DECEMBER, 1927. Vol. LII., No. 621.

THE ANALYST

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

An Ordinary Meeting of the Society was held on Wednesday, November 2nd, in the theatre of the Institute of Pathology and Research, St. Mary's Hospital, at the invitation of that Institute, Mr. E. Richards Bolton, F.I.C., President, being in the chair.

Certificates were read for the first time in favour of Messrs. Alfred Harry Bateman, B.Sc., A.I.C., Arthur Owen Blackhurst, M.D., William Clayton, D.Sc., F.I.C., Charles William Cornwell, B.Sc., A.I.C., and Thomas Riley, A.I.C.

Certificates were read for the second time in favour of Messrs. Leslie V. Cocks, A.I.C., Frederick Dixon, B.Sc., A.I.C., David Michael Freeland, A.I.C., Desmond Geoghegan, Claudius George Hyde, A.R.C.Sc., F.I.C., Vernon James Tilley, F.I.C., Leonard Wild, B.Sc., and Hugh A. Williams.

The following were elected Members of the Society:—Messrs. Charles Edwin Corfield, B.Sc., F.I.C., Harold E. C. Powers, B.Sc., A.I.C., John David Rogers, and Abraham Samson, A.R.C.Sc., A.I.C.

The following papers were read and discussed:—"The Biological Tests for Blood," by Sir William Willcox, K.C.I.E., M.D., F.I.C.; "The Technique of the Precipitin Test and its Forensic Value," by G. Roche Lynch, O.B.E., M.B., B.S., D.P.H.; and "The Use of the Blood Grouping Reactions in Forensic Investigation," by F. C. Martley, M.A., M.D., F.R.C.P.I.

Deaths.

With great regret we have to record the deaths of the following Members:—

Herbert Edward Burgess, on October 26th, 1927.

Thomas Featherstone Harvey, F.I.C., on October 22nd, 1927.

The Determination of Aldose Sugars by Means of Chloramine-T, with Special Reference to the Analysis of Milk Products.

By C. L. HINTON, F.I.C., and T. MACARA, F.I.C.

(*Read at the Meeting, October* 5, 1927.)

In the course of work on the determination of sugars in condensed milk, it became evident that the iodimetric method gave results comparing favourably with those which could be obtained by the copper methods, volumetric or gravimetric. There was, however, a tendency for the iodine figures for lactose to be higher than the copper figures, and a possible explanation of this appeared to lie in the incomplete removal of nitrogenous substances in the preparation of the milk serum. The clarification method used for the iodimetric tests was the zinc ferrocyanide method of Carrez. Any nitrogenous substances (*e.g.* amino acids) remaining in the serum might be expected to interact with iodine or with hypoiodite, and so give high results for the lactose.

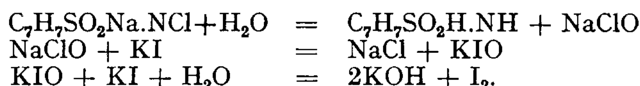
An experiment in which neutral iodine solution was allowed to stand with a condensed milk serum, showed that there was no absorption of iodine under these conditions. Any action on the non-sugar substances of the milk serum was apparently due, therefore, to the hypoiodite formed in the alkaline iodine solution. The ordinary iodimetric process thus affords no means of separating any possible iodine consumption of non-sugars from that of the sugars themselves. We were led, therefore, to examine the possibilities of chloramine-T, in conjunction with potassium iodide, as an alternative to alkaline iodine. This substance has recently been proposed as a substitute for iodine in many ordinary iodimetric operations (Noll, *Chem. Ztg.*, 1924, **139**, 845), but not, so far as we are aware, for methods depending on the use of alkaline iodine solution, in which hypoiodite is the active substance.

Chloramine-T, by itself, might be expected in the present case to react with any non-sugar interfering substances, and so prevent any effect on the hypoiodite. Provided that the sugars themselves did not react with the chloramine, then the extent to which the latter was attacked could be determined by a separate experiment in the absence of iodine, and therefore of hypoiodite.

First, therefore, a knowledge was required of the behaviour of the sugars with chloramine-T, with and without the addition of iodide.

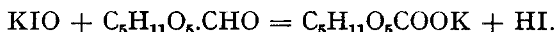
Mechanism of Chloramine-T Oxidation.—A solution of chloramine-T behaves like sodium hypochlorite in producing hypoiodite and a certain amount of free iodine when excess of potassium iodide is added. The action probably

takes place through an intermediate hydrolysis of the chloramine-T to hypochlorite. The following equations indicate the nature of the reactions which appear to occur:



$$C_7H_7SO_2Na.NCl + H_2O = C_7H_7SO_2H.NH + NaClO$$
$$NaClO + KI = NaCl + KIO$$
$$KIO + KI + H_2O = 2KOH + I_2.$$

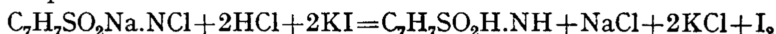
The free iodine (from the hydrolysis of part of the hypoiodite) is evident from the colour of the solution. The unhydrolysed hypoiodite can be used for the oxidation of aldoses:



$$KIO + C_5H_{11}O_5.CHO = C_5H_{11}O_5COOK + HI.$$

The hydriodic acid so formed appears to induce further hydrolysis of hypoiodite, and the colour of the solution darkens from the liberation of more iodine.

Finally, on acidification of the solution, the iodine equivalent of the unaltered chloramine and any unused hypoiodite from it can be determined by a titration with thiosulphate.



$$C_7H_7SO_2Na.NCl + 2HCl + 2KI = C_7H_7SO_2H.NH + NaCl + 2KCl + I_2$$

From the above equations (which represent only the essential stages of the reactions) it is clear that each molecule of chloramine-T is equivalent to 2 atoms of iodine, both in the oxidation of the sugar and in the final liberation of iodine on acidifying. The chloramine thus used up is conveniently expressed as its equivalent in iodine.

The oxidation of the aldoses by chloramine-T and iodide proceeds more slowly than the oxidation with alkaline iodine solution. Probably this is because the hydrolysis of the chloramine to hypochlorite is limited, so that at no time is there a considerable amount of hypoiodite available. The slower progress of the reaction renders it easier to control than the quicker alkaline iodine reaction.

The most convenient strength of solution to work with is $N/2$, containing 7·04 grms. per litre of the crystals with 3 Aq. The solution is standardised best at the time of its use by adding KI and acid and titrating with thiosulphate. It is preferable to make the thiosulphate a little stronger than $N/20$, so that 50 c.c. of the chloramine solution can be titrated without having to refill an ordinary 50 c.c. burette.

The following basis of experimental detail was adopted after a few preliminary tests. Usually 20 or 25 c.c. of a solution of sugar of suitable strength were pipetted into a 250 c.c. conical flask, and 20 c.c. of 10 per cent. potassium iodide solution were added, followed by 50 c.c. of $N/20$ chloramine-T solution. The flask was then closed with a rubber bung, and kept in a water bath at 17·5° C. for the required time, after which the solution was acidified with 10 c.c. of dilute (2 N) hydrochloric acid and titrated at once with thiosulphate, with starch solution as indicator. The temperature used for the bath was about 17·5° C., in order to make results comparable with those already found for alkaline iodine (ANALYST, 1924, **49**, 1). Special attention was paid to drainage of the burette, which was also calibrated in the same way as it was used for the titration. Readings were made to 0·01 c.c.

A control, in which water was used in place of the sugar solution, was, usually allowed to stand in the same way and for the same length of time as the sugar-containing solutions. The titration of this control with thiosulphate after acidification allowed the amount of chloramine (expressed as c.c. of the standard thiosulphate solution) used by the sugar to be obtained by difference. The thiosulphate was standardised against Kahlbaum's potassium dichromate, the procedure of Popoff and Whitman (*J. Amer. Chem. Soc.*, 1925, **47**, 2275) being used. To 25 c.c. of $N/10$ dichromate solution were added 20 c.c. of 10 per cent. potassium iodide solution and 10 c.c. of dilute ($2N$) hydrochloric acid; the flask was stoppered and allowed to stand in the dark for 10 minutes, and its contents then titrated with the thiosulphate.

Pure potassium iodate, dried at 100° C. for 1 hour, and used in the same way as the dichromate except that the solution was titrated at once, gave results in close agreement with the dichromate.

CONDITIONS FOR OXIDATION OF DEXTROSE.—A sample of dextrose, re-crystallised from water as monohydrate and dried at a low temperature, was employed. The percentage of dextrose was determined by polarisation.

Twenty-five c.c. quantities of a 0·30 per cent. solution of this dextrose, each containing 0·0678 grm. of anhydrous sugar were treated with chloramine and iodide, as above described, for increasing periods. The amounts of iodine equivalent to 1 grm. of dextrose were as shown:

TABLE I. OXIDATION OF DEXTROSE BY CHLORAMINE AND IODIDE FOR VARYING PERIODS.

Time.	Iodine per 1 grm. Dextrose (anhydrous).
15 minutes	1·235
30 ,,	1·377
45 ,,	1·403
1 hour	1·412
1½ ,,	1·415
2 hours	1·417
2½ ,,	1·418

The theoretical requirement for oxidation to monobasic acid is 1·410 grm. of iodine, and appears to be satisfied after about 1 hour, with the proportions of sugar to reagents here used. The oxidation, however, proceeds very slowly beyond that stage. The explanation is probably that there is a secondary oxidation of the molecule, akin to the small oxidations of sucrose and laevulose which were found with alkaline iodine (ANALYST, 1924, **49**, 1). This would mean that the main oxidation of the aldehydic group may not be quite complete in 1 hour, the deficiency being made up by the secondary oxidation, so that a result arbitrarily close to the theoretical is obtained.

This secondary oxidation has since been found also to occur when alkaline iodine acts on dextrose for an extended period.

The oxidation of the dextrose is incomplete if the amount of sugar used exceeds a certain value. This appears from the following experiment, in which varying amounts of dextrose were taken (Table II).

TABLE II. EFFECT OF AMOUNT OF DEXTROSE ON THE OXIDATION IN ONE HOUR.

Dextrose taken. Grm.	Iodine per 1 grm. Grm.
0·04	1·411
0·08	1·403
0·10	1·395
0·12	1·371

Since 0·068 grm. (Table I) gave a value of 1·412 grm. in 1 hour, the falling-off takes place when the dextrose exceeds this figure. At this point about 15 c.c. of the $N/20$ chloramine are used up by the sugar.

It was found later, in the analysis of milk sera, to be advisable to have the solution slightly alkaline before the chloramine is added. Hence it was of interest to know the effect, if any, of added alkali on the oxidation of dextrose. The added alkali, it should be noted, tends to suppress the hydrolysis of hypoiodite, judging from the lighter colour of the solutions, and might therefore be expected to have some influence in speeding up the oxidation of the sugar. The following experiments in which 0·08 grm. of dextrose was used, with 1½ hours' oxidation, show that the alkali has a negligible effect.

TABLE III. OXIDATION OF DEXTROSE WITH ALKALI ADDED.

(Dextrose: 0·08 grm.; 1½ hours' treatment.)

Alkali added, $N/2$ sodium hydroxide. C.c.	Iodine per 1 grm. dextrose. Grm.
0·0	1·408
0·4	1·409
0·8	1·410

OXIDATION OF LACTOSE.—For the experiments on lactose, a sample of the sugar, which polarised 100·0 per cent. monohydrate, was used.

Twenty-five c.c. of lactose solution containing 0·150 grm. of hydrated sugar gave the results below (Table IV).

TABLE IV. OXIDATION OF LACTOSE FOR VARYING PERIODS.

(Lactose 0·150 grm.)

Time. Hours.	Iodine per 1 grm. hydrated lactose. Grm.
1	0·703
1½	0·706
2	0·708
2½	0·709

The oxidation in this case is apparently complete in 1½ hours (theor. value 0·705), but then, as with dextrose, proceeds slowly beyond the theoretical value. In order to follow this oxidation further, quantities of 0·150 grm. of lactose were allowed to stand (in the dark) for 1 day and 2 days with the iodide and chloramine before titrating. Controls without the lactose were also allowed to stand for these periods, and the differences calculated into the iodine equivalents of the lactose. After 1 day the figure was 0·740; after 2 days 0·794.

It seems, therefore, that there is no very special virtue in the theoretical iodine equivalent of 0·705. Conditions may, therefore, be chosen so that the actual equivalent is practically constant for a reasonably wide range in the amount of sugar taken. They may be arranged to suit the conveniences of the determination.

The quantity of lactose taken is of importance, as with dextrose. Table V shows the oxidation of varying amounts of lactose in 1½ hours.

TABLE V. EFFECT OF AMOUNT OF LACTOSE ON THE OXIDATION IN 1½ HOURS.

Lactose taken. Grm.	Iodine per 1 grm. Grm.
0·05	0·705
0·10	0·706
0·15	0·705
0·20	0·701

The oxidation falls off distinctly when more than 0·15 grm. is taken (equivalent to about 17 c.c. of the chloramine solution).

The effect of small additions of alkali on the lactose oxidation is of no significance. This is shown, for quantities of 0·15 grm. of lactose, in Table VI.

TABLE VI. OXIDATION OF LACTOSE WITH ALKALI ADDED.

(Lactose: 0·15 grm., 1½ hours' treatment.)

Alkali added, sodium hydroxide. C.c.	Iodine per 1 grm. Grm.
0·0	0·7065
0·4	0·7055
0·8	0·706

ACTION OF CHLORAMINE-T ALONE ON DEXTROSE AND LACTOSE.—From experiments in which dextrose (0·08 grm.) was allowed to stand with the chloramine for 1½ hours, the solution being then acidified, treated with potassium iodide, and titrated, there was found to be no appreciable action on the dextrose in neutral solution. Addition of small quantities of alkali, however, resulted in some slight oxidation.

TABLE VII. ACTION OF CHLORAMINE-T IN THE ABSENCE OF IODIDE.

	Amount of Alhali added, $N/2$ sodium hydroxide. C.c.	Action on Sugar (as grm. iodine per 1 grm. sugar). Grm.
Dextrose, 0·08 grm.	0	0·001
,, ,,	0·4	0·010
,, ,,	0·8	0·015
Lactose, 0·15 grm.	0	0·000
,, ,,	0·4	0·007
,, ,,	0·8	0·010

A similar effect was found with lactose. Chloramine-T, alone, was unaffected by standing with lactose for 1½ hours, but in presence of small amounts of alkali, there was a slight action (Table VII).

With both of these sugars, it may be noticed that the first 0·4 c.c. of alkali is of greater significance than the second 0·4 c.c.

Chloramine has no action on these sugars when the solution is slightly acid with hydrochloric acid.

EXTENT OF OXIDATION OF SUCROSE.—The non-aldose sugars, sucrose and laevulose, with which we are usually concerned in an analysis of sugar products, have previously been shown to be appreciably attacked by alkaline iodine (*loc. cit.*). Their behaviour with chloramine and iodide was therefore examined.

The sucrose used for these experiments was a sample of a specially purified product supplied by Messrs. Tate & Lyle, Ltd., for standardisation purposes.

Quantities of sucrose up to 2 grms. had a fairly constant iodine equivalent of approximately 0·0065 ; but this fell to 0·0051 for 5 grms. of sucrose. Of more practical interest was the amount of oxidation of sucrose in presence of lactose. This was determined by using varying quantities of sucrose dissolved in 25 c.c. of a solution containing 0·15 grm. of lactose. A control, in which no sucrose was added to the lactose solution, permitted the extra consumption of chloramine, due to the sucrose in each case, to be calculated.

For amounts of sucrose from 0·2 grm. up to 5 grms. the oxidation in presence of the 0·15 grm. of lactose was practically constant, and averaged 0·0016 grm. of iodine per grm. of sucrose. Thus the presence of the more strongly reducing sugar considerably depresses the oxidation of the sucrose. The depression is more marked than was found with alkaline iodine, and is probably due to the slow rate at which hypoiodite is formed.

The oxidation of a constant amount of sucrose (0·5 grm.) was found to fall off rather rapidly at first with increasing amounts of lactose, and then more slowly. To obtain these results, duplicate quantities of lactose in water were treated by the chloramine-iodide oxidation, with and without the addition of 0·5 grm. of sucrose. The difference between the titration of each pair gave the effect on the sucrose. The results are to some extent irregular, but it should be noted that very small titration differences are dealt with, on to which are loaded all the errors of two titrations (Table VIII).

TABLE VIII. OXIDATION OF SUCROSE (0·5 grm.) IN PRESENCE OF INCREASING AMOUNTS OF LACTOSE.

Time. Hours.	Amount of Lactose present. Grm.	Sucrose Oxidation, as grm. Iodine per 1 grm. sucrose. Grm.
1	0·0	0·0070
	0·05	0·0036
	0·10	0·0032
	0·125	0·0022
	0·15	0·0016
$1\frac{1}{2}$	0·0	0·0099
	0·05	0·0067
	0·10	0·0035
	0·15	0·0027
	0·20	0·0014

It was later found desirable to know the effect of a small amount of alkali on the sucrose oxidation. The oxidations shown in Table IX were found in a similar manner to the last experiments, but in presence of an added 0·6 c.c. of $N/2$ sodium hydroxide solution.

TABLE IX. OXIDATION OF SUCROSE IN PRESENCE OF LACTOSE WITH 0·6 C.C. $N/2$ ALKALI PRESENT. (Time $1\frac{1}{2}$ hour.)

Amount of Lactose present. Grm.	Sucrose Oxidation as grm. Iodine per 1 grm. Sucrose.	
	With 0·56 grm. sucrose. Grm.	With sucrose = 3 times lactose. Grm.
0·0	0·0142	—
0·038	0·0098	0·0124
0·075	0·0062	0·0062
0·15	0·0032	0·0036
0·188	0·0027	0·0027

The oxidation was increased somewhat by the alkali (*cf.* Table VIII). The amount of sucrose had little effect, except when only small amounts of lactose were present.

OXIDATION OF LAEVULOSE.—For the laevulose experiments, a sample of laevulose, twice recrystallised, with a specific rotation $[\alpha]_D^{20} -92.7°$ in 10 per cent. solution on dry basis, was used.

Amounts of this sugar, increasing from 0·1 grm. up to 4·0 grms., showed an iodine equivalent in 1 hour which fell from 0·026 to 0·012, at first rapidly, then more gradually. When dextrose (0·100 grm.) was also present, however, the iodine equivalent of the laevulose, for amounts of 0·1 up to 3·0 grms. was practically constant, and averaged 0·0035 per grm. of laevulose.

Increasing the time during which the laevulose was acted upon, resulted in a distinct increase in the oxidation, whether dextrose was also present or not.

Thus, the iodine equivalent of 0·5 grm. of laevulose was 0·021 after 1½ hours, compared with 0·018 in 1 hour. If 0·075 grm. of dextrose was also present, these figures became 0·007 in 1½ hours, and 0·005 in 1 hour. The increase is of the same order as the small increases already noted with dextrose and lactose, and points, therefore, to the same kind of attack on the sugar molecule, quite different from the rapid aldose oxidation.

Addition of a small amount of alkali caused a considerable increase in the oxidation of laevulose. An iodine equivalent of 0·021 (for 0·5 grm. of laevulose) became 0·053 in presence of 0·8 c.c. of *N*/2 sodium hydroxide. With dextrose also present, this effect was still found, though partly suppressed; with 0·5 grm. of laevulose and 0·075 grm. of dextrose, the iodine equivalent of the former (in 1½ hours) was increased from 0·007 to 0·011.

Laevulose was found to be unacted upon when 0·5 grm. was allowed to stand with chloramine alone for 1½ hours. When, however, 0·8 c.c. of *N*/2 sodium hydroxide was also present, an apparent iodine equivalent of 0·007 was indicated. This, again, is similar to the effects found with dextrose and lactose. Hence it would seem that in the latter cases it is not an attack on the characteristic aldose structure which is in question.

The Oxidation of Inverted Sucrose.—The remarkable manner in which the oxidation of laevulose is sensitive to changes in conditions of experiment makes it necessary to specify definitely those conditions in establishing the oxidation factor for inverted sucrose. As will be shown later, it is advisable to work just on the alkaline side in applying the chloramine process to milk serum. The addition of 2·0 to 3·0 c.c. of *N*/10 sodium hydroxide to the neutral serum before adding the chloramine and iodide, while it ensures complete oxidation of the lactose, yet allows of the least amount of interference by non-sugars. The invert sugar oxidation also was therefore determined in presence of this small addition of sodium hydroxide.

Other conditions were more arbitrary. The time period adopted, *viz.* 1½ hours, as shown in Tables III and IV, allows oxidation of dextrose and lactose, in amounts of about 0·08 grm. and 0·15 grm. respectively, to practically the theoretical extent. A longer period would probably permit larger amounts of reducing sugars to be dealt with, but would inconveniently increase the total time required for the analysis. Temperature (17° to 18° C.) and quantities of chloramine and potassium iodide were the same as were used throughout these experiments.

An invert sugar solution of known concentration was prepared from a solution of 1·800 grms. of the pure sucrose in 40 c.c. of water. For the inversion, hydrochloric acid of strength 6·34 *N* was used. Five c.c. were added to the sugar solution; the flask containing the latter was placed in a bath maintained at 60° C., and rotated for 3 minutes (during which time it reached the bath temperature). It was then left in the bath for a further 9 minutes. After removal and cooling of the flask and contents, the solution was exactly neutralised with sodium hydroxide (litmus paper indicator), again cooled, and made up to 250 c.c

A series of quantities was carefully measured into flasks, treated with 3 c.c. of $N/10$ sodium hydroxide, potassium iodide, and chloramine as usual, for 1½ hours. Duplicate titrations of each amount of invert sugar solution, and of the blank, differed by not more than 0·02 c.c. Table X shows the oxidation, expressed as the equivalent iodine per grm. of invert sugar and of inverted sucrose.

TABLE X. OXIDATION OF INVERT SUGAR BY CHLORAMINE AND IODIDE IN 1½ HOURS AT 17–18° C. (3·0 c.c. N/10 sodium hydroxide added in each case.)

Amount of invert sugar in soln.	Iodine per grm. of	
	Invert Sugar.	Inverted Sucrose.
Grm.	Grm.	Grm.
0·1895	0·706	0·743
0·1516	0·708	0·745
0·0758	0·715	0·753
0·0379	0·737	0·776

In the first two results the oxidation of the laevulose is almost completely suppressed by reason of the large amount of dextrose present. As the amount of invert sugar, and therefore of dextrose, is decreased, the proportionate oxidation of the laevulose is very much increased. This is similar to preceding results with dextrose and laevulose mixtures.

A curve drawn from these results allows the factor to be readily ascertained for any intermediate amount of invert sugar. Between 0·15 grm. and 0·19 grm. of invert sugar the factor does not change greatly, and an average of 0·707 (0·744 for "inverted sucrose") for this range would be sufficiently close for practical use.

The replacement of a part of the invert sugar by lactose has but little effect on the oxidation factor of the invert sugar, at least for the larger amounts of total sugars.

