THE ANALYST

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

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, February 1st, the President, Mr. E. Richards Bolton, F.I.C., being in the chair.

Certificates were read for the first time in favour of: John Edmund Aps, Edward Eric Billington, M.Sc., Ralph C. Chirnside, Ralph David Owen, A.I.C., A.M.I.Chem.E.

Certificates were read for the second time in favour of: Andrew R. Buchanan and Arthur Gordon Francis, B.Sc., F.I.C.

The following were elected Members of the Society:—George Reginald Barnes, B.Sc., Cecil Abell Bassett, B.Sc., A.I.C., Ethel Irene Beeching, M.Sc., A.I.C., Harold Pease Buttrick, A.I.C., Cecil Owen Harvey, B.Sc., A.R.C.S., A.I.C., Harold Vivian Horton, B.Sc., A.I.C., Thomas Howard, M.Sc., A.I.C., Harold McKee Langton, M.A., B.Sc., A.I.C., William Alfred Nottage Markwell, Walter George Messenger, B.Sc., A.I.C., Edward John Newby, B.Sc., Horace Samuel Rooke, M.Sc., A.I.C., S. Sera, Claude Trevine Symons, B.A., F.I.C., David Rees Thomas, M.B., Ch.B., and Wilfred A. Whitley.

The following papers were read and discussed:—"The Determination of Butter in Margarine," by L. V. Cocks, A.I.C., and E. Nightingale; "The Deposition of Metals on Copper from Cyanide Solution : I. A New Method for the Separation and Determination of small amounts of Lead," by B. S. Evans, M.C., Ph.D., F.I.C.; "Investigations into the Analytical Chemistry of Tantalum, Niobium and their Mineral Associates : X. The Separation of Silica from the Earth Acids. XI. The Precipitation of Titanium by Tannin," by W. R. Schoeller, Ph.D., and A. R. Powell; "The Determination of Carvone in Dill Oil," by Prof. Joseph Reilly, D.Sc., F.I.C.; and "Seasonal Variations in the Composition of the Latex of *Hevea Brasiliensis*," by Norman Rae, M.A., F.I.C.

NORTH OF ENGLAND SECTION.

A meeting of this Section was held at Leeds on February 11th. Dr. Dunn presided, and thirteen members were present. The following papers were read and discussed:—"Some Experiences in the Determination of Small Quantities of Iodides," by J. T. Dunn, D.Sc., F.I.C.; "The Vieth Milk Ratio," by G. D. Elsdon, B.Sc., F.I.C.; and "Determination of Small Quantities of Alcohol," by John Evans, F.I.C.

Report of the Preservatives Determination Committee of the Chemists of the Manufacturing Confectioners' Alliance and of the Food Manufacturers' Federation.

DETERMINATION OF SULPHUR DIOXIDE.

(*Read at the Meeting, January* 11, 1928.)

THE Committee presenting this Report was formed at a meeting of chemists engaged in the food manufacturing industries, held on November 17, 1926. Its terms of reference were the investigation and selection of accurate methods of determining sulphur dioxide which should be sufficiently rapid for works' control purposes.

The Committee consisted of Messrs. J. W. Black (Lipton, Ltd.), L. K. Boseley (Crosse & Blackwell, Ltd.), H. R. Jensen (H. J. Packer & Co., Ltd.), Osman Jones (C. & T. Harris (Calne), Ltd.), A. W. Knapp (Cadbury Bros., Ltd.) (Chairman), H. M. Mason (J. Mackintosh & Sons, Ltd.), and T. Macara and L. E. Campbell (Convener) of the trade Research Associations. It has issued two condensed reports in the Bulletin of the Food Manufacturers' Federation, and was instructed at a meeting of the trade chemists, held on October 14th, 1927, to submit an account of its method to the Society of Public Analysts. This meeting also decided that the processes recommended by the Committee should be adopted for control in the laboratories of the various works.

It may not be out of place to describe briefly the lines on which the Committee has worked.

The first step was to circulate samples of confectioner's glucose and starch amongst members of the Committee, the sulphur dioxide in these to be determined by a specified distillation method and also by the method normally employed by the recipients. The specified method consisted in a plain distillation with phosphoric acid into iodine, using an ordinary still-head together with the normal type of condenser adapter. Although the variations in the results were not extremely divergent, it was decided that some attempt should be made to increase their accuracy.

Samples of potassium metabisulphite were then circulated, together with potassium dichromate, in order that each member might standardise his own metabisulphite solutions. The effects of carbon dioxide and of vacuum distillation were to be ascertained.

It was found that some members obtained low results, even when carbon dioxide was used. Vacuum distillation prevented this, as did also the addition of the metabisulphite solution after the contents of the flask had been brought to the boiling point.

From further experiments it appeared that low results were due to two principal causes, *viz.* (*a*) oxidation of sulphur dioxide in the distilling flask; (*b*) escape of sulphur dioxide with air in the receiving vessel.

If carbon dioxide is used, the danger of loss through the second of these causes increases and tends to neutralise any effect in preventing the first.

Eventually oxidation in the flask was found to be prevented to a very large degree if the contents were heated to boiling very rapidly, and if the distillation was speedy. The rapid heating and distillation were, however, rendered possible only by the design and use of two special pieces of apparatus, the bubbler adapter and the still-head.

It was found that with very rapid distillation the evolution of steam was such that the Reichert-Meissl and Kjeldahl still-heads did not always prevent the contents of the flask from being carried over into the distillate. A new form of still-head was therefore designed to overcome this trouble. The use of the bubbler adapter avoids the necessity of traps to prevent loss of sulphur dioxide, which otherwise occurs owing to the rapid heating and distillation.

Rapidity of distillation was also found to be desirable for another reason. This was that sulphur dioxide comes off from most substances within a very short distillation period, and any iodine-reacting substance obtained after this is of a very doubtful character. This point, however, is dealt with in a separate paper.

Investigations were also made as regards distillation by steam, both "wet" and superheated. Its use is advantageous only in special cases, *e.g.* to increase the speed of distillation of those materials which can only be distilled slowly by the ordinary process. "Wet" steam should be used where necessary. Superheated steam was found to be liable to give erratic results when the temperature was too high.

A large number of other points were dealt with, some of which are the subjects of papers which follow this. Among them may be mentioned—direct determination of sulphur dioxide in starch and glucose without distillation, rate of oxidation of solutions of bisulphites, and the use of hydrochloric and phosphoric acids. Other points investigated were differences obtained according to whether iodine is added to sulphite or sulphite to iodine, the use of hydrogen peroxide, the effect of fats, the use of glycerin for preventing oxidation of sulphites, the effect of acidity on the solubility of barium sulphate, and the use of paper pulp filters.

It was also found that the readiness with which both alkaline and acid sulphite compounds oxidise when their solutions are exposed to the air, particularly at the higher temperatures, is not sufficiently realised. For example, soaking the gelatin for even a quarter of an hour preparatory to distillation results in a decided loss of sulphur dioxide.

In all, over 800 quantitative determinations have been made. Although, therefore, the recommended process appears simple, it is not to be concluded that its simplicity is due to lack of development. The simplicity is, however, more apparent than real. The essential point about the ordinary method of determining

sulphur dioxide by distillation is that if the evolution of the gas from the liquid is slow, loss occurs by oxidation. If it is rapid, loss occurs owing to the SO_2-containing air bubbling too rapidly through the oxidising solution.

The process recommended here eliminates this second source of error by the use of a simple piece of apparatus. The first is eliminated by distilling as rapidly as possible.

It should be stated that the Committee was appointed and had completed the greater part of its work before the publication of the method of Dr. Monier-Williams (*Ministry of Health Report on Public Health and Medical Subjects*, No. 43; ANALYST, 1927, 52, 343; 415). The present report is not issued, therefore, in any sense as a criticism of that method. Indeed, the Committee suggests that where sulphides are present Dr. Monier-Williams's method can with advantage be adopted. For most food materials and for normal works laboratory purposes more rapid methods are, however, desirable, and those suggested in the report are put forward to supply this need.

PART I.

THE NORMAL PROCEDURE AND APPARATUS.

PREPARATION OF THE SAMPLE.—In all cases samples should be as finely divided as possible, so far as is compatible with prevention of loss of sulphur dioxide, For instance, in stone-fruit pulps if the fruit is hard an appreciable loss of sulphur dioxide may occur during breaking up, and in certain cases it may be necessary to determine the relative proportions of solid to liquid, and to determine the sulphur dioxide in each separately. The sulphur dioxide content of the whole sample can then be calculated.

In most cases, however, it will be possible to obtain the sample in a finely divided condition without appreciable loss. Glacé fruits, etc., should be minced. It is obvious that in such articles the sulphur dioxide may vary considerably. In confectionery goods, again, considerable variations are to be expected.

Flake gelatin should, if possible, be ground to a coarse powder. A Christy and Norris laboratory mill will, if available, carry out this operation very efficiently. The variations of the sulphur dioxide content in different parts of a flake gelatin are considerable. There should be no preliminary soaking in water, as this is known to give rise to oxidation.

Sausage meat should be well broken up by stirring in the flask with a long glass rod.

It may not be out of place to indicate that in many articles the loss of sulphur dioxide with time is considerable, and that want of agreement between one analyst and another is frequently to be explained on this ground.

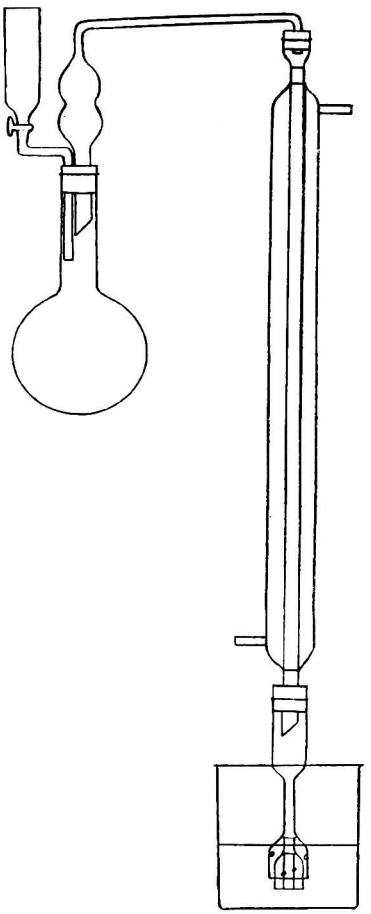
THE FLASK.—The flask should normally be of 500 c.c. capacity. It should be of resistance glass, as it is to be heated with a bare flame. It should be round in shape,

PRINTERS' APOLOGY.

Owing to a sequence of unfortunate errors serious misprints appear on page 121 (*March issue*). *As we are anxious that your volume should be correct, we now enclose the reprinted* 4 *pages.*

Please open up the wire stitches, remove pages 121, 122—183, 184, *and replace this corrected copy in position.*

as there is a danger of the froth being carried over into the distillate if a conical flask be employed. The rubber bung must fit tightly, and should not be new. It holds a tap funnel, the still-head, and, where necessary, the inlet-tube for steam.



THE STILL-HEAD.—The Reichert-Meissl and Kjeldahl still-heads have both been found unreliable when the quantity of steam passing is great. A new type has been designed which is better adapted to the process, and is to be obtained from Scientific Supplies Co., Ltd., 52, Hatton Garden, London, E.C.1. It is sold as the "B.A.R. Still-Head," and consists of two bulbs, each approximately $1\frac{1}{2}''$ wide, the diameter at the junction being about $\frac{7}{8}''$. The tube below the lower bulb is about $\frac{1}{2}''$ in diameter and $4''$ long, the end being cut off obliquely, as in filter funnels. There is a hole of from $\frac{1}{8}''$–$\frac{1}{4}''$ diameter, one inch from the tip.

