 c.c. of concentrated sulphuric acid. Warm and titrate with potassium permanganate solution until just pink. Cool and make to 1 litre (1 c.c. = 0·1 mgrm. Fe''); (2) A 5 per cent. solution of ammonium thiocyanate; (3) Hydrogen peroxide (10 vol. solution).

Procedure.—Taking ordinary commercial glucose as an example, from 1 to 10 grms. (or more if necessary) are dissolved in water (or ignited) and 2 c.c. of concentrated nitric acid (yellow, showing the presence of nitrous acid) run in from a pipette. The solution is transferred to a 100 c.c. Nessler cylinder, diluted to approximately 50 c.c. and left for 2 minutes. At the same time the control is prepared by diluting 2 c.c. of concentrated nitric acid to 50 c.c. in another Nessler cylinder. Two c.c. of hydrogen peroxide are added to each cylinder, and the liquids mixed and allowed to stand 1 minute. All the nitrous acid present is thus oxidised to nitric acid. Five c.c. of ammonium thiocyanate solution are then added to each tube, and after dilution to 100 c.c. the standard iron solution is run in from a burette to the control until the two solutions show an equal depth of colour. Comparisons are made by holding the Nessler cylinders over a white tile or white paper, not allowing them actually to stand on the tile or paper. The number of c.c. of standard iron solution required, divided by the weight in grms. of the substance taken, gives the amount of iron in parts per million.

Not more than 1 c.c. of standard iron solution should be used for matching, since the colours then become too dark to compare accurately. Should more iron solution be required, a smaller amount of substance to be tested should be

taken and the process repeated. If the solution is cloudy, it must be filtered, before adding the hydrogen peroxide, through an acid-extracted, iron-free filter paper. If this is not available, ordinary filter paper should be extracted with dilute sulphuric acid and permanganate until free from iron.

LIMITATIONS.—The thiocyanate method is well known to have its limitations. Sutton (*Volumetric Analysis*, 1911, p. 239) states that if other metals that form two series of salts are present, they must be in the higher state of oxidation, or the colour is destroyed. According to Lunge (*Scott's Chemical Analysis*, 1918, p. 222) oxalic acid, if present, destroys the colour. Oxidation with potassium permanganate or chlorate, with subsequent removal of chlorine prevents this interference. Scott (*loc. cit.*) states that the red colour of ferric iron with thiocyanate is destroyed by mercuric chloride, phosphates, borates, certain organic acids, and their salts, *e.g.* acetic, oxalic, tartaric, citric, racemic, malic, succinic, etc., whilst Treadwell (*Qualitative Analysis*) found that if the solution to be tested contains phosphoric, oxalic, citric, tartaric, iodic, arsenic, or hydrofluoric acids, the red colour is not obtained unless nitric acid is present. Other authors state that the coloration cannot be obtained in the presence of salts of silver, copper, mercury, or cobalt.

Examination of the above-mentioned limitations showed that:—1. In the presence of salts of silver, mercury or cobalt, unsatisfactory, if any, colorations are obtained. Small amounts of copper do not appear to interfere, but large amounts make a determination impossible.

2. With the method just described, satisfactory results are obtained in the presence of acetic, tartaric, citric, arsenic, and boric acids and their salts.

3. Unsatisfactory results are obtained in the presence of phosphoric, oxalic, and hydrofluoric acids and their salts.

The fact that the thiocyanate method gives unsatisfactory results in the presence of phosphoric acid and phosphates is of exceptional importance, since practically all foodstuffs contain a certain amount of phosphates.

Experiments showed that when not more than 0·05 grm. of phosphoric acid was present satisfactory results were obtained, but that with more than 0·05 grm. an error became noticeable.

Since it is not always known how much phosphate is present in certain materials it was decided to investigate other methods of determining iron, and it was found that methods in which potassium ferrocyanide is used give very accurate results in the presence of phosphoric acid.

FERROCYANIDE METHOD.

Here, again, nitrous acid was found to interfere by giving a yellowish green coloration with potassium ferrocyanide. The following tests illustrate the interference:—1. Dilute 3 c.c. of concentrated nitric acid (yellow, showing presence of nitrous acid) in a Nessler cylinder to 50 c.c. with water, and add 10 c.c. of 5 per cent. potassium ferrocyanide solution. A yellowish green coloration is given. Add 3 c.c. of hydrogen peroxide. No change is noticed.

2. Boil 3 c.c. of concentrated nitric acid (as above) in a platinum basin for a

few seconds to remove nitrous acid, dilute immediately and transfer to Nessler cylinder. Make up to 50 c.c. with water and add 10 c.c. of 5 per cent. potassium ferrocyanide solution. A very slight blue coloration due to trace of iron only is given. Add 3 c.c. of hydrogen peroxide. The yellowish green colour, equal in intensity to that of (1), is developed.

The intensity of the yellowish green coloration is proportional to the amount of potassium ferrocyanide, and is independent of the amount of nitrous acid or hydrogen peroxide present.

In the light of the above results it was found possible to determine small amounts of iron accurately with potassium ferrocyanide by two methods:—

(*a*) By removing nitrous acid from the test solution and blank by boiling, thereby obtaining only a Prussian blue coloration due entirely to iron.

(*b*) By developing the yellowish green colour in the test solution and blank, simultaneously with the Prussian blue coloration due to iron, by adding hydrogen peroxide.

Method (*a*) is undoubtedly the more accurate, since the colours are more easily matched.

SOLUTIONS REQUIRED.—(1) Standard ferric solution as in the thiocyanate method; (2) A 5 per cent. solution of potassium ferrocyanide.

PROCEDURE.—*Method* (*a*).—Ignite 1 grm. (or more) of material to be tested in a platinum basin, then warm gently with 3 c.c. of concentrated nitric acid to extract iron, and boil for a few seconds to remove nitrous acid, dilute (if necessary, filter through an iron-free filter paper), transfer to a 100 c.c. Nessler cylinder, and make up to 50 c.c. with water. At the same time prepare other cylinders containing 3 c.c. of concentrated nitric acid (boiled in a platinum basin to remove nitrous acid and diluted to 50 c.c.) plus 0·1, 0·2, 0·4, 0·6, 0·8 c.c. of standard ferric solution. To test solution and blanks add 10 c.c. of 5 per cent. potassium ferrocyanide solution. Dilute to 100 c.c. with water, rotate to mix, and leave for 5 minutes to allow colours to develop fully. Take the standard tint which is nearest to but not so intense as that of test solution, and add standard ferric solution, drop by drop, allowing the mixtures to stand for 1 to 2 minutes after each addition, until the tints are the same.

With this method only a Prussian blue colour due to iron is obtained.

Method (*b*).—Ignite 1 grm. (or more) of material to be tested in a platinum basin and add 3·3 c.c. of concentrated nitric acid. Warm to extract iron, dilute, filter, if necessary, and transfer to a 100 c.c. Nessler cylinder, making up to 50 c.c. with water. At the same time prepare other cylinders containing 3 c.c. of concentrated nitric acid plus 0·1, 0·2, 0·4, 0·6, and 0·8 c.c. of standard ferric solution. Dilute these to 50 c.c., and to test solutions and blank add 3 c.c. of hydrogen peroxide solution followed by 10 c.c. of potassium ferrocyanide solution. Make up to 100 c.c. with water, rotate to mix, and leave for 5 minutes to allow colours to develop fully. Take the standard tint which is nearest to but not so intense as that of test solution, and add standard ferric solution, drop by drop, allowing the mixture to stand for 1 to 2 minutes after each addition, until the tints are the same.

With this method, in addition to the Prussian blue coloration of the iron, there is the yellowish green colour produced by the nitrous acid or hydrogen peroxide, and so the colours are not quite so easily compared.

Large amounts of copper again interfere with the estimation.

NOTE ON THE METHODS.—It is essential in both thiocyanate and ferrocyanide methods that free nitric acid should be present, and so, when determining iron in salts such as calcium carbonate or calcium citrate, where a reaction or double decomposition takes place, it is often necessary to employ more than 2 or 3 c.c. of nitric acid. The corresponding increase, however, must be added to the blank.

Oxalic acid and oxalates give unsatisfactory results with both thiocyanate and ferrocyanide methods. It is necessary either to ignite or oxidise with potassium permanganate or chlorate, after which either method may be used.

Hydrofluoric acid and fluorides must be treated with concentrated sulphuric acid to remove all hydrogen fluoride, after which ferric iron can be determined by either method.

By means of the two methods described iron has been determined in various materials. Where possible, the thiocyanate method is preferable, as, for the reason given above, it yields the more accurate results. Several determinations have been made by both methods, and the results have been found to agree very well, as shown by the following:—

Substance.	Method Employed. Thio-cyanate. Parts per Million.	Ferro-cyanide.	Substance.	Method Employed. Thio-cyanate. Parts per Million.	Ferro-cyanide.
Hydrochloric acid (pure)	Nil	Nil	Cacao shell	—	300
,, ,, (coml.)	28	26	Cacao butter	2	—
Nitric acid (pure)	3	3	Milk chocolate	8	—
,, ,, (distilled)	Nil	Nil	Covering chocolate	28	27
Citric acid (direct)	5	5	Stick chocolate	28	28
,, ,, (after ignition)	5	—	Tea 1.	160	—
Tartaric acid (direct)	22	24	,, 2.	185	—
,, ,, (after ignition)	21	—	Bantam coffee	65	—
Sodium carbonate	8	8	Coffee beans	45	—
Cream of tartar	32	30	Ground coffee	45	—
Glycerin	1	—	Coffee extract	25	—
Glucose 1.	0·5	—	Condensed milk	1	—
,, 2.	2	2	Milk powder	—	22
,, 3.	27	28	Bread	8	8·5
,, 4.	60	58	Cooked meat	—	15
,, 4. (after ignition)	62	—	Cashew nuts	—	76
Cocoa 1.	56	54	Barcelona nuts	—	30
,, 2.	50	48	Blanched almonds	—	32
,, 3.	65	64	Almond skins	—	110
Cacao nib	—	18			

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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.

THE INCREASE OF FREE FATTY ACIDS IN CASTOR OIL.

THE British Pharmacopoeia, 1914, restricts the amount of free fatty acids in castor oil to a quantity not exceeding that represented by an acid value of 4. This limit is exceeded in a rather large proportion of samples submitted under the Sale of Food and Drugs Acts. Of twenty-six samples examined by the writer during the last five years, four exceeded the British Pharmacopoeial limit, having acid values of 5·0, 4·2, 13·0, and 5·0 respectively. The acid values of those below the limit ranged from 1·1 to 3·9. Considerable improvement resulted when the attention of pharmacists was drawn to the subject; the average of acid values, which before was 3·49, dropped to 2·09.

An attempt was made to ascertain the rate at which the acid value increased, so that vendors could be informed when only a short saleable life could be expected for their stock, and so that they could benefit by an "Observation," where such was called for, on the period elapsing since their stock, if now unsatisfactory, would have satisfied the Pharmacopoeia in this respect. Fifteen samples of castor oil were kept for periods varying from four months to thirty-eight months, and determinations of the acid values were made at the beginning and end of the periods, and, in some cases, also at intermediate times. The results are tabulated below:

	Acid value before interval.	Length of interval.	Acid value after interval.	Rate of increase in acid value per annum.
1.	4·2	6 months	4·4	0·4
2.	3·2	24 ,,	5·1	0·9
3.	3·0	18 ,,	4·5	1·0
4.	1·1	14 ,,	1·7	0·5
5.	1·6	14 ,,	5·3	3·2
6.	2·2	13 ,,	4·4	2·0
7.	2·6	13 ,,	4·3	1·5
8.	3·8	13 ,,	6·0	2·0
9.	1·7	13 ,,	2·4	0·6
10.	2·3	13 ,,	3·3	0·9
11.	3·3	13 ,,	4·2	0·8
12.	1·1	7 ,,	1·5	0·7
13.	1·4	4 ,,	1·5	0·3
14.	1·4	4 ,,	1·7	0·9
15.	3·3	38 ,,	7·9	1·5

With the exception of No. 12, which may have received sunlight at intervals, and No. 15, which was stored in the dark, all the samples remained in dull light at room-temperatures during the period. All were in corked bottles from one-third to one-half full.

These results show that a pharmacist may receive a consignment of castor oil of B.P. quality, and a few months later discover the oil to exceed the limit for acidity. It is to be presumed that the wholesale druggists are, as a rule, aware of the possibility, and supply oils that will remain saleable for eighteen months or so.

WILLIAM PARTRIDGE.

BELLIER'S MODIFIED TEST FOR ARACHIS OIL.