APPLICATION OF THE PROCESS TO ANALYSIS OF MILK PRODUCTS.

PREPARATION OF MILK SOLUTION FOR TITRATIONS.—In preparing the clear serum from milk the zinc ferrocyanide clarification of Carrez was at first used. This consists in adding equal volumes of 10 per cent. zinc acetate and 5 per cent. potassium ferrocyanide solution to the milk, making up to the required volume, shaking, and filtering. Arising out of some discrepant results which were obtained, however, experiments were made which showed that excess of zinc (necessarily present in the milk serum) might interfere with the oxidation of lactose by the chloramine and iodide mixture. This method, therefore, was abandoned.

Phosphotungstic acid solution was then tried. The formula used for the preparation of this reagent was reached as the outcome of a series of experiments with the object of preparing a suitable clarifying agent for polarimetric work. It was found that the acidity of the reagent had to be carefully adjusted in order to

secure a P_H value which was low enough: on the one hand (not above 2·5) for satisfactory coagulation, but not so low, on the other hand, as to cause trouble by the inversion of any sucrose present. Further, whilst a distinct excess of sodium phosphate was desirable (as a deficiency results in tungstic acid being thrown out during inversion with hydrochloric acid), yet an unnecessary excess was to be avoided, since it would be left in the serum and might affect the optical rotation of the sugars. The following is the method of preparing the reagent which was finally adopted.

Fifty grms. of sodium tungstate ($Na_2WO_4.2H_2O$) and 6 grms. of disodium phosphate ($Na_2HPO_4.12H_2O$) are dissolved in about 200 c.c. of water, and 220 c.c. of 2 *N* hydrochloric acid are stirred in slowly. The solution is made up to 500 c.c. and filtered. (A slight deposit of phosphotungstic acid crystals may separate during cold weather.) For clarifying fresh milk, 10 c.c. of reagent should be used for each 25 c.c. of milk; for condensed and evaporated milks, 10 c.c. of reagent per 10 grms. of milk. The serum then has a P_H of about 2·4 when the total volume from these quantities is 60 c.c.

For most of the work on fresh milk serum, 70 c.c. of milk and 28 c.c. of phosphotungstic acid reagent were made up to 100 c.c., well shaken, and filtered; 40 c.c. of the serum were then diluted to 200 c.c., and 25 c.c. of the resulting solution taken for each test. The amount of lactose was thus approximately 0·18 grm.

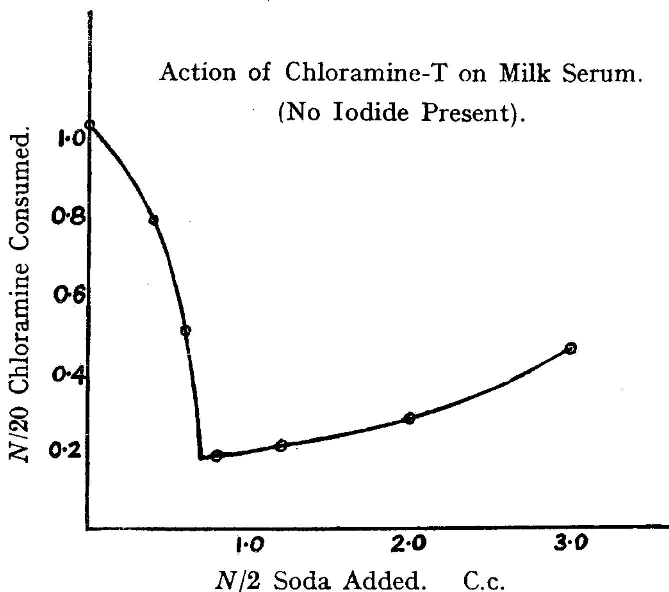
Action of Chloramine-T on Milk Serum.—As already explained, it was anticipated that the chloramine, in the absence of iodide, might react with certain non-sugar interfering substances in milk serum. Whilst it did not follow that the amount of chloramine thus consumed would be the same as that consumed when these substances react in presence of the iodide, yet it was hoped that the deduction of the non-iodide effect from the total chloramine-iodide oxidation, would give more satisfactory results for the sugar.

While the zinc clarification method was in use some fairly consistent figures for the action of chloramine on the serum were obtained, which averaged 0·65 c.c. of *N*/20 thiosulphate per 25 c.c. of serum (equivalent to 2·5 c.c. of the original milk). When the phosphotungstic acid clarification was adopted, however, much higher figures were obtained. This led to an investigation of the influence of acidity or alkalinity on the behaviour of the milk serum with chloramine.

A series of 25 c.c. quantities of a serum prepared with phosphotungstic acid, as above described, was treated with increasing amounts of alkali and allowed to react with 50 c.c. of *N*/20 chloramine for 1½ hours. Acid and iodide were then added, and the solution titrated as usual. When no alkali was present the difference between the blank titration of the chloramine and that with the serum was rather high, *i.e.* over 1 c.c. When alkali was present, however, this difference fell sharply to a minimum with about 0·8 c.c. of *N*/2 alkali. With still larger amounts of alkali it slightly increased (Table XI). The accompanying curve shows the sharpness of the drop with the first additions of alkali.

TABLE XI. ACTION OF CHLORAMINE ON MILK SERUM.

Amount of Alkali added (c.c. of $N/2$)	0	0·4	0·6	0·8	1·2	2·0	3·0
Chloramine consumed (as c.c. $N/20$ thiosulphate	1·03	0·79	0·51	0·19	0·22	0·29	0·47



When the addition of alkali to the serum reached 0·8 c.c. a whitish flocculent precipitate of calcium phosphate was produced, and the P_H (electrometric) was found to be 8·89. Thus the minimum point is reached when the solution is made slightly alkaline. Other milks, including two evaporated milks, were also examined in the same way with similar results. A minimum occurred when 0·8 c.c. of $N/2$ sodium hydroxide was added to the 25 c.c. of serum, and the amount of chloramine consumed at that point, for the several samples examined, was approximately 0·17 c.c. of $N/20$ solution. This was on quantities of solution containing the solids which were not precipitated by phosphotungstic acid from 3·5 c.c. of fresh milk or its equivalent, that is, containing about 0·18 grm. of lactose. It was thought that at some definite P_H value, rather below the 8·89 mentioned above, the action on both lactose and the non-sugar substances might be eliminated. This would mean that between the results for 0·6 c.c. and 0·8 c.c. of $N/2$ alkali, shown in Table X, the figure for chloramine consumed would fall to zero.

A series of tests within this range, however (small increments of $N/10$ sodium hydroxide were used), showed that the consumption of chloramine fell sharply to about 0·2 c.c. for an addition of 0·75 c.c. of $N/2$ soda. (This point corresponded with the first permanent formation of a precipitate of phosphate.) There was no indication that at any point was there no action at all on the chloramine. By

titration of 25 c.c. of the serum used, it was found that 0·6 c.c. of *N*/2 sodium hydroxide would be required to give a P_H of about 7. At this point there should be no action of chloramine on the lactose. Table XI shows that at this point there was, on the other hand, still quite a large action on the non-sugar substances. From the sharp nature of the change at 0·75 c.c. of added sodium hydroxide, it is evident that the effect of the non-sugars is eliminated at that point, but is replaced by the action of the chloramine on the lactose in slightly alkaline solution. The 0·2 c.c. of chloramine then consumed, expressed on the amount of lactose present, represents 0·007 grm. equivalent iodine per grm. of lactose, and this is approximately the same as the figure already found for the action of chloramine on pure lactose in slightly alkaline solution (Table VII).

This lactose effect, however, may be neglected, since if it occurs in presence of iodide it must clearly be incorporated in the main iodide and chloramine oxidation, and hence taken into account in the lactose factor.

The Action of Iodide and Chloramine on Milk Serum.—All necessity, then, for carrying out a special determination of the effect of non-sugar milk constituents is removed, provided that the oxidation is carried out in slightly alkaline solution. This is, to some extent, automatically provided for, if the iodide be added to the serum before the chloramine. As already shown, a decided alkalinity is at once produced by hydrolysis of hypoiodite. Judging from the colour of the solution, and hence the amount of free iodine produced by hydrolysis, the amount of alkali liberated by the hydrolysis at the outset is equivalent to about 1 c.c. of *N*/2 sodium hydroxide. Part of this, of course, is neutralised by the free acidity of the serum (due to the precipitant). About 0·4 c.c. of *N*/2 alkali remains, however, thereby ensuring that no action occurs between the chloramine and the non-sugars.

As the sugar oxidation proceeds, the colour of the solution deepens, until at the finish much of the iodine capable of being liberated by the remaining chloramine is already free in the solution.

To take a typical instance: if 20 c.c. of *N*/20 chloramine out of 50 c.c. are used up in the oxidation of the sugar, 30 c.c. are available for hydrolysis to hypochlorite, and thence to hypoiodite and free iodine and alkali, *i.e.* 30 c.c. of *N*/20 alkali. But of the 30 c.c. alkali thus possible, 10 c.c. are neutralised by the hydriodic acid produced in the sugar oxidation. So that finally, at most, there can be 20 c.c. of *N*/20 alkali in the solution, *i.e.* 2 c.c. of *N*/2 alkali. This is clear from a consideration of the equations given in the early part of this paper.

The alkalinity of the solution in which the milk serum reacts with chloramine and iodide increases, therefore, from about 0·4 c.c. to something less than 1·4 c.c. of *N*/2 alkali, 0·6 c.c. having been accounted for by the original acidity of the serum.

The effect of adding acid or alkali to the milk serum, before treatment with iodide and chloramine, was next examined. Twenty-five c.c. portions of serum

were treated with varying quantities of $N/2$ hydrochloric acid or sodium hydroxide, followed by the iodide and chloramine, as usual, for 1½ hours.

In the following table of results the acidity or alkalinity shown includes the acidity in the serum due to the precipitant. This, as already stated, amounted to the equivalent of 0·6 c.c. of $N/2$ acid.

TABLE XII. OXIDATION OF MILK SERUM OF VARYING DEGREES OF ACIDITY OR ALKALINITY.

Acidity (as $N/2$ acid).	Chloramine consumed (as c.c. of $N/20$ thiosulphate).
2·5	13·14
2·0	16·13
1·0	20·06
0·6	20·58
0·0	20·96
Alkalinity ($N/2$ sodium hydroxide.)	
0·5	21·05
1·0	21·09
1·5	21·12
2·5	21·22
4·0	20·70

The blank tests (potassium iodide and chloramine standing for 1½ hours) varied slightly according to the acidity or alkalinity of the test, and the above figures for chloramine consumption were therefore obtained from a blank corresponding in added alkali or acid to the alkali or acid in each specific case.

The results on the acid side are decidedly low. This is undoubtedly due to incomplete oxidation of the lactose, as similar low results can be obtained with a pure lactose solution when acidified. On the alkaline side there is first a slight increase in chloramine consumption, and then, as shown by the final figure, a distinct decrease.

The gradual increase over the lower ranges of alkalinity may be due to an attack on the non-sugar substances in alkaline solution. It appears to be advisable, therefore, in determining lactose, to take the value given by a serum which is neutral or only slightly alkaline. The action on non-sugars, while it may not be entirely eliminated, is then as low as is consistent with complete oxidation of the lactose.

DETERMINATION OF LACTOSE IN MILK SERUM.—As already shown, the equivalent iodine per grm. of lactose for amounts up to 0·15 grm. is 0·705 per grm., and falls off slightly, down to 0·701, when 0·20 grm. lactose is used. An amount of serum containing about 0·15 grm. of lactose is, therefore, the most convenient to take for analysis.

Twenty-five grms. of fresh milk are washed into a 200 c.c. measuring flask with about 100 c.c. of water, and 10 c.c. of phosphotungstic acid reagent are added.

The solution is then made up to 200 c.c., well shaken, and allowed to stand for some minutes, after which it is filtered. Twenty-five c.c. portions of the serum are neutralised with $N/10$ sodium hydroxide, the incipient formation of a flocculent precipitate serving as an indication of neutrality. A further 3 c.c. of $N/10$ sodium hydroxide are then added, followed by 20 c.c. of 10 per cent. potassium iodide solution and 50 c.c. of $N/20$ chloramine. The flasks are stoppered and allowed to stand in a bath at 17° to 18° C. for 1½ hours, after which 10 c.c. of 2 N hydrochloric acid are added to each flask, and the liberated iodine is titrated with thiosulphate. A blank experiment, with water, in place of the 25 c.c. serum, is made in the same way. The solutions, while standing and during titration, should be protected from strong sunlight. The difference between the thiosulphate titrations is calculated to grms. of iodine, and the latter, divided by 0·705, gives the lactose in 25 c.c. of the serum.

In bringing this figure to percentage of the original milk, allowance must be made for the volume of the precipitated fat, protein and precipitant. This may be calculated approximately from the sp. gr. of fat and protein, which are given by Richmond as 0·93 and 1·346, respectively; the volume of the precipitant may generally, in the case of phosphotungstic acid, be neglected.

The same procedure can be adopted for unsweetened evaporated milk, except that 10 grms. of sample should be weighed out initially, dissolved in hot water, and cooled before clarifying.

The factor 0·705 should be slightly reduced if rather larger quantities of lactose are present, or if different dilutions are used, giving larger amounts of lactose in each determination. A convenient method is to use a factor corresponding to the actual chloramine consumed (as given by the thiosulphate difference). Table XIII gives such factors based on the results of Table V.

TABLE XIII. LACTOSE FACTORS CORRESPONDING TO VARIOUS AMOUNTS OF CHLORAMINE CONSUMED.

Chloramine consumed (as c.c. $N/20$ thiosulphate.)	Factor.
16·7	0·705
18·0	0·704
19·4	0·703
20·8	0·702
22·2	0·701

For sweetened condensed milks the procedure is the same as for the unsweetened. Before calculating the lactose from the titration results, however, the iodine equivalent of the chloramine consumed by the sucrose must first be deducted from the total iodine equivalent. This deduction varies with the amount of lactose and of sucrose in the 25 c.c. of serum.

From Table IX we already have the iodine per grm. of sucrose corresponding to increasing amounts of lactose. The data may be given more conveniently as the actual deduction to be made from the total chloramine consumption, for

varying chloramine consumption on the one hand, and for different amounts of sucrose on the other. The latter figure, for any particular sample, must, of course, be found independently, either by a chloramine titration after inversion, or by polarimetric or other means. Table XIV gives these corrections for the sucrose.

TABLE XIV. CORRECTIONS FOR SUCROSE.

(C.C. of $N/20$ thiosulphate to be deducted from the total difference due to chloramine consumed.)

Total Chloramine Consumption. (as c.c. of $N/20$ thiosulphate).	Amount (Grm.) of Sucrose in the Serum Titrated.						
	0·40	0·44	0·48	0·52	0·56	0·60	0·64
12·0	0·30	0·33	0·36	0·39	0·41	0·44	0·47
14·0	0·25	0·28	0·30	0·33	0·35	0·38	0·40
16·0	0·21	0·24	0·26	0·29	0·31	0·33	0·35
18·0	0·18	0·21	0·23	0·25	0·27	0·28	0·30
20·0	0·16	0·18	0·20	0·21	0·23	0·25	0·26
22·0	0·15	0·17	0·18	0·20	0·21	0·23	0·24

A numerical illustration will help to make clear the manner of using the table. The thiosulphate titration of 25 c.c. of a diluted condensed milk serum, after standing with iodide and chloramine, was 32·00 c.c. of $N/20$. The blank result was 49·50 c.c. This gives 17·50 c.c. of $N/20$ as the equivalent of the chloramine consumed both by the lactose and the sucrose. The sucrose in the 25 c.c. of serum was known to be approximately 0·52 grm. From the table, therefore, the deduction to be made was 0·26 c.c., so that the actual $N/20$ thiosulphate equivalent of the chloramine used by the lactose was

$$17{\cdot}50 - 0{\cdot}26 = 17{\cdot}24 \text{ c.c.}$$

As iodine, this is $17{\cdot}24 \times 0{\cdot}006346 = 0{\cdot}1094$ grm.,

and as lactose hydrate $\dfrac{0{\cdot}1094}{0{\cdot}705} = 0{\cdot}1552$ grm.

DETERMINATION OF SUCROSE IN SWEETENED MILKS.—For this purpose two chloramine oxidations, before and after an inversion treatment, have to be carried out. The former is, of course, that already used for the lactose determination. For the inversion 25 c.c. of the original serum are pipetted into a 100 c.c. measuring flask, 15 c.c. of water are added, and then 5 c.c. of 6·34 N hydrochloric acid. The solution is heated, as already described, in a bath at 60° C. for 12 minutes, removed and cooled. Five c.c. of 6·34 N sodium hydroxide are then added, and the solution is finally just neutralised to litmus by means of $N/2$ sodium hydroxide, cooled again, and made up to 100 c.c. Twenty-five c.c. quantities are then treated, as before, with 3 c.c. of $N/10$ sodium hydroxide, iodide and chloramine, and finally titrated with thiosulphate. The difference from the blank titration is calculated as grms. of iodine equivalent to the chloramine consumed by the lactose and the inverted sucrose.

For convenience in discussion we will call the two iodine equivalents (*i.e.* of the uninverted and the inverted solutions) A and B. From the dilutions which have been made, the first solution has four times the concentration of the other, so that A is deducted from four times B, giving the difference, as iodine, due to the inversion of the sucrose, in 25 c.c. of the first solution. The lactose effect, being now brought to the same basis in each case, is thus eliminated. Corrections have still to be made, however, for the slight oxidation of the sucrose in the direct titration, and for the variation in the invert sugar factor with concentration. This can be more conveniently done by means of Table XV below, which has been calculated from the combined data in Tables IX and X.

The amounts of the sugars are expressed respectively as the thiosulphate differences before and after inversion.

TABLE XV. SUCROSE FACTORS CORRESPONDING TO VARYING AMOUNTS OF CHLORAMINE CONSUMED BEFORE AND AFTER INVERSION.

"Uninverted" Chloramine Consumption. c.c. $N/20$ thiosulphate.	"Inverted" Chloramine Consumption c.c. $N/20$ thiosulphate.				
	14	16	18	20	22
12	0·742	0·741	0·740	0·739	0·738
14	0·743	0·742	0·741	0·739	0·739
16	0·743	0·742	0·741	0·740	0·740
18	0·744	0·743	0·741	0·740	0·740
20	0·744	0·743	0·742	0·741	0·740
22	0·744	0·743	0·742	0·741	0·741

These factors can be applied to the determination of sucrose by inversion in other solutions than those from milk products, provided that there is no interfering substance present. In general, the cases where the methods can be used will be those in which the copper reduction methods might otherwise be used. It is advisable, however, to verify, by means similar to those adopted here, that there is no material present capable of acting on the chloramine itself under the conditions of experiment; or, if such is present, that it undergoes no material change as a result of the inversion process.

TEST ANALYSES WITH KNOWN QUANTITIES OF SUGARS.—Mixtures of lactose and sucrose were tested by the method, the above tables of factors being used.

(1) A solution was prepared containing 1·250 grms. of lactose hydrate and 5·000 grms. of sucrose in 200 c.c. This was titrated, before and after inversion, as described, except that the inverted solution had one-fifth the concentration of the other (instead of one-fourth as described above for milk).

The respective thiosulphate differences were 17·60 c.c. and 18·10 c.c. of $N/20$ solution. The correction on the former (Table XIV) is 0·30 c.c.; and the lactose factor (Table XIII) is 0·704. Hence the lactose in 25 c.c. of solution is:

$$\frac{(17{\cdot}60 - 0{\cdot}30) \times 0{\cdot}006346}{0{\cdot}704} \text{ grm.}$$

$$= 0{\cdot}1560 \text{ grm. (actual } 0{\cdot}1563).$$

The first thiosulphate difference, deducted from five times the other, gives 72·9 c.c., equivalent to 0·4626 grm., due to the inversion of the sucrose. The sucrose factor (Table XV) is 0·741.

Hence the sucrose in 25 c.c. of original solution is

$$\frac{0{\cdot}4626}{0{\cdot}741} = 0{\cdot}624 \text{ grm. (actual } 0{\cdot}625 \text{ grm.).}$$

(2) A similar experiment with different amounts of sugars gave the following results:

Lactose taken	0·1400 grm.	Found	0·1390 grm.
Sucrose ,,	0·5600 ,,	,,	0·5600 ,,

Analyses were also made on solutions of known sucrose content, prepared by adding sucrose to clarified milk serum.

(3) A serum was prepared by clarifying 140 c.c. of fresh milk with 56 c.c. of phosphotungstic acid reagent and filtering. To 40 c.c. of the serum were added 6 grms. of sucrose, the solution was neutralised and made up to 200 c.c.; 20 c.c. were then used for the direct titration. For the inversion, 40 c.c. were inverted, neutralised as usual and made up to 200 c.c.; again, 20 c.c. were used for titration. The thiosulphate differences were respectively 16·43 c.c. and 17·28 c.c., whence the sucrose factor is 0·741. The calculation then is:

$$[(17{\cdot}28 \times 5) - 16{\cdot}43] \times \frac{0{\cdot}006346}{0{\cdot}741} \text{ grms.}$$

$= 0{\cdot}599$ grm. of sucrose in the 20 c.c. of uninverted solution (actual 0·600 grm.).

As regards the lactose, there is, as yet, no method of determining this constituent which can be considered sufficiently beyond criticism to afford a reliable standard with which to compare results. However, we have compared the lactose figures for a number of fresh milks, as shown by the chloramine process, the polarimeter, and the volumetric Fehling's method of Eynon and Lane (Table XVI). For all three methods, the same clarified serum was used. No correction has been made for volume of precipitate.

Table XVI. Lactose in Milk by Different Methods.

(Grms. per 100 c.c. of fresh milk.)

Sample.	Chloramine.	Polarimeter.	Eynon & Lane.
Fresh Milk (1)	5·35	5·39	5·08
,, ,, (2)	5·20	5·23	—
,, ,, (3)	5·31	5·35	5·07

Summary.—(1) Chloramine-T, in conjunction with potassium iodide, may be used as a satisfactory substitute for alkaline iodine in the quantitative oxidation of aldose sugars. Its action is slower, the time necessary for oxidation of dextrose

and lactose to monobasic acid being from one to one and a half hours at ordinary temperature.

(2) Satisfactory conditions for the oxidation of dextrose and lactose by chloramine-T and iodide, were established. Addition of small amounts of sodium hydroxide solution had no effect on the oxidations.

(3) Chloramine-T alone was found to have no oxidising action on dextrose and lactose; in the presence of small quantities of alkali, however, oxidation occurred to a slight extent.

(4) Sucrose was oxidised less than by alkaline iodine under the conditions which gave full oxidation of the aldose sugars. Addition of alkali increased the oxidation slightly.

(5) Laevulose alone was oxidised rather more than by alkaline iodine, but the oxidation was very much repressed when dextrose was also present. Small amounts of alkali increased the oxidation. The oxidation of mixtures of laevulose and dextrose, in the form of inverted sucrose, was determined, under standard conditions.