The tube above the bulbs is of $\frac{1}{4}''$ diameter, and is bent over almost at right angles just above the upper bulb. The horizontal portion is about $6''$ long. It is then bent over at right angles again, the remaining portion being $2\frac{1}{2}''$ long. This end is fitted into the condenser.

THE CONDENSER.—The condenser is fixed vertically. The jacket should not be less than $18''$ long, and the condenser tube $\frac{1}{2}''$ in diameter. If condensation is not sufficiently good, a longer condenser must be used. The temperature of the condensate should be as low as possible and should certainly not exceed 27° C. The adapter is fitted to the end of the condenser tube.

THE ADAPTER.—The adapter is of a bubbler or "scrubber" type, and is sold by Scientific Supplies, Ltd., as the "B.A.R." adapter. It consists of an upper cylindrical portion, into the top of which the end of the condenser fits, about $1''$ in diameter and $3''$ long. To the bottom of this is fitted a tube $\frac{1}{4}''$ in diameter and $4''$ long. At the end of this is an extension surrounded by a bell-shaped portion about $1\frac{1}{2}''$ long and $1''$ wide. The bottom of this is level with the end of the tube. In it are two holes opposite each other, about $\frac{1}{8}''$ in diameter, and placed $\frac{3}{4}''$ from the bottom. Outside this is a further bell-shaped portion about $1\frac{3}{8}''$ in diameter. The bottom of this is about $\frac{3}{8}''$ above the bottom of the inner bell. Seven-eighths of an inch above it are two holes opposite to each other. A line through these two holes is at right angles to a line drawn through the two holes in the inner bell.

It has been proved that this device is an efficient scrubber for the rapidly emerging gas.

THE BURNER.—The burner should be of a powerful type, as it is necessary to heat the contents of the flask to boiling point within 2½ minutes. An asbestos screen is arranged to protect the condenser from the heat of the burner.

WATER USED IN THE FLASK.—The water used should be distilled and must be de-aerated by boiling for not less than 15 minutes. After boiling, it should be both cooled and stored in an atmosphere of carbon dioxide. There is good reason to believe that appreciable losses are due to the oxidation of sulphur dioxide by dissolved oxygen.

ACID.—Although phosphoric acid is conveniently employed with most substances, it has been found that for starch and gelatin hydrochloric acid is necessary (see Part II). With hydrochloric acid, however, there is more danger of charring. It has been found to give more rapid evolution of sulphur dioxide from gelatin, and may prove preferable to phosphoric acid in other cases.

OXIDATION OF THE DISTILLATE.—Iodine was selected as the oxidising substance, because it was desired that the process should normally be volumetric, although capable of being followed by a gravimetric determination if desired. Hydrogen peroxide was not adopted because of its known action on sulphides when hot. Dr. Monier-Williams has now shown that, in the cold, hydrogen peroxide does not oxidise appreciable amounts of hydrogen sulphide or volatile organic matter to sulphuric acid. This fact was, of course, unknown to the Committee at the time.

Dr. Monier-Williams has also rendered the hydrogen peroxide method capable of volumetric adaptation by means of the use of a reflux condenser which prevents volatile organic acids distilling over and renders possible the titration of the sulphuric acid formed in the receiving vessel.

The use of the reflux condenser naturally renders the process of distillation somewhat slow, and the Committee therefore still considers that for works' laboratory purposes the use of iodine has much to recommend it.

THE RECEIVING VESSEL.—The receiving vessel is a 600 c.c. beaker. The bottom of the adapter should be not less than ⅜″ from the bottom of the beaker, in order to prevent bubbles of gas passing outside the bells.

HEATING AND DISTILLATION.—The Committee desires to emphasise the fact that there is a great liability for the sulphur dioxide to be oxidised during the heating of the liquid. It is essential that the liquid should boil within 2½ minutes.

Distillation must also be rapid. It is found that with most substances the sulphur dioxide comes over within a few minutes. If it is found that more than ten minutes' distillation are required, as is frequently the case with dried fruits, for example, steam distillation should be employed (see Part II).

With most food materials there is, on distillation with acid, a continuous, though small, evolution of iodine-decolorising substances, even when no sulphur dioxide is present. It is, therefore, necessary to limit the time of distillation,

apart from the desirability of distilling quickly in order to avoid oxidation. The end-point of distillation may usually be taken as that at which more than one minute is required to decolorise 0·1 c.c. of $N/20$ iodine.

Volumetric and Gravimetric Determinations.

It is anticipated that even where reliance is placed chiefly on the gravimetric process, a volumetric determination will usually be made as a check.

Method of Determination.—Sufficient distilled water is placed in the receiving beaker to cover the outer bell of the adapter. To this are added 0·2 to 0·3 c.c. of a filtered 1 per cent. starch solution, and a few drops of $N/20$ iodine. Where a high percentage of sulphur dioxide is anticipated, a larger quantity, *e.g.* 1 to 5 c.c., of $N/20$ iodine may be added.

Two hundred c.c. of de-aerated water are placed in the distilling flask, followed by 25 to 100 grms. of the sample. The bung holding the still-head, etc., is inserted as rapidly as possible, and it is of course essential that it should fit well.

Twenty-five c.c. of 20 per cent. phosphoric acid are then run in through the funnel, and the contents of the flask heated to boiling as rapidly as possible by means of the naked flame of a powerful burner. The time taken to effect boiling should not exceed $2\frac{1}{2}$ minutes.

Volumetric Process.—As the distillation proceeds, $N/20$ iodine is added from a burette fixed over the receiving vessel, so that the colour remains. It is, in most cases, undesirable to add a considerable excess of iodine during the volumetric process, as there is a danger of loss of iodine. The distillate should be cool, and its temperature should not exceed 27° C.

Generally, at least 90 per cent. of the sulphur dioxide comes over in the first rush of gas, and only traces after five minutes' boiling. The end-point of the distillation was at first taken as that at which the colour due to 0·1 c.c. of $N/20$ iodine persists for more than 2 minutes, but it is probable that one minute would be a better time limit for this amount, with, possibly, some exceptions. The distillation should be complete within 10 minutes' boiling. Too prolonged boiling may produce reducing substances other than sulphur dioxide. If it is found that this time is exceeded, even when the most powerful flame practicable is used, recourse should be had to steam distillation (see Part II).

Gravimetric Process.—The distillate is filtered and brought to a volume of 200 to 250 c.c. If it is necessary to boil down to this volume, concentration should be carried out on an electrically heated plate, or precautions should be taken to prevent sulphur dioxide from the gas flame being absorbed. Ten c.c. of $N/10$ hydrochloric acid are then added, and the liquid is boiled for five minutes; 2·5 c.c. of 10 per cent. barium chloride solution are next added, drop by drop, and the solution boiled for five more minutes. Two and a half c.c. more barium chloride solution are added and the liquid is allowed to simmer for one hour, finally being allowed to cool. It should then stand for at least two hours, or preferably over-night, and finally be filtered either through a No. 40 Whatman

filter paper or by means of paper pulp. After washing and drying, the paper and precipitate are ashed as usual.

A blank determination should be made with the chemicals if special accuracy is desired.

PART II.

Materials requiring Special Treatment.

(*a*) Starch.—In the case of starch, the ordinary distillation process, as described in Part I, is employed, except that the flask should be of 1 litre capacity, the amount of sample taken 100 grms., and the acid hydrochloric instead of phosphoric.

The amount of concentrated hydrochloric acid should be 100 c.c., and that of de-aerated distilled water 400 c.c. The flask should be shaken gently at the start to keep the starch in suspension.

This concentration of hydrochloric acid prevents the starch from gelatinising, and is found to render the hot solution relatively mobile. The time required to heat the liquid to boiling point will be longer in this case, but should not exceed 5 minutes. Heating should be checked at the moment of boiling, as there is a risk of froth passing over.

The end-points of the titrations are affected by a red colour, which is apparent after the blue has been discharged by sulphur dioxide, although it, too, is discharged by still more of the gas. Some improvement has been obtained by postponing the addition of starch indicator to the beaker until near the end of the distillation.

If, after titrating with iodine, it is desired to make a determination by the gravimetric process, the distillate should be filtered, reduced to 200–250 c.c. if necessary, neutralised with ammonia, and 10 c.c. of $N/10$ hydrochloric acid added. The precipitation with barium chloride is then effected as described in Part I.

The same amount of all chemicals should, of course, be used in determining the "blank."

(*b*) Materials requiring more than 10 Minutes Distillation by the Process described in Part I. Gelatin, Meats, Dried Fruits, etc.—With certain materials, such as gelatin, dried fruits, meats, etc., it will be found that by the ordinary process, as described in Part I, more than 10 minutes will be required to distil off all the sulphur dioxide. In these cases the speed of distillation may be increased by means of steam. Wet steam should normally be employed, although the use of superheated steam may be advantageous in some cases, *e.g.* with substances giving rise to excessive frothing. Its temperature should not, however, exceed 150° C.

Preparation of Sample.—See Part I.

Steam Generator.—The steam generator may consist of any convenient apparatus, but the water should be boiled for some time before the steam is introduced into the distilling flask. Steam should be introduced into the liquid by means of a glass tube (see below).

SUPERHEATED STEAM GENERATOR.—The superheater consists essentially of a heated copper coil of three close turns of tubing, ½" in external diameter, the ends being reduced to carry ¼" tubing for connections to the boiler and the distillation flask. Steam should be led into the liquid by means of a glass tube, as it has been found that a copper tube may give rise to erratic results. The temperature of the steam should not exceed 150° C.

GELATIN.—In the case of gelatin, hydrochloric acid should be used instead of phosphoric acid. The concentration required is 25 c.c. of the concentrated acid to 250 c.c. of water, where 25 grms. of gelatin are employed. With 50 grms. of gelatin the amount of acid must be increased.

TIME OF DISTILLATION.—In these cases it is frequently impossible to distil over all the sulphur dioxide within 10 minutes, notwithstanding the employment of steam. Nevertheless, every step should be taken to render the distillation as rapid as possible.

It will generally be found that in the case of gelatin practically all the sulphur dioxide distils within 10 minutes unless the article is in the "flake" form.

Where sausages and other meat products are finely divided and well distributed in the liquid, 10 to 15 minutes are usually sufficient for complete distillation of sulphur dioxide. Other reducing bodies may continue to come over after this period.

Hard fruits require a longer time—normally from 20 to 30 minutes.

METHOD OF DETERMINATION.

(*b*) MATERIALS REQUIRING STEAM DISTILLATION.—The steam should be in the process of generation at least 15 minutes before the commencement of distillation.

The necessary water and acid, whether hydrochloric or phosphoric, are introduced into the flask, and the water, starch solution and a few drops of *N*/20 iodine placed in the receiving beaker, in accordance with the instructions given in Part I. The sample is then introduced into the flask and the contents heated to boiling as rapidly as possible by the introduction of steam and, if necessary, the employment of an Argand burner. The time taken in reaching the boiling point should not exceed 2½ minutes.

The rate of evolution of steam should be such that 250 c.c. are collected in ten minutes.

VOLUMETRIC PROCESS.—The distillation and the titration with iodine, are carried out as in Part I, but here, as has already been indicated, it may not always be possible to complete the distillation in 10 minutes. The end-point of the distillation is reached when more than one minute is required to decolorise 0·1 c.c. of *N*/20 iodine.

GRAVIMETRIC PROCESS.—The distillate is brought to a volume of 200 to 250 c.c. by concentration, neutralised with ammonia if hydrochloric acid has been used in the distillation flask, 10 c.c. of *N*/10 hydrochloric acid added, and precipitation and filtration of the barium sulphate carried out as before.