THERE is no doubt that there are on the market parcels of olive oil which give feebly positive results with various modifications of Bellier's test. One of these modifications is given in the B.P., but unfortunately, as only an upper temperature limit is prescribed, the results can be made to vary according to the temperature actually chosen for the test. We use a temperature of 14° C., and have obtained slight positive results with some of the oils to which Mr. Shelley refers (ANALYST, 1925, 182). With Luer's modification, to which he gives preference, we have found a cloudiness at a temperature as high as 17° C.

In our opinion it is not safe to rely on Bellier's test, without separating the fatty acids and taking the melting point after repeated crystallisation; in one sample of oil, which Mr. Shelley and we both analysed, we obtained eventually a melting point of 71° C., a figure which cast a grave suspicion on the oil. Another sample which gave a cloudiness with Luer's modification at 17° C., but a sufficiently satisfactory B.P. test, yielded fatty acids, the melting point of which on repeated re-crystallisation, did not exceed 69° C.

H. DROOP RICHMOND.
A. D. POWELL.

In the course of the examination of some 400 to 500 samples of olive oil, there have been met with from time to time oils which gave a suspicious reaction when examined by the rapid modification of Bellier's test, a turbidity being obtained at 16° to 17° C.

In the case of several of these oils the application of Bellier's original test, or of Luer's modification, gave negative results, but there still remained two or three which gave a turbidity at 16° C. The precipitate obtained was, however, different in character from that given by arachis oil, it being flocculent in appearance.

These oils were then examined by the Renard process (Archbutt's modification), and by this method entirely negative results were obtained. It would appear, therefore, that it is not safe to infer the presence of arachis oil in olive oil merely on the evidence of Bellier's test or one of its modifications, but that, in doubtful cases, confirmation should be obtained by the Renard test (or one of its modifications) in which the arachidic acid is definitely isolated and examined.

H. A. CAULKIN.

THE FAT OF GOATS' BUTTER.

MESSRS. KNOWLES and Urquhart's further note (ANALYST, 1925, 180) contains an argument that their reading of the expression: "P = mean Polenske figure from the table for a figure equal to the Reichert-Wollny figure found + half the Polenske figure"—is the obvious one; that is, that the phrase means that P′ = the mean Polenske figure from the table corresponding to the Reichert-Wollny figure determined, to which is added half the Polenske figure found. I contend that this view is quite illogical, as in this case the words "a figure equal to" are quite unnecessary and redundant, for the only figure equal to a figure is the figure itself, and it seems to my mind that the obvious meaning is that the phrase must be read as "P′ = mean Polenske figure from the table for the sum of the Reichert-Wollny figure found and half the Polenske figure."

Had I intended their interpretation the obviously simple way of writing the formula for calculating the percentage of coconut oil would have been

$$C = \frac{0{\cdot}5P - P'}{14{\cdot}4} \times 100,$$

and P′ would be the mean Polenske figure from the table equal to the Reichert-Wollny figure found.

I propose, however, in future editions, to amend the wording to render it incapable of being misunderstood.

The imputation that I misquoted my book is verbally true; I gave, however, two references, one to my book and one to the ANALYST, and the word "calculated," which does not occur in my book, is in the ANALYST.

I regret that the authors are devoting still more time to the allegation that goats' butter might be condemned, by introducing now the subject of mixing goats' butter with ordinary butter; I doubt whether as much as a ton a year of goats' butter finds its way on to the open market as "butter," and much less is likely to be mixed, and these quantities are commercially negligible.

I would urge Messrs. Knowles and Urquhart to continue their valuable experimental work, and especially to try and elucidate the differences between cows' and goats' butter, and not to dwell so much on the possibility of goats' butter being mistaken for adulterated butter and *vice-versa*.

H. DROOP RICHMOND.

ZINC IN TINNED AND BOTTLED PEAS.

MOST Public Analysts must have come across samples of tinned and preserved peas, notified as being free from copper, but which have, nevertheless, retained their green colour.

During the last six months we have examined a number of such samples, and in every case we have found zinc, in some cases as much as 3·1 grains per pound being present. We have been unable to discover the actual zinc salt employed in preparing the peas.

We were led to search for zinc because it has been used, for some years, for fixing the green colour of the chlophyll in botanical preparations of algæ and mosses. The chlorophyll in such structures is associated with magnesium, but the colour is fugitive. If, however, the magnesium is replaced by copper or zinc, the permanence of the colour is greatly increased.

In determining the zinc we operate as for a Kjeldahl determination, or else cover the peas in a porcelain dish with 50 per cent. nitric acid and 2 or 3 c.c. of sulphuric acid, on the lines suggested by Lander and Winter (ANALYST, 1908, 33, 450). With this method complete solution is not effected, and the undissolved organic matter is filtered off.

The clear solution is made alkaline, and the zinc, copper (if any) and iron are precipitated by hydrogen sulphide; the mixed sulphides filtered off, dissolved in hydrochloric acid, and the iron oxidised by nitric acid and removed by ammonia. Should there be only a trace of iron, it is well to add a little to prevent the precipitation of zinc phosphate. The zinc is then precipitated with ammonium sulphide, filtered off, washed with ammonium sulphate solution, then dissolved in dilute sulphuric acid and determined as sulphide nephelometrically.

CECIL H. CRIBB.
A. L. STILL.

ARTIFICIALLY AGED DOCUMENTS.

LUCAS, referring in his text-book, *Forensic Chemistry* (p. 80), to the artificial ageing of documents, states that he is not aware of any case where the use of tea or coffee extract has been definitely proved to have been employed for the purpose.

Quite recently I had occasion to examine some letters in an Irish-Australian will dispute case. Letters were exhibited in support of a claimant's case, which, from their dates, should have been upwards of sixty years of age. They were brownish in tint, and did not have a genuine appearance. Under the microscope (and less clearly by the naked eye) finger prints were visible. An aqueous extract of those portions of the letters on which there was no writing had a pale brown colour, gave a slow reaction with iron salts, was decolorised with sodium hypochlorite solution, and, on evaporation with hydrochloric acid and treatment in the usual fashion, gave the murexide reaction. A weak extract of tea gave identical results. I reported without hesitation my opinion that the paper had been coloured with weak tea. From the appearance of unmistakable brush-marks under microscopical examination, I added (at the request of the submitter) that I was of the opinion that the staining could hardly be accidental. Perhaps the method I employed might be useful as a routine, if other chemists should have occasion to carry out similar work. O. A. MENDELSOHN.

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 interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY OF KENT.

REPORT OF THE COUNTY ANALYST FOR THE FOURTH QUARTER, 1924.

DURING the quarter 768 samples of food and drugs were examined, of which 21 were found to be adulterated. Of the total samples, 644 were submitted by the county inspectors, 67 by officers of local authorities, and 57 by private purchasers.

MILK.—Of the 285 formal samples taken, 12 were adulterated, 1 containing about 50 per cent. of water and another showing a deficiency of over 30 per cent. of fat. One sample in every 8 taken on Sundays was of inferior quality, and the proportion of adulterated samples was greater than in the case of those taken on other days of the week.

Fourteen samples of Grade "A" milk contained an average amount of 3·8 per cent. of fat, which was nearly 0·2 per cent. below the average amount in the ordinary milk sold throughout the county.

BUTTER.—The average amount of water in the 92 samples of butter examined was 13·5 per cent. From 0·12 to 0·34 per cent. of boric acid preservative was found in 54 per cent. of the samples.

MARGARINE.—The amounts of boric acid present in 48 samples ranged from 0·10 to 0·34 per cent.

DRUGS.—Twenty samples, including 9 of dispensed medicines, were examined. All were of good quality, excepting two of the medicines, which were deficient in prescribed ingredients. F. W. ARNAUD.

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.

UNSTIRRED MILK.

BRIDGES *v.* GRIFFIN.

THIS case was an appeal from a decision of the justices of the Petty Sessional Division of Stow-on-the-Wold, and was heard on May 5 in the High Court, before the Lord Chief Justice and Justices Avory and Shearman. The appellant was an inspector under the Sale of Food and Drugs Act, and the respondent was a vendor of milk, from whose milkman a sample of milk had been taken on September 8, 1924, and had been found on analysis to be deficient in fat to the extent of 46 per cent. The defence was that the milk was in the condition in which it came from the cow, and that it had not been tampered with in any way, the deficiency in fat being attributable to the cream having risen to the top of the churn, whilst the milk was drawn off through a tap at the bottom. The Justices had dismissed the summons against the respondent for selling milk not of the nature, substance and quality demanded.

Mr. Willes, K.C., for the respondent, argued that the offence charged was not abstraction under sec. 9, but selling to the prejudice of the purchaser under sec. 6 of the Sale of Food and Drugs Act. The Milk Regulations did not lay down a standard for milk, and where (as in this case) the prosecutor relied entirely on the certificate of the Public Analyst, it was a complete defence to prove that the milk was in the same condition in which it came from the cow, and that there could have been no tampering with it. This was the effect of the decisions in the cases of *Williams* v. *Rees* (87 L.J., K.B., 639) and *Grigg* v. *Smith* (88 L.J., K.B., 488). Unless the Court was prepared to hold that stirring of milk was a statutory duty, unstirred milk must be considered as genuine as stirred milk.

The Lord Chief Justice, in giving judgment, pointed out that the Milk Regulations of 1901 did not purport to contain a definition; its object was to furnish a means of proof.

It was to be observed in the present case that the milk which was to be presumed under the regulation to be adulterated was the milk which was sold; not the bulk, but the actual sample. The analyst's certificate having been put in, the burden was shifted to the respondent to show that the milk was genuine. Accordingly, he undertook the kind of defence which had been well known since *Hunt* v. *Richardson* (32 *The Times*, L.R., 560; [1916] 2 K.B., 446), (ANALYST, 1916, **41**, 224–227) namely, that the milk was sold in the condition in which it came from the cow. But in *Hunt* v. *Richardson* it was expressly found that nothing had been added to, or subtracted from the milk.

The important moment was the moment of sale, and the important milk was the milk that was sold. It was not sufficient to say that there was a time when it formed part of milk which was in its natural state. In the present case the justices found that when the milk was put in the churn it was as it came from the cow; there was no finding that the sample was in that condition, and the argument was that the milk, having been allowed to stand for some time, the lower part was in a condition in which the cream had risen to the top.

In the case of *Dyke* v. *Gower* (1892; 1 Q.B. 220), milk had been served from the top of the vessel and the residue was deficient in fat. What was done there was said to be abstraction, but from what? From the portion of the milk which was sold. It was not by dipping a measure in the milk that the cream was drawn from the lower portion of the milk, it was by natural processes that the cream rose to the top. What was the distinction between that case and the present? The charge against the defendant was that he sold milk which was not genuine. If a seller put milk into a receptacle knowing that the cream would rise to the top, and afterwards sold from the bottom, could he say that the milk so denuded of its cream was in the condition in which it came from the cow?

That question had been discussed in two cases in Scotland (*Knowles* v. *Scott* [1918], S.C. (J.) 32; and *Pendrice* v. *Brander* [1921], S.C. (J.), 63). In the result those cases brought one back to the phrase employed in *Dyke* v. *Gower* (*supra*), "owing to a neglect to keep the milk stirred." The Scottish case, of course, was not binding on the Court, but was entitled to great respect, and the reasoning seemed to harmonise with that in *Dyke* v. *Gower* (*supra*).

In these circumstances he thought that there was nothing on which the justices could find that this milk was in the condition in which it came from the cow. The true conclusion was that the milk was not of the nature, substance, and quality demanded. There was evidence that the respondent knew well the consequences that would follow if the milk was not stirred. There was no evidence that it was impracticable to keep the milk stirred. In his opinion the appeal ought to be allowed.

Judgment to the same effect was given by the other Justices.

A full report of the judgment is given in *The Times Law Reports*, May 16, 1925.

SUMMONS UNDER THE CONDENSED MILK REGULATIONS.

On April 24, a street trader was summoned at Old Street Police Court for selling as full cream condensed milk a product which, on analysis, was found to contain less than the appropriate percentage of milk fat. The wholesale dealer and the importer of the milk were also summoned.

Mr. Jenkins, for the Bethnal Green Borough Council, said that the proceedings against the wholesale and retail dealers were taken under sec. 4, sub.-sec. 2, of the Public Health (Condensed Milk) Regulations, and those against the importer under sec. 9, sub-sec. 2.

Mr. Ricketts, for the defence, contended that these regulations only obtained force by the Act of 1896, and that Regulation 9 was therefore *ultra vires*. In reply to Mr. Jenkins' observation that the regulations were made under the Act of 1907, he pointed out that that Act only extended the powers of the 1896 Act. That Act contained the penalty clause, to which reference must be made to see if an offence had been committed. It was necessary to prove criminal responsibility or a refusal to comply with the regulations.