(6) The possibility of an action by chloramine-T (without iodide) on oxidisable substances which might be present in a clarified milk serum, was examined. It was found that, provided the serum was first made slightly alkaline, there was no indication of any action other than the small one due to the action of chloramine-T on lactose in faintly alkaline solution. If the solution is acid, however, quite a large consumption of chloramine may occur.

(7) Treatment of milk serum with chloramine-T and iodide gave complete oxidation of lactose, and a minimum oxidation of any possible interfering substances, when the solution was first made very slightly alkaline. The error due to such substances appeared to be not greater than 0·4 per cent. of the total lactose.

(8) A procedure is suggested, based on the results established in (2), (6) and (7), for the determination of lactose in fresh milk, and in condensed sweetened and unsweetened milk.

ADDENDUM.—Suitable conditions for the determination of sugars in milk products by the chloramine-T method having been established, it was considered desirable to compare these results with those obtained by the polarimetric method. During the course of this work various difficulties were encountered in the latter process, and, as some of these do not appear to have been previously recorded, it was thought that the following note might be of service to others who may use the polarimetric method.

In order to eliminate from the comparison all questions of volume of precipitate, degree of solution of lactose, etc., the same clarified serum was used for both methods, the precipitation being carried out by means of the phosphotungstic acid reagent already described.

At first, in view of the traces of nitrogenous substances still remaining in the serum, an attempt was made to apply the "neutral" double polarisation method for the polarimetric sucrose determination. Owing to certain difficulties which

arose, however, this was abandoned in favour of the usual double polarisation, without any addition beyond the acid necessary for inversion. The actual apparent specific rotations of sucrose, invert sugar, and lactose under the conditions of the method were determined (the first two in the presence of the proper amount of clarified serum from fresh milk), and these values were used in the calculation of the sugars from the readings.

Even in the ordinary method of polarisation, certain difficulties were encountered. It may be useful to summarise these, together with those experienced in connection with the "neutral" process, and in the preparation of the serum.

In the first place, trouble arose in various ways from the muta-rotation of the lactose and the variable nature of its equilibrium polarisation, or "specific rotation." Quite a moderate amount of heating of a lactose solution, in which muta-rotation at ordinary temperatures was complete, was found to increase the apparent specific rotation, $[\alpha]_D^{20}$, as much as 0·6°. The original value was only regained after some hours' standing at ordinary temperature. This led to the abandonment, for this particular work, of heating methods for dissolving the sample. The results found do not, therefore, represent the actual lactose contents of the milks (which may not have dissolved completely before filtering off the coagulum), but are satisfactory for comparison purposes.

When the solution, prepared in the cold, was clarified at once, and polarised, the direct readings showed initially a much more pronounced decrease than could be accounted for by inversion of the sucrose in the slightly acid serum. This must probably be ascribed to the muta-rotation of the freshly dissolved lactose. The trouble was overcome by dissolving the milk in cold water and allowing it to stand for 2 days before adding the precipitant, making up to volume, and proceeding with the analysis.

The direct reading was usually made within an hour after the addition of the precipitant. The amount of inversion of the sucrose which occurs in this interval is very small, and may usually be neglected. Measurements of the rate of inversion in a serum, prepared in the manner just mentioned, showed the following rates, at two temperatures.

Temperature. °C.	Total Sucrose inverted per hour. Per Cent.
17·5	0·12
22·7	0·20

If an inversion rate of 0·15 per cent. per hour at 20° C. is taken, the error introduced by neglecting the inversion, is only 0·07 per cent. for a sample containing 45 per cent. of sucrose, when the reading is made an hour after clarification. It is quite easy to make the direct reading within 30 minutes from clarification. In the results shown below a correction has been made for the inversion.

Coming to the inversion effect on the lactose, it was found that the amount of hydrochloric acid used produced an increase in the rotation of the lactose of about 1 per cent., *i.e.* about 0·5° on the specific rotation. No temporary heat effects seemed to be superimposed on this.

When the acid used for inversion was neutralised with sodium hydroxide, according to the "neutral" process, unexpected stabilisation effects took place over a long period, the polarisation becoming less negative, sometimes to a marked degree. Out of the phenomenon it was found possible to disentangle several concurrent effects. These were:—

(*a*) Local excess of alkali during the neutralisation caused a lowering of the rotation of the lactose, which was only slowly regained when the thoroughly mixed solution stood for several hours. This effect was much stronger with sodium hydroxide than with ammonia.

(*b*) Salts, such as sodium chloride or ammonium chloride, when added to laevulose solutions, were found to cause a sharp increase of (negative) rotation, which fell back with moderate rapidity to the rotation which the laevulose should possess in the presence of the particular amount of salt used. Stabilisation was complete with sodium chloride (about 3·7 grms. per 100 c.c. of solution) at about 21° C. in 40 minutes; with ammonium chloride (about 3·4 grms. per 100 c.c.) at 20° C. in 20 minutes. Extrapolation of the curves to the moment of addition suggested that the initial increase must be considerable—several degrees on the specific rotation.

It is very probable that a similar increase, and subsequent fall, takes place when sodium chloride or ammonium chloride are virtually added to an inverted sucrose solution by neutralisation of the inversion acid.

Both of these effects act in the same direction and would be large enough to account for the stabilisation phenomena observed in the inverted and neutralised solutions. In view of these effects, it was decided to abandon the "neutral" process.

(*c*) When an inverted sucrose solution was not neutralised the rotation found immediately after inversion was observed to increase appreciably (*i.e.* to become more negative) on standing for a time. This can be explained by a lag in the muta-rotation of the dextrose such as has been found by Pennycuick (*J. Chem. Soc.*, 1924, **125**, 2049). It is pronounced even up to 10 minutes after inversion, and, in order to avoid any error due to this cause, reading should not be taken within, say, an hour after inversion. This effect acts in the opposite direction to the others, so that it must have tended to reduce the other errors in the case of the "neutral" process. However, since it is not of such magnitude, and appears to work itself out more quickly, it would be masked in determinations where neutralisation was adopted.

With these phenomena in mind, the constants for the sugars were experimentally determined, as already stated, in milk serum, under the same conditions as were afterwards used in the analysis of the condensed milk. The values found for $[\alpha]_D^{20}$ were:

Lactose (as hydrated)	+ 52·52°
Sucrose	+ 66·37°
Inverted sucrose	— 22·22°

The small effect of hydrochloric acid on the rotation of the lactose in the inverted solution, referred to above, has to be allowed for before calculating the sugars by means of the above data.

Table XVII shows the percentages of the sugars found in three samples by the two methods.

TABLE XVII. SUGARS IN CONDENSED MILK BY CHLORAMINE-T AND POLARIMETRIC METHODS.

	Lactose, Per Cent.		Sucrose, Per Cent.	
No.	Polarimeter.	Chloramine-T.	Polarimeter.	Chloramine-T.
1	12·37	12·43	44·8	45·2
2	12·16	12·14	43·2	43·7
3	7·99	8·17	47·3	47·6

No. 3 sample had evidently deposited part of its lactose in the tin, the contents of which were not stirred up prior to the withdrawal of the portion for analysis.

The sucrose results are about 0·4 per cent. higher by the chloramine-T method than by the polarimeter; at present we have been able to find no satisfactory explanation for this; nor is there any criterion which gives the results by either method an undoubted validity in the special case of condensed milk.

In conclusion, we should like to acknowledge our indebtedness to the members of the Milk Products Sub-Committee, who have tested this process at various stages and have by their criticisms assisted in its development. We have also to acknowledge our indebtedness to the British Association of Research for the Cocoa, Chocolate, Sugar Confectionery and Jam Trades for permission to publish the results of this work, which was carried out in the Association's Laboratories.

DISCUSSION.

Mr. E. HINKS said that the Society was much indebted to the authors for this communication, as it had been for their previous work on iodimetric methods. This paper would be of great service in solving the difficult problem of the accurate determination of sugars in condensed milk, and it would appear that the chloramine-T method had definite advantages over the alkaline iodine method in this connection. It was clear that this process depended for accuracy, as did all sugar analyses, upon strictly controlled conditions, and the necessary control was here more capable of attainment than in the case of copper reductions. He called attention to a paper by Goebel (*J. Biol. Chem.*, 1927, **72**, 801) in which was shown again the influence of the rate of addition of the alkali upon the absorption of iodine by sugars; the small initial concentration of alkali in the chloramine-T process was, perhaps, a factor contributing to its success.

Mr. C. L. HINTON, in reply, said that the authors had not yet seen the paper mentioned, but that in their previous work on the alkaline iodine method they had shown how excess of alkali, when present from the start of the reaction, prevented complete oxidation of the sugar.

Determination of Manganese in Steel by the Proctor-Smith Reaction in Presence of Phosphoric Acid.

By BINAY CHANDRA MUKERJEE, M.Sc., A.I.C.

THE use of phosphoric acid has been held to give a sharper end-point in the titration with arsenious acid, and there is very little chance of precipitates being formed. The phosphoric acid also destroys the colour of the ferric salts, and hence the presence of iron does not interfere with the titration. The object of this paper is to review briefly the methods used by different observers with phosphoric acid and to find, by experimental investigation, the most suitable concentration of the phosphoric acid that should be present in the solution so as to fulfil the above-mentioned conditions.

SURVEY OF PREVIOUS METHODS.—The sources of possible error in the Proctor-Smith method can be traced either to incomplete oxidation of the manganese or to subsequent incomplete reduction. Aloke Bose (private communication to Ibbotson, June 15, 1917, and in *Chem. News*, 1918, 369), and Ibbotson (*ibid.*, 1918, **117**, 157) drew attention to the fact that in titrating permanganate solutions in acid media with arsenious acid, less arsenious acid is required than should have been the case if the reaction had been quantitative in accordance with the equation

$$4KMnO_4 + 5As_2O_3 = 2K_2O + 4MnO + 5As_2O_5.$$

Hall and Carlson (*J. Amer. Chem. Soc.*, 1923, **45**, 1615–1620) have further investigated the above discrepancy by electrometric titration, and find that the valency of the manganese drops from seven to an average of 3·3. The reduced condition corresponds to an oxide of manganese, Mn_3O_5, only $\frac{11}{15}$ of the available oxygen in $HMnO_4$ being reduced by arsenious acid in solutions of varying manganese concentrations. This is in close agreement with the observations of Geloso (*Bull. Soc. Chim.*, 1925, [iv], **37**, 641–656). The titration of potassium permanganate with sodium arsenite in 0·1 *N* solutions to a green colour gives consistent results within a certain range of concentration of sulphuric acid. The end-point is similar with certain concentrations of nitric acid, but never in presence of tartaric or phosphoric acid. The variation in composition of the reduction product with various conditions proves that the formulae Mn_3O_5 and Mn_3O_{11} do not represent definite compounds, the green liquid being a colloidal solution of MnO_2, with other substances adsorbed. Moore (*Chem. News*, **63**, 66) advances the theory that the manganese is oxidised to manganic metaphosphate by means of phosphoric acid and an oxidising agent, *e.g.* potassium chlorate. Brearley and Ibbotson hold that this is not an oxidation to permanganate.

According to Mathevet (*Ann. Chim. anal.*, 1923, **5**, 99–108), the influence of phosphoric acid is a very slight—much weaker than that of the other acids, the results being low if the quantity is very large. The phosphoric acid forms per-manganic phosphate which is either stable to heat, so that all the manganese present is transformed into manganic acid, there being no separation as manganese dioxide; or the perphosphoric acid yields up the oxygen easily and regulates the process of oxidation.

Travers (*Compt. rend.*, 1926, **182**, 1088–1090) holds that the oxidation of manganese to permanganic acid is hindered by secondary reactions. The concentration of nitric acid and sulphuric acid and the percentage of manganese are important factors in causing incomplete or complete oxidation. Hydrofluoric acid or metaphosphoric acid in proper concentration induces simultaneous formation of a manganic salt which is stable in presence of excess of acid and manganese dioxide, complete oxidation of manganese being effected. Complete oxidation is also effected in the presence of 2 per cent. of metaphosphoric acid and 3 per cent. of sulphuric acid, the minimum concentration of manganese in solution being 2·5 grms. per litre.

A. and H. Eder (*Chem. Ztg.*, 1922, **46**, 1085–1086) dissolve 0·5 grm. of steel in 25 c.c. of dilute (1:5) sulphuric acid, with the addition of 2 c.c. of 0·25 per cent. silver nitrate solution; 5 c.c. of nitro-phosphoric acid (nitric acid, 1; phosphoric acid, 1 vol.) are added, and the mixture evaporated until all nitric acid is expelled, diluted to 250 c.c. and boiled for five minutes, with the addition of 3 grms. of ammonium persulphate. After cooling, the solution is treated with 5 c.c. of 2·5 per cent. sodium chloride solution, and the permanganate is titrated with arsenious acid solution.

Mathevet (*loc. cit.*) dissolves 1 grm. of ordinary steel in 25 c.c. of a solution made up of a mixture in the following proportions: Water, 1250 c.c.; sulphuric acid (66° Be), 300 grms.; nitric acid (40° Be), 90 grms.; phosphoric acid (60° Be), 80 grms. The beaker is heated upon a sand-bath until the metal is completely dissolved, after which the solution is treated with 5 c.c. of silver nitrate solution, boiled for not less than 30 seconds. Thirty c.c. of hot water are then added, and ammonium persulphate solution, very slowly, until the froth becomes violet in colour, when the liquid is cooled, diluted with 50 to 100 c.c. of cold water and titrated at once with sodium arsenite solution until a yellowish-green colour appears.

Influence of Conditions.—In the experiments made in this laboratory, attention was closely directed to details, *e.g.* temperature, velocity of titration and concentration of acid, and the solutions were standardised under exactly the same conditions as in the actual analysis. The concentration of manganese in solution approximated to 0·53 grm. per litre. Various concentrations of the phosphoric acid solution were used, as detailed later, and 5 c.c. of acid of sp. gr. 1·7 (syrupy phosphoric acid, Merck) were used in one experiment.

The steel (0·2 grm.) was treated with the following reagents in the order named:—Five c.c. of dilute H_2SO_4 (1:5), 5 c.c. of dilute nitric acid (sp. gr. 1·135), and 5 c.c. of the phosphoric acid solution. After warming to facilitate complete solution, the liquid was treated with solid ammonium persulphate (about 1·5 grm.), with the addition of 5 c.c. of silver nitrate solution as catalyst. It was then slightly diluted with water (the total volume being about 30 c.c.) and warmed until a violet-amethyst coloration appeared. The solution was then cooled and titrated with sodium arsenite solution containing hydrochloric acid, prepared by dissolving a mixture of 0·8 grm. of arsenious oxide and 2 grms. of sodium hydroxide in boiling water, cooling the solution and making it up to 2 litres by the addition of water and 100 c.c. of strong HCl. This was kept as a stock solution. The silver nitrate solution was prepared by dissolving 5 grms. of the extra-pure salt in a litre of water.

The end-point was the disappearance of the pinkish tint. Some of the results actually obtained are given below:—

TABLE I.

Strength of phosphoric acid solution.		Nature of sample and percentage of manganese found.						
No. of solution.	H_3PO_4 present.	Rail steel.	Rail steel.	Rail steel	Very mild steel.	Mild steel.	Boiler plate.	Ni-Cr. alloy steel.
	Grm.	(A).	(B).	(C).	(D).	(E).	(F).	(G).
1	0·235	0·71	0·75	0·87	0·04	0·22	0·44	0·75
2	0·470	0·74	0·79	0·89	0·06	0·23	0·49	0·79
3	0·588	0·75	0·79	0·92	0·04	0·19	0·47	0·76
4	0·118	0·72	0·75	0·89	0·06	0·21	0·44	0·75
5	0·056	0·72	0·74	0·87	0·06	0·20	0·45	0·77

The following table shows, by way of comparison, the values for manganese obtained: (i) When only nitric acid was present in solution, no phosphoric acid being used; and (ii) by methods other than the persulphate method.

TABLE II.

Nature of sample.	Percentage of manganese found.	
	With only HNO_3 present in solution.	By methods other than the persulphate method.
Rail steel (A)	0·73	0·72 (bismuthate)
Rail steel (B)	0·74	0·76 (,,)
Rail steel (C)	0·87	0·85 (,,)
Very mild steel (D)	0·05	0·04 (,,)
Mild steel (E)	0·21	0·22 (chlorate)
Boiler plate (F)	0·44	0·46 (gravimetric)
Ni-Cr. alloy steel (G)	0·75	0·75 (,,)

REMARKS ON THE RESULTS.—(*a*) When 5 c.c. of 1·7 phosphoric acid were used with one particular sample, the end-point of the titration could not be determined, as the pink tint persisted, and thus no reading could be taken.

(*b*) With solution 1 the end-point was sharp, the precipitate coagulated and quickly settled down, leaving the supernatant liquid clear.

(*c*) With solution 2 the end-point was not distinct; although the precipitate coagulated and quickly settled down, the supernatant liquid had a persistent pink tinge, due probably to interaction between permanganic acid and phosphoric acid.

This may possibly account for the higher results obtained.

(*d*) With the other solutions—3 to 5—the end-point was not so sharp as with solution 1.

CONCLUSIONS.—(1) Contrary to Mathevet's observation (*loc. cit.*), the use of nitric acid alone was not found to give higher results than when a mixture of nitric and sulphuric acids was used for dissolving the steel.

(2) The *optimum condition* for titrating manganese in presence of phosphoric acid is when solution 1 is used for dissolving the steel, in conjunction with nitric and sulphuric acids, *i.e.* when 1 c.c. of the phosphoric acid solution contains 0·047 grms. of phosphoric acid.

(3) Higher concentrations of phosphoric acid tend to produce slightly higher results, whilst with lower concentrations the end-point was not so sharp as with solution 1.

My acknowledgments are due to Mr. E. A. Wraight, A.R.S.M., F.I.C., Metallurgical Inspector to the Government of India, for looking through the paper; and to the Chief Controller of Stores, Indian Stores Department, for permission to publish it.

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A General Method for the Determination of Aldehydes in Essential Oils, with Particular Reference to the Determination of Citronellal in Java Citronella Oil and Citral in Lemon Oil.

BY C. T. BENNETT, B.Sc., F.I.C., AND M. S. SALAMON, B.Sc.

WE have recently had communicated to us a new method for the determination of citronellal in Java citronella oil. We have not been able to ascertain who is the actual originator of this method, but the details given to us were as follows:

"Two grms. of citronella oil are carefully weighed into a flask, and to these are added 20 c.c. of a 5 per cent. solution of hydroxylamine hydrochloride in 80 per cent alcohol, made neutral to methyl orange. On the addition of the hydroxylamine hydrochloride solution to the oil the yellow colour of the methyl orange becomes pink, and $N/2$ alcoholic alkali is then added, drop by drop, with constant shaking, until the pink colour no longer returns, and a permanent yellow shade is established."

The percentage of citronellal is then calculated by the following formula:

$$\text{Per cent. of citronellal} = \frac{100 \times 0{\cdot}077 \times \text{c.c. } N/2 \text{ alkali}}{\text{Weight of oil taken}}.$$

The advantages of such a method over that usually employed for the determination of citronellal in citronella oil, namely, Dupont and Labaune's method, are: (1) The determination can be carried out in a comparatively short space of time; and (2) The method allows of a direct determination of the citronellal, instead of depending on a difference figure.

In the method of Dupont and Labaune the determination of the citronellal depends on the determination of the so-called geraniol content of the oil, before and after shaking with a solution of hydroxylamine, and assumes that the difference between these figures is citronellal.

Unfortunately the formulae used for calculating these values are not altogether strictly accurate; moreover, it is now well established that citronellal does not always undergo quantitative conversion in the acetylation process.

Hence the figure obtained by the Dupont and Labaune method is, at best, only an approximation, and is apt to err on the high side; moreover, their method involves two acetylations and two saponifications.

In view of these considerations, we felt that the method communicated to us was well worth experimenting with, and we consider that the results obtained are of sufficient interest for publication.

When the method was first tried some difficulty was experienced in obtaining a sharp end-point, but by substituting bromphenol blue for methyl orange this difficulty was overcome. It is necessary, however, that neither too little nor too much of the indicator should be used, and, as the results of our experiments, we find that the following method of preparing the test solutions gives the most satisfactory results:—

Five grms. of hydroxylamine hydrochloride are dissolved in 9 c.c. of hot water, and to this is added 80 c.c. of 90 per cent. alcohol (sp. gr. 0·833); 2 c.c. of bromphenol blue solution are added, and the whole neutralised, if necessary, with $N/2$ alcoholic alkali (this is merely a precaution, because with the usual grade of rectified spirit and hydroxylamine hydrochloride of good quality, no neutralisation is usually necessary), and then made up to 100 c.c. with more 90 per cent. alcohol. Only rectified spirit should be used to prepare the hydroxylamine solution and the $N/2$ alkali, as the ordinary "Industrial Spirit" contains too many impurities. The bromphenol blue solution is made by grinding 0·1 grm. of indicator with 3 c.c. of $N/20$ aqueous sodium hydroxide and making up to 25 c.c. with water.

If 20 c.c. of this solution are used, no further amount of indicator should be added, but, if necessary, the free acidity of the oil may be determined in a separate portion, bromphenol blue, of course, being used as the indicator.

The following are some of the results obtained on samples of citronella oil, etc., and mixtures containing a known amount of citronellal:

	New method. Per Cent.	D. & L method. Per Cent.	Total acetylisable Per Cent.	Sp. Gr.
Commercial citronellal (*a*) ..	82·8	—	—	—
Ditto + orange terpenes ..	30·0	31 by calculation.	—	—
Commercial citronellal (*b*) ..	85·0	—	—	—
Ditto + lemon terpenes ..	44·0	43 by calculation.	—	—
Java citronella oil	34	36·5	—	—
,, ,, ...	38	41·0	92	0·888
,, ,, ...	36	—	89·5	0·893
,, ,, ...	29	31·0	87·0	0·896
,, ,, ...	30·5	—	87·5	0·896
,, ,, ...	30·5	—	84·5	0·895
,, ,, ...	26·5	—	83·5	0·898
,, ,, ...	32·5	38	87·5	0·894
,, ,, ...	33·6	—	84·0	0·895
West Indian citronella oil ..	22	—	83·0	0·901
Ceylon citronella oil	9	—	—	—
Bourbon geranium oil ..	Less than 0·5			
Palmarosa oil	Less than 0·5			

It will be seen that in the case of citronella oil this method gives lower percentages than those given by the Dupont and Labaune method, but, for the reasons stated, we believe that the lower figures are probably the more correct.

In view of these results, it appeared probable that the method might be useful for the determination of citral in lemon oil, and this we found to be the case. As, however, the aldehyde content of this oil is so much lower than that of citronella

oil, it is necessary to use more than 2 grms., as otherwise the amount of alkali used for neutralisation is so small that the experimental error is too great.