(*c*) MEATS, ETC., CONTAINING DECOMPOSING PROTEIN AND MATERIALS CONTAINING SULPHIDES.—With regard to meats, etc., it should be noted that where decomposed protein is likely to be present precautions will have to be taken to differentiate between sulphur dioxide and hydrogen sulphide. This may be done by adopting the procedure of Dr. Monier-Williams.

In general, it has been found that with old samples of potted meat and sausages the sulphur compounds appeared to affect the results of the proposed method only very slightly.

TABLES.

These show:—

(1) The improvement obtained, early in the Committee's proceedings, by the employment of the special ("B.A.R.") adapter, combined with rapid heating and distillation, although the time to be occupied in bringing the contents of the flask to the boiling point has since been shortened still further.

(2) and (3) The results obtained by members of the Committee or their assistants in determining the sulphur dioxide in gelatin by both the Committee's and Dr. Monier-Williams's methods.

(4) Results of the determination of sulphur dioxide in two samples of starch by the Committee's methods.

In Tables (2)—(4), abnormal results have been placed in the line below the others, and the average figure, as well as the variations, calculated both excluding and including them. In two cases, however, specially marked in the Tables, certain abnormal figures have not been taken into account in calculating averages.

I.

IMPROVEMENT OBTAINED BY RAPID BOILING AND THE USE OF THE "B.A.R." ADAPTER.

50 c.c. of a 0·1 per cent. solution of potassium metabisulphite were distilled with phosphoric acid.

The results are expressed as:—

$$\frac{\text{Sulphur dioxide obtained}}{\text{Sulphur dioxide introduced}} \times 100.$$

								Mean.
(*a*) Ordinary distillation method	91·0	79·0	84·1	90·7	100·0	79·5	96·9	88·7
(*b*) Rapid method with earlier type of "B.A.R." adapter	91·9	92·6	95·0	95·6	95·7	96·4	94·6	94.5
(*c*) Rapid method, with latest type of "B.A.R." adapter	95·8	95·3	98·9	97·7	99·4	98·2	98·5	97·7

N.B.—It should be noted that with regard to both (*b*) and (*c*) the time of heating to the boiling point was longer than was afterwards found to be desirable, being 4 minutes instead of 2½ minutes.

II.

DETERMINATIONS OF SULPHUR DIOXIDE IN GELATIN BY THE COMMITTEE'S METHOD CARRIED OUT IN SEVEN DIFFERENT LABORATORIES.

	Parts per million.	Mean.
(*a*) Volumetric,	502, 502, 453, 466, 474, 454, 460, 499, 499, 470, 464, 477, 475	477±25
	422* 427*	—
(*b*) Gravimetric	477, 477, 442, 459, 447, 450, 478, 452, 456, 442, 440	456±22
	490, 502, 504	465±39
	430*	—

* Samples accidentally left uncovered for some time.

III.

DETERMINATIONS OF SULPHUR DIOXIDE IN GELATIN BY THE MONIER-WILLIAMS METHOD CARRIED OUT IN SIX DIFFERENT LABORATORIES.

	Parts per million.	Mean.
(*a*) Volumetric	470, 480, 452, 486, 461, 455, 474, 486, 461, 454, 461, 461, 469, 461, 454	466±20
	432, 441	462±30
(*b*) Gravimetric,	466, 477, 459, 473, 465, 463, 465	467±10
	503,* 493*	—

* Precipitate of barium sulphate washed three times with boiling water, but not boiled with water.

IV.

DETERMINATIONS OF SULPHUR DIOXIDE IN STARCHES IN SEVEN DIFFERENT LABORATORIES BY THE COMMITTEE'S PROCESS.

	Parts per million.	Mean.
(*a*) Volumetric,	163, 164, 164, 163, 160, 169, 173, 176, 176, 176	168± 8
	151, 157	166±15
(*b*) Gravimetric,	159, 172, 157, 163, 166, 170, 176, 167	166±10
	143	164±21
(*a*) Volumetric,	61, 65, 60, 59, 54, 56, 55, 66, 68, 58, 53 ..	60± 8
	45, 48, 48	57±12
(*b*) Gravimetric,	42, 41, 42, 44, 49, 43, 45, 50	44·5±5·5
	30, 32, 58	43±13

NOTE.—With regard to errors in determinations, it may not be out of place to indicate that where only 25 grms. of sample are taken, 0·1 c.c. of $N/20$ iodine corresponds to 6·4 parts per million when the Committee's volumetric process is used. In the Monier-Williams volumetric process, 0·1 c.c. of $N/10$ sodium hydroxide corresponds to 12·8 parts per million when 25 grms. have been taken. Dr. Monier-Williams, however, recommends the use of 100 grms., and it is, of

course, obvious that up to a point the larger the quantity of sample taken, the smaller will be the error. For a given quantity of sample the titration figure (in $N/10$ sodium hydroxide) obtained by the Monier-Williams process is half that (in $N/20$ iodine) obtained by the Committee's process.

It will be seen that in working with small quantities of substance the end-point of the titration is of considerable importance. Generally speaking, the end-point with iodine is good, except in the case of starch, already referred to in the text.

(Signed) A. W. KNAPP (*Chairman*).
L. E. CAMPBELL (*Secretary*).

DISCUSSION.

Dr. MONIER-WILLIAMS said that there appeared to be a number of quick methods, depending either on distillation, or even on simple titration (as in Ripper's method), which could be used satisfactorily for most foods, but which were liable to give inaccurate results in certain cases, for instance, with foods containing nutmeg or other spices. The method which he had recently suggested had been put forward as a general method applicable to all cases. It had, no doubt, the disadvantage of being considerably longer than the one now proposed, but against this must be set the advantage of having a method which could be depended upon to give reliable results with all foods, including spices.

Mr. PERCY MAY suspected that dried fruits belonged to the nutmeg type, for which the only methods were the Monier-Williams and the gravimetric. He had always found that the use of iodine gave high results.

Mr. E. HINKS said that he had adopted a combination of the Monier-Williams and the present process—namely, reflux distillation into iodine. He visualised a time when it might be necessary to apply a different process to each substance. He had sometimes used nitrogen instead of carbon dioxide, and he mentioned that oxidation really took place in solution rather than in the gaseous state.

In the case of vinegar he found that with the present method an acidity came over, which was prevented by previous "refluxing." He had not found that the suggested adapter altogether prevented the escape of gas.

With regard to the disappearance of sulphur dioxide over a period of time he confessed that periodically he felt that accuracy was a useless achievement. He instanced the case of a particular preservative, largely used by sausage makers, which, though alleged to contain 14 per cent. of SO_2, gave the following figures in the course of a week: 3·3 per cent., 2·1 per cent., 1·25 per cent., 0·8 per cent. The sausages themselves behaved in the same way, the sulphur dioxide content halving itself in two days. Finally, he mentioned the old precaution of adding copper sulphate.

Mr. BRISTOWE HARRISON recalled that Giles and Shearer, in 1884, had shown that aqueous solutions of sulphite oxidised rapidly. It was usual, he said, to add sulphite to iodine rather than the reverse. With regard to sulphate losses he asked Mr. Jensen if he had tried igniting barium sulphate on a wet filter paper—which procedure was said to give the most accurate results. He could confirm the loss of metabisulphite in sausages. He regarded the present method as

being especially suitable for control work, but recommended the Monier-Williams process where finality was desired.

Dr. CAMPBELL, in replying to general questions as to the Committee's process, said that for most food products and for normal works' laboratory purposes, they thought the process to be as accurate and more rapid than most others. The Monier-Williams volumetric process was undoubtedly of more universal application than the Committee's, and, where sulphides were present, it would probably be better to rely on the Monier-Williams method altogether. Nevertheless, it had not been found that, even in the case of old samples of potted meats and sausages, any considerable error had arisen when the Committee's process was used. Dried fruits had been mentioned by Dr. May as being very difficult to deal with. In this case the Committee recommended the use of steam to speed up the rate of distillation of sulphur dioxide.

At the commencement of heating the expanding air carried over much sulphur dioxide, and to avoid the danger of the bubbles being flattened against the bottom of the beaker and some of them passing outside the bells, the Committee had suggested that there should be a space of at least three-eighths of an inch between the bottom of the adaptor and the bottom of the beaker.

Mr. J. W. BLACK agreed that, in the volumetric process, nutmeg presented a real difficulty, which was not present to the same extent in the case of other spices. A study of the curves supported the view that at the point or area where the change of direction of the curves took place, there was a close approximation to the amount of sulphur dioxide in the spice. The curve for dried fruits showed marked change of direction. The distillation period corresponding to this change was between 10 and 12 minutes, and thereafter the increase was gradual.

Mr. OSMAN JONES, in reply to a question regarding the rapid loss of sulphur dioxide by sausages, stated that in his experiments the sodium metabisulphite had been added to the sausages in powdered form and that the examination was begun 3 hours after the sausages were manufactured. This fact, no doubt, explained the differences between his figures and those shown on the curve exhibited by Mr. Black, who had added the sulphite in solution and then immediately proceeded to its determination.

Mr. JENSEN said that he used dry filter paper for barium sulphate because decarbonisation was quicker. He had found Ripper's method, to which Dr. Monier-Williams had referred, satisfactory for glucose, sugar, etc., and as a sorting test for starch.

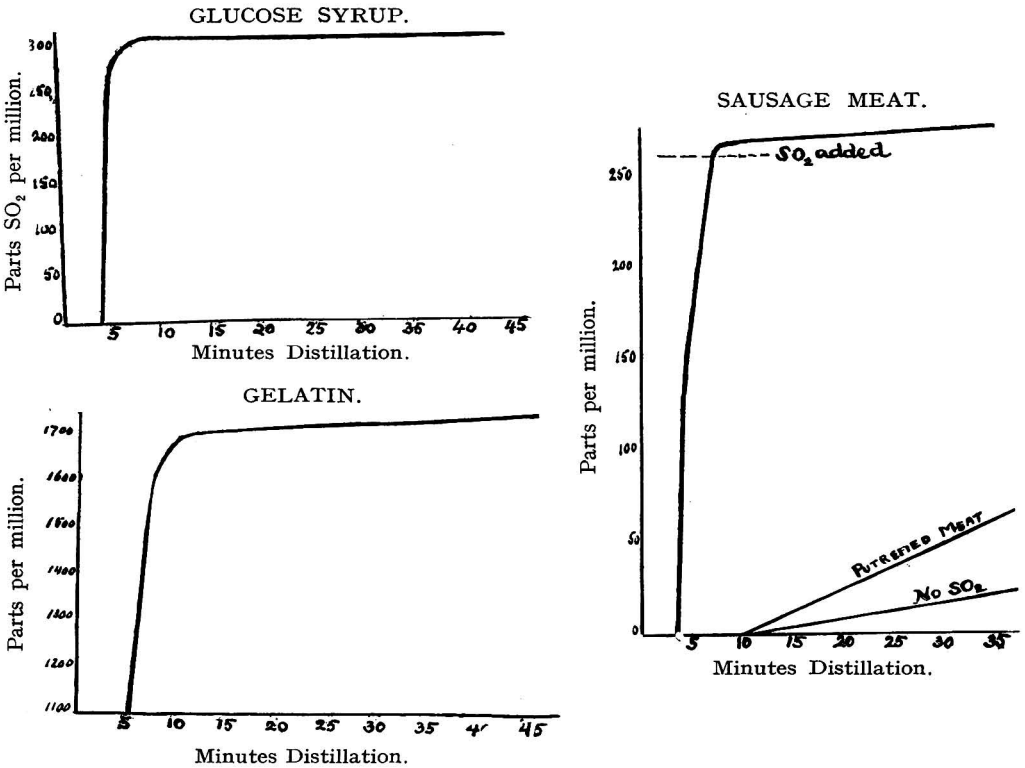
THE PRESIDENT expressed the thanks of the Society to the authors and to the Institute of Chemistry, where the meeting was held.