The Magistrate (Mr. Clarke Hall) said that, having heard the opening for the prosecution, he did not see how Mr. Jenkins was going to prove any offence. It was for the prosecutor to prove that each of the three defendants had "wilfully neglected," and the opening speech showed no evidence of "wilful neglect." He agreed to the suggestion of Mr. Jenkins that there should be an adjournment, and thought that the Ministry of Health should be represented at the next hearing. In his opinion it was a matter of the greatest importance to all the Borough Councils. He did not see why it should be permitted to sell this imported milk, any more than milk, without the appropriate amount of fat.

"FRENCH COFFEE" WITH DISCLOSURE OF CHICORY.

A GROCER was summoned on April 24, at Pont Mottyn (Glamorgan) for selling a tin of French coffee without directing the attention of the purchaser to the fact that it was a mixture which, on analysis, had been found to contain at least 15 per cent. of chicory.

Counsel for the defence urged that the defendant was protected by sec. 8 of the Sale of Food and Drugs Act, as it was sufficiently and plainly disclosed on the label that the product supplied was a genuine mixture of coffee and chicory. The insistence of customers for this brand of French coffee negatived any suggestion of prejudice to the purchaser, and the fact that for some years this product had been sold with a distinctive label, giving its composition, was an answer to the allegation of fraud. Moreover, the price at which the article was sold was some indication that it was not offered as pure coffee. The purchasers knew what they were buying.

The Bench dismissed the case, but made no order as to costs.

BAD SHRIMPS: KNOWLEDGE PRECLUDES "PREJUDICE."

ON April 25 a firm of wholesale fishmongers was summoned at Stamford, Lincs., for selling to the prejudice of the purchaser potted shrimps not of the nature, substance and quality demanded. The inspector said that the defendants' manager had refused to sell him two pots of the shrimps, stating that they were not for sale, but had offered to give them to him. He had pointed out, however, that they were exposed for sale, and taking two of the pots, had put the money on the counter. He admitted that he was aware that the shrimps were bad.

For the defence it was contended that there was no case to answer, for the gravamen of the charge was that the sale was "to the prejudice of the purchaser," whereas the inspector knew that the shrimps were bad.

The Bench accepted this contention and dismissed the case, but without allowing costs.

DUTCH "CHESHIRE" CHEESE.

ON April 29 three firms were summoned at Liverpool for having sold Cheshire cheese which showed a deficiency of 24 to 30 per cent. of fat, and was not of the nature, substance and quality demanded.

Mr. D. P. Oliver, for the prosecution, said that the inspector's agent, having asked for Cheshire cheese, had been served with Dutch cheese, which was inferior in quality to the genuine Cheshire cheese. The latter was made from whole milk, whilst the former was made from skimmed milk.

Mr. W. H. Roberts, City Analyst, said that the samples he had examined were made from skimmed milk. "Cheshire cheese" was a term given to a cheese that had a particular flavour produced by certain ferments. At one time Cheshire cheeses were only made in Cheshire, but they were now made in other places, including Canada.

One of the defendants stated that Cheshire cheese was known in the trade as good-class cheese made in Cheshire, but there were endless varieties of Cheshire cheese. In future this class of cheese would probably be described as "Dutch cheese," and not as "Dutch Cheshire cheese."

The Magistrate suggested that if this undertaking were given, the three summonses should be withdrawn. This was done, the defendants agreeing to pay £3 3s. 0d. costs.

Additions to Poisons Schedule.*

A LETTER has been sent by the Secretary of the Pharmaceutical Society to all authorities granting licences under Sec. 2 of the Poisons and Pharmacy Act, 1908. In this letter attention is directed to the following amendment effected by an Order in Council approving a resolution of the Council of the Pharmaceutical Society:—

(1) The deletion of the word "medicinal" from the words "Arsenic and its medicinal preparations" occurring in Part I. of the Schedule.

(2) The addition to Part I. of the Schedule of the words "Tobacco": any preparations or admixtures of (other than tobacco prepared for smoking and snuff) containing the poisonous alkaloids of "Tobacco."

The effect of these two amendments is to bring into Part I. of the Schedule all sheep dips containing arsenic, and preparations containing the poisonous alkaloids of tobacco, such as weed-killers containing nicotine.

In future, sales of these substances will be subject to the following restrictions:

(1) The seller must, before delivery, enter or cause to be entered in the Poison Book the date of the sale, the name and address of the purchaser, the name and quantity of the article sold, and the purpose for which it is required.

(2) The purchaser must be known to the seller or must be introduced by a person known to the seller.

(3) The entries in the Poison Book must be attested by the signature of the purchaser and of his introducer, if any.

The following requirements as to labelling remain in force:—The box, bottle, vessel, wrapper, or cover in which the poison is contained must be distinctly labelled with the name of the poison, the word "Poison," and the name and address of the seller.

After January 1, 1926, the article must, in addition, be labelled with the proportion which the poison present bears to the total ingredients of the preparation.

Failure to comply with the above requirements, which came into effect on April 3 (after publication in the *London Gazette* for March 3), constitutes an offence under sec. 17 of the Pharmacy Act, 1868.

* *Pharm. J.*, 1925, 114, 468.

National Physical Laboratory.

METROLOGY DEPARTMENT.

VERIFICATION OF WEIGHTS, TESTING OF BALANCES, DETERMINATION OF DENSITIES.*

VERIFICATION OF WEIGHTS.—Two alternative bases of standardisation are introduced for the first time, viz. "mass" and "weight in air," and weights submitted for verification may be entered under the following varieties of test.

* Obtainable at the National Physical Laboratory, Teddington, Middlesex.

Class A:—A1.—Standardisation on a mass basis with values of the mass and (except in the case of fractions) of the actual mean density of each weight. A2.—Standardisation on a "weight in air" basis with individual values. A3.—Test for compliance with tolerances on a "weight in air" basis (individual values of weights not given).

Class B:—B.—Test for compliance with tolerances on a "weight in air" basis (individual values of weights not given).

Weights from 10 grms. and upwards are certified to a uniform proportional accuracy, instead of, as before, to a single unit in a particular decimal place. A Class A certificate, with calibration errors enables weighings to be corrected to an order of accuracy of about 1 part in 1 million on either basis. A Class A tolerance certificate enables weighings to be made to an order of accuracy of about 1 part in 100,000, without the necessity of applying corrections for individual errors of weights, and a Class B tolerance certificate gives an accuracy of about 1 part in 20,000.

THE TESTING OF BALANCES.—The general working of balances constructed on the principle of a beam with equal arms and 3 knife edges is tested, as well as details of adjustment. Specific gravity balances are tested, provided the final accuracy of registration is $\pm\frac{1}{2}^{\circ}$ sp. gr. for a 10 c.c. (nominal) sinker, and $\pm 1^{\circ}$ for a 5 or 2 c.c. sinker.

DETERMINATION OF DENSITIES.—An average accuracy ranging from 1 part in 1000 to 1 part in 3000 is usually called for and obtainable.

Fees for all types of tests are given, including rejection fees, and lists of accuracies and tolerances for metric, avoirdupois and troy weights. For metric weights the ± tolerances are as follows:—*Class A*:—50 kilos., 0·5 grm.; 20 kilos., 0·2 grm.; 10 kilos., 0·1 grm.; down to 1 kilo., 0·01 grm.; 500 grms., 5 mgrms. 200 grms., 2 mgrms.; 50 grms., 0·5 mgrm.; 20 grms., 0·2 mgrm.; 10 grms. to 100 mgrms., 0·1 mgrm.; 50 mgrms. to 1 mgrm., 0·05 mgrm.; and 0·5 mgrm., 0·02 mgrm. *Class B*:—50 kilos., 2 grms.; 20 kilos., 1 grm.; 10 kilos., 0·5 grm.; down to 1 kilo., 0·05 grm.; 500 grms., 0·02 grm.; 200 grm., 0·01 grm.; 100 grms., 0·005 grm.; 50 grms., 2 mgrms.; 20 grms., 1 mgrm.; 10 grms., to 100 mgrms., 0·5 mgrm.; 50 mgrms. to 2 mgrms., 0·2 mgrm.; and 1 mgrm., 0·1 mgrm.

D. G. H.

The International Critical Tables.

AT the meeting of the International Union of Pure and Applied Chemistry, held in London in 1919, the American delegates submitted a proposal for the international compilation of critically prepared tables of the physical properties of chemical substances and technological materials. The proposal was approved by the Union, and the American National Research Council at Washington has since undertaken the financial and editorial responsibility for the undertaking. A Board of Trustees has undertaken to raise the sum of $200,000 or such part thereof as may be necessary. The editorial responsibility is invested in a Board of Editors, the Editor-in-Chief being Dr. E. W. Washburn, formerly Professor of Physical Chemistry at the University of Illinois.

To ensure the international character of the Tables, Corresponding Editors have been appointed in the principal countries of the world. It may be added that the Tables are in no sense a commercial undertaking, and the members of the

Boards of Trustees and Editors and the Corresponding Editors serve in an honorary capacity.

The work of critically examining the data and of compiling the various tables is being carried out by well-known chemists, physicists, engineers, etc., some three hundred in number, who have been chosen for this purpose in the various countries of the world, largely on the basis of recommendations from the Corresponding Editors and their advisory committees. Each portion of the tables will be published over the name of the co-operating expert who has assumed responsibility for the selection, reliability and accuracy of the data in question.

The main language employed in the Tables will be English, but the introduction, table of contents, definitions, general explanatory text and a very complete index will be in English, French, German, and Italian.

The Tables will contain all available information of value concerning the physical properties and numerical characteristics of (*a*) pure substances, (*b*) mixtures of definite composition, (*c*) the more important classes of industrial materials, (*d*) many natural materials and products, and (*e*) selected data for certain bodies or systems, such as the earth and its main physical subdivisions, the solar and stellar systems, and certain biological organisms, including man. Publications of the world in many languages have been combed for data and much unpublished information has been collected.

For pure chemical substances the data will be assembled in tables of properties, but a certain amount of latitude and duplication will be permitted in some instances, and tables of materials will be employed where it proves to be more convenient.

In some cases no definite value of a constant can be put down, but only upper and lower limits. In other cases a graph may be the best means of indicating the variation of the particular property in question.

The Tables will be issued in a series of volumes comprising a total of about 2500 pages ($9\frac{1}{2}$ in. $\times$ 7 in.), publication extending over about a year and a half. The progress made has been such that the first volume is now in the press and may be shortly expected.

The published price of the Tables will be from $60 to $75 for the set, but the Trustees are reserving the privilege of purchasing from the publishers at the rate of $35 per set whatever number of sets may be required to fill all advance subscriptions received by the National Research Council of America up to a definite fixed date, after which the privilege will lapse, and subsequent sales will be handled exclusively by the publishers at the higher rate. Although $35 represents only the cost of printing, the Trustees and the National Research Council are anxious that all scientific men and women shall be given the opportunity of taking advantage of the lower rate. Accordingly, arrangements are being made so that (1) members of a recognised scientific, technical or engineering society, or (2) universities, research laboratories, libraries, government departments or the like, will shortly be given preferential facilities for purchasing sets at the lower figure. Only one such set may be subscribed for by one individual, but a reasonable number of sets may be purchased by organisations such as the above.

The National Research Council will deal with such applications, but all orders placed in the ordinary way through the trade will be handled by the publishers at the higher figure.

The Advisory Committee for the British Empire (excluding British North America) consists of Dr. G. W. C. Kaye (Corresponding Editor), Sir Robert Robertson, F.R.S., Dr. W. Rosenhain, F.R.S., Prof. A. W. Porter, F.R.S., Dr. T. E. Stanton, F.R.S., Mr. J. E. Sears (Jr.), Mr. A. C. G. Egerton, and Mr. W. F. Higgins as Secretary. Dr. Rosenhain is also acting as Special Editor for Metals and Alloys.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Rapid Colorimetric Testing of Flour. P. Bruère. (*Ann. Falsificat.*, 1925, **28**, 161–165.)—Instead of determining acidity on an aqueous or alcoholic extract of the cereal, the P_H is determined colorimetrically in the presence of the starch by indicators after the well-known manner of Clark and Lubs. The test is adapted for work in warehouses or at the quayside. Four indicators are required, each in 0·04 per cent. solution in 50 per cent. alcohol, viz. bromphenol blue, methyl red, bromocresol and bromothymol. A small quantity of the sample is placed on a flat dish, side by side, with a like quantity of a known neutral starch, and the pile pressed flat with a glass plate; on each surface so formed is put a drop of each of the 4 indicators, and the dish is then immersed for a few seconds in distilled water; the observed coloration gives an indication of the P_H:—

Blue	P_H	$\geqslant$	4·6	bromphenol blue.
Yellow	P_H	$\geqslant$	6·0	methyl red.
Violet	P_H	$\geqslant$	6·8	bromcresol violet.
Greenish	P_H	=	6	bromthymol blue.