Amounts of 10 c.c. (8·5 grms.) to 20 c.c. (17 grms.) were therefore tried, and the latter is quite a convenient quantity. In calculating the results one must, of course, substitute the factor for citral, namely 0·076, for that of citronellal.

The results obtained were as follows:—

	New method. Per Cent.	B.P. (1914) method. Per Cent.
Lemon oil (A)	3·85	3·9
(B)	4·0	4·0
(C)	4·43	4·37
(D)	3·95	3·99
(E)	3·80	3·90
(F)	4·7	4·6
(G)	4·3	4·2
(H)	4·2	4·2
Distilled lemon oil	2·1	1·9
,, ,, ...	2·2	2·2
,, ,, ...	2·5	2·4

It will be seen that the results obtained by this method agree quite well with those given by the method of the B.P., 1914; the determination is more easily and rapidly carried out, and the end-point of the reaction is, in our experience, sharper than that obtained in the method of the B.P., 1914.

It is, however, very important in making a determination, that the alkali should be added slowly and the whole thoroughly shaken, as otherwise low results may be obtained.

We have also applied this method to several other aldehyde-containing oils, with the following results:—

	New method. Per Cent.	Other methods. Per Cent.
Hand-pressed lime oil	8·5 citral.	—
Lemongrass oil	80·3 citral.	80 (bisulphite).
Cassia oil	79·6 cinnamic aldehyde.	83 (bisulphite).
Cinnamon bark oil	59·4 ditto	60 (neutral sulphite)
Almond oil	99·2	—
Eucalyptus citriodora	54·3	—
Mixture of orange terpenes and lemongrass oil	3·78	4·06 (calculated).
Mixture of ethyl phthalate and lemongrass oil	5·55	5·52 (calculated).
Commercial citral	85·06	90 (bisulphite)

As far as we have been able to form an opinion from our somewhat short experience with this method, we think that it should prove an extremely useful one for the general determination of aldehydes in essential oils, but particularly for citronellal in citronella oil, and citral in lemon oil.

We would express our thanks to our assistants, Miss S. Marshall and Mr. D. C. Garratt, who are largely responsible for the experimental work.

The Detection of Dyeing with the Colouring Matter of Sandal Wood.

By LEO SOEP.

In Holland the use of colouring matters for foodstuffs is controlled by a special law (*Warenwet*) of 1919, supplemented by Royal Edicts applied to special products. For instance, vinegar may only contain a little caramel; milk must not contain any artificial dye; and in meat and meat products "colouring matters other than those naturally occurring in meat" must not be present.

In order to escape from these stringent rules certain manufacturers have reverted to the use of natural colouring matters, the detection of which is still more difficult than that of artificial dyes, and which often enough pass through the net of analysis. Leach[1] describes a number of reactions of natural colours, and gives a few methods to distinguish between them, but these are, without exception, very imperfect, being only colour reactions.

As there was some reason to think that a particular sausage had been dyed with the colouring matter of sandal wood, or barwood, I was led to study more closely the analytical behaviour of some natural colouring matters, and, in particular, that of sandal wood.

The pure colouring matter was obtained by treating an alcoholic extract of a sample of commercial sandal wood with basic lead acetate. Dieterle and Stegemann[2] assert that the precipitation is not complete, and that barium hydroxide precipitates a further quantity of colouring matter, and that complete precipitation can only be effected with barium hydroxide or with neutral (normal) lead acetate. I cannot confirm this, as my filtrates from the basic lead precipitate have always been quite colourless, and I have never been able to obtain a precipitate with barium hydroxide from the filtrate, provided that the basic lead acetate had been added in excess. Moreover, the lead precipitate is much more readily formed and separated, and less slimy than the barium precipitate, and lead acetate can be used in a concentrated solution, so that the necessary volume of reagent is smaller.

The violet lead salt of the colouring matter (santalin, or better, santalic acid; Schulz, Tables, No. 937) was washed several times with hot alcohol, after being separated on a Buchner funnel, and was then treated with dilute sulphuric acid. The suspension was filtered again, and the filtrate evaporated to a small volume. A reddish brown precipitate was formed which was readily soluble in alcohol. It was dissolved in absolute alcohol, and the solution filtered, and evaporated to dryness, this operation being repeated a few times, and then twice more, but with dilute acetic acid instead of alcohol.

In this way a small quantity of the colouring matter was obtained as small but well formed blood-red needles, arranged in stars. Between crossed nicols they

appeared blood-red. A saturated solution of these crystals in dilute acetic acid was used for the analytical work.

The solution gave the following reactions: The salts of metals gave more or less amorphous precipitates. *p*-Nitrosodimethylaniline and diethylaniline gave amorphous precipitates (Reaction of phenols). Neither with quinone nor with phenanthrenequinone was there any notable reaction, nor with the salts of a number of alkaloids.

With zinc iodochloride larger crystals were formed than by evaporation of the pure solution. The type, however, was closely corresponding. It is not impossible that the reagent merely accelerates crystallisation. After some time the surface of the crystals shows small colourless prisms which will be considered more closely afterwards.

Heating with hydrogen peroxide, or with bromine solution, and evaporation of the liquid on glass causes the formation of small colourless needles (in addition to an amorphous substance), completely corresponding to the needlets formed in presence of zinc iodochloride. There is a good deal of evidence for concluding that in the three cases the same oxidation product is formed. As the crystals had some resemblance to those of oxalic acid, and as Franchimont[3] has detected oxalic acid among the oxidation products of santalic acid with potassium permanganate, I sought for this substance in the solution of santalic acid after oxidation with hydrogen peroxide, but in vain. It was not possible to detect oxalic acid by means of any of the usual microchemical reactions. Nor were there any precipitates formed in the oxidised solution if salts of metals were added, with the exception of calcium acetate, which yielded small twinned crystals on evaporation of the solution. Possibly these are characteristic; in any case, they are absolutely different from calcium oxalate, and are soluble in water. The substance produced by oxidation is, therefore, very probably not even an acid. Neither can it be a phenol, as it does not react with ferric chloride or with the nitroso derivatives of aniline.

Oxidation of the solution with chromic acid did not give anything worth noting; benzene did not dissolve anything from the oxidised solution (*cf.* Franchimont, *loc. cit.*, resorcinol).

With potassium nitrite, however, the solution gave a pronounced reaction. A brown precipitate was formed instantly, and the solution turned yellow. If the solution was then evaporated on a glass slide, long yellow needles were formed, coalescing to form fibrous structures and leaves. In many cases these leaves occurred as twins, crossing each other and projecting.

The spectrum of the alcoholic solution shows according to Formanek and Grandmougin[4] maxima of absorption at $0{\cdot}511\mu$, $0{\cdot}4775\mu$, and $0{\cdot}4665\mu$. An alcoholic solution of my preparation, examined with a simple crystal spectroscope of Zeiss-Loewe, showed two strong absorption bands between $0{\cdot}47\mu$ and $0{\cdot}48\mu$, and between $0{\cdot}495\mu$ and $0{\cdot}51\mu$, besides a weaker band close to $0{\cdot}46\mu$. The correspondence is very satisfactory. The absorption spectra of the acetic acid solution and of the ethereal solution were not measured by Formanek and

Grandmougin, and with my apparatus no differences from the alcoholic solution could be detected. Yet they must exist, as the alcoholic solution of santalic acid shows a reddish to blood-red colour, whilst the ethereal solution is of a yellow to orange shade, with greenish fluorescence.

The intensity of the first bands is very pronounced, and they can be observed at great dilutions.

Santalic acid dyes wool pink (salmon), or more yellowish at lower concentrations. The dyed fibre turns violet on contact with ammonia. (For the colour reactions on the dyed fibre see Loomes.[5]) Wool mordanted with iron is dyed dirty bluish-violet; on alumina, chrome or tin mordant a pink shade is produced, just as on uranium mordant; in the last case somewhat more intense.

By making use of the above-mentioned reactions of santalic acid I have been able to detect it in sausage which I had dyed moderately pink with the colouring matter of sandal wood (concentrated alcoholic solution). The test is applied as follows:—Fifty grms. of sausage are boiled with absolute alcohol for a few minutes, and, after cooling, the solution is filtered. The clear filtrate is examined with the aid of the spectroscope. and the 3 bands can easily be recognised.

The alcoholic extract of uncoloured sausage shows only very little absorption at $0{\cdot}59\mu$, $0{\cdot}54\mu$ and $0{\cdot}44\mu$. This spectrum corresponds closely to that of oxyhaemoglobin, but it is distinctly different from that of santalic acid.

The lead salt of santalic acid is then precipitated by means of basic lead acetate. If added colouring matter is absent the precipitate is greyish white, but even very small quantities of santalic acid produce a violet tinge.

The precipitate is collected on a Buchner funnel, thoroughly washed with hot alcohol, and then suspended in 50 c.c. of N sulphuric acid, and the solution again passed through a Buchner funnel. The clear filtrate shows in the spectroscope the 3 typical bands. It is then extracted with ether for a few hours, the passage of the santalic acid into the ether being shown by means of the spectroscope.

The ethereal solution is washed twice with water, evaporated to dryness, and the residue is dissolved in dilute acetic acid. With this last solution the tests with hydrogen peroxide and with potassium nitrite are made, and finally spectroscopical examination is applied as a confirmation.

If the alcoholic solution is evaporated in contact with woollen fibre in presence of some bisulphate, the fibre is dyed orange to pink (it is washed with water, and then with a little ether to dissolve traces of fat). On fibre mordanted with ferric chloride a dirty violet colour is produced. (In this last test no bisulphate is used.)

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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.

PRODUCTION OF UNIFORM STAINS IN THE GUTZEIT TEST FOR ARSENIC.

In the Gutzeit test for arsenic, as described in Appendix VI of the *British Pharmacopoeia* (1914 edition), directions are given that the mercuric chloride paper is to be placed over the end of the glass tube and secured by means of a rubber ring. This method of fixing the paper is not found, in practice, to be satisfactory, because it is very difficult, if not impossible, to get the paper to bear uniformly on the end of the glass tube. The paper creases, and the stain is consequently irregular in outline.

It is very desirable, when two stains have to be compared, that both should be of the same shape and area and also sharp in outline. For several years I have used the following simple arrangement which fulfils these conditions; I have not seen it described previously. Its object is to ensure that all the evolved gas passes through that portion only of the test paper which covers the end of the glass tube.

Two corks, about 1 inch in diameter, are bored centrally to the external diameter of the glass tube. This tube, which is unflanged, and has its end ground flat, is inserted in one cork so as to be just flush with its upper surface. A glass collar, about $\frac{3}{4}$ in. long, is made from glass tubing of about 1 inch internal diameter. Into this collar the cork, bearing the glass tube, is fitted from below, and the other from above. When both corks are pressed home they should meet at about the middle of the collar. A disc of mercuric chloride paper is placed on the surface of the lower cork before inserting the upper one. By this means the paper is held firmly against the ground end of the glass tube, ensuring stains of sharp outline, and thus facilitating comparisons.

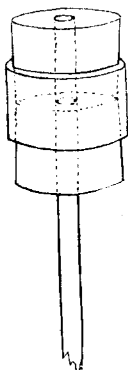

Fig. 1.

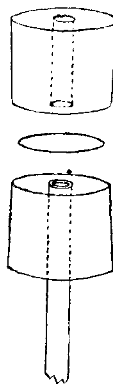

Fig. 2.

Fig. 1 shows the arrangement fitted up ready for use, and Fig. 2 shows the two corks separated and the disc of mercuric chloride paper between them.

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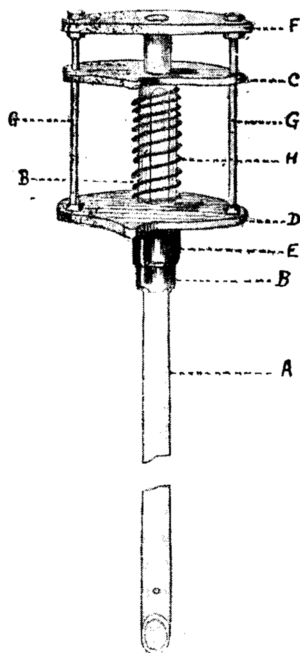
SPRING CLIP FOR GUTZEIT TUBE.

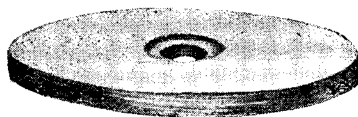
THE clip is cemented to the top of the tube, A, which is of standard dimensions, *viz.* 200 mm. in length and 5 mm. in internal diameter.

It consists of a metal cylinder B, to the top of which is fixed a metal plate, C. The cylinder is cemented to the tube so that the plate is about 10 mm. from the top. A movable metal plate, D, provided with a cylindrical base, E., is connected with a bakelite plate, F., by two metal rods, GG, which pass through holes in the plate C.

The bakelite plate is held in position at the top of the tube by a spring H, and can be moved upwards to allow insertion of the mercuric chloride paper by holding the plate C and pressing the plate D towards it. The bakelite plate is provided with a hole of the same diameter as the internal diameter of the glass tube, and is slightly counter-sunk on the lower side. This ensures good contact between the paper and tube. The paper receives an impression at the point of contact with the tube, and the stain is uniform and well-defined.



The tube, which has a hole, about 2 mm. in diameter, about 10 mm. from the bottom, may be fitted by means of a bung into a suitable wide-mouthed bottle of about 120 c.c. capacity. The bung should also have a hole, through which passes a small



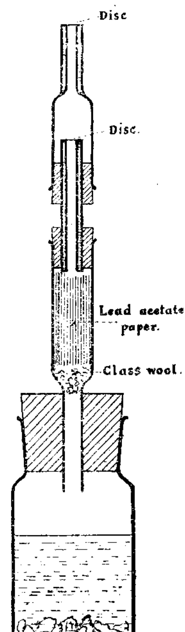
F. Showing counter-sunk hole (inverted).

dropping funnel provided with a tap for the addition of acid, as required to maintain a uniform evolution of hydrogen. This apparatus was devised by the late J. M. Wilkie, and was shown to me by him.

JOHN WHITE.

METHOD OF APPLYING THE GUTZEIT TEST FOR ARSENIC.

THE sketch is almost self-explanatory. Small discs of mercuric chloride paper, of standard size, are cut with a cork borer and uniformly and securely gummed to the upper ground ends of the two thick walled glass tubes, so that all the gas evolved *must* pass through the discs. The tubing employed has an external diameter of not less than 11 mm. and a bore of 5 mm.



The stains produced by the arsenic should be circular, sharply defined, and show a white margin corresponding to the ground surface of the tubes. With 0·01 mgrm. of arsenic a very faint stain will appear on the lower disc, which becomes of a bright red-brown after treatment with hydrochloric acid, but, of course, a much smaller quantity gives a plainly visible stain. If the arsenic exceeds 0·02 mgrm. the upper disc will be more or less stained as well. The intensity of the colours depends, to some extent, on the thickness of the filter paper used.

As the determination is based on a comparison with a stain produced by 0·01 mgrm. of arsenic, the quantity of material operated on should be adjusted accordingly. The volume of the liquid, plus zinc, in the generating bottle (3 ozs.) should not exceed 60 c.c., and the usual precautions for a slow evolution of gas should be taken.

CECIL H. CRIBB.

DIGALLIC ACID AS A REAGENT FOR EARTH ACIDS.

In connection with the precipitation of the earth acids by tannin (Analyst, 1925, **50**, 485), mention may be made of the results of some qualitative tests with a small quantity (0·8 grm.), kindly supplied by Dr. Nierenstein. An acidified solution of sodium tungstate gave a dark brown precipitate (*cf.* Analyst, 1927, **52**, 504). Oxaloniobic acid solution gave a red colour, and on partial neutralisation a crimson precipitate; a solution of oxalotantalic acid gave a yellow colour, but precipitation was quite incomplete, even when the solution was neutralised. Further tests could not be carried out for want of reagent, but it seems unlikely that digallic acid can successfully replace tannin in the separation of tantalum from niobium.

W. R. Schoeller.

Notes from the Reports of Public Analysts.

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

CITY AND COUNTY OF KINGSTON-UPON-HULL.

Annual Report of the Public Analyst and Bacteriologist for the year 1926.

During the year 1926 the number of samples of all kinds examined was 6957, of which 1130 were samples under the Food and Drugs Acts. These included 532 formal samples (52 suspicious, 32 adulterated), and 440 informal samples (20 suspicious, 12 adulterated). The number of samples taken per 100,000 of population was 338, as compared with 314 for England and Wales during 1925.

"Dirt" in Milk.—Of 493 samples of milk received under the Acts, 50 contained unwarranted amounts of dirty sediment. In 46 of these the quantity of moist extraneous sediment was estimated to exceed 2 parts by vol. per 100,000, and in the remaining four samples the amounts were 1·3, 3·2, 2·0, and 2·4 parts, respectively (dung present in all cases). The percentage of "dirty" milks for the year was thus 10·1, as against 10·4 for 1925. In this connection it is stated that :—

" It is not contended here that a limit for sediment in milk is the best criterion by which to judge of the cleanliness of milk; but I am strongly of opinion that milk which can be proved in the laboratory to be dirty (*i.e.* to contain more than 2 parts by volume of moist extraneous sediment per 100,000 parts of the milk, such sediment consisting partly or largely of *dung*) has certainly not been produced under the conditions laid down in the Milk and Dairies Order, 1926, of the Ministry of Health, and that evidence that milk is so contaminated should be sufficient to obtain the conviction of the producer in the Courts. Milk which has been sieved until it is free from dirty sediment, and yet has not been produced under satisfactory conditions, can be dealt with in other ways. A bacterial standard for all milk sold for human consumption is very desirable, but great difficulties would be met with at the present time in working such a standard under the Sale of Food and Drugs Acts. The greatest step forward towards clean milk will be

made when it is enacted that all milk must be sold in sealed bottles. A bacterial standard would then be a practicable basis for judging of the cleanliness of the product sold."

CREAM.—A sample of *tinned cream* was a sterilised Dutch product, labelled "Contains the largest proportion of butter-fat with due regard to its keeping qualities." Since this product contained only 19 per cent. of butter-fat (milk fat), this statement cannot be regarded as accurate. It is regrettable that the Ministry of Agriculture and Fisheries cannot be prevailed on to fix a fat standard for cream, which has been asked for in several quarters, and frequently supported in these Reports. In my opinion, cream should contain not less than 35 per cent. of milk fat, and there is no reason why tinned cream should be of the poor quality all too frequently found.

SUET.—Nine samples of shredded or flaked suet contained cereal flour, the presence of which was declared in all cases, though it can scarcely be said that 18 per cent. of such addition is correctly described as "a little rice-flour." Six different brands examined during the year contained 14 to 25 per cent. of cereal flour. "Whilst I agree that a small addition is necessary in warm weather to prevent coalescing of the shreds, I am of opinion that it is unreasonable to expect an article of this kind to be kept on the shelves of small shops for many months. Such a stale article will have lost part of its value as food during the prolonged storage, often under undesirable conditions. A brand, which, in four samples, was found to contain from 21 to 25 per cent. of rice flour, was condemned and the makers cautioned. In my opinion 10 per cent. of such addition is reasonably sufficient, and a maximum of 15 per cent. of dry rice flour should not be exceeded under any circumstances."

WHITE BREAD AND BROWN BREAD.—The following figures, obtained in the City Laboratory during recent years, show the average composition of three types of bread:

	White bread. Per Cent.	Brown bread. Per Cent.	Standard bread. Per Cent.
Moisture	36·1	39·5	34·9
Proteins ($N \times 5{\cdot}7$)	7·0	8·9	9·2
Fat	0·2	0·6	54·6 (Fat, Starch, Cellulose together)
Starch	55·2	48·3	
Cellulose (Indigestible fibre)	0·2	1·0	
*Mineral Matters	1·3	1·7	1·3
	100·0	100·0	100·0
*Containing phosphoric acid, (P_2O_5)	0·20	0·42	—

These results show that the differences in composition, though appreciable chemically, are very slight, and as they appear in the table are in part due to the varying amount of moisture in the breads. Any real difference in nutritive values between these various types of bread cannot therefore be due to their gross chemical composition, and, as a fact, the main practical differences lie in the slightly greater vitamin content and mineral matters of brown bread, and in its rather higher percentage of indigestible fibre, which latter acts as a mild irritant in the bowel.

GLASS CONTAMINATION OF FOOD.—While I am in general accord with the comments in the Ministry of Health Report (ANALYST, 1927, 284) on this subject,

I would point out that an appreciable number of foods examined in the City Laboratory contained glass particle of considerable size, readily visible to the naked eye. Such particles were not due to atmospheric dust. The results obtained during the year were as follows:

Food.	Number of samples examined.	Number free from glass.	Number containing glass fragments.	Characters of glass particles.
Jam and Marmalade ..	18	13	5	Minute particles
Mincemeat	1	1	0	—
Honey	5	1	4	Minute particles
Preserved ginger ..	1	0	1	Glass splinters and minute particles
Sugar	14	12	2	Minute particles
Potted meat and fish ..	10	10	0	—
	—	—	—	
Total during the year ..	49	37	12	(=24·4 per cent.)

These results show a definite improvement on those of 1925, when 36 per cent. of glass-contaminated foods were detected (*cf.* ANALYST, 1926, **51**, 626).

COD LIVER OIL EMULSION.—Of 3 samples of cod liver oil emulsion, B.P. Codex, asked for by the inspectors, only 1 contained the correct amount of cod liver oil (*viz.* 50 per cent.), the two other samples containing 33 and 42·5 per cent., respectively.

BACTERIOLOGICAL EXAMINATIONS.—A total of 5725 specimens and samples were examined, including 97 milks, 9 waters, 1 disinfectant, 4 shaving brushes, for anthrax bacilli (1 doubtful), blood, urine, shellfish, and 1 ice-cream (purity doubtful). Two rats were also examined, but were found to be healthy and free from any suspicion of plague infection. One sample of "Certified" and 11 samples of "Grade A" milk failed to pass the required standards.

CHEMICO-LEGAL CASE.—CHARRED PAPER.—Some fragments of much-charred paper, recovered by the City Police in suspicious circumstances, were examined to determine whether they were the remains of burnt Treasury notes, as was thought possible. The opinion formed from the results of several chemical and microscopical tests was that the ashes were those of a plain thin paper without any written or printed characters.

A. R. TANKARD.

CITY OF PORTSMOUTH.

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1926.

OF the 1381 samples examined during the year, 1202 were Foods and Drugs, being a "sample rate" of 5·1 per 1000 persons. Of these, 23 were inferior and 5·7 adulterated.

ARSENIC IN APPLES.—Six of 22 samples contained arsenic in excess of one-hundredth of a grain per lb. (1/40th to 1/90th grain per lb. of whole apple). The amounts of arsenic in the peel of these six samples were 1/5th, 1/10th, 1/9th, 1/13th, 1/6th and 1/8th grain per lb., respectively.