Notes on the Effect of other Reducing Substances on the Determination of Sulphur Dioxide.

By J. W. BLACK, B.Sc., A.I.C., and B. J. W. WARREN, F.I.C.

(*Read at the Meeting, January 11th*, 1928.)

During the discussions and investigations of the Committee appointed by the chemists of the Food Manufacturers' Federation, it became increasingly evident that the key to obtaining uniformity was speed of operation and distillation—

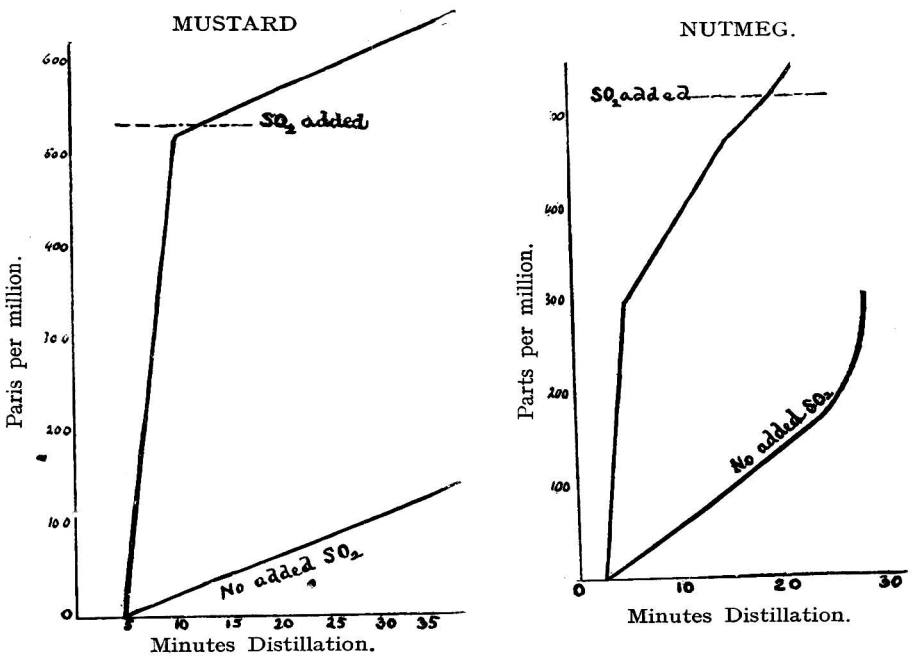


a point most strongly insisted on in the details of the process as now laid down. It therefore occurred to one of us that, as the great bulk of the sulphur dioxide comes over in a few minutes after distillation has started, this might form a means of differentiating between sulphur dioxide and other iodine-reducing substances in certain materials in which the presence of interfering substances may be very misleading. It is not pretended that the differentiation is absolute, but it will,

we think, be shown that it is sufficiently sharp, not only to give a very reasonable approximation to the actual amount of sulphur dioxide, but also to avoid certain errors of relatively considerable magnitude which might otherwise arise.

For this purpose we distilled a variety of substances both before and after the addition of sulphur dioxide; and by means of rapid titration during the evolution of the sulphur dioxide, particularly in the first few minutes after distillation had begun, we were able to plot the curves, a few of which are shown herewith.

The titration of the sulphur dioxide during the distillation presents slight mechanical difficulties, particularly in the earlier stages, but, apart from a possible lag, the curves are a correct representation of fact. It will be observed that all the curves have a certain similarity, in that they show a steep upward slope which at a certain point in the distillation period (approximately 10 minutes) takes



a bend in the horizontal direction, more or less pronounced according to the character of the material being tested.

In the case of glucose the curve is fairly sharp, and thereafter runs in what is practically a horizontal direction. Gelatin shows a somewhat similar curve. On the other hand, speaking generally, spices free from sulphur dioxide yield during distillation a quantity of iodine-reducing substance which is proportional to the time, and is indicated by the steepness of the curve beyond the point of change, in spite of the fact that a distinct change of direction is still clearly seen.

The following points should be noticed: (1) The change of direction usually occurs after about 8 to 10 minutes' distillation. In one or two cases this takes place earlier. (2) The change of direction in the graph occurs approximately when the added sulphur dioxide has been evolved. (3) The curve or angle made by the passage of the steep upward part of the graph into the more horizontal portion indicates the point at which nearly all the sulphur dioxide is disengaged, and where the curve is beginning to be affected in a greater or less degree by interfering substances. This is shown by the fact that there is a close similarity between the curves given by the pure substances and the curves described by them after the sulphur dioxide has been driven off.

In some cases, *e.g.* glucose and gelatin, the interference is negligible; in others, *e.g.* nutmeg, mustard, ginger, etc., it is considerable, and the results, in our opinion, show that it is incorrect to continue boiling for indefinite periods—as we believe is sometimes done—but that, as provided for in the method given, a time limit must be set. The time limit laid down by the Committee was fixed by determinations on pure salts and on simple substances; the results here appear to confirm these results very closely.

It may be stated, in passing, that where, as in the case of some dried fruits, it appears to be necessary to boil for a longer period than 10 minutes, and where interfering substances may simulate considerable quantities of sulphur dioxide, a comparison of the graph of the sulphited article with the graph of the same article unsulphited, would enable more correct conclusions as to the true amount of sulphur dioxide to be drawn. It may be of interest, in conclusion, to draw attention to the curves for sausage meat. Three curves are shown, one for fresh sausage containing about 260 parts of sulphur dioxide per million. In this graph it can be seen that the directional change takes place at a point corresponding to about $8\frac{1}{2}$ minutes' boiling. After 40 minutes there is not much change, only about 15 parts per million being evolved. If the meat is putrefactive, however, the interference is greater, and 75 to 100 parts per million may be added to the true amount if sour or decayed meat is distilled for a length of time substantially greater than 10 minutes.

Rapid Determination of Sulphites by Alkaline Liberation or Extraction, and Titration.

By H. R. JENSEN, M.Sc., F.I.C.

(*Read at the Meeting, January 11th*, 1928.)

Ripper's principle for determining traces of sulphites, especially in wines, where they are partly or wholly combined with aldehydes and sugars, has been fully discussed in the Ministry of Health's exhaustive report on sulphur dioxide determination (Monier-Williams).

Without distillation, a direct titration with iodine is used, after the formation, first, of fully hydrolysed sulphite by cold digestion for 15 minutes with potassium hydroxide or sodium hydroxide followed by strong acidification, whereby recombination to bisulphite sugar aldehydes (not acetaldehyde) is sufficiently delayed to permit titration.

Modifications of this test have been used by technical chemists for many years, and, for some purposes, have been found more satisfactory than the designation of a rough sorting test would imply. With the procedure quoted, the standard glucose (corn) syrup of commerce appears not to contain any other iodine-absorbing substance, and, in practice, to give results as accurate as those obtained by efficient distillation and a determination. The proportions so deduced as combined sulphite vary from 22 to over 90 per cent., ordinarily about 60 per cent. Thus 50 grms. of glucose syrup are dissolved in 50 c.c. of water at 50° C., cooled to 15° C., and 20 c.c. of 5 per cent. sodium hydroxide solution added. After fifteen minutes a mixture of 30 c.c. of 20 per cent. sulphuric acid with 100 c.c. water is added, and the liberated sulphur dioxide at once titrated with $N/20$ iodine, until a blue starch colour, permanent for at least one minute, is produced. It should be noted that addition of excess of iodine and back-titration gives slightly higher results. In the following table, results thus obtained are critically compared with those given by other methods.

Sulphites in Glucose Syrup
(Parts per million).

	Direct Volumetric Method.	Distilled (Phosphoric Acid)	
		Volumetric.	Gravimetric.
(1)	275	253	* 258, 259
	6 others, 273 to 284.		
(2)	291	—	† 264, 266.
	6 others, 288 (aver.)		
(3)	380	—	* 330
(4)	282, 283.	273	(Research Association method.)

* Indicates alkalisation before acid distillation,—absence of sulphur dioxide absorbing trap.

† Distillation effected after addition of the glucose solution last to the fully boiling acid water. The residue in the distillation flask still absorbed 0·5 c.c. of $N/20$ iodine, equivalent to 11 parts per million; if sulphur dioxide, a barium correction of 0·002 grm. would correct the result to 292 parts, in agreement with direct titration. Several of the above figures require increasing by 5 to 11 parts per million in respect of barium loss.

To glucose No. (1) metabisulphite was added in the proportion of 188 parts per million; on re-determination 15 minutes after alkalisation, only 437 parts were found (and less on distillation), indicating that 26 parts per million were masked by combination, or loss by volatilisation on neutralising.

A boiled sucrose and glucose tablet, to which metabisulphite solution had been added just before boiling, gave the relative figures:—Direct, 488 parts; distilled, gravimetric 473 parts (six others 473–532). The sulphite in plain confectionery fondant may be directly determined in a similar manner.

SUCROSE.—Pure sucrose is stated not to combine with sulphur dioxide and to be, moreover, a negative catalyst, retarding oxidation of the sugar by air. Commercial sugar may contain invert sugar and iodine-absorbing substances other than sulphite in sufficient amount to interfere with direct titration. Nevertheless the maximum figure by the alkalisation methods can often be employed as a sorting test.

SULPHITES IN SUGAR.

		Standard method with phosphoric acid (distilled).	
	Direct Volumetric method.	Volumetric.	Gravimetric.
Mauritius (1)	36·5 6 others 33 to 35.	35, 37* 6 others 33 to 37.	31 † 6 others av. 34·5
Mauritius (2)	77	—	71 *
Raw Sugar (3) ..	96	—	67
Golden Syrup (4) ..	192	—	30

* Sugar added to boiling acid, with glycerin.

† This gravimetric figure will probably be raised to 34 parts by the correction of 0·001 grm. of barium sulphate. It was observed here that the residual liquid in the distillation flask absorbed 0·2 c.c. of $N/20$ iodine liquid; if not sulphite, this will reduce the direct figure by 3 parts.

CORNFLOUR.—It is known that the sulphite present is mainly combined with starch and not quickly oxidised by iodine, and, indeed, is only slightly diminished by roasting. It may therefore be considered physiologically inert. The difficulty in determining the sulphite by alkaline extraction (as also by any volumetric test) is the presence of small amounts of other iodine-absorbing substances, volatile in steam, possibly fatty acids. A non-sulphited starch showed an absorption equal to 10 parts per million not extractable by petroleum spirit. With most samples of edible maize starch the following procedure gives a quick indication of the maximum sulphur dioxide content:—Add 100 grms. of starch powder to a cold mixture of 303·5 c.c. of water, with 40 c.c. of 5 per cent. sodium hydroxide solution. Leave, with occasional rotation, for 15 minutes, and filter off through pleated paper 200 c.c. (= 50 grms. of starch). To the filtrate add a mixture of 30 c.c. of 10 per cent. hydrochloric acid with 20 c.c. of water (even at 30 parts per million the odour of sulphur dioxide is then detectable). At once filter off and titrate 200 c.c. (=40 grms. of starch) with $N/20$ iodine. A total displacement value of 69·2 c.c. was found for 100 grms. lf starch, and an insoluble

volume of 12·7 c.c. by double dilution; this indicates a volume of 56·5 c.c. for the soluble starch under the action of sodium hydroxide. This provisional value corrected an apparent 79 parts to 92 parts in No. 1).