Normal samples show a P_H value between 5·2 and 6·0, whereas recently chlorinated flour gives a value below 4·6; dichlorethyl sulphide (ypérite), which is sometimes employed for the same purpose, has a similar effect. H. E. C.

Specific Rotation of Invert Sugar and the Clerget Divisor. F. W. Zerban. (*J. Amer. Chem. Soc.*, 1925, **47**, 1104–1111.)—Critical study of the literature gives for the specific rotation of invert sugar, $[\alpha]_D^{20} = -(19{\cdot}415+0{\cdot}07065c-0{\cdot}00054c^2)$, and for the temperature correction, $[\alpha]_D^t = [\alpha]_D^{20}+(0{\cdot}283+0{\cdot}0014c)(t-20)$. These results indicate that the value 32·00, usually accepted for the negative constituent of the divisor of the Clerget formula, is slightly lower than the true value. T. H. P.

Air Content of Butter. O. Rahn and W. Mohr. (*Milchwirtschaft Forsch.*, 1924, **1**, 211–221; *Chem. Abstr.*, 1925, **19**, 546):—A metal cylinder, 8 cm. long, with a diameter of 20 mm. at the top and 30 mm. at the bottom, is filled with butter and weighed. It holds about 30 to 40 grms. of butter. Over the opening of the cylinder is an inverted glass cap filled with water and sealed by means of a rubber band. The apparatus is placed in a glass cylinder of water maintained at 40° C. As the butter melts the air rises into the cup, and its volume is ultimately determined by measuring the expansion under diminished pressure. For this purpose the glass cylinder is connected by means of a ground glass joint with a pipette, which in turn is connected with a manometer and air pump. The volume of the air is calculated from the equation $V_0P_0 = V_1P_1$, where V_0 represents the

unknown volume x, when $P_0 = 760$ mm.; V_1 = the volume under reduced pressure P_1; and $V_1 = x +$ the measured increase in volume, dv. Then

$$x \times 760 = (x + dv) \times P_1; \quad x(760 - P_1) = dvP_1; \quad \text{or} \quad x = P_1 \times \frac{dv}{(760 - P_1)}.$$

As the measurement is taken at 40° C., a correction is made for the moisture in the air, and the volume of the air is then calculated for a normal temperature of 20° C. The average amount of air in 290 samples of butter tested over a period of 18 months was 4·2 c.c. per 100 grms. For normal butter values ranging from 0·97 to 8·33 c.c. were obtained. The air content varies with the season, the proportion being highest during the summer. Some dairies made butter with consistently low air content, whilst in other dairies the air content was high.

Non-volatile Acids of the Strawberry, Pineapple, Raspberry, and Concord Grape. E. K. Nelson. (*J. Amer. Chem. Soc.*, 1925, **47**, 1177–1179.)—Determinations by the ester distillation method show that the non-volatile acids of the strawberry are citric (about 90 per cent.) and *l*-malic (about 10 per cent.); of the pineapple, citric (about 87) and *l*-malic (about 13); of the red raspberry, citric (about 97) and *l*-malic (about 3); of the black raspberry, citric; and of the Concord grape, *l*-malic (about 60) and *d*-tartaric (about 40 per cent.).

T. H. P.

Glucosides of the Navel Orange. J. A. Hall. (*J. Amer. Chem. Soc.*, 1925, **47**, 1191–1195.)—The endocarp of mature navel oranges appears to contain a soluble compound of glucose and hesperidin, this being probably accompanied by a second similar compound. Another compound, related to hesperidin, but most likely not combined with glucose, also occurs in the endocarp. T. H. P.

Occurrence of Acetaldehyde in the Fruit and other Parts of Plants. C. Griebel. (*Zeitsch. Unters. Nahr. Genussm.*, 1925, **49**, 105–110.)—The presence of acetaldehyde has been demonstrated in a wide range of fruits by means of the micro-chemical test given below. A tiny covered beaker about one-quarter full of the well-bruised tissue is heated on the water bath for a few minutes, the underside of the cover having been moistened with two drops of a clear freshly prepared solution of *p*-nitrophenylhydrazine hydrochloride in 15 per cent. acetic acid. After allowing the cover to cool for about 15 minutes it is examined under the microscope for the presence of minute crystals of acetaldehyde-*p*-nitrophenylhydrazone. A long list of plants which do and do not contain acetaldehyde or acetaldehyde-producing substances is given. In general, it was found that alcohol could be detected in those species which showed a positive reaction for acetaldehyde. H. E. C.

Determination of Benzoic Acid in Wine. J. Dubaquie. (*Ann. Falsificat.*, 1925, **28**, 149–150.)—Some of the difficulties encountered in the estimation of benzoic acid in wine are discussed, and the following method is advocated, which is sensitive to 20 mgrms. of benzoic acid per litre. Two separate quantities of 50 c.c.

are evaporated on the water-bath to low bulk and then extracted with 60 c.c. of ether. The ether is washed with 10 c.c. of water and allowed to evaporate in a cool place. Each of the two extracts is rinsed into a test tube with 5 c.c. of water. To one is added 0·3 c.c. of hydrogen peroxide, 0·2 c.c. of acetic acid, 0·5 c.c. of copper sulphate solution and 1 c.c. of 5 per cent. invert sugar solution; this mixture is heated in boiling water for 40 minutes, then cooled and shaken out with 10 c.c. of petroleum spirit; the petroleum spirit layer is withdrawn by means of a pipette, and washed with 2 c.c. of water, and to it is added 1 c.c. of iron alum solution, which gives the characteristic colour of salicylic acid formed by the oxidation of the benzoic acid. The absence of salicylic acid in the wine is proved by carrying out the same procedure on the contents of the other test tube, but omitting the hydrogen peroxide.

H. E. C.

Presence of Dextran in Wines and its Consequences. A. Vasseur. (*Rev. Pathol. Comp. Hyg. Gen.*, 1924, **24**, 240; *Chem. Abstr.*, 1925, **19**, 374.)—Dextran is a complex gum, having a composition corresponding to the formula $(C_6H_{10}O_5)_n$; it is formed by the action of certain fungi (*Botrytis cinerea* of grey rot) on saccharine matter, and it differs from dextrin in being insoluble in dilute alcohol and in giving no coloration with iodine. Wine that contains it closely resembles in composition wine containing added glucose, in which dextrin is invariably present. The two carbohydrates are distinguished by isolating and identifying the dextran. Vinegar made from such wines will also contain dextran.

Determination of Copper and Zinc in Wine. C. von der Heide. (*Zeitsch. anal. Chem.*, 1925, **66**, 24–38.)—Copper and zinc present together in wine may be determined as follows: A quantity of 500 (or up to 2000) c.c. of the wine is shaken with 10 (or 40) c.c. of 1 per cent. tannin solution; 10 (or 40) c.c. of 10 per cent. potassium ferrocyanide solution and 10 (or 40) c.c. of 1 per cent. gelatin solution (prepared below 30° C.) are then added and the liquid shaken, left for 24 hours, and filtered bright through a pleated filter. The filter paper and precipitate are dried and ashed in a quartz dish, the cold ash being treated with a little water, evaporated to dryness, and again ignited to burn the last traces of carbon. The residue is heated on the water-bath with 22 to 25 c.c. of *N*-sulphuric acid until only a small amount of flocculent matter remains undissolved, evaporated water being replaced from time to time. The liquid is filtered and the residue washed with hot water until neutral, the total filtrate being evaporated to 20 c.c. and treated with hydrogen sulphide, which impinges on the surface of, but is not passed through, the liquid. After about 30 minutes the current of gas is interrupted and the covered beaker warmed and shaken over a gently boiling water-bath to cause the precipitate to flocculate. After 30 minutes the treatment with hydrogen sulphide is repeated and, if necessary, the liquid left for some hours to clear; the precipitate is collected on a filter, washed thoroughly with hydrogen sulphide solution containing 1 per cent. of sulphuric acid, and the wet paper and precipitate ashed in a glazed porcelain crucible, which is heated for 15 minutes in a blowpipe flame before the cupric oxide is weighed.

The filtrate is evaporated to 10 c.c., well cooled, rendered alkaline to methyl orange by means of ammonia and then made acid by addition of 2 c.c. of $N/6$ sulphuric acid. The volume is brought to 20 c.c. and the boiling liquid treated with hydrogen sulphide as before, shaken with a little pulped filter-paper, and filtered, The first filtrate should give no white turbidity if treated, drop by drop, with ammonia and well shaken. If such turbidity appears, the filtrate is mixed with the liquid obtained by washing the precipitate with hydrogen sulphide solution containing acetic acid, the latter acid removed by evaporation with sulphuric acid, and the whole again acidified and treated with hydrogen sulphide as described above. Any residual precipitate, after washing, is dissolved from the beaker in nitric acid and this solution evaporated to dryness and ignited in a platinum dish, in which also the filter and precipitate are ashed. The residue is treated with a few drops of water and 1 to 3 drops of nitric acid, evaporated to dryness, heated over a Bunsen burner and weighed as zinc oxide. T. H. P.

Identification of Tea by the Phloroglucinol Test. C. J. Stracke. (*Pharm. Weekblad.*, 1924, **61**, 124–126.)—A fragment of tea leaf is soaked in warm water, and a section containing epidermis cells is placed on a microscope slide, treated with a drop of concentrated hydrochloric acid, left for 30 minutes, and then covered with a cover glass. Genuine tea develops a characteristic red coloration, whereas *Camellia japonica*, which belongs to the same family, gives no coloration unless phloroglucinol is added. Many other plants also give negative results in this test.

Biochemical, Bacteriological, etc.

Pectin Liquefaction during ripening of Rosaceous Fruit. C. Griebel. (*Zeitsch. Unters. Nahr. Genussm.*, 1925, **49**, 90–94.)—The process of pectin formation has been followed by the microscopical examination of prepared sections of *Pyrus domestica*, and it appears that true pectin originates in the intracellular tissue by hydrolysis of protopectin. As soon as a sufficient stage of ripeness has been reached by fermentation, hydrolysis of the intracellular pectose or protopectin begins and proceeds at a rate dependent upon the temperature, producing a viscous fluid, "pectinschleim," which is an intermediate product between the insoluble protopectin and the more soluble pectin. The mechanism of these changes is discussed in detail. H. E. C.

Methods for the Determination of the Products of the Hydrolysis of Proteins. J. Froidevaux. (*Ann. Falsificat.*, 1925, **28**, 151–161.)—The methods available for the determination of the products of proteolysis are discussed and criticised. For its quantitative evaluation three forms of nitrogen must be determined, *viz.* total nitrogen, ammoniacal nitrogen, and amino-nitrogen. The first presents no difficulty, the second can be satisfactorily determined by well-known methods, *e.g.* by the use of an alkaline earth for the liberation of the ammonia;

the third, however, involves the determination of amino-nitrogen+ammoniacal nitrogen, from which figure the ammoniacal nitrogen is subsequently deducted. For this determination two methods are available—van Slyke's nitrous acid process and Sörensen's "formol" titration. The former is not altogether satisfactory because certain products of hydrolysis, such as purines, react very slowly and incompletely, and others, such as uric acid, do not react at all. Sörensen's method, however, is quite satisfactory. Details are given of a slight modification of this method and, as the results of the formol titration are a little low in the presence of the other forms of nitrogen, they are multiplied by the factor 1·04. Tables of results on known products of proteolysis are given. H. E. C.

Vitamin-*A* Content of Fresh Eggs. J. C. Murphy and D. B. Jones. (*J. Agric. Res.*, 1924, **29**, 253-257.)—Feeding experiments show that eggs are rich in vitamin-*A*. This substance is probably associated with the egg-oil in the yolk, and this, it is calculated, has a vitamin-*A* potency from 2 to 4 per cent. of that of the most potent cod-liver oil. From 0·5 to 0·75 grm. of whole egg daily provides sufficient vitamin for the growth of young rats, and 0·25 grm. sufficed to cure advanced cases of xerophthalmia. H. E. C.