CREAM ICES AND ICE CREAM.—The higher grade of ice cream is made by mixing milk or milk products with cane sugar, cream and flavouring agents, together with a small amount of a stabilising agent, such as gelatin. This product

is correctly sold as "cream ice." The cheaper quality of ice cream, which consists of corn flour custard, sweetened and chilled, is frequently sold as "cream ice" at a relatively high price. In 10 of the samples asked for by the Inspector as "cream ice," the amount of fat was 10 per cent. or more. In six cases it exceeded 5 per cent., and it is probable that a small amount of cream had been added. In five cases the fat was less than 5 per cent. (0·85 per cent. in one), and it is improbable that any cream had been added. I submit that the sale of such products as "cream ices" is contrary to Sec. 6 of the Food and Drugs Act.

REGINALD P. PAGE.

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.

LABELLING OF WINE AS "SPANISH PORT."

ON October 25 a wine merchant was charged before the Chichester City Bench with applying a false trade description, to wit, "Spanish Port," and for applying the description "Port" to the contents of the bottles.

Mr. R. T. Monier-Williams, appearing for the prosecution (a firm of wine importers), said that a bottle of wine purchased at the defendant's shop bore the words "Spanish Port" in prominent letters, and below these words, in very much smaller letters, the words "red wine" and "type." Although the case for the prosecution was covered by the Merchandise Marks Act, the Statutes passed to enforce the commercial treaty with Portugal, in 1914, carried the matter further. Under these statutes the description "Port" or "Madeira" could not be applied to any wine other than that produced in Portugal and Madeira, respectively, and such application was, under these statutes, deemed to be a false trade description.

Counsel pointed out that by reading downwards, instead of across the label on the defendant's bottle, the words ran "Spanish red wine" and "Port type," but reading downwards was an unusual method, and he contended that the label had been designed by some one who knew the law, in an attempt, if possible, to find a loophole in the statutory provisions.

There was no question of trade rivalry about this prosecution, but proceedings to enforce the treaty rested entirely upon private individuals. For some reason the Board of Trade did not institute them.

Defendant, giving evidence, said that one legal point had been omitted, *viz.* that if Tarragona wine was re-exported from this country the exporter was entitled to call it "port." The label in question had been in use for very many years, but when the trade agreement of 1914 came into force he realised that the label as then printed, without the words "red wine" and "type," was wrong. In order to make as little alteration to the label as possible, a firm of trade printers had suggested putting a full-stop between the words "Spanish" and "Port," with the words underneath to make it read "Spanish Red Wine" and "Port Type." The phrase "Port type" was in constant daily use, and was constantly applied to Colonial and other cheap wine, and he submitted that it was a perfectly legitimate term to apply. The wine in question was not a cheap wine.

After the Bench had discussed the case in private, the Mayor announced that they had decided to convict, but that they considered it a technical offence only, and that there had been no intention to defraud. The Magistrates fined the defendant two guineas, but declined to grant costs or to make an order for the forfeiture of wines labelled as described.

"PORT" ON WINE LABEL.

On November 1, 1927, a firm of wine merchants was summoned at the Mansion House for having, on September 16, contrary to the Merchandise Marks Act, 1887, applied to certain bottles of wine a false trade description, to wit, "Port," and for having sold and had in their possession wine so described.

Mr. Monier-Williams, for the prosecutors (a firm of port shippers), produced in Court a bottle with a label on which was the word "Port" in prominent letters. Beneath this was the word "Tawnidor," and a statement that the wine had been produced in England from imported grape juice. Counsel pointed out, however, that the word "Tawnidor" made the label still more misleading, since that word had been registered in respect of a red wine imported from Portugal. Under the Anglo-Portuguese Commercial Treaty Act, 1914, it was quite clear that wine described as "Port" or "Madeira" which did not come from Portugal or the Isle of Madeira was being given a false description.

Sir Henry Curtis Bennett, for the defence, said that it was quite clear from the label that the wine was actually made in this country and was a British wine. At most, a technical offence had been committed by the prominence given to the word "Port." This would be rectified in future.

The Alderman (Sir L. Newton), giving judgment, imposed a fine of £5, but said that in a case of this kind he did not think it desirable to allow adequate costs, and there would therefore be nominal costs of £10 10s. Whatever he allowed, he was unable to estimate the value of the advertisement which the prosecutors had got out of the case.

STANDARD FOR BAKING POWDER.

On October 8 a tradesman was summoned at Lincoln for selling a packet of baking powder not of the nature, substance and quality demanded.

Mr. L. O. Need, for the prosecution, said that they recognised as the standard for the amount of carbonic acid in baking powder 8 per cent., of which not less than 6 per cent. should be "available" carbonic acid, but the sample in question was deficient to the extent of 45 per cent. in total carbonic acid, and contained little more than two-thirds of the "available" carbonic acid. It was obvious that the actual seller could not be expected to know the ingredients of a proprietary article sold in packets, but by law the retailer was responsible, and the manufacturer could not be proceeded against for "aiding and abetting" unless he was present at the sale.

The inspector, in cross-examination, admitted that a damp atmosphere would cause baking powder to deteriorate unless it was very carefully stored.

The Bench decided that, while they accepted the evidence and recognised that a technical offence had been committed, justice would be met by the imposition of a nominal fine of 5s. and payment of the analyst's fee.

The Use of the Analytic Quartz Lamp for Testing Drugs.

By P. W. DANCKWORTT and E. PFAU
(*Attached to the Chemical Institute of the School of Zoology, Hanover*).*

THE Hanovia Analytic Quartz Lamp, which has recently been put on the market, has within a very short period proved itself to be an extraordinarily efficient medium for analytical work. For this reason it has now been adopted as a means of testing drugs.

The Analytic Quartz Lamp is a quartz mercury vapour lamp which has already been used in photo-chemistry and in medicine. For analytical purposes a special glass filter is used which only passes the rays of wave-lengths between about 4400 and 2800 A.U.[1] The rays within this narrow range have proved very useful in the identifying and testing of paper, pearls, fabrics, dyes,[2] etc., of oils,[3] and varnishes[4]; in discriminating between natural and artificial tannins[5]; in testing glues[6]; in chemico-dietetic and toxicological work[7]; and in chemico-analytical tests.[8]

Since Robl[8] has undertaken the investigation of organic compounds to obtain data as to their constitution from their fluorescence, we have confined ourselves in this paper to an investigation of the most important pharmaceutical alkaloids and of a number of drugs. In doing so, we have been able to set the capillary-analytical method of tests on an entirely new basis.

CLASSIFICATION OF CHEMICAL SUBSTANCES.—Robl divides chemical substances into the following three classes according to their behaviour under the Analytic Quartz Lamp:

(1) *Passive substances* :—These appear dark or display a scarcely perceptible bluish shimmer.

(2) *Fluorescent substances* :—These light up with more or less pronounced intensity, but, if they are quickly removed from the influence of the rays, this luminosity disappears.

(3) *Phosphorescent substances* :—These display a secondary luminosity when removed from the influence of the rays, of the same or of a different colour.

A few alkaloids occur in the first division, but, for the most part, these are in the division of the fluorescent substances. In the first place a number of alkaloids in dry form were tested, stock preparations being used without previous purification ; a white porcelain dish was used as a receptacle. The crystalline powder, when brought under the rays of the lamp, was distinguishable by a more or less intense luminosity from the dark violet colour assumed by the dish.

Little or no fluorescence was observed in the cases of brucine, quinine tannate, quinine ferro-citrate, cocaine and its salts, daturine and strychnine, which only

* Translation made by the authors from their paper in the *Archiv der Pharmazie und Berichte der Deutschen Pharmazeutischen Gesellschaft,* Vol. I, 1927 (publ. Chemie G. m. b. H., Berlin, W. 10).

had a faint blue shimmer. To the second class belong alkaloids which showed the following colourings:—

Alkaloid	Colouring	Alkaloid	Colouring
Aconitine	distinct light blue.	Colchicine	distinct yellow-green.
Atropine sulphate	faint bluish.	Emetine	distinct yellow-red.
Apomorphine	deep blue.	Hydrastine	distinct light green.
Berberine	distinct yellow.	Morphine	pronounced light blue.
Berberine hydrochloride	distinct yellow-green.	Narceine	pronounced yellow-green.
Quinine hydrochloride	pronounced light blue.	Narcotine	light greenish.
Quinine sulphate	ditto.	Papaverine	pale light yellowish.
Cinchonine	light bluish.	Pilocarpine	white.
Cinchonine sulphate	distinct clear white.	Piperine	faint bluish.
Codeine	light clear yellow.	Solanine	pronounced light yellow.
		Thebaine	reddish yellow.
		Veratrine sulphate	marked light blue.
		Yohimbine hydrochloride	deep yellow-green.

COLOURS OF SOLUTIONS.—One is tempted to assume that the colours would be easier to observe in solutions. This, however, is not the case. Tests of this kind should not be undertaken in ordinary glass test-tubes, although the very thin glass allows a sufficient quantity of the rays of the given wave-lengths to pass through it. But the glass tubes have, to a certain degree, their own characteristic colour; for this reason the solutions were, without exception, observed in small test-tubes of quartz, and the solution was made with a preponderance of sulphuric acid after the addition of sodium hydroxide. Under these conditions it was observed that most alkaloid salt solutions display no luminosity. On the other hand, apomorphine in an acid solution showed a faint blue, and in an alkaline solution a cloudy olive colour. Berberine hydrochloride solution appeared dark golden yellow, quinine hydrochloride and sulphate, in an acid solution, light blue, the surface having a clear luminosity, whereas the alkaline solution appeared dark violet. Morphine remained uncoloured in an acid solution, and in an alkaline solution it became dark blue. Apart from morphine, it may be said generally that if an alkaloid salt fluoresces in a neutral solution, on the addition of acid the luminosity becomes more intense, and on the addition of an alkali the luminosity disappears. R. Mellit and M. A. Bischoff[6] have therefore made use of quinine as a fluorescence indicator in titrating strong acids and bases. It is our intention to try the reverse experiment, to see whether the alkaloid content of quinine preparations cannot be directly titrated with the aid of the analytic quartz lamp.

The clouding of individual solutions is a form of Tyndall effect. Perhaps from investigations of this kind it may be possible to deduce an *a posteriori* conclusion as to the diffusibility of alkaloid salt solutions, and thus as to their durability.[10]

ALKALOID SOLUTIONS.—Except in a few cases, such as quinine, the observation of alkaloid solutions under the lamp is hardly to be regarded as a suitable test for alkaloids. But an adequate method is found if the alkaloids are allowed to permeate a filter-paper, as in capillary analytical methods. Coloured zones are observable in very high dilutions—even in solutions which with definite alkaloid precipitate tests, such as Mayer's, do not produce any reaction. Indeed, several zones can frequently be observed, which may possibly have some connection with the purity of the preparation, but this is a point which has still to be investigated. The following alkaloid salt solutions, of which corresponding capillary specimens are further described below, were subjected to capillary analysis in an acetic acid solution. In these cases the alkaloid appears in the top zone. We therefore give

descriptions of the capillary specimens, all of which appear colourless in ordinary daylight, from the top zone downwards. The strips must be quite dry when they are placed under the lamp.

Arecoline hydrobromide:—Upper zone faint bluish; below, another yellow zone.

Atropine sulphate:—A broad dirty blue zone.

Quinine salts:—Upper zone distinct light blue, dark blue below; lower part of strip red-violet.

Colchicine:—Whole strip deep yellow-green; a darker zone above.

Daturine:—Upper zone pale blue.

Digitoxine:—Narrow bright zone; broad, very bright zone below.

Emetine:—Upper sharp zone blue; brown below; remainder of strip downwards clear white.

Hydrastine:—Pronounced light blue zone, yellow zone below; lower part of strip blue.

Hyoscyamine hydrobromide:—Pale blue zone; lower part faintly blue.

Morphine hydrochloride:—Upper zone bluish; very pale yellow zone below (*vide infra*).

Strychnine nitrate:—Pale dirty bluish zone.

Veratrine sulphate:—Upper zone light bluish.

The reaction is so marked that with morphine, for example, even when diluted in the proportion of 0·001 mgrm. in 30 c.c. of liquid, the light blue zone can easily be detected. As has already been mentioned, we have, up to the present, made use of stock preparations without preliminary purification. The formation of two differently coloured zones points undoubtedly to an impurity. With a morphine solution which was rendered alkaline with sodium hydroxide and diluted with very little hydrogen peroxide, the upper light blue zone no longer appeared, and the yellow zone produced by oxymorphine resulted. When the strip was put aside, the light blue zone also disappeared gradually.

USE OF THE LAMP IN CAPILLARY ANALYSIS.—The Analytic Quartz Lamp provides, therefore, an adequate means of detecting the presence of certain alkaloids in solution. The chief advantage of this method, however, is that the alkaloidal content, even of coloured solutions, such as extracts or tinctures, can also be detected in this simple manner. For the investigation of drugs and their extracts the method of capillary analysis has often been recommended. This method was inaugurated by Schönbein, elaborated by Göppelsröder, and first used for testing pharmaceutical products by Kunz-Krause. Recently one of the authors (Pfau) has written a report on "Capillary Analysis and its application in the Pharmacist's Laboratory."[11]

There must be some intrinsic reason for the fact that this method, in spite of repeated recommendations, has not found favour. This intrinsic reason is quickly discovered if the capillary strips are placed under the analytic quartz lamp. Take, for example, an extract of opium. The ordinary capillary specimen, examined in daylight, shows an upper brown zone due to colouring matters. But colouring matters are not the typical substances we look for in drugs. A drug may display the correct appearance and yet contain too little alkaloid; or an appearance differing from the standard strips, such as we have in the laboratory, may be obtained, and yet the alkaloidal content may be correct. If the strips are now placed under the lamp, the light blue zone of the morphine can be distinctly seen over the colouring-matter zone. Therefore it may be stated generally that the capillary strips, if observed under the quartz lamp, firstly reveal zones

which cannot be seen by daylight, but which show us the substances which are of therapeutic value; and secondly, that colour zones undergo a change of colour and intensity.

The following capillary appearances have been observed by the method which E. Pfau recommends for general use. Three extracts are taken of each drug—one neutral, one acid and one ammoniated. As the reaction of the acid extract was identical with that of the neutral extract, we omit the latter in the following table:

In Acid Solution.	In Alkaline Solution.
Tincture Cinchonae comp. :—Upper zone deep blue, lower strip red-violet.	No blue zone, no red-violet colouring.
Folia Belladonnae :—Upper zone broad yellow-green, underneath light bluish.	Dirty green, below red-brown underneath no bluish shade.
Folia Digitalis :—Above narrow blue-green zone, then green-brown.	No upper zone, deep dirty brown.
Folia Hyoscyami :—Upper zone light blue-green, dirty green, then bright.	Blue-green, underneath dirty green-brown.
Folia Stramonii :—Faint narrow pale yellow zone.	Similar to the acid solution.
Opium :—Upper zone distinct light blue, underneath two yellowish zones.	Light blue, underneath several zones.
Tinctura Opii :—Distinct blue zone, underneath brown.	Very pale bluish, dirty brown.
Radix Ipecacuanhae :—Dark blue, underneath light blue.	No blue zones, faint light yellowish.
Rhizoma Hydrastis :—Upper zone dark blue, the other strip deep yellow.	Faint bluish wider zone, underneath deep yellow.
Semen Arecae :—Upper zone distinct blue, underneath coffee-brown.	Fainter blue, underneath green-brown.
Semen Colchici :—Broad light yellow zone, underneath colourless.	Yellow zone fainter.
Tinctura Strophanthi :—Narrow bluish zone, underneath darker zone, then lighter.	Wider lighter zone, yellow-brown, then light.
Tinctura Strychni :—Faint bluish, underneath at first dark green, then blue.	Light bluish, underneath no green zone.
Tinctura Veratri :—Dirty yellow-brown, underneath light greenish, then violet blue.	Above faint light-bluish wider brown zone, then light green, later bluish.

Other Drugs.—Investigation of the capillary strips is not limited to drugs containing alkaloids. Capillary reactions of other drugs, to some degree, also reveal zones which are not discernible in daylight. Thus with *Rhizoma Calami*, the dark zones have a bright luminosity, with *Radix Gentianae* a light zone is seen in acid extracts. With *Cortex Frangulae* the lower strip, which otherwise is colourless, becomes a deep red-brown. The experiments just mentioned were carried out with capillary strips which had been preserved in the Institute as standard strips for months. But it must be pointed out that storage is, in general, liable to bring about changes in the reactions, as has already been shown in the case of morphine.

Colloid Solutions.—The capillary analytical method of investigation with the analytical quartz-lamp can also be applied to pure colloid solutions. A red-violet colloid gold solution showed in the strips an upper distinct light blue zone, only the lower strip being red-purple. Colloid silver showed a similar zone, the upper strip being yellow-brown. Colloid arsenic sulphide (de Haën) had a faint yellow zone, below which was a broad light blue zone passing into a dirty

yellow brown. It would be worth experimenting to see how far the degree of dispersion or the protective colloid influenced these colourings.

DIRECT EXAMINATION OF POWDERED DRUGS.—Finally, drugs and powdered herbs may be directly investigated under the lamp. Here, again, colours appear in places which by daylight are not at all or barely to be distinguished from their surroundings. Thus *Cortex Granati* displays light patches on the outside, *Cortex Condurango* shows deep yellow patches. With *Cortex Cinchonae,* too, these distinctly luminous yellow patches can be seen, but, side by side with these, a few light blue patches. If the inside is touched with acid, the patch immediately becomes blue. If Cinchona bark powder is sifted into water in a porcelain pot it remains dark, but, on the addition of acid, the whole liquid becomes light blue. With *Radix Ipecacuanhae* all the places from which the bark has come away and where the wood is visible are brightly luminous; if acid is applied they become light blue. *Radix Levistici* turns blue on application of acid, which is due no doubt to its umbelliferon content, this being a strongly fluorescent substance. With *Radix Rhei* the grain is highly luminous. In a cross-section of *Semen Arecae* the endosperm has a beautiful light blue luminosity. *Rhizoma Veratri* displays intensely light blue spots, and *Radix Colombo* is intensely yellow in cross-section, whilst the cambium ring and the vascular bundles appear dark green. Most wonderful of all, however, is the luminosity with *Rhizoma Hydrastis.* In all places where the bark has been removed, *i.e.* where it has been broken or where a twig has been broken off, a deep golden-yellow shimmer is displayed, which produces a really magical colour-effect.

USE OF MICROSCOPE WITH THE LAMP.—The microscope may also be used with the lamp by tilting so that the rays are caught by the reflecting mirror. In such experiments slides made of quartz should not be used, as this would cause too great a strain on the eyes. Ordinary slides made of glass allow the luminosity to be seen sufficiently well. We do not wish to emphasise any particular point in our individual experiments, but we should like to draw the attention of botanists and chemists to the adaptibility of the analytical quartz lamp.

The use of the analytic quartz lamp for experiments with medicinal drugs opens up a very wide field. Both inorganic and organic preparations lend themselves, in some degree, to this method of investigation. But one circumstance must be reckoned with, namely, the fact that certain firms add to their original preparations a certain quantity of some strongly fluorescent substances to enable them to trace imitations. Further reports will be made on our future experiments.

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Ministry of Health.

SALE OF FOOD AND DRUGS ACT.

EXTRACTS FROM THE ANNUAL REPORT OF THE MINISTRY OF HEALTH FOR 1926–27 AND ABSTRACT OF REPORTS OF PUBLIC ANALYSTS FOR THE YEAR 1926.*

OUT of a total of 120,617 samples (an excess of 1677 over those of 1925), 7044 (5·8 per cent.) were regarded as adulterated.

MILK.—This was again the chief subject of analysis, and 4625 (7·4 per cent.) samples were reported against, 80 as contaminated by dirt, with 20 cases of successful legal proceedings; there were 41 cases of added colouring matter, in one of which 50 per cent. of added water was also present, and 13 cases of milk with preservative, showing a continued declension.

CREAM.—Of 982 samples of preserved cream, 25 contained over 0·4 per cent. of boron preservative.

BUTTER AND MARGARINE.—One hundred and seventy-five (1·5 per cent.) samples of butter were reported adulterated, 82 consisting wholly or partly of foreign fats, 6 containing excess preservative, and the rest excess of water. Excess water was present in 21 samples of margarine, and preservative in 12, whilst 10 contained mineral oils.

LARD AND OTHER FATS.—Of lard 11, of dripping 8, and of suet 28 samples were adulterated, the chief adulterants being, respectively, vegetable oil, excess water or free fatty acids, and rice flour.

CHEESE.—Thirty-one of 1462 samples were adulterated.

BREAD AND FLOUR.—One sample of bread contained 0·12 per cent. of sand, and 8 samples of flour contained persulphates.

CUSTARD AND EGG POWDERS.—Acid dyes were present in 6 of 442 samples. One egg powder consisted of 63 per cent. of maize flour, 20·6 per cent. of sodium bicarbonate, and 16·4 per cent. of tartaric acid, with a trace of colouring matter.

JAMS AND MARMALADE.—The 15 cases (out of 1100) of adulteration were due to substitution of glucose for cane or beet sugar, and addition of apple pulp to jams from other fruits.

VINEGAR.—Of 1782 samples, 111 were adulterated or below standard, mostly owing to deficiency of acetic acid.

SPIRITS AND BEER.—Of 2258 samples of spirits, 291 were adulterated, and of 487 samples of beer there was no case of adulteration.

CHOCOLATE AND SWEETS.—Samples contained foreign fats, starches, traces of lead and oxide of iron; 3 samples of butter toffee contained, respectively, 1·5, 5 and 6 per cent. of butter fat; a sample of chocolate rock was made with burnt sienna containing an excessive amount of arsenic.

COFFEE AND TEA.—Seven samples of 1709 were adulterated, and iron filings were still found in a few samples of tea.

SAUSAGES.—Preservative, usually boric acid, was present in 18·5 per cent. of the samples.

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

DRUGS.—Out of 5287 samples of 185 different kinds of drugs, 4·5 per cent. were adulterated. A sample of Seidlitz powder contained only 20·7 per cent. of sodium bicarbonate in the blue paper, and 2 cases of "double strong Seidlitz powders" contained only 78·4, instead of 85·7 per cent., of Rochelle salt in the blue paper. Ground ginger and ground cinnamon contained mineral matter, and petroleum products were found in turpentine, and traces of lead and cornflour in cream of tartar. Tablets for obesity consisted merely of Epsom and Glauber salts.

D. G. H.

Safety in Mines Research Board.

LABORATORY METHODS OF DETERMINING THE INFLAMMABILITY OF COAL DUST.*

IN order to measure the degree of inflammability of a particular coal, relative to some standard coal or series of coals, in a laboratory apparatus, it is necessary to estimate the influence of any set of conditions likely to arise in a coal mine, but difficult to reproduce in the laboratory, and it is also necessary to discover the properties of coal influencing the inflammability of its dust. The report aims (1) at co-ordinating knowledge on the subject, (2) deals with the influence of various factors on the inflammability of dust clouds, and (3) discusses relative inflammabilities of coal dusts.