STARCH SULPHITE RESULTS.

	Direct extraction. Alkali-acid.		Distillation.
	Volumetric.	Gravimetric.	Gravimetric.
(1)	92	—	96, 98
(2)	99	†85 †86	81, 88

Values obtained by difference of total sulphates before and after iodine oxidation (396 – 311) and (390 – 304).

(3)	104	—	87
(4)	37	—	30·5
(5)	43	—	29
(6)	36	—	19
(7)	11	—	11
(8)	34	—	26 (H_2O_2 oxidation)
(9)	124	—	116
(10)	43	—	29
(11)	169	—	153, 155 (NaOH-HCl) (14 other tests, 158).
(12)	144	—	96.

Several of these gravimetric figures require correcting by at least 5 parts for barium sulphate loss.

Starch may be distilled after complete de-aeration, by alkalisation, and addition by funnel to already boiling acid.

Flours have been found on hydrochloric acid distillation (after alkalisation) to give 3, 10, 11, 20, 22 and 28 parts (gravimetric) and a Russian wheat mixture (with hydrogen peroxide oxidation) gave an apposent 11 parts per million SO_2.

Similar adaptations for limit tests are often possible for approximate content with jam and fruit pulps, and probably with dried fruits, with which a long alkaline digestion is needed after thorough mincing. Otherwise, long distillation with hydrochloric acid is required to break up certain resistant tissues and cellulose sulphites.

Barium Sulphate Losses in Gravimetric Determination.

By H. R. JENSEN, M.Sc., F.I.C.

(*Read at the Meeting, January 11th,* 1928.)

It seems fully established that the solubility of barium sulphate, in water, ranges from 0·0002 to 0·00025 grm. per 100 c.c. at 15°–20° C. (Kohlrausch, Fresenius, etc.).

The solubility in hydrochloric and other acids, however, is uncertain, Seidell recording 0·0067 grm. in 100 c.c. of 0·5 *N* hydrochloric acid, and 0·0089 grm. in 100 c.c. of *N* hydrochloric acid.

The optimum acid concentrations recorded for accurate gravimetric precipitation differ. These are:

0·016 *N* 250 c.c. per 0·5 grm. $BaSO_4$	(Cumming and Kay).
0·036 *N* 300 c.c. per 2·3 grms.	(J. M. Taylor, *J. Soc. Chem. Ind.*, 1923, **42**, 294 T.)
0·125 *N* 400 c.c.	(Scott).

Accordingly a series of tests was made with three independent standards to check the losses—or gains—both within and below this range of acidity. In addition, the possible effect of hydrogen iodide, usually formed in sulphite determinations was investigated. Too low an acid concentration appears to be favourable to a high adsorption of barium chloride; consequently, when acidities are of necessity kept at a minimum to avoid solubility loss, it is especially desirable to add this reagent through a very fine jet. Excess is necessary to reduce barium sulphate solubility and alkaline sulphate adsorption.

In view of the very small amount of sulphuric anhydride involved, tests 13 to 16 show that the limits of visual recognition and of solubility in acid are there approached. No. 13 showed visible precipitation in a minute or two, and No. 16 only became visible in an hour. These tests also showed that the technique of measurement was fairly good.

There is no indication of adsorbed barium chloride (5 c.c. of 10 per cent. used throughout) giving results too high, unless several of the solubility losses are diminished in that way. On the contrary, there is a slight invariable loss, averaging 0·0009 (0·0003–0·0022) grm. for 9 special determinations with free hydrochloric acid up to 0·02 *N* (350 c.c.). With acid concentrations higher than this, and volumes of 350 c.c. or over, significant losses (averaging 0·007 grm. (0·005–0·01) are frequent, but not invariable. The loss tends to be highest when precipitates are filtered off within 18 hours; solubility is the only apparent explanation of this loss, although other factors, such as retarded crystallisation, may possibly contribute to it.

GRAVIMETRIC BARIUM SULPHATE CONTROL LOSSES.

	Volume. c.c.	Acid Concen. Normality.	Vol. Acid used. c.c. *N*.	Time before Filtration.	Weight of Barium Sulphate. Equiv. Present. Grm.	Found. Grm.	Correction. Grm.
M 1	65 conc.	0·02	1	20 mins. conc.	0·182	0·182	0·000
M 2	75	0·02	1	2 hrs.	0·182	0·18	0·002
S 3	65 conc.	0·02	1	20 mins. conc.	0·18	0·1788	0·0012
S 4	250	0·004	1	18 hrs.	0·36	0·3597	0·0003
M 5	250	0·004	1	18 hrs.	0·364	0·3629	0·0011
S 6	350	0·003	1	2 hrs.	0·36	0·359	0·001
M 7	350	0·003	1	2 hrs.	0·364	0·363	0·001
S 8	350	0·02	6	4 hrs.	0·2977	0·2955	0·0022
			10 per cent. acid c.c.				
S 9	350	0·04	5	4 hrs.	0·36	0·3515	0·0085*
M10	350	0·04	5	18 hrs.	0·182	0·177	0·005
M11	350	0·04	5	2 hrs.	0·182	0·1762	0·0058
S 12	350	0·04	5	2 hrs.	0·18	0·1696	0·0104*
			c.c. *N*				
S 13	250	0·005	1·25	18 hrs.	0·004	0·0034	0·0006
S 14	250	0·008	2·0	18 hrs.	0·003	0·0026	0·0004
S 15	250	0·0147	3·7	18 hrs.	0·004	0·0039	0·0001
S 16	250	0·0147	3·7	18 hrs.	0·003	0·0025	0·0005
KMB 17, 18	250 conc.	0·037	1	18 hrs.	0·2088	0·2052 0·2067	0·0021 (Minimum)
KMB 19, 20	100	0·037	1	18 hrs.	0·2088	0·2059 0·2066	0·0036 (Maximum)

M. —Represents a standard pure magnesium sulphate solution.
S. — Represents a standard sulphuric acid solution, neutralised (NaOH).
K.M.B. — a standard metabisulphite solution.
Conc. refers to volume reduction by boiling.

Certain of the losses occasionally observed are much too large to be occasioned by adsorption of alkaline sulphates by barium sulphate first precipitated. From this cause, on the scale used, losses could not much exceed 0·001 grm.

For the determinations Nos. 17 to 20 portions of a standard potassium metabisulphite solution were used, to obtain an independent check on the solubility losses under such further acidities as are produced with a typical sulphur dioxide determination. It must be noted that with iodine oxidation there is an equivalent formation of hydrogen iodide; also, with distillates an equivalent of hydrochloric acid from barium chloride interaction. In these experiments 26·5 c.c. of 0·1 *N* acids were produced, in addition to the 10 c.c. normally added, and such acidity was actually found in the filtrates by titration, even after concentration. With high sulphite products, distilled into too low a volume, undesirable final acidities can occur in this way, apart from specific addition of acid. The losses registered here indicate a similar solvent action for the mixed acids as for hydrochloric

acid, and probably confirm the conclusion that the oxidation is wholly due to sulphuric acid, which Kühn and Rühle have denied (*Z. Unters. Nahr. Genussm*, 1910). These experiments showed that concentration of the volume by boiling was not an advantage, and could be a disadvantage, and there was no evidence, in general, that long boiling consistently aggregated colloid particles or prevented loss.

The metabisulphite used showed a purity of 98·6 per cent. by titration. In a gravimetric determination for sulphate originally present, 5 grms. were dissolved in a mixture of 150 c.c. of water (de-aerated) with 50 c.c. of *N* hydrochloric acid (a slight excess), at once precipitated in the cold with 5 c.c. of barium chloride, and filtered after one hour. Barium sulphate found was equivalent to 1·74 per cent. of potassium sulphate, and after eighteen hours there was further precipitation equivalent to 0·27 per cent. of potassium sulphate, which may indicate oxidation at the rate of 0·015 per cent. per hour. Hence, the theoretical total barium sulphate from 5.0 grms. is calculated as 0·2088 grm.

The conditions of precipitation normally used were those adopted for use by the Committee, *viz.*, the barium chloride (2·5 c.c. of 10 per cent. solution) was added, drop by drop, with stirring, to the sulphuric acid in a volume of 200–300 c.c. Then, after 5 minutes' boiling, a further similar addition of barium chloride solution was made, followed by one hour's simmering and filtration after 18 hours' standing.

This series of careful determination, carried out to check different stages of the work of the Committee, shows the desirability of systematic re-investigation of all the conditions for the determination of very small amounts of barium sulphate.

The Determination of Sulphur Dioxide in Sausages

AND

The Determination of Sulphur Dioxide in Foods by Distillation in a Vacuum.

By H. OSMAN JONES, F.I.C.

(*Read at the Meeting, January 11th*, 1928.)

I. Determination of Sulphur Dioxide in Sausages.—Sodium metabisulphite was added to a 35-lb. chopping of sausage meat in an amount equivalent to 450 parts of sulphur dioxide per million.

It should be noted that there is always an almost immediate loss of sulphur dioxide in a sausage when the sulphite is added to it; when 450 parts per million

are added, the loss is very approximately 150 parts, so that the amount of sulphur dioxide found is invariably lower than that added. Further, when working on a manufacturing scale it is a difficult matter to obtain an absolutely uniform mixture; some discrepancy in two or more determinations on the same sample is therefore to be expected.

The results given below were obtained by the method described by Dr. Campbell, with the use of wet steam, the results being compared with those obtained by the method outlined in Leach's *Food Inspection and Analysis*, except that the determinations were made volumetrically by means of standard iodine solution. The amount of sulphur dioxide added to the sausages was 50 parts per million.

(1) *Amount of sulphur dioxide found in sausages* 3 *hours after making.*

Committee's method (p. 120) ..	309 parts per million.
Leach's method	236·2 ,, ,, ,,

(2) *Amount of sulphur dioxide found in sausages* 24 *hours after making.*

Committee's method	208 parts per million.
Leach's method	192 ,, ,, ,,

(3) *Amount of sulphur dioxide found in sausages* 48 *hours after making.*

Committee's method	214·4 parts per million.
Leach's method	192·0 ,, ,, ,,

It will be seen that in every case the Committee's method gives a higher figure.

The rate of liberation of sulphur dioxide is slower with sausages than with many other substances; at least 20 minutes are required to distil all this gas after the contents of the flask begin to boil.

Further examples comparing the Committee's method with others will be given under the description of the Vacuum Process.

II. Determination of Sulphur Dioxide by Distillation in a Vacuum.—Among various methods tried by the Committee, one (for which I was responsible) was an attempt to determine the sulphur dioxide in foods by vacuum distillation. The following is a description of the method and apparatus employed:

Apparatus.—This comprises a distilling flask of at least 500 c.c. capacity; a receiving flask, consisting of a distilling flask of 250 c.c. capacity; and an ordinary 15-inch Liebig's condenser.

The end of the delivery tube of the condenser is connected with a bent tube so as to dip under the surface of the liquid in the receiving flask.

Carbon dioxide is introduced into the distilling flask by means of a tube drawn out to a capillary, and dipping underneath the liquid in the distilling flask. A small glass T-piece, fitted with a screw clip, is connected with the distilling flask and the top end of the condenser tube. This serves as a vacuum release.

An iodine trap is connected with the side tube of the receiving flask; a calcium chloride tube containing crystals of potassium iodide serves the purpose. A vacuum gauge is placed in the circuit between the trap and the pump.