The Vitamin Content of Soya Beans. C. Hornemann. (*Zeitsch. Unters. Nahr. Genussm.*, 1925, **49**, 114–120.)—By feeding experiments on rats it was found that soya beans are rich in vitamins; the fat contains vitamin *A* which is also found in the extracted oil, and the hulls or waste products or soya cake contain vitamin *B*. The proteins of the soya bean are very fattening and promote growth in rats. H. E. C.

Further Report on Imparting Antirachitic Properties to Inert Substances by Ultra-Violet Irradiation. A. F. Hess and M. Weinstock. (*J. Biol. Chem.*, 1925, **63**, 297–304.)—Wheat which has been activated by means of ultra-violet irradiation retains its antirachitic potency for a period of weeks. Etiolated yellow wheat as well as green wheat can be rendered active in this way. The same is true of the etiolated (yellow) leaves of lettuce. When irradiated with the mercury vapour lamp for a period of 1 hour at a distance of 1 ft., they acquired antirachitic value. These etiolated plants contained carotinoid pigments, but little, if any, chlorophyll. A solution of chlorophyll is not endowed with antirachitic power by irradiation, nor are haemoglobin, red blood cells, cream, the phosphatide of yolk of egg, or glycerol. On the other hand, refined wheat flour undergoes activation. Vegetable oil retains its protective power for a period of at least 6 months. It can be activated by an exposure to the lamp for a period of 2 minutes or less. Oxygen plays no rôle in this process, which takes place in an atmosphere of nitrogen. Fractionation showed that the active principle is present only in the unsaponifiable portion of the irradiated oil. Irradiated linseed oil was used. The active principle is only present in the non-saponifiable fraction of cod-liver oil; thus it would seem that irradiation of linseed oil had produced a substance similar in its properties to that contained in cod

liver oil, especially since the unsaponifiable fraction of irradiated linseed oil increased the percentage of inorganic phosphorus in the blood of rats. The results of the experiments are shown in tables. P. H. P.

Antirachitic Value of Irradiated Phytosterol and Cholesterol. I. A. F. Hess, M. Weinstock and F. D. Helman. (*J. Biol. Chem.*, 1925, **63**, 305–308.)—Since the main constituent of the non-saponifiable fraction of vegetable oil consists of phytosterol, experiments were carried out to ascertain whether phytosterol could be activated by means of irradiation. Phytosterol, nearly pure, prepared from cottonseed oil, was given to rats which were receiving the standard low phosphorus diet. A table shews that the irradiated preparation conferred protection, whereas the non-irradiated phytosterol did not protect against rickets. Similarly, crystalline cholesterol extracted from brain tissue conferred absolute protection when irradiated, yet ordinary cholesterol possessed no antirachitic value. Irradiated lanoline conferred slight protection. Cholesterol has been regarded as chemically inert. A hypothesis is offered in regard to the bearing of these results on the pathogenesis of rickets. It is suggested that possibly cholesterol in the skin is activated and rendered antirachitic by the solar rays and similar artificial radiations. This presupposes the formation of active cholesterol within the skin and its further transport by way of the circulation.

P. H. P.

The Diagnosis of Decay in Wood. E. E. Hubert. (*J. Agric. Res.*, 1924, **29**, 523–567.)—Methods for the complete diagnosis of the decays commonly found in wood are given, together with a study of a large and representative number of wood-destroying fungi. The macroscopic, microscopic, and cultural characteristics of the various organisms are given in detail, providing the necessary data for the complete identification of the fungus decomposing the wood. Study is made of the size and shape of the various bore holes, hyphal characters and methods of penetration of the cell walls. There are numerous photomicrographs and tables of cultural characters for which it is necessary to consult the original.

H. E. C.

Preparation of Polychrome Methylene Blue and Thiazine Red. F. Proescher and A. P. Krueger. (*J. Lab. Clin. Med.*, 1924, **10**, 153–159; *Chem. Abstr.*, 1925, **19**, 529.)—Polychrome blue for staining sections may be prepared by adding 20 to 20 mgrms. of sodium peroxide to 100 c.c. of a 1 per cent. solution of methylene blue, and heating the mixture for 15 minutes on the water-bath, after which the solution is neutralised with 1·18 c.c. of 0·1 *N* hydrochloric acid for each 5 mgrms. of sodium peroxide used.

The thiazine reds are prepared by treating a solution of 50 grms. of methylene blue in 200 c.c. of water with 5 grms. of sodium peroxide at 75° to 80° C., filtering off the precipitate on a Buchner funnel, drying it at 37° C., powdering it, and finally drying it over calcium chloride. Frozen sections can be rapidly stained with a solution of 0·5 grm. of thiazine red in 100 c.c. of 1 per cent. acetic acid.

An Apparatus for Measuring the Oxygen Consumption of Tissues. A. E. Koehler. (*J. Biol. Chem.*, 1925, **63**, 475–477.)—Various methods for measuring oxidation in tissue suspensions and cultures are discussed. The author uses a 500 or 700 c.c. Erlenmeyer type flask for the material to be oxidised, because of the large surface exposed for oxygen consumption. A slight shaking motion keeps the tissue suspension sufficiently saturated with the oxygen at the tension within the flask, so that this does not become a limiting factor. A levelling manometer at the side measures the oxygen consumed. The carbon dioxide liberated is absorbed by the soda-lime tube through which the air is circulated by means of a rubber bulb fitted with valves at the top of the flask or by a special rotary gear pump in place of the bulb. The apparatus is used singly or in groups, mounted in a frame in a constant temperature water or air bath. Fifteen to 30 grms. of finely cut fresh tissue are suspended in about an equal amount of Ringer's solution or blood plasma. The stop-cock at the top of the apparatus is opened to the air and the liquid in the manometer burette set at a low level. After temperature equilibrium has been obtained, the stop-cock is closed, the carbon dioxide absorbed by about 20 compressions of the bulb and the original volume observed. Clove oil may be used in the manometer, or distilled water with a few drops of 0·01 *N* sodium hydroxide and phenolphthalein. The alkalinity of the solution decreases the surface tension of the meniscus. Check readings on the burette must be taken by oscillating the meniscus by means of moving the levelling bulb and noting whether it comes to rest at the same value as before. A diagram of the apparatus is given. P. H. P.

Toxicological and Forensic.

Destruction of Organic Matter by "Perhydrol" and its Application to Toxicology. G. Magnin. (*J. Pharm. Chim.*, 1925, **117**, 333–336.)—Perhydrol (100 vol. hydrogen peroxide) may be successfully used to destroy organic material, and has the advantage of giving rise to no unpleasant fumes. The reagent should be slowly added from a dropping funnel, and the presence of a little sodium hydroxide hastens decomposition. The mass is subsequently acidified with hydrochloric acid and filtered, and sulphur dioxide passed to reduce the oxidised compounds. The following substances, 0·01 per cent. of which had been added, were easily detected after decomposition with perhydrol:—Arsenic, copper, bismuth, mercury, lead, barium, antimony, zinc, and tin. The barium must be looked for in the residue from the filtration. D. G. H.

Detection of Hydrocyanic Acid in Cases of Poisoning. G. Magnin. (*J. Pharm. Chim.*, 1925, **117**, 336–339.)—In 12 cases of poisoning from hydrocyanic acid the viscera were tested for the acid after periods varying from 3 to 6 years, both by the direct phosphoric acid method and by Chelle's method, which consists in the oxidation, by means of potassium permanganate in dilute solution, of the thiocyanic acid formed, with production of sulphuric and hydrocyanic acids.

Not all the original hydrocyanic acid is, however, transformed into thiocyanic acid. In spite of this, positive results with Chelle's method were obtained in every case, whilst the direct method gave negative results. Four controls were run with each method. D. G. H.

Water Analysis.

Forms of Nitrogen found in Certain Lake Waters. B. P. Domogalla. C. Juday and W. H. Peterson. (*J. Biol. Chem.*, 1925, **63**, 269–285.)—Since it had previously been shown that the water of Lake Mendota contains more than nine times as much soluble nitrogen as total plankton (plant material) nitrogen, a study of the different forms of soluble nitrogen and soluble organic matter in Wisconsin lake waters has been made with a more detailed study on the Mendota waters. Investigations, made over a period of two years, are described and it is shown that there is a seasonal variation in the different forms of nitrogen found in Lake Mendota. This variation was noted in the surface water, in the bottom water, and in the inflowing water. Ammonia, nitrites, nitrates, amino acids, and proteins reach a maximum in the winter and fall to a minimum during the summer. A sudden and marked increase in ammonia and nitrates occurs in February. The bottom water always contains more of the different forms of soluble nitrogen than the surface water. The plankton nitrogen increases as the soluble nitrogen decreases, but shows marked spasmodic changes due to the different crops of plankton which follow one another in rapid succession. The forms of nitrogen in twelve other inland lakes of Wisconsin and in Lake Michigan are approximately the same as those found in Lake Mendota. The seasonal variation in the different forms of soluble nitrogen indicates that these compounds form part of the nutrients of both plant and animal life of these waters. The samples of water analysed varied in size from 1 gallon to 525 litres. P. H. P.

Occurrence of Amino Acids and other Organic Nitrogen Compounds in Lake Water. W. H. Peterson, E. B. Fred and B. P. Domogalla. (*J. Biol. Chem.*, 1925, **63**, 287–295.)—The presence of proteins and amino acids in lake waters has been established both by qualitative and quantitative methods which are described. Tables shew the results. Large samples of water from different types of Wisconsin lakes and also from Lake Michigan were concentrated and gave positive results for proteins with ten different reagents. The amounts of tryptophane, tyrosine, hystidine, arginine, and cystine were determined in each water. The average of the first three amino acids was about 13 mgrm. and for cystine about 4 mgrm. per cubic metre of water. The quantity of amine, amide and purine nitrogen was determined in top and bottom water samples from Lake Mendota. The lower stratum contained more than the upper. The soluble nitrogen was separated into twelve different forms, and the quantity of each determined, thus enabling about 90 per cent. of the total to be assigned to different fractions. The production of soluble nitrogen takes place principally at the bottom of the lake,

and is brought about by the action of bacteria on the plant and animal debris which accumulates there, but little is consumed there by plant forms. The plankton nitrogen is lower at the bottom, since plant and animal life is less abundant.

P. H. P.

Organic Analysis.

Micro-Determination of Methoxyl. J. C. Smith. (*J. Chem. Soc.*, 1925, 912.)—Attention is drawn to the low results obtained by Pregl's method when 20 grms. of silver nitrate per 200 c.c. of 95 per cent. alcohol are used, as recommended in the English edition of Pregl's *Die Quantitative Organische Mikroanalyse* (Springer, Berlin, 1923). The German edition has 20 grms. of silver nitrate per 500 c.c. of 95 per cent. alcohol, and the author of this note gives figures showing the latter solution to be the correct one. R. F. I.

New Method for the Rapid Determination of Phenols in Essential Oils. L. Reti. (*Chem. Zeit.*, 1925, **42**, 306.)—This is a modification of Gildemeister's process and is of special value where only small quantities of material are available. The absorption vessel, which is of a type similar to a Gerber butyrometer, holds 20 c.c., and has a long neck, about 3·5 mm. diameter and 9 cm. long, graduated in $\frac{1}{100}$ c.c., the scale extending over a volume of 0·8 c.c. One c.c. of the oil is pipetted into the vessel and sufficient sodium hydroxide solution (5 per cent. in strength for oils containing thymol and carvacrol and 3 per cent. for oils containing eugenol) added to bring the layer of oil up to the graduations. The vessel is then closed with a rubber stopper, repeatedly shaken, and centrifuged for 3 minutes, and the volume of the oil read. Air-bubbles must be avoided. The advantages of the method are:—(1) Small amounts of material may be used; (2) a determination takes only 10 minutes; (3) there are no droplets of oil adhering to the vessel; (4) the sharp line of separation enables an exact reading to be obtained. The method can also be applied to the determination of basic bodies, *e.g.* pyridine and quinoline in coal tar, by shaking with 20 per cent. hydrochloric acid. R. F. I.

Simple and Rapid Method for the Determination of Acetyl Values of Fats. E. André. (*Bull. Soc. Chim.*, 1925, **37**, 335–339.)—About 2 grms. of fat are weighed into each of two 60 c.c. flasks, and to one are added 5 grms. of acetic anhydride (b.pt. 135–138° C.) and 25 c.c. of xylene of the same boiling point, and to the other the xylene only. The contents of each flask are boiled for 1 hour under a reflux condenser, and then distilled with the oil bath at 175° C., 22–23 c.c. being collected in each case. Twenty-five c.c. of xylene are then dropped into each flask and distilled, and the operation repeated. On shaking the three distillates from the first flask with water the third should show no acid reaction. The saponification values of the contents of each flask are now determined, and the difference represents the proportion of potassium hydroxide absorbed by acetic acid for 2 grms. of fat, and the proportion of acetic acid fixed by 1 grm. of

fat, *i.e.* the acetyl value correctly defined, may thus be calculated. The agreement of results obtained by this method with those obtained by the ordinary method is usually good, although variations of 2 to 3 units are sometimes found.