The historical survey discusses the following articles:—Vital, "L'Inflammabilité des Poussières de Charbon," *Ann. des Mines*, 1875, Ser. **7**, 180–197; Mallard and Le Chatelier, "Du Rôle des Poussières de Houille dans les Accidents des Mines," *Ann. des Mines*, 1882, Ser. **8**, 1–98; Holtzwart and von Meyer, "Ueber die Ursachen von Explosionen in Braunkohlen-Briquette-Fabriken," *Dingl. polytech. J.*, 1891, **280**, 185–190; Engler, "Einfacher Versuch zur Demonstration der gemischten Kohlenstaub-und Gasexplosionen," *Chem. Ztg.*, 1907, **31**, 358–359; Bedson and Widdas, "The Inflammability of Mixtures of Coal Dust and Air," *Trans. Inst. Min. Eng.*, 1906–7, **32**, 529; 1907–8, **34**, 91; 1909–10, **39**, 719; Taffanel and Durr, "Cinquième Série d'Essais sur les Inflammations de Poussières," *Comité Central des Houillères de France*, Brochure No. 1117, Aug. 1911; *Explosions in Mines Committee*, Second Rept., London, 1912; Morgan, (1) "Dust Explosions," *Trans. Inst. Civ. Eng.*, 1913–14, **196**, 334; (2) "Coal Dust Explosions," *Trans. Inst. Min. Eng.*, 1915, **49**, 220; *U.S. Bureau of Mines*, "The Explosibility of Coal Dusts," by Frazer, Hoffman and Scholl, *Bull.* 50, 1913; (2) Clement and Scholl, *Bull.* 102, 1916; (3) Clement and Lawrence, *Techn. Paper* 141, 1917; Beyersdorfer, "Zur Kenntniss des Explosionen organische Staubarten. Experimentaluntersuchung am einfachen Beispiel des Zuckerstaubes," *Ber.*, 1922, **55**, 2568; Allison, "The Explosibility of Coal and other Dusts in a Laboratory Steel Gallery," *Iron and Coal Trades Rev.*, 1925, **111**, 317.

According to the last-named author the explosibility of a dust can be divided into three groups:—(1) Initial explosibility, *i.e.*, explosibility at the minimum concentration which increases the flame length in the gallery (34 oz. per 1000 cb. ft. for Pittsburg coal dust in the laboratory steel gallery). Some combustible dusts were explosive even at this concentration; (2) "Building up" explosibility, *i.e.*, the rate at which the explosibility increased with increasing concentration of the

* Paper No. 31, by A. L. GODBERT; obtainable at Adastral House, Kingsway, W.C.2. Price 1s. 6d. net.

dust; and (3) Maximum explosibility, *i.e.*, explosibility at its optimum concentration. The order of the relative explosibilities of several dusts was as follows:—(1) Initial explosibility: Starch, sugar, aluminium, coal dust (Pittsburg). (2) Building up explosibility: Aluminium, coal dust, sugar, starch. (3) Maximum explosibility: Aluminium, sugar, starch, coal dust.

MEASUREMENT OF INFLAMMABILITY.—However inflammability of a given coal dust is measured, it will chiefly depend on the concentration of the dust in the cloud; the surface area per unit mass of the coal; presence of added incombustible matter; chemical composition of the coal, and nature of the atmosphere. Relative inflammability may be measured: (1) by determining ignition temperature; but different methods may give different orders of inflammability, and dusts with high ignition temperatures may give rise to more violent explosions. (2) By measuring the speed of flame in clouds of different dusts under standard conditions of experiment. This is a more satisfactory method, but presents experimental difficulties. (3) By determining the amount of inert dust necessary to render the coal dusts non-inflammable. This last method is the most satisfactory, and results are immediately applicable to prevention of explosions. The method which is now being developed by the Safety in Mines Res. Board has followed from Taffanel's experiments (*loc. cit.*), but, instead of the amount of inert dust to be mixed with the coal dust to produce a certain volume of flame at the mouth of a heated furnace being determining, the amount of inert dust required to suppress the flame is determined. By this means it is found that results can be repeated with great accuracy, and no arbitrary measurements are involved; the results are independent of furnace temperature and blast pressure, and the relative ignitibilities of a series of coals are measured, and direct information obtained for prevention of ignition in the particular mine involved.

D. G. H.

The Duty on British Wines.

OFFICIAL NOTICE BY THE COMMISSIONERS OF CUSTOMS AND EXCISE.*

THIS Official Notice, No. 728, supersedes the Notice, No. 145, issued in April, 1927. It gives the Regulations concerning the collection of duties on British wines.

The Regulations of March 8, 1912, prohibiting or restricting the mixing of British wines with spirits or with foreign wines, remain in force. Attention is here directed to No. 6 of those Regulations, which provides that British wine must not, by reason of admixture therewith of foreign wine during manufacture in conformity with the Regulations, be sent out, or sold, or exposed for sale, otherwise than under the designation of a British wine. It is also to be noted that the term "foreign wines," as used in those Regulations, includes all imported wines, whether of Empire or non-Empire production.

Sec. 2 defines in law the expression "sweets" as any liquor which is made from fruit and sugar, or from fruit or sugar mixed with any other material, and which has undergone a process of fermentation in the manufacture thereof, and includes British wines, made wines, mead and metheglin. For convenience, the commodities chargeable with the duty are referred to as British Wines.

Basis or neutral wine is within the charge for duty on delivery.

Sec. 3 deals with the licence for the manufacture of British wines for sales, and Secs. 4 to 9 with the methods of control and collection of the duty.

* Statutory Rules and Orders, 1927, No. 728.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Relation of the Hydrogen Ion Concentration to the Titratable Acidity of Milk. P. F. Sharp and T. J. McInerney. (*J. Biol. Chem.*, 1927, **75**, 177–184.)—It might be assumed that the hydrogen ion concentration and not the titratable acidity of milk, as such, is the factor which causes some of the properties of milk to change with the acidity. However, the fact that the titratable acidity of milk has been so successfully used in following the changes in milk due to the development of acid, shows that these changes are related to the titratable acidity, and, therefore, there must be a rather close relationship between the titratable acidity and the hydrogen ion concentration of milk. Samples of fresh milk, some abnormal, were obtained which ranged in titratable acidity from 0·50 to 0·05 per cent., expressed as lactic acid, and in P_H from 6·0 to 7·73. A relation between the P_H and the titratable acidity of fresh milk was found, by means of which the P_H can be determined from the titratable acidity, with an average error of $\pm$ 0·06 P_H, provided that the titratable acidity is greater than 0·10 per cent. This error is the same as that found in the colorimetric method of Sharp and McInerney (*J. Biol. Chem.*, 1926, **70**, 729). A different relationship exists between the titratable acidity and P_H of sour milk, as compared with fresh milk, by means of which fresh milk which has a high acidity can generally be recognised. The titratable acidity of milk is an index of the acidity factor, but this investigation indicates that, as an adjunct, a determination of the P_H value may, in many cases, be of great value in determinations of the conditions of acidity of the milk.

P. H. P.

Determination of Chlorine and Sodium in the Milk of Certain Mammals. L. Barthe and E. Dufilho. (*Compt. rend.*, 1927, **185**, 613–615.)—In human milk and mare's milk, the proportion of chlorine exceeds that of sodium, and even that of sodium chloride deduced from the sodium determined directly. During the colostral period the chlorine in human milk becomes greater than 1 grm. per litre, the subsequent amount being 0·6–0·7 grm. per litre; sodium is present in weighable quantity only after about the forty-fifth day, and both chlorine and sodium increase as the period of lactation proceeds. Thus, it appears that sodium is not useful to the new-born organism. With mare's milk the amount of chlorine exceeds 1 grm. per litre during the colostral period, and subsequently is 0·5–0·7 grm. per litre; sodium is present in traces only during all stages of lactation. The milk of a herd of Dutch cows contained, on the average, 0·345 grm., and that of a herd of Bordeaux cows 0·445 grm., of sodium per litre.

T. H. P.

Direct Precipitation of Calcium in Human Milk. C. S. Rothwell. (*J. Biol. Chem.*, 1927, **75**, 23–26.)—It has previously been shown by the author (*J. Biol. Chem.*, 1925, **65**, 129; ANALYST, 1925, **50**, 562–563) that calcium can be directly precipitated from cows' milk with ammonium oxalate; by a slight modification of the original procedure calcium can now be quantitatively precipitated from human milk. The protein composition of the two milks differs, and the following method has been developed, based on the statement that calcium caseinate is soluble in 5 per cent. sodium chloride solution, and that sodium can replace calcium in basic caseinates:—Shake the sample of human milk and pipette 1 c.c. into a 15 c.c. tapered centrifuge tube. Add 2 c.c. of 10 per cent. sodium chloride and 1 c.c. of saturated ammonium oxalate. This gives a final concentration of 5 per cent. sodium chloride. Mix and leave for 30 minutes to 1 hour, centrifuge, pour off the supernatant milk and cream, and wash once with about 0·5 c.c. of ether and 2 c.c. of ammonium hydroxide solution (2 c.c. of concentrated ammonia to 100 c.c. of water). Repeat the washing with 2 c.c. of the ammonia solution alone, according to the technique of Clark and Collip (*J. Biol. Chem.*, 1925, **63**, 461). Avoid disturbing the precipitate while washing. Titrate with 0·01 *N* potassium permanganate in the usual manner. For the analysis of colostrum, the mucus and cellular detritus must be removed by centrifuging for 5 minutes at 1500 r.p.m. before pipetting. The results were checked against those obtained by ashing in platinum. They were correct within 2 per cent. when the final concentration of sodium chloride was more than 1·25 per cent. A table of results shows an average error for the colostrum of + 0·3 per cent., and for the normal milks of − 0·2 per cent. P. H. P.

Marzipan and its Substitutes. O. Keller. (*Z. Unters. Lebensm.*, 1927, **54**, 78–83.)—The author criticises the suggested criteria for marzipan and its substitutes, and for the raw materials used in its manufacture (Fincke, *ibid.*, 1926, **52**, 423, and 1927, **53**, 172). For the raw material the usual water content is 14 to 16 per cent., the added sugar often exceeds 35 per cent. of the solid matter, and unblanched almonds may be used. The author proposes that substitutes other than apricot or peach kernels, almonds or hazel-nuts, should not be permitted. Glucose syrup may be added to the finished material to an extent of more than 3·5 per cent. Products similar to marzipan are also discussed; these may contain nuts, almond-nuts, nougat and macaroon. The important analytical numbers are moisture, fat, starch, reducing sugars and sucrose. The moisture is determined on 5 grms. of sample well mixed with pure alcohol and dried at 100° C. till constant in weight. For the fat 10 grms. of sample are finely ground with anhydrous sodium sulphate and extracted in a Soxhlet apparatus with petroleum spirit. The method of Baumann and Grossfeld (ANALYST, 1927, **52**, 481) is recommended for the determination of starch, in preference to the extraction or Mayrhofer method, since it gives consistent results with the same sample over long periods of time. A fairly wide latitude should be allowed for the determination of sugars. J. G.

Sulphur Dioxide in Beer. N.C.B. (*Brewers' J.*, 1927, **63**, 436–437; *J. Inst. Brew.*, 1927, **33**, 523–524.)—Sulphur dioxide in beer may not exceed 70 parts per million, and an average addition of two-thirds the permitted amount was found to bring a beer of normal stability into a really excellent one with regard to keeping qualities. Thus, of potassium metabisulphite, ½ oz. per barrel (48 parts per million); of calcium monosulphite 0·5 oz. (39 parts), or of calcium bisulphite 0·25 part (46 parts) may be added. There is no advantage in using calcium monosulphite, as it will at once part with its sulphur dioxide in ordinary beer. Sulphur dioxide does not disappear from beer to any appreciable extent from a full vessel. Addition of other materials to the beer after fermentation must be watched with regard to sulphur dioxide content, since finings, if "cut" with sulphurous acid, will contain 400–500 parts per million, meaning an addition of about 3 parts per million to a barrel; dry hops average 1000 parts per million of sulphur dioxide, and each addition of 4 oz. per barrel means an addition of 1 part of sulphur dioxide per million; some syrups contain large quantities of sulphur dioxide. As a rule, the sulphur dioxide determined by the standard method will work out at 5 to 10 parts per million above that purposely added as preservative.

D. G. H.

Occurrence of Vanillin in Wine Distillates, Brandy and Artificial Brandy. G. Reif. (*Z. Unters. Lebensm.*, 1927, **54**, 90–101.)—Certain substances commonly present in wine distillates (fusel oil, aldehydes, etc.) may interfere with the usual tests for vanillin, since they have similar reactions. These substances, and their reactions to six tests, are tabulated. Phenolic bodies derived from the wooden vessels used for storage may also be present to an extent indicated by the depth of brown colour of the wine distillate. Determinations of vanillin in these distillates and in alcoholic extracts of wood (oak) showed that the reaction obtained depends on the size of the vessel, the time of storage and the strength of the alcohol. Mean values of 0·2 and 0·1 mgrm. per litre of vanillin were found for a number of wine distillates and brandies, respectively, but, of the six tested, one sample of artificial brandy only gave a reaction (0·05 mgrm. per litre). The following method is employed to obtain the vanillin in a pure state:—The alcohol is removed from 100 to 200 c.c. of sample by repeated distillation with water. The residue (10 c.c.) is shaken twice with 10 c.c. of ether (three times in the case of wood extracts), and any emulsion removed by means of the centrifuge. Three c.c. of a saturated solution of sodium bisulphite are then added, the whole well shaken and washed into a test-tube with 3 c.c. of sulphuric acid (1 : 1) and 1 c.c. of water. The solution is warmed, cooled, returned to the funnel, extracted with ether, and the ethereal layer then separated, washed twice with water and dried over fused calcium chloride. It is then gently evaporated at 50 to 60° C., and the residue sublimed quantitatively from a watch-glass at 120° C. The residue should then have no odour of vanillin. The sublimate may best be determined quantitatively by the bromine and iron sulphate method (Mork, *Z. anal. Chem.*, 1893, **32**, 242) or by the phosphotungstic and phosphomolybdic acid method (Folin and Denis, *Chem. Zentr.*, 1913, **1**, 848). The reagent for the latter method is best prepared from

10 grms. of sodium tungstate, 2 grms. of phosphomolybdic acid (free from nitrate and ammonia), mixed with 10 grms. of phosphoric acid (85 per cent.) and 70 c.c. of water, and heated for 2 hours. The reagent is filtered, when cold, and diluted to 100 c.c. The standard comparison solution should be freshly prepared. J. G.

Decomposition of Free and Combined Cystine, with Special Reference to certain Effects produced by heating Fish Flesh. L. H. Almy. (*J. Amer. Chem. Soc.*, 1927, **49**, 2540–2545.)—Fresh fish, heated in a sealed tube at 120° C. for 45 minutes, yields little or no hydrogen sulphide, but stale flesh yields comparatively large amounts. Addition of cystine only increases the residual hydrogen sulphide in the case of stale flesh, and it is established that the fresh fish flesh has the power of destroying hydrogen sulphide, probably by oxidation. It is suggested that detection of large amounts of hydrogen sulphide in canned products points to the use of stale fish in the first instance, and that in flesh products, in general, heated to temperatures over 100° C., some cystine is destroyed, and the hydrogen sulphide from it may be detected in the product, provided it has not been oxidised.
D. G. H.

Oil from Seeds of *Digitalis purpurea*. I. S. Mellanoff. (*Amer. J. Pharm.*, 1927, **99**, 549.)—The amber-coloured, semi-drying oil obtained from these seeds had the following characters :—Sp. gr. at 15·5° C., 0·9231 ; n_D^{20} 1·4755 ; acid value, 9·3 ; saponification value, 207·5 ; unsaponifiable matter, 6·12 per cent. ; soluble fatty acids, 1·66 per cent. ; insoluble fatty acids, 90·0 per cent. ; liquid fatty acids (n_D^{20} 1·4670), 75·8 per cent. ; solid fatty acids (n_D^{20} 1·4685), 9·2 per cent. ; glycerol, 11·4 per cent. ; iodine value (Hanus), 127·9. T. H. P.

Reactions of Anaesthetic Ethers with Potassium Hydroxide and with Mercury, and the Test for Foreign Odours. E. Mallinckrodt, Jr. (*J. Amer. Chem. Soc.*, 1927, **49**, 2655–2666.)—The U.S.P. (10th edition) test for anaesthetic ether requires that no colour shall develop within 2 hours when 10 c.c. of ether are mixed with 1 c.c. of potassium hydroxide test solution and occasionally shaken. It was found that less than about 0·05 per cent. of aldehyde is not likely thus to be detected, but that if solid potassium hydroxide is used 0·01 per cent. may be detected if precautions are taken. In the presence of peroxides and alcohols characteristic modifications in the appearance of the test occur. The potassium hydroxide (lump) test is unreliable in the presence of peroxide, except when only small traces are present, and the appearance of turbidity which remains undiminished in intensity for some hours, points to an alcoholic ether containing considerable amounts of peroxide; but alcohol itself produces a turbidity not easy to distinguish from that due to peroxides, turbidity being in no way indicative of the presence of aldehyde. The potassium hydroxide test will not indicate aldehyde in the complete absence of water. Organic peroxides naturally occurring in old ethers are decomposed by mercury, with liberation of aldehyde. Foreign odours are detected by evaporating the ether to small bulk, pouring the residue, drop by drop, on to a piece of filter paper, and smelling the spot at the moment of evaporation of the ether. The presence of more than minute traces of peroxides may then be detected. D. G. H.

Biochemical, etc.

Reducing Non-Sugars and True Sugar in Human Blood. M. Somogyi. (*J. Biol. Chem.*, 1927, **75**, 33–43.)—The methods commonly used for blood sugar determination yield higher values than the sugar actually present. In a note concerning reactions between yeast and various sugars, the author reported (*Proc. Soc. Exp. Biol. and Med.*, 1927, **24**, 320) the extremely rapid disappearance of glucose from solutions under certain conditions. From this a method has been devised for the determination of true sugar in blood (and other biological fluids) by the separation and determination of the reducing non-sugars or residual reduction. It is unnecessary to incubate the blood with yeast, even for brief periods, as the sugar is completely removed at room temperature in the course of the Folin-Wu precipitation of the blood proteins, if the water for dilution and laking is replaced by a 10 per cent. (moist weight) yeast suspension. Into 7 volumes of a 10 per cent. yeast suspension (yeast free from reducing substances) introduce 1 volume of blood, thoroughly mix and agitate for a few seconds, then add 1 volume of 10 per cent. sodium tungstate, mix, and finally add 1 volume of 0·66 N sulphuric acid; shake well, leave for 5 minutes, and filter. The mixture may be centrifuged before filtration if small amounts of blood are used. The amount of reducing non-sugars in human blood is found to be very uniform, averaging 27 mgrms. per 100 c.c. of blood, in terms of glucose, as determined by the Shaffer-Hartmann method with the modified reagent. It is independent of the blood sugar level, and rises above the normal only in cases of high nitrogen retention. The distribution of reducing non-sugars in corpuscles and plasma is unequal; the average value for corpuscles is 47 mgrms. per 100 c.c., for plasma 10 mgrms. per 100 c.c. In human blood the subtraction of 27 mgrms. per cent. from the apparent sugar, as determined with the modified Shaffer-Hartmann reagent, gives the true sugar, with a maximum error of $\pm$ 4 mgrm. per cent. P. H. P.

Colour Test for Radio-Sensitive Substances. C. J. Bond. (*British Med. J.*, 1927, 637.)—The following starch and iodine colour test is a delicate test which reveals the presence of very small amounts of radiated ergosterol; it shows the different intensity of radiation in ergosterol radiated through water and in the air. A small quantity of crystalline ergosterol is rubbed with a heated glass rod on a warm microscopic slide, on which a thin, translucent and adherent band of the rubbed crystals is thus formed. Half the slide is exposed to the rays from a mercury vapour lamp (Hanovia) for half an hour at 12 inches, the other half of the film being protected from the rays. The whole film is then covered with hot starch solution which has been boiled in water to which about 5 per cent. of potassium iodide has been added. After a short incubation period (10 minutes to three-quarters of an hour, depending on the amount of radiated sterol present, and the concentration of the potassium iodide in the starch solution) the film of ergosterol on the radiated half of the slide assumes a rich pink colour, owing to the dissociation of the potassium iodide and the fixation and retention of the

iodine as a starch iodide on the radiated sterol smear. On irrigation with distilled water the pinkish-brown colour will change into the characteristic blue colour of iodised starch. Samples of egg yolk, coconut stearine, cream and certain other fatty substances have been found to give this test, but some samples of cholesterol fail to do so. The test should prove useful for the demonstration of the presence of certain radiated fatty substances, in place of lengthy feeding experiments.

P. H. P.

Vitamin *A* Potency of Irradiated Milk. G. C. Supplee and O. D. Dow. (*J. Biol. Chem.*, 1927, **75**, 227–239.)—Numerous investigators have shown that the antirachitic potency of milk can be increased by exposure to the rays of the quartz mercury vapour lamp. The desirability of this procedure for enhancing the nutritive properties of milk which serves as the sole dietary of the infant, has been questioned, because certain experimental evidence has indicated that the vitamin *A* of milk is destroyed by irradiation. The irradiated product has now been subjected to further critical studies in order to determine whether or not measurable vitamin *A* destruction could be detected. Results show that milk, after irradiation either in dry or liquid form, for short periods under suitable given conditions, presents no evidence of vitamin *A* destruction, or other toxic effects. The milk was tested on rats. P. H. P.

Separation of a Substance from Oils which Inhibits the Destruction of Vitamin *A* by Ferrous Sulphate. H. W. Estill and E. V. McCollum. (*J. Biol. Chem.*, 1927, **75**, 157–162.)—It has previously been shown that ferrous sulphate in a food mixture causes the destruction of vitamin *A* in fats, rapidly with butter fat, but more slowly with cod liver oil. This destruction, or possibly, inactivation, is inhibited by the inclusion of a small amount of wheat germ oil in the diet. The separation is now described of a most interesting substance from cod liver oil in the form of its lithium chloride derivative, prepared by means of lithium chloride dissolved in pyridine ; this substance, or active fraction, is very effective in inhibiting the destruction of vitamin *A* by ferrous sulphate. It induces in rats a recovery from the " salt ophthalmia," due to their having been given ferrous sulphate, in a manner comparable to the inclusion of wheat germ oil in the ration. Results indicate that this substance may be vitamin *E*. An attempt to remove the same substance from wheat germ oil resulted in the separation of the active principle with lithium chloride, but, in contrast to the case of cod liver oil, a clean-cut physical separation from accompanying substances has not yet been effected. The alcohol and salt addition product type of reaction promises to be useful in the isolation of the fat-soluble vitamins. P. H. P.