Method.—Twenty c.c. of *N*/20 iodine solution are diluted to about 80 c.c. and introduced into the receiving flask, the delivery tube from the condenser being so arranged that it will dip beneath the surface of the iodine solution. An appropriate quantity of the substance to be examined (usually 50 grms.) is placed in the distilling flask, together with about 250 c.c. of freshly boiled and cooled distilled water and 20 c.c. of a 10 per cent. solution of phosphoric acid. The apparatus is connected together and carbon dioxide passed through it for ten minutes, after which time the supply is reduced and the vacuum formed. In order to prevent bumping and foaming, it is desirable to maintain as rapid a stream of carbon dioxide as possible, consistent with a 20-inch vacuum. As soon as the evacuation is started a bath of hot water is introduced under the distilling flask.

About 100 c.c. are distilled, and the vacuum reduced by means of the screw clip on the release. Care is necessary here to prevent sucking back of the distillate into the apparatus. When the pressure is normal the source of heat is removed, the condenser washed through with a little water, and the liquid in the receiving flask (to which has been added the potassium iodide in the trap) titrated with *N*/20 sodium thiosulphate in the usual manner.

The following are some results obtained by six members of the Committee. The figures are given as a percentage of the amount of sulphur found in a sample of metabisulphite by direct titration. (Amount found by direct titration equals 100 per cent.).

	Gravimetric, Per Cent.	Volumetric, Per Cent.		Gravimetric, Per Cent.	Volumetric, Per Cent.
A. ..	99·5	96·2	D. ..	97·8	96·1
B. ..	100·7	99·5	E. ..	101·2	97·7
C. ..	94·7	94·6	F. ..	99·7	99·7

It should be noted that no iodine trap was used when the above results were obtained.

COMMENTS OF MEMBERS OF THE COMMITTEE.—The following comments on the method were made by members of the Committee:—

(1) It is probable that with the apparatus described there is an unavoidable loss, owing to the high speed of distillation, with incomplete absorption. Even with modification it is unlikely to give reliable figures higher than those obtained with the best distillation method at ordinary pressures.

(2) All the sulphur dioxide can be removed by vacuum distillation. The gravimetric method, as already carried out, is recommended, except that a trap is necessary to guard against loss due to rapid bubbling of the gas through the iodine solution in the receiver. The size of the bubbles can be reduced by standing the receiver in cold water in order to increase the condensation

of the water vapour. It is doubtful if any advantage is gained by sweeping out with carbon dioxide before applying the vacuum, which has the effect of removing the air and enabling the distillation to be done at a low temperature. During the distillation the use of carbon dioxide is desirable.

Volumetric determination.—This may be possible if a second trap is introduced to catch the iodine carried away by gas at the low temperature.

(3) The vacuum distillation process seems to give slightly higher figures than any other method (gravimetric)—actually only about 1·6 per cent. higher than our ordinary method. The process is rather more complicated and has more pitfalls. I should hesitate to recommend it.

(4) The vacuum method, although good, is too slow for ordinary work.

COMPARATIVE RESULTS.—During the time that has elapsed since the method was tried by the Committee, I have had the opportunity of applying it to routine samples of sausages, and I have found that, with practice, the process is not so difficult of manipulation as was thought, and that it gives good results.

The following figures show the results of determinations on samples by various methods, all determinations being made volumetrically.

	Sulphur dioxide, Per Cent.
Sodium Metabisulphite	
Vacuum method ..	62·08
Committee's method..	61·90
Monier-Williams's method	60·50
Direct Titration ..	63·04
Gelatin	Parts per million.
Vacuum method ..	1011
Committee's method	1011

	Sulphur dioxide, Parts per million.
Sausages.	
Leach's method ..	179·2
Committee's method	192·0
Vacuum method ..	187·5
Sausages	
Leach's method ..	153·6
Committee's method	179·2
Vacuum method ..	179·2
Monier-Williams's method	172·8

A modification of this method would be to substitute hydrogen peroxide for standard iodine, and then determine the amount of sulphur dioxide either gravimetrically or volumetrically.

Note on the Oxidation of Sulphites by Air.

By H. M. MASON, M.Sc., F.I.C., and G. WALSH.

(*Read at the Meeting, January* 11, 1928.)

An important feature of the method of determining sulphites adopted by the chemists of the Food Manufacturers' Federation is the rapid distillation, which is intended to minimise the loss of sulphur dioxide by oxidation in the distilling flask.

It is known that sulphites are easily oxidised by air at the room temperature, and that neutral and alkaline solutions are changed more rapidly than acid solutions, but, during the determination of sulphites by distillation, the acid solution is in contact with air at temperatures up to 100° C., and so it seemed desirable to find how the velocity of the oxidation is influenced by temperature.

For this purpose, flasks, half filled with dilute solutions of potassium metabisulphite and sodium sulphite, respectively, were placed in a thermostat at 20° C., and the sulphite contents were determined by titration with standard iodine solution after fixed intervals of time.

The experiments were repeated with sodium sulphite solutions kept at 60° C. and 90° C., but, as the meta-bisulphite solution is not sufficiently stable, it could not be tested at these temperatures.

The freshly-prepared solutions contained 0·1 per cent. of the anhydrous salts. The percentages of unchanged sulphites after the stated intervals are shewn in the following tables:—

Table I.

Oxidation of 0·1 per cent, sulphite solution by air at 20° C.

Time	Unchanged sulphite. Potassium metabisulphite. Per cent.	Unchanged sulphite. Sodium sulphite. Per cent.
0 hours	100·0	100·0
12 ,, ...	96·5	79·5
24 ,, ...	95·4	64·1
36 ,, ...	94·2	49·4
48 ,, ...	93·1	37·6

Table II.

Oxidation of 0·1 per cent. sodium sulphite solutions by air.

At 60° C. Hours. Time.	Per cent. Unchanged sulphite.	At 90° C. Hours. Time.	Per cent. Unchanged sulphite.
0	100·0	0	100·0
1	77·8	0·5	63·6
2	49·4	1·0	40·1
4	8·6	1·5	19·8
6	0·0	2·0	1·9

These results shew that neutral sulphite solutions are rapidly oxidised by air at temperatures approaching 100° C., and it is probable that acid solutions behave in a similar manner; but as the latter are oxidised comparatively slowly at the room temperature, the oxidation at higher temperatures may not be sufficiently rapid to cause serious errors in the distillation process, if this is completed in the shortest possible time.

In order to estimate the magnitude of the oxidation losses under extreme conditions, distillations were made in which the time taken to start boiling was varied to a greater extent than is usual in ordinary distillations.

The distilling flask contained 200 c.c. of water which had been boiled and cooled, and 20 c.c. of 10 per cent. phosphoric acid and 50 c.c. of 0·1 per cent. potassium meta-bisulphite were added after the apparatus had been swept clear of air with carbon dioxide. In another set of experiments carbon dioxide was not used. The end of the condenser dipped into dilute iodine solution. When the distillation began it was continued as rapidly as possible, and traps were used to make sure that neither sulphur dioxide nor iodine was lost.

The results are compared with that of a distillation in which the sulphite solution was added gradually to the boiling phosphoric acid solution, under which conditions the time up to the beginning of boiling was negligible.

TABLE III.

Time before boiling.	Sulphur dioxide recovered.	
	CO_2 passed. Per Cent.	No CO_2. Per Cent.
Instantaneous	—	98·8
5 minutes	91·2	91·5
50 ,, ...	82·3	67·7
135 ,, (80° C) ..	77·7	—

The percentages were calculated from the ratio of the volumes of standard iodine required by the distillate and by direct titration. These results suggest that the distillation process is fairly accurate when the sulphite solution is added to boiling acid solution, that oxidation of some of the sulphur dioxide occurs in the distilling flask during the time taken to start boiling, and that the loss increases with this time.

Although the distilled water used for preparing the sulphite solution, and for diluting, had been boiled free from air, it is probable that air was redissolved on cooling, and that this air caused oxidation when the temperature was raised.

Carbon dioxide partly prevented oxidation when the heating period was prolonged, but its effect was insignificant when the time was short. That it did not prevent oxidation altogether may be explained by the assumptions that it is seldom free from air, and that air is also present in the distilled water. The gas used in our experiments was supplied from an iron cylinder, and it was not completely absorbed when passed slowly through potash bulbs.

Our results suggest that carbon dioxide must be quite free from oxygen if it is used in a sulphite distillation which lasts for more than a few minutes. When sulphur dioxide in a foodstuff is determined by distillation it is difficult to remove all the oxygen from the distilling flask before the temperature is raised, as many foodstuffs contain absorbed air, and therefore oxidation losses are sure to occur in most determinations.

Removal of the air by the use of a vacuum before heating begins, appears to us to be the most reliable method of preventing oxidation losses, but extremely rapid heating and distillation give good results which are well within the possibilities of errors resulting from the age and uneven consistence of the sample.

In conclusion, it is necessary to mention that these experiments were made before the standard process was fully developed, and that the speed of distillation was distinctly slower than is required for that method.

Note on the Titration of Dilute Sulphite Solutions with Standard Iodine Solutions.

By H. M. MASON, M.Sc., F.I.C., and G. Walsh.

It has long been known that when iodine solution is run into sulphite solutions, the volume of iodine solution required to oxidise a given volume of sulphite solution is less than when the sulphite solution is run into the iodine solution.

The explanations which have been put forward are summarised in Monier-Williams's *Report on the Determination of Sulphur Dioxide in Foods* (Analyst, 1927, **52**, 343.)

It is generally agreed that the low result obtained when iodine is run into sulphite is only noticed when the sulphite solution contains more than 0·04 per cent. of sulphur dioxide, but we find that the error occurs with solutions containing only 0·008 per cent. of sulphur dioxide, unless precautions are taken to avoid it.

The accuracy of the determination of sulphites by titration with iodine is important when this test is used to determine the proportion of sulphur dioxide recovered by distillation, as a low result by the direct titration gives a high result for the proportion recovered. Thus, if the direct titration figure is 20·0 c.c. of $N/20$ iodine, whereas the true result should be 20·1 c.c., the apparent efficiency of the distillation is approximately 0·5 per cent. higher than the actual efficiency. For smaller quantities of sulphites, the error is greater.

During a distillation the iodine is always in excess, and the possibility of error in the direct titration can be avoided by adding the sulphite to iodine, but, as it

is more convenient to add iodine to sulphite and as this is the general practice, it is important that the limitations of the method should be fully realised.

Our attention was drawn to this subject in the course of attempts to explain why one worker always got lower results than other workers in the titration of a solution of confectioner's glucose with iodine. Although the solutions used were identical and every detail of manipulation was copied, the difference persisted, and the only explanation which we could offer was that the worker who got low results was left-handed.

Reference to the literature showed that abnormal results had been obtained by other workers, but, as the explanations suggested by different observers were contradictory, we decided to carry out a number of iodine and sulphite titrations in which the working conditions were made as dissimilar as possible, in order to find out how far manipulation was responsible for the abnormal results.

The burettes used were of certified accuracy, and each solution was measured from the same vessel for all the tests. Exactly 10 c.c. of $N/20$ iodine were run into 200 c.c. of water, and the solution was titrated with a 0·1 per cent. solution of potassium meta-bisulphite. This quantity of the sulphite solution was run into 200 c.c. of water, and the solution was titrated with $N/20$ iodine.

The conditions of the latter titration were varied in regard to the speed of addition of iodine solution, the shape of the vessel and the amount of agitation during titration; the distilled water used for dilution was also varied in quantity and in its liability to contain dissolved oxygen, but these conditions did not influence the results.

The results of these experiments are summarised in Table I.

TABLE I.