D. G. H.

Constitution of Natural Unsaturated Fatty Acids, Part II. Some Acids present in a South Georgian Whale Oil. E. F. Armstrong and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1925, **44**, 180–194; *cf.* ANALYST, 1925, 50.)—The isolation and oxidation of the unsaturated acids is a long and complex process, and summaries of results and experimental work only are included in the paper, any abstract of which must necessarily be inadequate. Ethylenic linkages in the acids derived from a South Georgian whale oil of good quality were located as follows:—C_{14} acids, myristoleic acids (about 1·4 per cent. of the whale oil) mainly $\Delta^{9:10-}$ tetradecenoic acid. C_{16} acids, palmitoleic (about 15 per cent. of the whale oil) entirely $\Delta^{9:10-}$ hexadecenoic acid. C_{18} acids, oleic (about 35 per cent. of the whale oil) about 95 per cent. $\Delta^{9:10-}$ octadecenoic acid, and not more than 5 per cent. of an isomeric acid. C_{20} and $_{22}$ acids, polyethylenic acids, no double linkages nearer than the $\Delta^{9:10-}$ position, much, and with C_{22} acids, most, of the unsaturation beginning further along. Unsaturation (in common with the acids of the majority of vegetable oils) does not commence before the $\Delta^{9:10-}$ position except in special circumstances, and it is probable that the 14, 16 and 18 carbon atom acids are not markedly unsaturated (important proportions of the 16 unsaturated acid are however present) and are usually of the formula $R.CH{:}CH.[CH_2]_7.COOH$, whilst with acids of higher carbon content this structure may be subordinate to one in which the first double bond is still further removed from the carboxylic residue ($R.CH.CH.[CH_2]_9COOH$). The 20 and 22 carbon atom acids only possess traces of saturated acids, little of the mono-ethylenic acids, but (expressed in terms of ethylenic linkages) the average total unsaturation amounts to 4 or 5 times the mono-ethylenic acids. Unsaturated derivatives are not produced in large amount unless there are enough carbon atoms to enable the first ethylenic linkage in the preferred $\Delta^{9:10-}$ position to be in a more or less central position in the chain. The experimental work was on the general lines of that previously described (*J. Soc. Chem. Ind.*, 1925, **44**, 45T and 64T). The oil was saponified and the fatty acids converted into methyl esters which were then fractionated, and the purified unsaturated acids treated by oxidation, hydrogenation, etc. D. G. H.

Insecticidal Properties of the Fatty Acid Series. E. H. Siegler and C. H. Popenoe. (*J. Agric. Res.*, 1924, **29**, 259–261.)—Arising out of the well-known use of soaps as insecticides, experiments have been made as to the toxicity towards aphides of the various members of the acetic series. The toxicity increases with the molecular weight up to a point, a practical amount being reached at C_6 and the peak at or about C_{10}. The free acids are much more potent than their soaps, but some of the more delicate foliages are liable to injury when the free acids are used. Of commercial mixtures, coconut fatty acids are the most useful, as they embody those members approximating to the peak of toxicity.

H. E. C.

Examination of Peat by the Methods of Foodstuffs Analysis. A. P. Dachnowski. (*J. Agric. Res.*, 1924, **29**, 69–83.)—Different kinds of peat have been analysed by the ordinary method of analysis usually applied to feeding stuffs, and the results are discussed in detail. Such figures afford as much information on peat as do the more elaborate methods, and indicate the close connection which exists between the botanical and chemical composition of the main groups of peat. The observed ratio between the nitrogenous and non-nitrogenous organic matter serves as a basis indicating the relative usefulness of the different kinds as food either for livestock or soil micro-organisms. A lengthy bibliography is given. A selection from the results is as under:—

Type of peat.	Depth below surface.	Water.	Ash.	Crude protein.	Crude fibre.	*N*-free extract.	Fat.
Sedimentary, colloidal	4 ft.	2·58	65·48	9·63	12·21	9·81	0·29
Fibrous, sedge	4 ,,	7·71	4·97	17·81	30·16	36·51	2·84
Fibrous, bog moss	1 ,,	9·82	2·54	2·75	40·69	42·73	1·47
Woody, forest peat, coniferous	3½ ,,	10·81	6·38	10·13	24·67	46·08	1·93

H. E. C.

Inorganic Analysis.

Qualitative Test for Weak Bases. R. Robinson. (*J. Chem. Soc.*, 1925, **127**, 768–769.)—Most carbon compounds containing oxygen, nitrogen or sulphur will form ferrichlorides on treatment in petroleum spirit solution with a solution made by saturating concentrated hydrochloric acid with crystalline ferric chloride. Three layers usually form, the lowest consisting of a dilute solution of ferric chloride and hydrochloric acid, the middle green or brown layer containing the weak base, ferric chloride and hydrochloric acid, and the top layer consisting mainly of petroleum spirit. Of two hundred substances tested, all gave positive results, except carboxylic acids, acid chlorides (but not anhydrides, amides or ester chlorides) thiophen, safrole and diphenyl ether. Of the simple alcohols, methyl and ethyl alcohols alone give negative results, owing to their solubility in water. Below a minimum strength the reaction fails. The reaction may be used, for example, to remove traces of oxygenated and nitrogenous compounds from hydrocarbons, and safrol from camphor oil. D. G. H.

Use of *p*-Nitrobenzoic Acid as an Acidimetric Standard. W. M. Thornton Jun., and D. Getz. (*Chem. News*, 1925, **30**, 277–278.)—Para-nitrobenzoic acid is a satisfactory primary standard in acidimetry, readily obtainable in a state of purity, and it appears likely that it will also prove useful in oxidimetry. D. G. H.

Colorimetric Determination of the P_H Values of Solutions. E. Richard. (*J. Pharm. Chim.*, 1925, **117**, 328–333.)—The P_H value is determined from one of the two following equations according to whether $E/e-E$ is greater or less than 1.

$P_H = P_K + \log E/e - E$, $P_H = P_K - \log e - E/E$, where E is the thickness of the standard liquid, e that of the unknown solution, and K is a constant varying with the indicator used. Ten c.c. of the solution whose P_H value is required are measured into a beaker, and 10 c.c. of 0·01 *N* sodium hydroxide solution into another, and exactly 20 drops of a monochrome indicator of suitable strength added to each. After shaking, the colours are matched in a colorimeter, and the values e and E determined. If K is not known, the operation is repeated, using a solution of known P_H value and matching with the same sodium hydroxide solution. It is advisable to use a 0·02 *N* sodium hydroxide solution in the case of alizarine yellow, which has a P_H limit of 12, but provided the whole of the indicator is transformed, it is not necessary to know the exact strength of the alkali solution. D. G. H.

Potassium Tripyrocatechol Ferrate as Indicator in Acidimetry and Alkalimetry. K. Binder. (*Zeitsch. anal. Chem.*, 1925, **66**, 1–13.)—In 1·25 per cent. aqueous solution, this salt, which forms a red anion, $[Fe(OC_6H_4O)_3]$, serves as an excellent indicator. It is decomposed on heating and is extremely sensitive towards carbon dioxide, which must be removed from the water used in preparing the alkali hydroxide solution used in conjunction with it. For titrations with 0·1 *N* (or *N*) solutions, 1 drop (or 10 drops) of the indicator should be used. The indicator is highly stable towards alkalis, but addition of two equivalents of an acid to a molecule of the alkali salt changes the red to a deep violet colour, owing to the formation of the anion, $[Fe^{(C_6H_4O_2)_2}_{H_2O}]$; further addition of acid produces a green colour. Like phenolphthalein, it is applicable in the determination of very weak inorganic and organic acids. Thus, acetic, lactic, oxalic, tartaric, salicylic, and phthalic acids are titratable directly with 0·1 *N* alkali hydroxide in its presence; with citric acid, the solution may be either titrated direct or treated with excess of alkali and then titrated with acid; the latter procedure is followed also with benzoic and cinnamic acids.

The indicator may be used in the same way as phenolphthalein for determining the base in alkali hydroxide containing carbonate, a small quantity of the indicator being added at first to show when the added acid is in excess, and a larger quantity (see above) after the carbon dioxide has been expelled by boiling and the liquid cooled.

Ammonia may be determined by addition of excess of hydrochloric acid and titration with alkali hydroxide. When the ammonia solution obtained by distilling an ammonium salt with alkali is to be titrated, double the usual amount of indicator should be employed. To the volumetric determination of pyridine the indicator is not applicable. This is the first recorded case in which the change in colour of an indicator depends on alteration in complex ions. T. H. P.

Detection of Cobalt occurring separately or in Presence of Nickel and other Salts in Neutral Solution. S. J. Jindal. (*Chem. News*, 1925, **30**, 34–35.)—A blue precipitate, dissolving in excess of the reagent to a blue solution, is formed when sodium silicate is added to a dilute neutral solution of a cobalt salt.

On addition of bromine water the colour changes to greenish yellow and then black, and, on heating, the black colour is produced at once. The blue colour is characteristic of cobalt, which may thus be detected in the presence of precipitates of barium, nickel and other silicates. D. G. H.

Determination of Vanadium. W. Hartmann. (*Zeitsch. anal. Chem.*, 1925, **66**, 16–23.)—The method considered by the author is that in which the vanadium is oxidised to alkali vanadate either by fusion with sodium peroxide and hydroxide or by boiling the concentrated solution, as free as possible from iron and acid, with alkali hydroxide and peroxide. Hydrochloric acid, etc., is expelled by evaporation with sulphuric acid, water being then added, and the hot liquid reddened with permanganate to destroy organic matter. The solution is afterwards reduced with either sulphite or hydrogen sulphite, and the filtered liquid, after removal of sulphur dioxide or hydrogen sulphide by boiling, is titrated with permanganate at 60° to 70° C. The titre of the permanganate solution must be ascertained by means of a vanadic acid or potassium vanadate solution of known vanadium content. Even the purest vanadic acid on the market contains, not only lower oxides of vanadium, but also various impurities, which must be determined (see below). A weighed quantity of 2 to 3 grms. of the acid, either air-dry or dried at 200° C., is heated at about 350° C. in a platinum crucible, the moisture content being thus determined. The crucible is then gradually heated to dull redness in a current of oxygen until of constant weight, any lower oxides of vanadium being thus converted into vanadic acid. This is covered with about 5 grms. of sodium carbonate and a very small quantity of sodium peroxide, and the covered crucible heated gently until the commencement of the reaction, at the termination of which the mass is heated until it becomes a clear liquid. When cool, it is dissolved in hot water, any residue being again fused, etc. The united filtrates are made up to 500 c.c., and several separate amounts of 50 c.c. treated as described above and titrated with permanganate until 2 drops of this give a red tint persisting for 10–15 seconds. This titre must be corrected for the various impurities present. After separation and weighing of the silica, the phosphoric acid is determined by Kropf's method (*Chem. Zeit.*, 1917, **41**, 877) in 150 c.c. of the vanadic acid solution. Another volume of 150 c.c. is acidified with sulphuric and hydrochloric acids and treated warm with hydrogen sulphide under pressure; the precipitate formed is filtered off and calcined with the paper in a porcelain crucible, the residue being fused with a little sodium carbonate, extracted with a small quantity of water, and the molybdenum determined colorimetrically with potassium xanthate. Determinations are also made of the arsenic (by distillation with hydrochloric acid, potassium bromide and a hydrazine salt,) and of the alkali.

The presence of iron interferes with the titration with permanganate. Ferrovanadium, therefore, is treated so as to convert the vanadium into alkali vanadate, and the iron-free solution titrated with permanganate; at the same time a second titration is made with an alkali vanadate solution of similar and known vanadium content.

Owing to the unpleasant effects produced by vanadic acid, persons handling vanadium compounds frequently, or in large quantities, should wear masks.