Vitamin *A* in Evaporated Milks made by Vacuum and Aeration Methods. R. A. Dutcher, H. E. Honeywell and C. D. Dahle. (*J. Biol. Chem.*, 1927, **75**, 85–94.)—Experiments have been made to determine whether or not vitamin *A* is destroyed when cow's milk is subjected to commercial methods of evaporation. Rats were given a vitamin *A*-free, irradiated basal ration, and

the curative technique was used. Evaporated milks, made by vacuum and aeration methods, were given by mouth, at various levels, in direct comparison with the raw milk from which they were made. It is concluded that evaporated milks made by the vacuum process have lost some of their nutritive value during the manufacturing process, and that this loss, although it does not appear to be unduly great, is probably due to destruction of vitamin *A*. It would appear also that aeration and sterilisation increase this destructive effect to some extent. A table shows the percentages of growth injury. Quantitative interpretations of the destruction of vitamin *A* are discussed, but no accurate conclusion can be drawn. The amount destroyed appears to vary from 10 to 30 per cent. according to the treatment the milk has received. P. H. P.

Quantitative Study of the Problem of the Multiple Nature of Vitamin *B*. H. C. Sherman and J. H. Axtmayer. (*J. Biol. Chem.*, 1927, **75**, 207–212.)—The authors use the terms vitamin *F* (rather than *B* or *B-P*) for the antineuritic factor, and vitamin *G* (rather than *B* or *P-P*) for the second factor, which several investigators have now shown to be essential, along with the antineuritic factor, for growth, and which Goldberger believes to be also a preventive of pellagra. When baker's yeast was heated in an autoclave at 15 pounds' steam pressure for 150 minutes, most, but probably not quite all, of the vitamin *F* (antineuritic) value of the yeast was destroyed. Rats receiving a good basal diet devoid of vitamin *B* were given this autoclaved yeast and gained in weight for a short period only, after which the average weight curve and food intake of these animals were like those of parallel animals which received the basal diet only. It is definitely shown that vitamin *B* consists of more than one factor essential to the growth of rats, by the supplementation which results from giving a mixture of ground whole wheat and autoclaved yeast, as compared with the giving of each separately in doubled amount, and the feeding experiments carried out demonstrate the practicability of using this method to determine which of the two now recognised factors of this complex is the limiting factor in the vitamin *B* value of a given food ; and, also, whether the food is relatively richer in the other factor. Thus the autoclaved yeast, rendered poor in vitamin *F*, is still a relatively rich source of vitamin *G*. Vitamin *G* is found to be the limiting factor of the vitamin *B* complex of whole wheat, which is therefore relatively richer in vitamin *F* than in vitamin *G*. Vitamin *F* is the limiting factor of the vitamin *B* complex of milk, which is thus richer in vitamin *G* than in vitamin *F*. These conclusions were further confirmed by systematic examination of the experimental animals for symptoms of polyneuritis. P. H. P.

Relation between the Vitamin *B* Content of the "Feed" Eaten and that of the Milk Produced. S. I. Bechdel and H. E. Honeywell. (*J. Agric. Res.*, 1927, **35**, 283–288.)—Determination of the vitamin *B* potency of milk from three cows fed for over two years, throughout their period of growth, on an experimental ration decidedly deficient in vitamin *B*, gave results equal to that of herd milk from

cows receiving a good winter ration. Hence the presence of vitamin *B* in milk is not dependent on the presence of this vitamin in the feed, and apparently cows, and possibly all ruminants, differ from other animals in their ability to grow to maturity, to produce normal offspring, and to maintain vitamin *B* in their milk when forced to subsist on rations deficient in such vitamin. Experiments are in progress to determine if this apparent synthesis of vitamin *B* is due to micro-organisms normally present in the rumen. T. H. P.

Vitamin Content of Beer. A. Scheunert and M. Schieblich. (*Chem. der Zelle und Gewebe*, 1926, **12**, 45; *J. Inst. Brew.*, 1927, **33**, 522.)—Vitamins *A* and *C* appeared to be absent from a pale bottom fermentation beer of Pilsen type and from a dark top fermentation porter, first evaporated to thick syrups *in vacuo* at about 42° C. The growth-promoting factor of vitamin *B* was present in just perceptible amounts in the Pilsen beer, and in sufficient quantity in the porter to maintain ordinary growth, but not to correct the effects of previous deficiency. The antineuritic factor of vitamin *B* appeared to be absent from the Pilsen beer and present in small amounts in the porter, whilst black beer brewed from rye germs contained less vitamin *B* than the porter. D. G. H.

Bacteriological.

Action of Free Chlorine on Microbes. F. Dienert and P. Etrillard. (*Compt. rend.*, 1927, **185**, 621–623.)—Micro-organisms removed from a culture on peptonised gelatin and suspended in water to the number of 10^6 per 1 c.c., are rendered sterile by the following numbers of mgrms. of free chlorine per litre of the suspension: *B. coli*, 0·1; Eberth's bacterium, 0·1; Flexner bacterium, 0·18; Shiga bacterium, 0·15; *entero-coccus*, 0·25; *Saccharomyces cerevisiae*, 0·30; *B. subtilis*, 1; amoebae, 1·0; bacteriophage, 8. In surface waters, organisms capable of withstanding more than 3 mgrms. of chlorine per litre are found. When a large seeding of the treated suspension is employed, more resistant organisms appear, and it is often necessary to use four or five times the above proportions of chlorine to bring about complete destruction. The presence of dissolved organic matter in the water favours resistance of the organisms to the chlorine, although the power of resistance diminishes if the bacteria remain for some hours in the water. Agitation of the liquid has no specific influence on the sterilising power of chlorine. T. H. P.

Production of Certain Enzymes by Bacterium Pruni. S. L. Jodidi. (*J. Agric. Res.*, 1927, **35**, 219–221.)—When grown aerobically in skim milk, *Bacterium pruni* forms characteristic crystals composed of tyrosine, leucine, and stearic, palmitic and myristic acids. Proteolytic and lipolytic enzymes are produced by the organism. (See ANALYST, 1927, 486.) T. H. P.

Toxicological.

Alkaloid Trichloracetates. II. Separation of Alkaloids from Viscera. M. G. Florence. (*Bull. Soc. Chim.*, 1927, **41–42**, 1242–1244.)—Trichloracetic acid may be used to precipitate albumins, and at the same time to form soluble salts with alkaloids, by means of which they may be isolated. *Milk.*—The sample is made distinctly acid with a 20 per cent. solution of the reagent. After coagulation is complete the solution is kept at 35° C. for 15 minutes, filtered limpid, and the residue washed with a 4 per cent. solution of the reagent. The filtrate and washings are extracted with ether and petroleum spirit, and then several times with alcohol-free sulphuric ether. The acidified ether then contains the glucosides in a pure and weighable state. The acid liquor is made alkaline with potassium bicarbonate, filtered quickly through glass wool, extracted with ether, and then with chloroform (after removal of the ether), in order to obtain strychnine, if present. *Blood.*—The procedure is the same as for milk, except that a weight of a 20 per cent. solution of reagent equal to that of the sample is used, and the mixture made with a pestle in a mortar till coagulation is complete. The first extractions with ether and petroleum spirit are here unnecessary. *Viscera.*—The minced sample (300 grms.) is coagulated in a mortar, with 200 grms. of a 20 per cent. solution of reagent in the same way as the blood. The filtrate, which should always be limpid, is extracted in the usual manner. Alternatively, the acid liquor may be extracted in succession with petroleum spirit, benzene and chloroform, then made ammoniacal and re-extracted with these same solvents followed by amyl alcohol (Dragendorff's method). Good results have been obtained with a number of typical samples to which alkaloids and other substances were added (cf. ANALYST, 1927, 655). J. G.

The Industrial Contamination of Food with Copper. C. G. King and G. Etzel. (*Ind. Eng. Chem.*, 1927, **19**, 1004–1005.)—Investigation of the copper content of foods commonly prepared in copper or brass apparatus showed that the amount of the metal in pasteurised milk and in aerated beverages was usually about 0·5 part per million. In the case of jams and fruit preserves the quantities of copper found varied considerably, and ranged from 3 to 110 parts per million. The xanthate method was used in the determination of the copper, and attention is drawn to the fact that nickel gives a coloration very similar to that yielded by copper. When nickel is present in appreciable amount another method must be used, or the nickel must be removed before the copper is determined. W. P. S.

Water Analysis.

Dissolved Oxygen Absorption Test. E. A. Cooper and W. H. Read. (*J. Soc. Chem. Ind.*, 1927, **46**, 413–414T.)—Preliminary experiments have shown that sodium permolybdate added to sewage effluents in concentrations of the order of 1 in 10,000 produces a considerable increase in the rate of dissolved oxygen

absorption, as determined by Winkler's method. A solution of the permolybdate was prepared by the careful addition of hydrogen peroxide to a solution of sodium molybdate of known strength, until effervescence and a deep red colour were produced. The mixture was then incubated at 37° C. until the excess of hydrogen peroxide had been decomposed by the catalytic action of the permolybdate. Since the solution also increases the rate of absorption by tap-water in the presence of tartrates, its action is probably to induce a more rapid oxidation of the fatty acids in the sewage. It cannot be used, however, to intensify the effect of hydrogen peroxide itself (cf. *ibid.*, 1927, **46**, 154). J. G.

Organic Analysis.

Quantitative Estimation of Selenium in Organic Compounds. E. H. Shaw, Jr., and E. E. Reid. (*J. Amer. Chem. Soc.*, 1927, **49**, 2330–2334.)—The sample (0·2–0·4 grm.) is mixed with 0·3 grm. of cane sugar, 0·1 grm. of potassium nitrate and 14 grms. of sodium peroxide, a thin layer of sodium peroxide spread over the charge, and combustion made in the usual way. The fused mass is dissolved in water, boiled, cooled, acidified with hydrochloric acid, filtered and diluted to 350 c.c., and from this solution selenium is precipitated either by (1) sulphur dioxide (Rose, *Pogg. Ann.*, **113**, 471; *Z. anal. Chem.*, 1862, **1**, 73), adding 200 c.c. of concentrated hydrochloric acid to the boiling liquid, passing sulphur dioxide into the hot solution until the precipitate has coagulated, adding 200 c.c. of water and filtering the selenium on a Gooch crucible; or (2) by potassium iodide (Peirce, *Z. anorg. Chem.*, 1896, **12**, 409), adding 50 c.c. of concentrated hydrochloric acid and 3 grms. of potassium iodide, and boiling the solution gently to remove iodine, replacing water lost by evaporation, and filtering off the selenium.

D. G. H.

Use of Nitrogen Tetroxide in place of Nitric Acid in Organic Nitrations. L. A. Pinck. (*J. Amer. Chem. Soc.*, 1927, **49**, 2536–2539.)—The method suggested involves an intermediate reaction of the nitrogen tetroxide with the sulphuric acid, whereby nitrating and dehydrating reagents are simultaneously formed. The apparatus consists of a wide-mouthed bottle with a ground glass joint, with a mercury seal for a stirrer, and a dropping funnel and capillary tube with stopcock, sealed below the neck. As applied to benzene, the method used was to place a solution of 1·05 moles of nitrogen tetroxide in 1·25–1·75 moles of sulphuric acid having a concentration ranging between 85 and 95 per cent., in the bottle, and to add a mole of benzene slowly from the funnel, maintaining the temperature at 5–15° C. After mixing, the temperature is raised to 40–60° C., the mixture agitated until completion of reaction, and the stopcock of the capillary tube opened whenever a difference between internal and external levels of the mercury in the seal becomes appreciable. Nitrotoluene was obtained by adding 1 mole of toluene to a solution of 1·05 moles of nitrogen tetroxide in 1·6 moles of 95 per cent. sulphuric acid, agitating for 3½ hours at 50–55° C., the yield being

87·5 per cent. of theory ; α-nitronaphthalene was formed by the reaction of 1·0 mole of naphthalene with a solution of 1·1 mole of nitrogen tetroxide and 1·5 moles of 95 per cent. sulphuric acid, the yield being 88·4 per cent. of theory. D. G. H.

Volumetric Determination of Alkoxyl Groups in Organic Compounds. Modification of the Zeisel Procedure. E. P. Eaton and E. S. West. (*J. Biol. Chem.*, 1927, **75**, 283–288.)—A modification of the Zeisel method for the determination of alkoxyl groups is proposed, based upon absorption of the alkyl iodide in pyridine followed by oxidation of the pyridinium alkyl iodide with potassium iodate, distillation of the iodine, and titration with thiosulphate. The apparatus consists essentially of a decomposition flask with an inlet for carbon dioxide, a water-cooled reflux tower, and a U absorption tube. When this is used the procedure is applicable to both methoxyl and ethoxyl compounds and to those which contain sulphur. The values obtained by this method correspond favourably with those given by the Zeisl procedure. Great care need not be taken to use hydriodic acid entirely free from sulphur, since any hydrogen sulphide may be easily removed before oxidation with iodate, and the analysis is more rapid ; a disadvantage of the method is that it is necessary to have an apparatus for the quantitative distillation of iodine. P. H. P.

Determination of Isopropyl Alcohol in the Presence of Acetone and of Methylethyl Ketone in the Presence of Secondary Butyl Alcohol. H. A. Cassar. (*Ind. Eng. Chem.*, 1927, **19**, 1061–1062.)—Acetone does not interfere with the determination of isopropyl alcohol by oxidation with chromic acid. A quantity of the mixture containing about 15 grms. of isopropyl alcohol is diluted to 500 c.c., and 25 c.c. of this solution are added to 100 c.c. of 45 per cent. sulphuric acid ; 50 c.c. of *N* sodium dichromate solution are then added slowly during ten minutes, while the temperature of the mixture is kept below 25° C. After thirty minutes the mixture is diluted to 500 c.c., and the excess of dichromate is determined iodimetrically in an aliquot portion. One c.c. of *N* dichromate solution is equivalent to 0·03003 grm. of isopropyl alcohol. To determine methylethyl ketone in the presence of secondary butyl alcohol, 10 c.c. of a solution of the two substances containing about 0·24 grm. of the ketone are added to 50 c.c. of *N* sodium hydroxide solution, and 25 c.c. of 0·1 *N* iodine solution are added slowly. After ten minutes the mixture is acidified with sulphuric acid, and the excess of iodine is titrated with 0·1 *N* thiosulphate solution. Under these conditions each c.c. of 0·1 *N* iodine solution is equivalent to 0·001089 grm. of methylethyl ketone, a figure which is 10·2 per cent. less than the theoretical factor. The quantity of secondary butyl alcohol present may be determined by the dichromate method described above. W. P. S.

Behaviour of Fish Oils with Uranium Nitrate and Pyrogallol. W. H. Dickhart. (*Oil and Fat Ind.*, 1927, **4**, 326–328.)—The following procedure is suggested as a means of distinguishing between pure and contaminated cod liver oil. Ten mgrms. of powdered uranium nitrate and 3 c.c. of the oil are heated

in a test-tube in a steam-bath for 20 minutes, with occasional shaking. Under this treatment pure cod liver oil develops an amber colour and shows a greenish shade when examined in transmitted light ; Norwegian sperm oil, a pale amber colour, which appears the same in transmitted light ; menhaden oil, crimson ; pilchard oil, light red ; whale oil, light brownish-red ; herring oil, sardine oil, and Newfoundland cod oil, blood red. Samples of cod liver oil which answered all the requirements of the U.S. Pharmacopoeia, except that the proportions of unsaponifiable matter were high, gave a red colour within six minutes when tested in this way, and were declared contaminated. Distinctive colorations were also observed on heating 5 c.c. of the respective oils with 10 mgrms. of uranium nitrate and 5 c.c. of a 1 per cent. solution of pyrogallol in 95 per cent. alcohol until the alcohol had evaporated, and then cooling the tube. T. H. P.

Body Oil from Sperm Whale. Y. Toyama. (*J. Soc. Chem. Ind. Japan*, 1927, **30**, 137B–139B.)—I. *Fatty Acids.*—The body blubber of the sperm whale (*Physeter macrocephalus*, L.) yields an oil (not freed from spermaceti) of an orange yellow colour depositing a crystalline solid at 20° C. It had the following characteristics :—Sp. gr. at 20° C./4° C., 0·8806 ; at 30° C./4° C., 0·8733 ; n_D^{30}, 1·462 ; saponification value, 131·6 ; iodine value (pyridene sulphate dibromide method), 82·4 ; acid value, 1·24 ; unsaponifiable matter, 36·4 per cent. ; fatty acids, 64·13 per cent. *Fatty Acids.*—Sp. gr. at 20° C./4° C., 0·8918 ; at 30° C./4° C., 0·8847 ; n_D^{20}, 1·4602 ; neutralisation value, 199·2 ; iodine value, 87·4 ; ether-insoluble bromides, 5·55 per cent. The fatty acids were found to consist of about 10 per cent. of saturated acids, myristic, palmitic (preponderating) stearic and a little arachidic having been identified. Of the oleic acid series, zoomaric, oleic, cetoleic, and acids with the formulae $C_{20}H_{38}O_2$ and $C_{14}H_{26}O_2$ were found to be present, but no evidence was obtained of the presence of " physetoleic " acid, as described by Hofstadter and Tsujimoto ; this is regarded as having probably been an impure zoomaric acid.

II. *Unsaponifiable Matter.*—The unsaponifiable matter of the sperm body oil is a yellow crystalline solid. The sample gave : Sp. gr. at 20°C./4° C., 0·8508 ; at 30° C./4° C., 0·8413 ; n_D^{30}, 1·455 ; saponification value of the acetylated product, 186·6 ; iodine value, 72·2 ; cholesterol content, 0·44 per cent. A crystalline solid is deposited at 20° C. The chief constituents are oleyl (preponderating) and cetyl alcohols, octadecanol, and small quantities of alcohols more unsaturated than oleyl alcohol. Hexadecanol is absent, and tetradecanol could not be detected. The acetate of oleyl alcohol yields, on oxidation with potassium permanganate in acetic acid solution, nonoic acid and acetyloxynonoic acid, giving the formula for oleyl alcohol as $CH_3(CH_2)_7CH:CH(CH_2)_7CH_2OH$. D. G. H.

Constitution of Cetoleic Acid. Y. Toyama. (*J. Soc. Chem. Ind., Japan*, 1927, **30**, 154B.)—The cetoleic acid used was isolated from sei-whale oil. Oxidation of its methyl ester with potassium permanganate in acetone solution produced *n*-undecylic acid and a nonane-dicarboxylic acid. The ozonide peroxide of

cetoleic acid, on being boiled with water, yielded *n*-undecylic acid, *n*-undecanal, and a nonane-dicarboxylic acid. The author concludes that cetoleic acid has the following formula :—$CH_3(CH_2)_9CH:CH(CH_2)_7COOH$. He suggests that the so-called erucic acid occurring in marine animal oils is identical with cetoleic acid.

R. F. I.

Constitution of Zoomaric Acid. Y. Toyama. (*J. Soc. Chem. Ind., Japan*, 1927, **30**, 155B.)—The zoomaric acid used was isolated from sei-whale oil. Oxidation of its methyl ester with potassium permanganate in acetone solution produced heptoic acid and azelaic acid. The ozonide peroxide, on being boiled with water, yielded heptanal (oenanthol) and azelaic acid. Hence, the structure of zoomaric acid can be represented as follows :—$CH_3(CH_2)_5CH : CH(CH_2)_6COOH$. This acid appears to be identical with the palmitoleic acid of Armstrong and Hilditch.

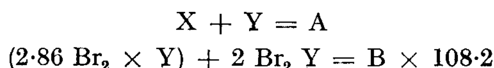
R. F. I.

Solubility of Paraffin Wax in Petroleum Oils. F. W. Sullivan, W. J. McGill and A. French. (*Ind. Eng. Chem.*, 1927, **19**, 1042–1045.)—Graphs are given showing the solubilities of paraffin wax of varying melting points in different petroleum oils. The solubility of the wax rises as the melting point decreases, and falls with increasing viscosity of the oil. Differences in solubility due to variations in the melting point of the wax or in the viscosity of the solvent decrease as the temperature is lowered. W. P. S.

Peat and Peat Wax from Chatham Islands. (*Bull. Imp. Inst.*, 1927, **25**, 243–250.)—The peat from the Chatham Islands was found to be low in moisture content and high in its yield of wax (about 25 per cent.). The yield and nature of the wax varied according to the solvent used for extraction. Benzene, or mixtures of benzene and alcohol, were nearly as efficient solvents as chloroform, and preliminary trials with kerosene were promising. Petrol yielded a hard dark yellow wax ; acetone and chloroform, brittle and dark brown waxes, and benzene a black brittle wax. The wax bore a considerable resemblance to montan wax, and could be used for many similar purposes, but it is not readily bleached. Peat wax, prepared at the Imperial Institute (1), and in New Zealand (2), had the following charactertistics : M. pt. (1) 70–74° C., (2) 73° C. ; saponification value : (1) 120, (2) 146·4 ; acid value (1) 55, (2) 40·4. D. G. H.

Bromination of Cresols. Y. Oshima and T. Takahashi. (*J. Soc. Chem. Ind., Japan*, 1927, **30**, 163B.) :—The authors discuss the Ditz method for the determination of *m*-cresol in a mixture of cresols. They point out that *m*-cresol does not completely take three molecules of bromine, but a definite amount independent of temperature and excess of bromine. They recommend for the Ditz method one minute's shaking at 18° to 20° C., and that the equation should be corrected as follows :—

$$X + Y = A$$



$$(2{\cdot}86\ Br_2 \times Y) + 2\ Br_2\ Y = B \times 108{\cdot}2$$

where A is the weight of cresols ; B the weight of bromine taken ; Y the weight of *o*- or *p*-cresol ; and X the weight of *m*-cresol. R. F. I.

Reactions of Rubber Hydrocarbons with Metallic Halides. H. A. Bruson, L. B. Sebrell and W. C. Calvert. (*Ind. Eng. Chem.*, 1927, **19**, 1033–1037.)—When a benzene solution of rubber in an atmosphere of nitrogen is treated with anhydrous stannic chloride a coloured addition compound is formed, having the formula $(C_5H_8)_{10}SnCl_4$. If the compound is treated with alcohol the stannic chloride is eliminated and a polymer of rubber is obtained. The latter consists of a white powder which may be separated into two portions by treatment with benzene; the portion which is soluble forms a white powder when the solvent is removed, m. pt. about 280° C. The insoluble polymer is a white, fibrous, inelastic substance resembling shredded asbestos; it softens and decomposes at about 300° C., and is insoluble in all the usual solvents. In the preparation of addition products with titanium tetrachloride, antimony pentachloride, and ferric chloride, the rubber must be dissolved in carbon tetrachloride, since benzene reacts with the halides; the two latter halides yield only insoluble polymers, but titanium tetrachloride behaves like stannic chloride, giving both soluble and insoluble polymers of the rubber. Isoprene and balata also yield polymers when treated with stannic chloride. W. P. S.