Expt.	Vessel.	Conditions.	Volumes of Solns. N/20 Iodine. c.c.	Volumes of Solns. 0·1 per cent. $K_2S_2O_5$. c.c.
1.	Beaker flask.	Sulphite added to iodine. ..	10·00	28·42
2.	,, ,,	Iodine added to sulphite ..	9·70	28·42
3.	,, ,,	Ditto, drop by drop, in 5 minutes	9·40	28·42
4.	,, ,,	Ditto, 9·3 c.c. added rapidly, and the titration finished ..	9·95	28·42
5.	Porcelain dish.	Ditto, drop by drop, with vigorous stirring	8·4	28·42
6.	Beaker flask.	Sulphite added to iodine ..	10·00	28·51

The difference between the first and last titrations is due to oxidation of sulphite on standing during the time required for the other experiments, but it is too small to affect the significance of the other results.

The low results of the iodine titrations may be due to several causes, such as oxidation, volatility of sulphur dioxide, and the reduction of sulphur dioxide by the hydriodic acid which is formed during the titration.

Time, agitation and local concentration of iodine all appear to influence the magnitude of the loss of sulphur dioxide, so that it is necessary to study the effects of these factors more definitely.

The effects of volatilisation reduction and oxidation by air, were investigated by repeating the titration which shewed the greatest loss of sulphur dioxide and determining the sulphur trioxide gravimetrically at the end of the titration. Table II shows the titrations and the volume of $N/20$ iodine solution equivalent to the weight of barium sulphate obtained.

TABLE II.

Ex.	Conditions.	Titration. c.c.	From $BaSO_4$ c.c.	Wt. of $BaSO_4$. Grm.	Loss, titration. c.c.	Loss, gravimetric. c.c.	Ratio of losses. g/t.
1.	Sulphite added to iodine.	10·00	10·23	0·0597	—	—	—
2.	Iodine added, drop by drop, to sulphate stirred in dish for 5 minutes.	9·25	9·70	0·0566	0·75	0·53	0·705
3.	Ditto, stirred in dish for 12 minutes.	8·55	9·22	0·0538	1·45	1·01	0·696
4.	Air passed through sulphite soln. for 45 mins. Soln. added to excess of iodine and back titrated.	9·32	9·76	0·0570	0·68	0·47	0·690

In all these experiments the volume of diluting water was 200 c.c. and the volume of potassium metabisulphite solution was 28·52 c.c., which was the volume required in the first experiment. After the last experiment it was found that 28·63 c.c. were necessary in a repetition of the first experiment, but this slight loss of sulphur dioxide is insignificant in comparison with the other losses shown in the table.

In experiment No. 1, the iodine equivalent of the barium sulphate is a little greater than the volume used in the titration, but this is either due to occlusion of salts in the barium sulphate or to slight oxidation of the metabisulphite during the preparation of the solution. The weights of barium sulphate obtained in these experiments were of necessity small; and although every precaution was taken to obtain accurate results, as 0·001 grm. of barium sulphate corresponds to 0·17 c.c. of $N/20$ iodine, absolute agreement can hardly be expected.

The second experiment shows a loss of 0·75 c.c. of $N/20$ iodine in the titration result, and a loss of 0·53 c.c. in the gravimetric result. The former represents the total loss of sulphur dioxide, the latter the sulphur dioxide not lost by oxidation by air, and the difference is the effect of oxidation by air during the titration. Thus 30 per cent. of the total loss is due to oxidation, and 70 per cent. is due to volatilisation of sulphur dioxide and other possible causes. The third experiment also shows a 30 per cent. loss by oxidation, and the fourth experiment gives the

same result. The total loss in these experiments varies with the time and method of agitation of the solution, but in all cases the ratio of loss by oxidation to total loss is constant.

In order to determine the cause of the loss not due to oxidation, it is necessary to agitate the diluted sulphite solution and then complete the titration by adding it to excess of iodine, for under these conditions the possibility of loss by reduction of sulphur dioxide by hydriodic acid is eliminated.

Experiment No. 4, in which the ratio of oxidation loss to total loss remains unaltered, was made in this way, and the result suggests that oxidation and volatilisation are the sole causes of loss.

Further evidence in support of the theory that reduction by hydriodic acid does not contribute to the total loss was obtained by shaking diluted solutions of potassium metabisulphite in a beaker flask for five minutes, pouring them into a measured quantity of iodine solution, and completing the titration with a few drops of iodine. In one experiment the sulphite solution was acidified with 10 c.c. of $N/20$ hydriodic acid, in another with 10 c.c. of $N/20$ sulphuric acid, and in a third no acid was added. Table IV summarises the results.

TABLE IV.

Volume of $N/20$ iodine required by 28·5 c.c. 0·1 per cent. $K_2S_2O_5$.

Expt.	Conditions.	Iodine, c.c.
1.	No added acid. without agitation..	10·0
2.	No added acid, shaken for 5 minutes	9·95
3.	10 c.c. $N/20$ HI, shaken for 5 minutes	9·55, 9.45
4.	10 c.c. $N/20$ H_2SO_4, shaken for 5 minutes	9·65, 9·55

These results indicate that hydriodic acid, set free during an ordinary titration of iodine into sulphite does not reduce sulphur dioxide, but, by increasing the acidity of the solution facilitates the loss of sulphur dioxide by volatilisation.

The low results obtained when sulphite solutions are titrated with iodine are therefore caused by oxidation and by the escaping of sulphur dioxide set free by the hydriodic acid formed during the titration, the latter being responsible for 70 per cent. of the loss.

When the reliability of titrations of iodine into sulphite was first considered by the Committee of the Food Manufacturers, Chemists it was thought that the errors associated with this method of titration were too small to influence our results, as we were working with very dilute solutions. One member was unable to obtain any difference between the two methods of titrating.

Other workers were, therefore, asked to repeat experiments Nos. 1 to 4 in Table I, and two independent observers confirmed the fact that titrations of iodine into sulphite give low results.

There is not a constant difference, and this is explained by slight differences in apparatus and manipulation. That such conditions affect the amount of loss of sulphur dioxide was confirmed by the following experiments:—

TABLE III.

Ex.	Vessel.	Conditions.	Dilution.	Volumes. $N/20$ Iodine.	Volumes. 0·1 per cent. $K_2S_2O_5$
			c.c.	c.c.	c.c.
1.	300 c.c. Florence flask.	Sulphite into iodine.	200	10·00	28·33
2.	Ditto.	Iodine into sulphite, drop by drop, during 5 minutes.	200	9·64	28·33
3.	500 c.c. Ditto.	Ditto.	200	9·87	28·33

The volume of air in the larger flask evidently restricted the escape of sulphur dioxide by diffusion or exchange with air outside the vessel.

In the experiments which have been described, the conditions were exaggerated in order to find the causes of the errors which occur when iodine is run into sulphite solutions, and the losses are very much greater than those obtained in ordinary working conditions.

Three chemists, working in different laboratories, were asked to compare the effect of the two ways of doing the titration in the ordinary method of working, and their results are given in Table V.

TABLE V.

Quantity of iodine required by a given volume of sulphite.

Experiments.	Iodine added to Sulphite.	Sulphite added to Iodine.
	c.c.	c.c.
a.	9·85	10·0
b.	10·0	10·0
c.	9·9	10·0
d.	9·75	10·0

For these determinations no details were given regarding the size of the vessels and the times taken, but the solutions were all similar in concentration.

It is quite evident that, even when the dilute sulphite solution with which one has to work in testing foodstuffs is titrated with iodine solution, agitation of the solution may cause loss of sulphur dioxide, unless precautions are taken to avoid it.

When great accuracy is important, as, for example, when a direct titration is used as the standard for estimating the efficiency of a distillation process, it is advisable to titrate the iodine solution with sulphite solution, but when extreme accuracy can be sacrificed for convenience, satisfactory results can be obtained by running the bulk of the iodine solution into the standing sulphite solution, and after gently mixing the two solutions, completing the titration by adding the few drops of iodine solution required to reach the end-point.

Finally, we are of the opinion that, in iodine into sulphite titrations, loss of sulphite may occur, even in very dilute solutions, that the loss is due partly to oxidation, but mainly to volatilisation, and that it is not due to reduction of sulphur dioxide by the hydriodic acid formed during the titration.

These investigations were made in the laboratory of Messrs. John Mackintosh & Sons, Ltd., of Halifax, and we have to acknowledge our indebtedness to the Directors for permission to publish the results.

The Determination of Sulphur Dioxide in Fatty Substances.

By A. W. KNAPP, M.Sc., F.I.C., and R. J. PHILLIPS, F.I.C.

(*Read at the Meeting, January* 11, 1928.)

In the course of sulphur dioxide determinations on fat-containing caramels it was thought that volatile bodies from the fats present might have an influence on the results obtained in the Committee's Rapid Volumetric Distillation process.

Blank tests on cacao butter and cow's butter, both moderately fresh, were made, in which 25 grms. of each fat were subjected to the standard distillation process. The results showed an iodine absorption equivalent to 10 and 6 parts of sulphur dioxide per million in the cow's butter and cacao butter, respectively, by the volumetric method; no trace of barium sulphate was found by the gravimetric method.

A further experiment was made to determine what the effect of a very rancid fat would be on the sulphur dioxide figure. Three 25 grm. samples of very rancid cow's butter were distilled, and gave iodine absorption figures equivalent to 29 parts of sulphur dioxide per million by the volumetric process; by the gravimetric process, however, they showed no trace. When tested similarly, a sample of full-cream milk powder, eight months old, showed an iodine absorption equivalent to 19 parts of sulphur dioxide per million.

As a result of these few tests, it would appear that in all cases where rancid fats might be present in samples under examination for sulphur dioxide, although the volumetric process would still be sufficiently accurate for rough sorting tests, the gravimetric process alone should be relied upon for accurate results.

Research Laboratory, Bournville.
25*th November*, 1927.

Note on the Stability of Solutions of Potassium Metabisulphite.

By R. J. PHILLIPS, F.I.C.

It is quite well known that solutions of metabisulphites rapidly undergo decomposition, and that sulphur dioxide is oxidised or volatilised, or both. The following test was carried out to determine approximately the rate at which sulphur dioxide is lost when carrying out a series of determinations of sulphur dioxide on a dilute metabisulphite solution.

A 0·1 per cent. solution of potassium metabisulphite was made up in a stoppered litre flask. Fifty c.c. were pipetted from it after each 24 hours, and a direct titration carried out with $N/20$ iodine solution. The flask and contents were maintained at 60° F., as nearly as possible. The sulphur dioxide content was as follows:—

Hours	0	24	72	96	120	144
Sulphur dioxide content, per cent.	100·0	98·2	94·6	93·5	92·2	91·3

Of course, each 50 c.c. removed by pipetting meant the introduction of 50 c.c. of air into the flask, volatilisation and oxidation, therefore, occurring under ideal conditions.

Research Laboratory, Bournville.

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.

REFRACTION OF MILKS WITH LESS THAN 8·5 PER CENT. OF SOLIDS-NOT-FAT.

When a paper was read by us on the use of the Immersion Refractometer in milk analysis (Analyst, 1927 **52**, 193) considerable interest was shown in Table XXI, which gave the refractions of those milks having solids-not-fat below 8·5 per cent., and also the refractions of the corresponding "appeal-to-cow" samples. It was shown that in every case a low solids-not-fat was accompanied by a low refraction, and that the corresponding "appeal-to-cow" samples had in every case a higher refraction.

We have continued to apply the refractometric method to all those milks, having a percentage of solids-not-fat less than 8·5, which have been received during the year that has elapsed since the reading of the above paper, and we have not met with any case that has caused us to revise in any degree the opinions therein expressed, *viz.* "That the determination of the refraction of the serum offers no advantage over that of the solids-not-fat of the milk; in fact, that it may be even less valuable."