T. H. P.

Separation and Determination of the Alkali Metals by the use of Perchloric Acid. III. Normal Butyl Alcohol and Ethyl Acetate as Mixed Solvents in the Separation and Determination of Potassium, Sodium, and Lithium. G. F. Smith and J. F. Ross. (*J. Amer. Chem. Soc.*, 1925, **47**, 1020–1026; *cf.* ANALYST, 1925, 254.)—The following procedure has now been evolved. The mixture of potassium, sodium, and lithium chlorides is converted into perchlorates by evaporation of the solution with excess of pure perchloric acid, the excess of which is removed by evaporation to dryness twice, with intermediate solution in water. The sodium and lithium perchlorates are then extracted for 2 to 3 minutes with 10 to 20 c.c. of a mixture of *n*-butyl alcohol and ethyl acetate in equal volumes heated to nearly its boiling point. The potassium perchlorate thus obtained is, after decantation of the cold solvent through a weighed Gooch crucible, washed thrice by decantation and then dissolved in the minimum amount of hot water. This solution is evaporated to dryness and the extraction with the hot mixed solvent repeated. The precipitate is filtered through the crucible, washed with the extracting solvents, dried at 350° C., cooled and weighed. If sodium is absent, the second extraction is unnecessary. The united filtrate and washings, totalling 50 to 70 c.c., are evaporated on the hot plate until the ethyl acetate is removed, and the hot solution of the sodium and lithium perchlorates in 20 c.c. of *n*-butyl alcohol is treated with 8 c.c. of 20 per cent. hydrochloric acid solution, the first c.c. being added, drop by drop, and with stirring; this gives a 6 per cent. concentration of the acid, which decomposes the sodium salt with formation of sodium chloride. This is filtered off by means of a Gooch crucible, washed 8 or 10 times with a 6 to 7 per cent. solution of hydrogen chloride in butyl alcohol (made by diluting 100 c.c. of the alcohol with 40 c.c. of 20 per cent. hydrochloric acid), dried at 110–250° C. and finally ignited for a few minutes at a barely visible red heat. The sodium chloride thus obtained is dissolved in water and titrated with silver nitrate solution in presence of potassium chromate as indicator. The filtrate is diluted with 10 c.c. of water and evaporated to expel organic matter, the lithium salt being then converted into sulphate in the usual way. T. H. P.

Determination of Small Amounts of Iodine as Iodide or Iodate. N. A. Lange and L. A. Ward. (*J. Amer. Chem. Soc.*, 1925, **47**, 1000–1003.)—The blue-green colour given by *o*-tolidine with iodine in neutral solution serves as a basis for the determination of iodine in amounts between 0·01 and 0·1 mgrm. Test-tubes (1·8 × 15 cm.) of uniform diameter are used, and 10 standard tubes are prepared by means of varying quantities of potassium iodide solution corresponding with 0·01, 0·02,....., 0·1 mgrm. of iodine; the volume is made up with water in each case to 15 c.c. and the liquid shaken with 0·5 c.c. of a solution prepared by dissolving 1 grm. of *o*-tolidine in 150 c.c. of 95 per cent. alcohol and adding 5 c.c. of 3 per cent. hydrogen peroxide solution. The sample to be tested, containing

iodine as either iodide or iodate, is made slightly alkaline with sodium hydroxide, 10 c.c. of hydrogen peroxide are added to oxidise any nitrites present, and the mixture is evaporated to 20 c.c. The residue is filtered and washed with hot water, and the filtrate is made neutral to litmus by addition of sulphuric acid, evaporated to somewhat less than 30 c.c. and divided into two equal parts. One of these is made up to 15 c.c. and treated with 0·5 c.c. of the tolidine solution; this shows the iodide iodine only. The other is saturated with hydrogen sulphide, the excess of which is expelled by boiling; the cooled liquid is treated with 0·5 c.c. of the tolidine reagent and made up to 15 c.c. and shaken, this showing the total iodine present as iodide and iodate. To each of the tubes containing the standards and the sample, 5 c.c. of hydrogen peroxide are added quickly so that the reaction times are nearly the same. The tubes are shaken and compared after the lapse of 5 minutes.

Sulphates have no effect on the results. Bicarbonate gives a colour, but is removable by boiling; chlorides or bromides in amount exceeding 1500 parts per million influence the results, and if these are to be accurate, the liquid is treated with ferric sulphate, acidified with sulphuric acid, and steam-distilled, the iodine being collected in dilute sodium hydroxide solution containing hydrogen peroxide to reduce the hypo-iodite to iodide. Salts of metals like iron, copper, mercury, etc., would cause precipitation of the tolidine and must be removed from the sample before the test. T. H. P.

New Reactions of Nitrates and Nitrites. S. Vági. (*Zeitsch. anal. Chem.*, 1925, **66**, 14–16.)—When 5 c.c. of 0·15 to 1·5 per cent. aqueous sodium nitrate solution are mixed with 5 c.c. of concentrated sulphuric acid and 3 to 4 drops of 2 per cent. alcoholic benzidine solution, a yellow coloration appears. This is an oxidation reaction, occurring also with ferric chloride or a chlorate, and is especially sensitive with the last. Thus, 5 c.c. of 0·1 per cent. potassium chlorate solution, 5 c.c. of concentrated hydrochloric acid, and a few drops of the benzidine solution yield a deep red coloration, which is still discernible with a 0·03 per cent., and is detectable as a deep yellow coloration with a 0·0001 to 0·0002 per cent. solution of the chlorate; at none of these concentrations is any coloration obtained with potassium nitrate. A solution prepared by dissolving 1 to 2 grms. of benzidine in 100 c.c. of 50 per cent. acetic acid and adding 300 c.c. of water does not react with either nitrates or chlorates, but gives an intense yellow coloration with nitrites, this being still detectable after 15 minutes if 100 to 200 c.c. of a solution containing 0·00005 grm. of N_2O_3 per litre is treated with 10 c.c. of the reagent. T. H. P.

Physical Methods, Apparatus, etc.

Application of Ultra-Violet Spectroscopy to Food Chemistry. R. Dietzel and K. Täufel. (*Zeitsch. Unters. Nahr. Genussm.*, 1925, **49**, 65–75.)—An exposition is given of the application of the ordinary methods of ultra-violet spectroscopy to the examination of various organic compounds occurring in foods. Results are given of an investigation of lactic acid and saccharin by plotting their absorption curves and interpreting the results according to the usual laws. Details

have been given in the *Zeitsch. angew, Chem.* (1924, **37**, 806). The following constitutions (*inter alia*) are deduced:—

Lactyl-lactic acid $CH_3CHOH.COO.CHCH_3.COOH$

Di-lactic acid $HOOC.CH.CH_3\ H_3C.CH.COOH$ (O bridge)

Lactide $CH_3.CH\text{-}CO$ / $O\ O$ / $CO.CH.CH_3$

Di-lactic anhydride $CHCH_3.CO$ / O O / $CHCH_3.CO$

H. E. C.

Reviews.

THE THEORY OF QUANTITATIVE ANALYSIS AND ITS PRACTICAL APPLICATION. By HENRY BASSETT, D.Sc., Ph.D. Pp. ix+308. London: George Routledge & Sons. Ltd. 1925. Price 15s. net.

This volume is the first in Routledge's Twentieth Century Chemistry Series, and the author's aim, as indicated in the preface, is to interpret the operations of quantitative analysis in terms of the general chemical laws. The plan adopted is to outline the theoretical principles underlying the main operations in quantitative analysis, each principle being subsequently illustrated by descriptions and discussions of appropriate methods employed in analytical work.

A number of chapters are devoted to the consideration of the equilibrium conditions attained in classified processes of gravimetric and volumetric analysis from the point of view of the law of mass action applied to dilute solutions. These chapters contain a full exposition of the equilibria obtaining in a large number of typical cases encountered in the laboratory, and the methods of analysis described in this connection are extremely well chosen. The condition of ammonia in aqueous solution—a vexed problem which continues to intrigue the mind of the chemist awaiting a satisfactory solution—is considered in a special chapter. An outline is given of the experimental work done to determine the equilibrium conditions and the dissociation constant of ammonium hydroxide, followed by very good descriptions of typical determinations made in ammoniacal solution. The chapter on colloidal chemistry contains an interesting discussion on the conditions which govern the precipitations of compounds from the colloidal state, and analytical chemists will find much that is of value in this connection. An outline is given

of Werner's theory of co-ordination, the constitution of complex salts being discussed in the light of Langmuir's views of the electronic structure of the constituent atoms. The application of complex salt formation to the quantitative separation of the metals is fully discussed, detailed directions being given for separations involving the use of α-nitroso-β-naphthol, dimethyl-glyoxime, guanyl urea, nitrosophenyl, hydroxylamine, etc.

In treating of the theoretical aspects of quantitative analysis many writers confine their remarks to carefully chosen examples of phenomena for which a perfectly satisfactory explanation is available, no comments being made on cases where theory is at a loss to account for the observed facts. A feature of the book under review is the impartiality shown by Dr. Bassett in discussing cases of each category, and great credit is due to him for his courage in this respect. It must, however, be frankly stated that a few of the explanations suggested are unconvincing, cases in point being the explanation of the slight solubility of aluminium hydroxide in ammonia (p. 128), the retention of alumina by ferric hydroxide (p. 131), the contamination of stannic oxide by iron (p. 135), and the separation of zinc from nickel and cobalt (p. 185). The description "inert" (p. 7), applied to hydrogen as a gas in which certain sulphides should be ignited is not happy, and in this connection it might have been mentioned that the presence of sulphur is also necessary.

These adverse criticisms are intended merely to indicate minor blemishes in a well-planned and conscientious work. The book is thoroughly up-to-date, and will not fail to stimulate the analyst to a deeper consideration of the principles underlying the determinations which he makes, whilst the student of physical chemistry will find here a wealth of illustrations of the chemical laws discussed. The printing and binding leave nothing to be desired, and both author and publishers are to be congratulated on the production.

GEORGE HOGAN.

THE EXAMINATION OF WATERS AND WATER SUPPLIES. By JOHN C. THRESH, D.Sc., M.D., F.I.C., and JOHN F. BEALE, B.A., D.P.H. Third Edition. Pp. xiii.+590 (with 59 illustrations). London: J. & A. Churchill. 1925. Price 25s. net.

The first edition of this book was reviewed in THE ANALYST of October, 1904; that notice, if reprinted, might well apply to this volume, on broad lines.

The authors have contributed greatly to our knowledge of water analysis, they have solved some real difficulties connected with water supply, and they write with obvious anxiety to be of the greatest service to their readers.

An early page repeats the sayings of a pioneer in pathological bacteriology "that an inspection of the source and arrangements of the water supply, carried out with the unaided senses, is the most desirable method, and seldom needs to be supplemented by chemical, bacteriological, or microscopical investigations." The subject matter of the book, in effect, substitutes the words "but always" for "and seldom."

The authors have done good service to the public health by their study of the action of water on lead. Their analyses of moorland waters, their advocacy of treatment with sodium silicate, and their study of the enormous variations in lead content of water in the same supply are as important as any other modern investigation.

Dealing with the question of the action of waters on iron, the authors describe how a very faintly acid moorland supply is treated at Dartmoor with sodium silicate and conveyed in trunk mains for a distance of some seventeen miles, leaving a clear, where previously there was a turbid, water and where sodium carbonate treatment had been a failure.

Eight of the twelve interesting pages on chlorination give the reports of six waterworks engineers on results obtained in practice. A short chapter on the "Excess Lime Method" is supplemented by mention in the Preface of some Langford experiments of the authors, which show "that by acting on Sir A. Houston's suggestion to use excess lime, better results can be obtained than by the use of chlorine."

Dr. Thresh has continued his study of the underground travel and alteration of water, and to his classic on Lincolnshire limestone must be added one on the alkaline waters of the London basin.

Methods of analysis, chemical and bacteriological, generally follow orthodox lines. Many chemists will protest that they do taste water-samples sent for analysis and do test for zinc; the authors declare such to be rare.

A chapter entitled "What Constitutes a 'Pure and Wholesome Water'" reprints an "Annotation" from a medical journal which deals with organic matter in water thus: "In fact, there is no proof that, in the absence of objectionable bacteria, this organic matter is more deleterious than that contained in an infusion of tea." It might well be protested that the tea leaf is plucked while above and off the ground. Next to be discussed are arguments for and against the presence or absence, and the respective amounts of, sundry inorganic substances. These arguments are pertinent and excellent, even if somewhat surprising on occasion, as, for example, "it may be asserted that under 100 parts of salt" (the paragraph is on sodium chloride) "per gallon should not cause a water to be considered impure or unwholesome." Opinions may differ over parts of the following: "One well yielding water containing 120 pts. $MgSO_4$ and 50 pts. Na_2SO_4 per 100,000 was used until recently, although it caused diarrhœa from time to time amongst the users, and even caused 'scour' in cattle. Under ordinary circumstances, a water containing half this quantity would be regarded as unsuitable for domestic use, though it would be unwise to certify that it was unwholesome. Possibly this is a typical example of a water which, though not definitely unwholesome or injurious to health, yet contains sufficient saline matter to affect its suitability for domestic use, and could therefore be regarded as 'impure' from the hygienic point of view."