Determination of Nicotine in Tobacco and in Tobacco Smoke. B. Pfyl and O. Schmitt. (*Z. Unters. Lebensm.*, 1927, **54**, 60–77.)—The methods for the determination of nicotine in tobacco and tobacco smoke are discussed critically, with special reference to the influence of bases and other substances naturally present, or produced during the manufacture or treatment of the tobacco. The following methods are recommended:—Ten grms. of the disintegrated tobacco are well shaken in a flask with 150 c.c. of water and 50 grms. of common salt for 30 minutes. Two grms. of finely ground magnesium oxide are then washed in, the volume made up to 200 c.c., and exactly 300 c.c. of liquid distilled over by means of steam. The salt assists the quantitative separation of the nicotine, and the weak alkali inhibits decomposition of the nitrogenous substances. To one-third of the distillate (100 c.c.), neutralised to methyl red with 0·1 *N* acid, are added 50 c.c. of a 0·05 *M* solution of picric acid, and the nicotine dipicrate allowed to settle out for two hours in the cold. It is then filtered off, washed with two 4 c.c. portions each of picric acid solution and of water, and titrated in a 100 c.c. stoppered flask, in the presence of 10 c.c. of water and 4 drops of phenolphthalein (1:100), with 0·1 *N* sodium hydroxide solution. When a red colour is obtained 25 c.c. of toluene are added, and the titration carried to the end-point. The mixture must be well shaken, so that the nicotine which results from the decomposition of the dipicrate by the alkali passes into the toluene layer, whilst the sodium picrate which remains in the water-layer alone is titrated. Three times the volume of alkali required gives the "picrate number," whence the factor 0·081 gives the percentage of nicotine. The titrated mixture is then made up to 20 c.c. with water, 1 c.c. of the 0·1 *N* alkali added, and the liquid filtered into a separating-funnel, where the water-layer is removed and the toluene dried with about 1 grm. of anhydrous sodium sulphate. To an aliquot portion (20 c.c.) are added equal

volumes of water and of ether and 2 drops of an alchoholic solution of iodeosin (1:500), and the whole titrated with 0·1 *N* acid till the water-layer is colourless and the toluene layer red. Three times the volume required gives the "iodeosin number" (half the "picrate number,") from which the factor 0·162 gives the percentage of nicotine. The method gave concordant results for 1 to 10 c.c. of a 0·1 *N* solution of nicotine and was unaffected by the addition of substances such as pyridine, α- and β-picoline, pyrrole, etc. Nicotinine and nicotyrine, both of which form picrates, do not affect the results, since the former is present in too small a quantity, and the latter forms a salt neutral to methyl red. Qualitative tests for nicotine and to determine the purity of the precipitate may be carried out on the dipicrate or on the titrated solution. The maximum disagreement between the two sets of results for experiments with ordinary tobacco, cigars, and cigarettes, and for those treated so as to remove the nicotine or to render it harmless is 0·02 per cent.

Tobacco smoke, produced by burning the cigar or cigarette in a holder or the tobacco in a pipe, by means of a steady stream of aspirated air, is bubbled through a sintered glass filter plate in a wash-bottle which contains 30 c.c. each of chloroform and 0·1 *N* sulphuric acid, and then through 0·1 *N* hydrochloric acid in two similar bottles. The filtered liquids and washings from the apparatus are freed from chloroform, neutralised with 0·1 *N* alkali to methyl red, again shaken with chloroform and the separated water-layer analysed in the above manner. The method eliminates the effect of substances produced during the burning process, but depends on the rate at which this occurs. At the ordinary rate of smoking a number of treated and untreated samples, which contained from 0·5 to 1·7 per cent. of nicotine, yielded from 14 to 42 per cent. of it in the smoke. The distinction between nicotine-free and nicotine-fixed tobacco is emphasised. J. G.

Inorganic Analysis.

Determination of Antimony in White Metals, etc. H. R. Fitter. (*J. Soc. Chem. Ind.*, 1927, **46**, 414T.)—The following method gives accurate results for white metals, solders, brasses and bronzes which contain up to 15 per cent. of antimony:—Two grms. of the filings are dissolved in 20 c.c. of concentrated nitric acid, the nitrous fumes boiled off, and the solution diluted to 200 c.c. The mixed oxides of tin and antimony which remain are filtered off, well washed, and dissolved immediately in 100 c.c. of a hot 30 per cent. solution of oxalic acid. The clear solution is diluted to 200 c.c. with boiling water, and the antimony precipitated while it is hot, by a stream of hydrogen sulphide. The filtered and washed precipitate is warmed with sodium hydroxide solution (10 per cent.), and the liquid separated from the dark insoluble sulphides, neutralised with oxalic acid, and the antimony re-precipitated after the addition of an extra 30 grms. of oxalic acid. The absence of tin, copper or lead is indicated by the colour of the antimony sulphide, and, if necessary, it should be again precipitated. The antimony is then determined by any of the usual methods. Oxidation to Sb_2O_4 by means of fuming nitric acid, followed by ignition, is recommended. J. G.

Diphenylamine as a Quantitative Reagent for Zinc. W. H. Cone and L. L. Cady. (*J. Amer. Chem. Soc.*, 1927, **49**, 2214–2215.)—The filtrate containing the aluminium group is acidified with hydrochloric acid, ammonium chloride added, and aluminium precipitated with ammonium hydroxide. The filtrate is acidified with acetic acid, and one part tested for chromium and the other for zinc. To the latter 5 drops of diphenylamine acetate solution (1 grm. in 100 c.c. of glacial acetic acid) and 5 c.c. of the 0·5 per cent. potassium ferricyanide solution are added, and the immediate appearance of a dark brown, green or purplish-black turbidity indicates the presence of zinc. Zinc may thus be tested for in the presence of dichromate. The test is more delicate than the cobalt zincate test, and the amount of zinc present may be estimated by the depth of the colour produced. D. G. H.

Detection of Magnesium by Diphenylcarbazide. F. Feigl. (*Z. anal. Chem.*, 1927, **72**, 113–119.)—An alcoholic alkaline solution of the reagent, $CO(NH.NH.C_6H_5)_2$, is added to the boiling solution free from ammonium salts; the liquid is run through a filter, and the precipitate washed with hot water till the washings are colourless. If magnesium is present, the precipitate is of a more or less intense reddish-violet colour. Magnesite reacts directly, dolomite and dolomitic limestones only after previous ignition. The powder is boiled with the reagent in a test tube, the liquid poured off, and the residue washed with hot water till the latter is colourless. A bluish-violet colour of the powder proves the presence of magnesium. W. R. S.

Distribution and Transport of Chlorides in the Atmosphere. F. Bordas and A. Desfemmes. (*Compt. rend.*, 1927, **185**, 603–605.)—Preliminary analyses of dust and rain collected in a region in the South of France show that the atmosphere may hold in suspension quantities of chlorides which, when precipitated by rain, represent as much as 8·41 grms. of sodium chloride per square metre of the earth's surface. These chlorides may be transported much further inland than is usually assumed possible. T. H. P.

Determination of Sulphur in Ores. K. K. Järvinen. (*Z. anal. Chem.*, 1927, **72**, 81–100.)—The causes of error in the usual procedures are discussed. The following gravimetric scheme is recommended as being accurate to about 0·1 per cent.: in a 300 c.c. flask 0·5 grm. of the ore powder is treated with 10 to 15 c.c. of dilute *aqua regia* or nitric acid (3:7 water) on the waterbath. The flask may be closed with a looped bulb tube containing bromine water, as a means of testing for volatilised sulphur. After 15 to 30 minutes the flask is cooled, and 1 c.c. of bromine added, followed after 15 minutes by 1 to 2 c.c. of ether. The flask is shaken until the sulphur bromide has disappeared. The liquid is evaporated in a basin on the waterbath, the residue treated with hydrochloric acid (1:1; 5 c.c.) and again dried, and dissolved in 2 c.c. of the same acid and hot water. The liquid is filtered, diluted to 150 c.c., heated, and treated with 2 c.c. of 10 per cent. hydroxylamine hydrochloride, followed by 60 c.c. of cold 0·25 *N* barium chloride solution. The

latter is added in the space of about five minutes (4 drops per second), when an additional 10 c.c. are added. The precipitate is collected and washed with 100 c.c. of cold water ; decantation is unnecessary. The wet precipitate is incinerated slowly, and ignited gently for ten minutes. The result shows a slight negative error. This is determined by precipitation of (*a*) a synthetic solution of sulphuric acid, iron, and any other constituent of the ore under the same conditions as before, and (*b*) of the same quantity of pure sulphuric acid with the barium solution. The difference ($b - a$) is added to the assay. A mean correction of 0·0033 grm. per gramme of $BaSO_4$ was found necessary. Directions for the volumetric benzidine method are also given. W. R. S.

Physical Methods, Apparatus, etc.

Electrolytic Analysis with the Mercury Dropping-Cathode. J. Heyrovsky. (*Bull. Soc. Chim.*, 1927, **41–42**, 1224–1241.)—The mercury dropping-cathode consists of a vessel in which droplets of mercury fall continually, from a fine glass capillary-tube fed by a reservoir, through the solution to be tested. With such an arrangement the continual renewal of the mercury surface avoids concentration-polarisation during electrolysis, whilst the hydrogen overvoltage is at the maximum and a reversible anode with a constant potential is formed by the layer or mercury on the bottom of the vessel. The anode and cathode are connected with a variable supply of electromotive force, such as a potentiometer circuit, and the exponential changes in the intensity of the current as the polarisation-potential is increased gradually from zero to 2 (or 4) volts (polarisation curves) are registered photographically by means of a polarograph controlled by a galvanometer. Hydrogen is bubbled through the solution for 3 hours before the experiment, to eliminate oxygen, and the potential of the anode at the beginning of electrolysis is determined by comparison with a normal calomel electrode. When the amount of reducible matter in the solution is very small, the loss of ions round the cathode, caused by their deposition, is relatively great. The polarisation curves then indicate a saturation-current independent of the potential, the actual curve being broken up into a number of " waves " from the positions and heights of which traces of metals in solution may be identified and determined, respectively. Thus, the method has been used to determine 10^{-7} grm. equivalents of lead per litre in 2 to 10 c.c. of solution, all of which is available and uncontaminated after the experiment. The sensitiveness of the method is limited by that of the galvanometer, on which the heights of the waves depend. The method may be used for the detection of impurities, for solubility determinations, electrolytic titrations, the identification of complex compounds, and in numerous theoretical investigations. In analyses of mixtures the waves may overlap, and solutions of the same mixture in four different solvents are used. Quantities of the order of 10^{-5} to 10^{-6} grm. equivalents per litre should be used, and traces of reducible anions (such as nitrates, chlorates, permanganates, etc.) avoided, as they complicate the cathodic processes. A table of deposition-potentials of metals and radicals in different solutions is provided. J. G.

Electrical Resistance of Wood as a Measure of its Moisture Content. A. J. Stamm. (*Ind. Eng. Chem.*, 1927, **19**, 1021–1025.)—The method is practicable only within narrow limits. In the case of wood stock, where the moisture content is below the fibre saturation point, and where there is no surface film of condensed moisture tending to short circuit the electrodes, the average moisture content can be determined by the resistance method, with an error of about 1 per cent. The method might be of use with thin veneers, which soon attain moisture equilibrium with their surroundings, and for any wood, such as furniture stock, which has been seasoned thoroughly and kept for a considerable time under fairly constant humidity conditions. W. P. S.

Polishing and Etching Lead, Tin, and some of their Alloys for Microscopic Examination. J. R. Vilella and D. Beregekoff. (*Ind. Eng. Chem.*, 1927, **19**, 1049–1052.)—The following procedure is recommended for obtaining a polished surface free from disturbed metal:—The specimen is ground successively on emery papers of increasing degrees of fineness, each of which is smeared with a concentrated solution of paraffin wax in kerosene. The polishing is then continued on a broadcloth smeared plentifully with soap, and finally on a pad of velvet soaked with soap and alumina. The specimen is then warmed in hot water and immersed in an etching solution consisting of nitric acid, 1, acetic acid, 1, and glycerol, 4 parts ; in the case of pure tin, the proportion of nitric acid should be decreased to prevent deposition of metastannic acid on the prepared surface. After a few seconds' immersion, the specimen is examined under the microscope, polished on the velvet pad, again etched, and these operations repeated as long as the structure appears to improve. W. P. S.

Reviews.

SPECTROSCOPY. By E. C. C. BALY, C.B.E., M.Sc., F.R.S. Vol. II. (pp. 398) and III. (pp. 532). 3rd edition. London: Longmans, Green & Co. 1927. Price 18s. and 22s. 6d. net, respectively.

The opinion expressed in the review of the first volume (ANALYST, 1925, **50**, 157) applies, in even greater measure, to the two later volumes. This is due mainly to greater space afforded by increasing the capacity of the work from the intended two volumes, the first of which embraced only 298 pages, to four volumes, each larger than foreshadowed. The work is now the most comprehensive English treatise on the subject, and it is probably not equalled in its own field in any other language, while its appeal to the reader is well maintained. The long delay since the appearance of the first volume has thus been justified. Volume II deals with the application of interference methods to spectroscopy, methods of illumination, nature of spectra, fluorescence, phosphorescence, and photography of the spectrum. Volume III is engaged mainly with the Bohr theory and its bearing

on atomic structure and series of lines in spectra, followed by chapters on the Zeeman effect, the Stark effect, and emission band spectra.

The subject is viewed mainly from the standpoint of the physicist, but the chemist will find most of his requirements within focus. Sometimes the focus may be regarded as "virtual"; for example, the detailed description of "Electrical Resistance Furnace Spectra," their production and investigation, may appear to apply the knowledge of the chemist to the service of astronomy, but the knowledge thus reviewed may now assist the chemist to a much more vivid and practical comprehension of the conditions obtaining in his furnace, whether fuel heated or electrical. Such reciprocity has already been realised with the study of spectra associated with "Explosion of Wires" dealt with in the next section. The great possibilities of quantitative work are discussed in a detailed review of the work of Hartley and Pollock and of de Gramont. Several instances of such close approximation are given, that they command the attention of the analyst. Each of these workers utilises the spark only; the application of the arc method to quantitative work is not discussed.

The better known phenomena of fluorescence and phosphorescence are described with care, followed by a section on the theoretical aspects, but there is no reference to some of the more recent work on the quantitative relationship between the fluorescence of a solid organic body and its chemical nature, nor to numerous fluorescent properties which are applicable to the purposes of the analyst and the industrial chemist.

The concluding chapter on photography of the spectrum will interest a wide circle of readers, including the microscopist in his more critical investigations; the physical equipment used by Barnard and Gye in their cancer inquiry is explained.

The digression (pp. 132, 133) protesting against the ultra-scientific view taken by many in these days, to the exclusion of all consideration of the experimental and romantic progress of science, is welcome.

Most of the third volume is of interest to few except those concerned with the theory of spectroscopy, especially the experimental development of Bohr's theory. The purely scientific chemist will revel in its contribution to the study of atomic structure, and this will, in turn, find expression in applications to ordinary practice. An item of laboratory procedure is the use of microphotometers for determining the densities of photographs of spectrum lines. The descriptions of the Moll and Koch instruments, illustrated by five plates in addition to other figures and tables, are valuable to many who are not spectroscopists.

The index is not so complete as it should be; for example, the last-named theme is not to be found under either "Koch," "Moll," "microphotometer" or "photometer." This is the more unfortunate, since cross references are extremely rare.

One anticipates with pleasure the appearance of the fourth volume.

S. JUDD LEWIS.

RECENT ADVANCES IN ORGANIC CHEMISTRY. By A. W. STEWART, D.Sc. In 2 Vols. Pp. xiv + 387 and xiv + 382. 5th edition. London: Longmans, Green & Co. Price 21s. per vol.

To those who have followed the various editions of Stewart it has always been a matter of regret that each succeeding one has suffered from the deletion of certain chapters, to make room for the newer work. This has now been rectified by issuing the book in two volumes, so that much that is left out in some editions is again incorporated, and, of course, much new matter has been added, whilst some old chapters have been entirely rewritten. Volume I is mainly for third year honours students, whilst Volume II is suited to the needs of post-graduate workers. Rather more than half the book is devoted to compounds derived from natural sources, and the author has many a quiet dig at the mere maker of synthetic compounds.

Volume I opens with an excellent essay on the main currents in organic chemistry. The remainder of the book is devoted to five main themes: (1) Reagents, (2) Natural substances from plants and animals, (3) Synthetic compounds, (4) Theories and (5) Historical development. Among the essays devoted to these subjects one finds splendid chapters on the Terpenes, the Alkaloids, and the Purines.

The whole is so very readable and so clearly put that it may, perhaps, cause the reader to forget the enormous amount of difficult laboratory work which the subject-matter represents. The volume ends with a good account of the application of the modern electronic theories to orient influences in the benzene system.

In Volume II we get accounts of the newer fields of organic chemistry, and about half the volume is quite new. It opens with a survey of the subject in the twentieth century, and is suggestive of new research. Such subjects as the carbohydrates, sesquiterpenes, anthocyanins and depsides receive adequate treatment, but the chapter on structural formulae and their failings, although very interesting, is open to criticism. The final chapters on the Electronic Theory and some unsolved problems are well worth reading.

Dr. Stewart's book is essentially for those who, having acquired a ground work of organic chemistry, wish to go on and gain a real knowledge of the subject, and to such it makes fascinating reading; for the treatment, if far removed from that of the systematic text-book, is in fact, a series of brilliant essays, written in a critical spirit, yet giving a generally balanced statement of the main facts and theories of modern organic chemistry. The book is well written, and can be throroughly recommended to all who are interested in the intellectual appeal of organic chemistry.

HAROLD TOMS.

FLAME AND COMBUSTION IN GASES. By WILLIAM A. BONE, D.Sc., Ph.D., F.R.S., and DONALD T. A. TOWNEND, Ph.D., D.I.C. Pp. xvi + 548. 30 Plates and Diagrams in the Text. London: Longmans, Green & Co., Ltd. 1927. Price 32s. net.

This volume is a critical review of the principal researches on gaseous

combustion from the year 1660 onwards, special attention being devoted to the developments of the last fifty years. The senior author is one of the most famous pupils of Prof. H. B. Dixon, the founder and doyen of the Manchester School of Combustion Research, to whom the book is dedicated, and who has inspired much of the work described in it. It bears, therefore, the stamp of authority, and its appearance is greatly to be welcomed, in view of the increasing importance to this country of means for the economic generation of power by combustion.

The subject is discussed under five heads:—(1) A concise Historical Introduction, (2) Initiation of Flame and Detonation in Gaseous Explosions, (3) Explosions in Closed Vessels, (4) the Mechanism of Gaseous Combustion, and (5) Catalytic Combustion. There is also an Appendix containing classified experimental data relating to Ignition, Flame Propagation and Detonation.

The presentation of the subject-matter has been particularly well done. Though a vast literature, to which a bibliography bears ample witness, is here brought together in a reasonable compass, this book is more than an indexed collection of facts for reference purposes only. It is made readable by a literary style, too often foreign to the scientist, and it is made vivid by frequent quotation from the original papers discussed. It should appeal to all who are interested in science, because it is written in a true scientific spirit, being a model of the logical exposition of complicated facts and of the philosophical outlook necessary truly to interpret them.

A few quotations may help to illustrate this. Thus (p. 53–54) ". . . the science of combustion is being profoundly influenced by the truly astounding advances which have been made in our knowledge of atomic structure, . . . and already there are signs of the new wine bursting the old skins. For, just as the advent of the kinetic theory of gases . . . changed men's outlook upon combustion, and impelled them to . . . extend the knowledge of the previous generation, so now we are at the threshold of a new era which will assuredly be at least as prolific of new discoveries . . . as the one now closing. The progress of scientific discovery continually teaches us the truth of the ancient proverb that 'it is the glory of God to conceal a thing; but the honour of kings is to search out a matter'." And again (p. 298) "Two principal hypotheses . . . have thus been advanced to explain 'knock' . . .; but neither of them is free from difficulty, and as the subject is still in a very experimental and speculative stage, the wise will ponder and scrutinise carefully such facts as have been proven or alleged, but will keep an open-mind as to their interpretation." Again, on p. 400 we have "It (the 'hydroxylation' theory of Prof. Bone) should . . . not be interpreted or applied too rigidly, because doubtless in the long run the steady accumulation of new facts will necessitate some modifications, and it would be unphilosophical to regard it as more than a serviceable tool for accomplishing further advances."

It is difficult adequately to discuss within the limits of a review any one of the many researches described in this book. Reference may be made, however, to the Bonecourt system of "incandescent surface combustion," which is a striking

example of the manner in which academic research may lead to results of the highest technical importance. In this process a mixture of a combustible gas and air is brought in contact with incandescent porous surface, whereupon rapid flameless combustion ensues, with the development of a large amount of radiant energy. It is possible in this way to obtain effective temperatures of 2000° C., using coal gas or a high grade water gas without any heat recuperation, and to maintain any given temperature with a great economy in gas consumption. In spite of its advantages the system is being only slowly adopted in this country ; in the United States, on the other hand, where there is not the same inertia and conservatism to be overcome, and where new ideas are more readily received, it has made great progress, and is reported to have revolutionised some of the re-heating processes in metallurgy.

This book seems certain to become a classic. The printing and binding are excellent, and the proof reading has been thorough. T. S. WHEELER.

TITANIUM. WITH SPECIAL REFERENCE TO THE ANALYSIS OF TITANIFEROUS SUBSTANCES. By WILLIAM M. THORNTON, JUNR. Pp. 262. New York: The Chemical Catalog Company, Inc. 1927. Price $5.

This work is one of the series of monographs published under the auspices of the American Chemical Society. The first chapters, comprising 60 pages, deal—on the whole, rather briefly—with the occurrence, chemistry, and industrial applications of the metal: they convey the impression that the author is impatient to get to grips with the analytical part, a subject to which he has devoted years of study.

A careful perusal of the book has satisfied the writer that, from the analyst's point of view, it must rank as a masterpiece of compilation of all relevant work, amongst which Mr. Thornton's own methods occupy an honourable place. It is also a masterpiece of completeness, accuracy, and lucid exposition, the fruit of practical experience. An exhaustive collection of references and notes, covering 26 pages of small type, is a prominent feature of the work.

On p. 112, Lundell and Knowles' separation of zirconium from titanium by the phosphate method is described, the zirconium being finally weighed as pyrophosphate (ZrO_2 factor, 0·4632). We now know that zirconium may be accompanied by variable amounts of hafnium, which also yields a very insoluble phosphate (ANALYST, 1925, **50**, 637). In view of the great difference between the atomic weights of zirconium and hafnium, it is preferable to convert the phosphate precipitate into, and weigh, the oxide. Todd's procedure for the analysis of minerals containing tantalum, niobium, and titanium (p. 196) has met quite recently with criticism by Schoeller and Deering (ANALYST, 1927, 630).

The proof-reading has been carefully done: the writer could detect but three unimportant mis-spellings, in addition to two printer's slips ("cold-hot" tube: p. 45, line 20; and "large" amount, should read "small": p. 105, line 33).

Titanium enjoys an enviable distinction amongst the more recently studied elements—for the present, at any rate—in having been made the subject of such a thorough monograph on analytical chemistry. W. R. SCHOELLER.