To guide someone new to such work in the interpretation of the results of water analysis is difficult in the extreme. The book gives a lot of sound advice

and makes some very sensible remarks, though it retains the Frankland and Tidy table which classified water on the amount of "Oxygen Absorbed" in 100,000 parts. This described as "waters of great organic purity" upland surface water with not more than 0·10, and other waters with not more than 0·05, etc.; many analysts of to-day consider the description unduly flattering. With regard to nitric nitrogen, the authors say: "No standard can possibly be adopted as to the amount of nitrates permissible in a potable water." While perfectly true in the sense of a universal standard, this overlooks the fact that the analyst who goes to the trouble of making his standard for a patch of stratum or for a particular supply, has in this determination a figure of great utility and significance. A sentence on page 223 reads: "Water yielding over 0·01 part per 100,000 of albuminoid ammonia, if associated with free ammonia to the extent of 0·006, must be looked upon with grave suspicion." Some analysts would divide the second of these figures by 2.

The chapters on bacteriology follow the now long-used scheme. There is a very good table showing instances of relation of agar to gelatin counts to point the unwisdom of the assertion that the ratio should never be less than 1:10. This book retains the name *Bacillus enteritidis sporogenes* for the group of organisms commonly re-christened.

Many of the criticisms of analysts and bacteriologists are carried over from the first edition. It would be an act of justice—after twenty-one years—to review them and delete all but those necessary to point a moral.

Errors appear to be few. The worst found is on page 21, where hardness in parts of calcium carbonate per 100,000 (the authors use this, the Continental, degree) is converted into Clark's degrees by multiplying by 1·7 instead of 0·7. In two places, pp. 21 and 214, degrees of hardness are classified—with differences of expression in the case of 5° to 10° (which is "moderately soft" in one place and "fairly soft" in the other) and in the case of 10° to 15°, ("neither hard nor soft" on one page and "slightly hard" on the other).

Page 146 says that sodium nitrate is never used in medicine. It is official—according to Squire's *Companion*—in the French, German, Russian, Swiss and U.S. Pharmacopœias, with an average dose of 15 grains.

The terms "albuminoid" and "organic" ammonia are used indiscriminately. Outside this book the latter is sometimes used for total organic nitrogen reckoned as ammonia.

Altogether, some fifty pages are devoted to records of analyses made by the authors on about 678 samples. Of these, 456 include the mineral analysis, and are classified by the strata of origin. These are of considerable service, and the wide selection is unique.

This book is a work of sheer merit. The more it is consulted, the greater is the appreciation of the whole-hearted work the authors have done.

WILLIAM PARTRIDGE.

PHYSICAL CHEMISTRY FOR STUDENTS OF MEDICINE. By ALEXANDER FINDLAY, M.A., D.Sc., F.I.C. Pp. ix+227. London: Longmans, Green & Co. 8s. 6d. net.

Anyone who has ever tried to combat the instinctive antagonism of the average medical student for his preliminary courses in chemistry and physics will find an excellent ally in Professor Findlay's latest book. The gas laws, the properties of solutions, colloids, and permeability, are dealt with, and the connection between physical chemistry and the functioning of the body is made so clear that it must be obvious even to that class of student who chooses his hospital by the prowess of its football team.

In a book which deals with the wide subject of physical chemistry with such amazing brevity and lucidity, it is difficult to pick out special portions for criticism. Nevertheless, the chapters dealing with the laws of mass action (Chaps. VI. and VII.) can be mentioned as especially illuminating. The chapter on "Hydrion" (Chapter VIII.) contains the best short account the present reviewer has yet seen of this extremely important subject. The technique of measuring hydrogen ion concentrations is now so simple that it can be carried out efficiently by a junior laboratory assistant. The fundamental principles on which the methods are based are clearly and simply stated here, and no student of the subject will have any excuse in future for burking an intelligent practice of the technique on the ground that the theory is beyond him. The chapters on the bio-colloids (Chaps. X.–XII.) have suffered rather more from the necessity for condensation than some of the other parts of the book. The statement made on p. 174 that "on cooling an emulsion sol, a jelly or gel is formed," is a little too sweeping. While it is true that gelatin sols form gels, even at very great dilution, on being sufficiently cooled, the writer cannot recollect a single example of, say, an albumin gel or a globulin gel being formed as a result of cooling. Starch gels, too, are not heat-reversible. The "Hofmeister series" of salts seem to have received, in so short a book, a rather disproportionate amount of attention, especially in view of recent work casting doubt on its true significance. The problem of the "permeability" of the plasma membrane is another subject which needs re-examination in the light of modern work.

The reviewer admits a personal dislike to some of the nomenclature in the book. "Albuminoid substances" and "albuminoids" applied to the proteins of the plasma and the serum have an archaic ring. In modern usage their meaning is restricted to the keratins and scleroproteins only, or to the first stages of protein degradation, the metaproteins. In view of their ambiguity they are best avoided.

The only obscure phrase throughout the whole book occurs on p. 48, where the expression "with the blood plasma or serum" occurs. An inexperienced student might possibly be led by this to think that "plasma" and "serum" were alternative titles for the same fluid. The trivial nature of these minor criticisms may, however, be taken as evidence of the general excellence of this text-book.

D. JORDAN LLOYD.

INTRODUCTION TO ORGANIC RESEARCH. By E. EMMET REID. Pp. viii+330. London: Constable & Co. 1925. Price 24s. net.

In the opinion of the reviewer the writing of a text-book on research is an inherently impossible task, and the perusal of this volume has strengthened that opinion. With a number of notable exceptions text-books are regrettable necessities for elementary classes and for teachers who teach merely for a living. By the time a man has passed through the years of rigorous training in the various branches of chemistry which are a necessary preliminary to his undertaking research, he should not stand in need of a text-book on research.

Prof. Reid's book may be divided roughly into three parts:—(*a*) The spirit and ideals of research, (*b*) literature searching, and (*c*) laboratory work.

The first part, occupying roughly one-fifth of the book, makes interesting reading for a wet Sunday afternoon. It applies to all scientific research, and was much better done by Sir Richard Gregory nearly ten years ago in his "Discovery."

The second part, on scientific literature, is the best part of the book. It contains a fairly full account of the chemical periodical literature of the world and includes the great handbooks and dictionaries. Then comes a brief account of libraries; their function, use and arrangement. This is followed by a critical account of the world's patent literature and some really good advice on literature searches. This part occupies more than one-fourth of the book.

The section on laboratory work is frankly padded. It contains nothing that is new and much that is commonplace, even to elementary students. Most of the space is occupied with matter with which the student should have become familiar in his degree course. Then there are a few chapters contributed by the author's colleagues and friends. Three of these gentlemen have badly let the author down. The writer of the chapter on medicinals has quoted a formula for strychnine (p. 225) without any comments, thus implying that the constitution of this substance is known with certainty, which is far from being the case; the same remarks apply to the formula given on p. 231 for morphine, and on p. 232 for codeine; the formula given on p. 235 for papaverine is not the usually accepted one, whilst that given on the same page for narcotine is certainly incorrect; the formulæ ascribed to chloramine-T (p. 239) and to quinine (p. 241) are also erroneous. The author of the chapter on reaction velocity has written an account which is strikingly reminiscent in phraseology of, and often verbally identical with, a chapter on the same subject written by him for Taylor's *Treatise on Physical Chemistry*, published last year. The subject matter of these two chapters, occupying some fifty pages, appears to be totally irrelevant and might have been omitted. Lastly, in the chapter on plant processes (p. 307) there is an apparently pointless numerical calculation on the reduction of nitrobenzene, in which a charge of more than two tons of material is handled in a vessel which is apparently less than one quarter of an inch thick. Further, the heat of reaction is totally ignored, and the heat loss from the walls of the vessel is hopelessly under-estimated.

The chapter on "writing up results" is distinctly funny.

In preparing the book for the press, the author has committed many of the faults against which he warns his readers. He points out that full acknowledgment must be given to earlier workers and then attributes the story of the discovery of roast pig—shade of Elia!—to "a humourist" (p. 45). He tells us to be sure not to go to the trouble of discovering old facts and suggests (p. 58) that the discovery of a third law of thermodynamics is a worthy object of research. Perhaps, as an organic chemist, he repudiates Nernst's Heat Theorem. Lastly, he violates some of his precepts with regard to literary presentation. The nomenclature is neither systematic not consistent, phosphorus is mis-spelled several times (pp. 170, 173), and commas are apparently put in with a pepper pot in places (p. 72).

The price of the book is very high; the section on scientific literature might be enlarged and sold separately for about 5s.

JOSEPH KENYON.

THE "CHEMICAL AGE" DICTIONARY OF CHEMICAL TERMS. Pp. vii+158. London: Ernest Benn, Ltd. 1924. Price 16s.

Chemistry has now become so specialised that the workers in one branch are unfamiliar with many of the terms used in another branch of the science. Such a word, for example, as *chemotaxis* will frequently convey as little to the physicist as does *ionic synergism* to the biochemist. We have *copper values* with a specialised meaning in the chemistry of cellulose, and *gold values* in colloid chemistry, not to speak of *bromine values*, which, by the way, are one of the few omissions to be noted in this dictionary. It was with the object of bridging this gulf in terminology that the dictionary was undertaken, and everyone who studies the book will own that the attempt has been most successful.

The ground covered comprises the terms used in general inorganic, organic and analytical chemistry, in physical and electro-chemistry, including the chemistry of colloids, in biochemistry, and in physiological and pharmacological chemistry. The definitions, which have been drawn up by specialists in the respective subjects, are concise yet clear, and give sufficient information to enable anyone with a chemical training to grasp the meaning of the particular terms.

One of the most useful features of the book is the large number of concise outlines of tests, solutions, and theories associated with the names of individual chemists (*e.g. Locke's Solution, Fick's law, Laue diagram*, etc.), a general knowledge of which is usually assumed by the authors of papers on subjects in which the respective terms are commonplaces. The cross-references to cognate terms are also valuable.

The printing is clear, and the book is of a convenient size for constant reference. The publishers may be congratulated on the production of a dictionary which every chemist should have.

EDITOR.

British Engineering Standards.

AN Indexed List of British Standard Specifications and Reports has been issued by the British Engineering Standards Association. The first section gives a numerical list comprising 210 items, and including bitumens, cements, pipe fittings, electrical machinery and apparatus, iron castings, lamps, rails, and railway material stock, etc., etc. The second section refers to ship and ship machinery fittings, and the third to automobile parts and materials. There is also a list of translations of the specifications into French, Italian, Portuguese, and Spanish, and a subject index of 14 pages.

SECTIONAL COMMITTEES ON CHEMICAL ENGINEERING AND PETROLEUM PRODUCTS FOR ENGINEERING PURPOSES.

LIST OF BRITISH STANDARD SPECIFICATIONS AT PRESENT AVAILABLE.

No. 76–1916.	British Standard Nomenclature of TARS, PITCHES, BITUMENS and ASPHALTS when used for Road Purposes and British Standard Specifications for TAR and PITCH for Road Purposes. (*The Specifications for* TAR *are temporarily withdrawn.*)
No. 121–1923.	British Standard Specification for MOTOR and AVIATION SPIRIT.
No. 135–1921.	British Standard Specification for BENZOL for MOTOR FUEL.
No. 144–1921.	British Standard Specification for CREOSOTE for the Preservation of Timber.
No. 148–1923.	Tentative British Standard Specification for INSULATING OILS for use in Transformers, Oil Switches and Circuit Breakers.
No. 186–1923.	British Standard Specification for Cast Iron and Enamelled Cast Iron STEAM-JACKETED PANS.
No. 188–1923.	British Standard method for the DETERMINATION of VISCOSITY in Absolute Units.
No. 209–1924.	British Standard Specifications for FUELS for HEAVY-OIL ENGINES (Petroleum and Shale Oils).
No. 210–1924.	British Standard Classification of PURE MINERAL LUBRICATING OILS.

Copies of the List and of the Specifications can be obtained from the Publications Dept. of the Association, 28 Victoria Street, S.W.1. Price 1s. 2d. each, post free.

Publications Received.

YEAR BOOK OF SCIENTIFIC AND LEARNED SOCIETIES FOR 1924. London: Chas. Griffin & Co., Ltd. Price 15s.

BRITISH CHEMICALS: THEIR MANUFACTURERS AND USERS. Being the Official Directory of the Association of British Chemical Manufacturers for 1925. London: E. Benn, Ltd. Price 10s. 6d. net.

THE BRITISH GOAT SOCIETY'S YEAR BOOK FOR 1925. Price 1s. 6d.