We have not yet met a sample of milk having solids-not-fat of less than 8·5 which has given a high refraction, although we have found an occasional sample of perfectly genuine milk which has combined a low refraction with a normal figure for solids-not-fat.

The following table is an extension of the Table XXI mentioned above. It contains all those milks (taken from a total of about 2400 samples) which we have examined during the last twelve months, which have contained less than 8·5 per cent. of solids-not-fat and where corresponding "appeal-to-cow" samples have been available. A few samples having less than 8·5 per cent. solids-not-fat are not included in the above table, because no corresponding "appeal-to-cow" samples were received. In every case, however, the refraction figure was less than 37·0.

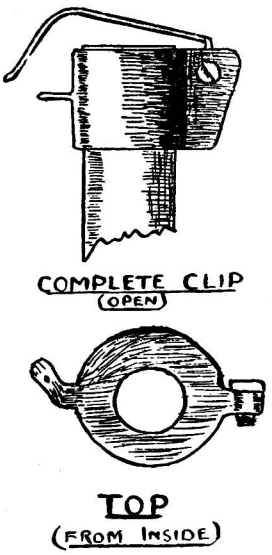
	Refraction.	Acidity.	Total Solids.	Solids-not-fat.	Fat.	"Appeal to Cow" samples: Refraction.	"Appeal to Cow" samples: Solids-not-fat.
Irlam 160	35·2	2·2	12·0	7·8	4·2	37·6	8·7
,, 161	36·7	2·1	11·5	8·5	3·0	38·2	9·1
R.D. 759	33·9	1·4	10·1	7·1	3·0	38·0	8·8
R.D. 779	36·0	1·8	10·8	8·0	2·8	38·3	9·0
S.D. 806	36·7	2·4	11·2	7·9	3·3	38·0	8·7
Lytham, St. Annes 442	34·4	1·6	10·5	7·3	3·2	38·0	8·9
L.D. 871	36·3	2·2	11·9	8·1	3·8	38·3	8·8
,, 872	35·3	2·3	10·5	7·4	3·1	38·3	9·0
O.D. 760	36·6	2·0	11·9	8·0	3·9	37·9	8·7
,, 761	36·6	2·4	11·4	8·0	3·4		
G.D. 1096	31·4	1·4	13·1	5·9	7·2	36·0	8·6
P.D. 417	35·7	2·0	13·7	7·5	6·2	38·0	8·7
Ws. D.731	36·5	2·0	11·2	8·0	3·2	38·5	9·0
,, 732	37·0	1·9	11·7	8·5	3·2		
Km.D.877	36·6	2·2	11·3	8·0	3·3	37·7	8·6

These figures support our contention that the mixed milk of a herd seldom gives a refraction of less than 37·0 with copper sulphate serum at 20° C., and that the refractometric method offers no diagnostic advantage over the determination of the solids-not-fat.

G. D. ELSDON.
J. R. STUBBS.

LANCASHIRE COUNTY COUNCIL LABORATORY.
LIVERPOOL.
January 31, 1928.

THE PRODUCTION OF UNIFORM STAINS IN THE GUTZEIT TEST FOR ARSENIC.



In a recent issue (ANALYST, 1927, **52**, 699–701) three different devices for the production of uniform stains are described. For some time another simple appliance, which I devised, has been used in my laboratory, with very satisfactory results.

It consists of a metal band encircling the top of the glass exit tube and fixed by means of a small screw nail, which serves the dual purpose of tightening the band and also acting as a hinge for the top. The latter is a flat disc with a circular hole in the centre exactly the same size as the bore of the exit tube, and having projections at two opposite sides which, as shown in the diagram, are fashioned into a hinge and spring fastener. There is a tiny hole in the spring to hold the catch pin.

Small strips of mercuric chloride paper are slipped under the top or lid and clipped down. The stains are uniform and sharp to the edge. The device is entirely composed of brass, is easily made, and may be adapted for use in other processes where uniform stains are required.

A. SCOTT DODD.

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Notes from the Reports of Public Analysts.

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

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE FOURTH QUARTER, 1927.

OF the 1331 samples examined during the quarter, 1166 were submitted under the Food and Drugs Acts. Of these, 1094 were informal samples (22 adulterated) and 72 were bought under the provisions of the Acts (7 adulterated).

SULPHUR DIOXIDE IN GROUND GINGER.—Eleven of 16 informal samples of ground ginger were free from sulphur dioxide. The amounts in the remainder were, 1500, 3000, 1900, 1900, and 800 parts per million. In the first case a caution was sent to the wholesaler who had sent it to the retailer about a week before the purchase of the sample. The other four samples came from shops where the supplies had been bought two or three years previously. A letter was sent to the local Grocers' Association asking that the attention of their members should

be called to this form of adulteration and that steps should be taken to prevent it in future.

WHITE PEPPER.—Eighteen informal samples examined last quarter were genuine, the mineral matter varying from 0·64 per cent. to 1·76 per cent. Three connected samples were adulterated. These were all sold in penny packets, containing about one-fifth of an ounce, labelled, "Genuine White Pepper." An informal sample contained 4·9 per cent. of mineral matter; a subsequent formal sample from the same shop had 5·1 per cent. and a formal sample taken at the request of the shopkeeper, in course of delivery, from the wholesale dealer, had 4·9 per cent.

The wholesale dealer was cautioned and undertook to withdraw the article from sale. He in turn had received a warranty from the packers, with the goods, stating that the article was "Genuine White Pepper." The firm who packed the article undertook to withdraw it from sale. They had received it with a guarantee from a wholesale house that it was "Genuine Pepper," and assumed it was genuine *white* pepper, overlooking the fact that a mixture of black and white pepper may be sold as "Pepper" but not as "White Pepper."

BLACK PEPPER.—Three samples of black pepper corns contained from 4·3 per cent. to 4·5 per cent. of mineral matter and 0·1 per cent. of sandy matter and were passed as genuine.

Eight of the 11 informal samples of ground black pepper contained from 4·4 per cent. to 6·6 per cent. of mineral matter and were passed as genuine, although the latter quantity is rather high. Three informal samples, contained from 7·0 to 7.4 per cent. of mineral matter and were condemned. The sandy matter varied from 1·6 to 2·9 per cent. One of them had 1·1 per cent. of chalk and another an unusual amount of iron oxide. The vendors of these three samples were cautioned.

PUDDING SPICE.—There is no standard for this article, and any sample made from a mixture of suitable spices must be passed as genuine. Spices of a fair quality do not contain much mineral matter or sand. In some spices, such as nutmeg, mace, allspice and cloves, the sandy matter may be about 0·1 per cent. The mineral matter, in the 14 informal samples examined, varied from 5.2 per cent. to 7·7 per cent. and the sandy matter in them from 0·72 per cent. to 2·5 per cent.

The two worst samples were certified as containing 2·3 per cent. and 2·5 per cent. of sand, respectively. These two samples were obtained from two branches of a Company's shop, and the vendor was cautioned. He had a warranty from his wholesale dealer, and the latter, in turn, had one from the spice grinders.

SYRUP OF TOLU.—Syrup of tolu is prepared by heating balsam of tolu with water to remove the odorous constituents, adding sugar to the liquid and dissolving by the aid of heat.

The 1864 British Pharmacopœia required that three pounds of the syrup should contain two pounds of sugar (66.7 per cent.) and no alteration was made in subsequent Pharmacopœias until 1914. That edition orders less heat to be used for treating the balsam of tolu, and the resulting liquid to be diluted to 400 ml. It is directed that 660 grms. of sugar are to be dissolved in the liquid by the aid of heat, and finally distilled water to be added to produce 1000 grms. The total weight before the solution of the sugar is thus 1060 grms. The official directions, therefore, expect that the heat used will evaporate more than 60 grms. of water, and that by making it up to 1000 grms. the syrup will contain 66 per cent. of sugar. In practice, less than 60 grms. of water are evaporated, and therefore, the weight to be diluted to 1000 grms. *is more than* 1000 *grms.* If the

B.P. had required less water to be used at first, or directed the necessary evaporation to reduce the volume, there would have been no difficulty.

The strength of the syrup will depend on the amount of evaporation that takes place during the solution of the sugar. If there were no evaporation at all, the syrup would contain 62 per cent. of sugar, a small proportion of which might be changed during heating.

I am indebted to several wholesale drug houses for information as to the preparation of the syrup. In each of the Pharmacopœias the name of the preparation is "Syrupus Tolutanus," and the earlier pharmacopœias gave the corresponding English equivalent as "Syrup of Tolu," whilst those of 1898 and 1914 translate the same Latin heading as "Syrup of Balsam of Tolu." The nomenclature is further complicated by the fact that there is a recent preparation "Syrupus Tolutanus, B.P.C." which is prepared by mixing 1 part of "Solution of Tolu" with 7 parts of simple syrup containing 66·7 per cent. sugar. This syrup is described as being more aromatic than the B.P. preparation.

The editors of the B.P.C. appear to have acted unwisely in using "Syrup of Tolu" to describe a different article from that so long known by that name. Of these two preparations, the B.P. syrup of tolu is 50 years older than the B.P.C. preparation and is undoubtedly the article which has been in popular use. I do not think the later term "Syrup of Balsam of Tolu" has been used at all by the public, and it is not likely that there is any knowledge of the B.P.C. preparation. Neither the B.P.C. syrup nor solution is mentioned in several wholesale price lists.

These facts suggest that when syrup of tolu is asked for, the B.P. preparation should be supplied, unless the B.P.C. "more aromatic preparation" is specially asked for.

I obtained a solution of tolu for making the syrup. It was labelled, "To make Syrupus Tolutanus.—Add 1 fluid ounce to 7 fluid ounces of Simple Syrup." This solution contained no sugar, and a syrup prepared according to these directions would contain only 58·3 per cent. of sugars, instead of 66 per cent. as intended by the B.P. I consider this label is incorrect and misleading, as it suggests that the syrup so made will be the syrup of tolu of the B.P.

None of the 7 samples of syrup of tolu examined last quarter attained the limit of 62 per cent. of sugars suggested above. Their specific gravities varied from 1·257 to 1·295. The earlier B.P. gave the specific gravity of the syrup as 1·330. These samples of syrup differed considerably from one examined in the previous quarter, which contained 67·1 per cent. of sugars and had a specific gravity of 1·330.

Each of the 7 samples was labelled, "Syrup of Tolu," and it appears probable that some of them, at any rate, had not been prepared according to the B.P., and that the incorrect strength was due to the use of a solution of tolu.

It is questionable if there is any justification for making a syrup of tolu from the solution, though at times it may be convenient. If a solution of tolu for making the syrup can be prepared containing a fair amount of cane sugar, a mixture of one part of it with seven parts of simple syrup would produce a product more closely approximating to the B.P. syrup of tolu than the samples examined last year.

Three samples contained from 60·6 to 61·6 per cent. of sugars and approached the minimum. Three others contained from 58·3 to 59·8 per cent. and were of poor quality. One contained only 54·7 per cent. of sugars and was condemned as adulterated. The vendor was cautioned.

VINEGAR.—Three samples of artificial vinegar sold as "Vinegar" contained from 2·2 to 3·3 per cent. of acetic acid. The sale of such artificial vinegar in Birmingham as "Vinegar" is very rare. During the past thirty years only about

10 previous vendors out of over a thousand samples have supplied such an adulterated article.

The makers of the vinegar who supplied the shop were prosecuted, and each of three brothers was fined £1. The case against the retailer was withdrawn.

An informal and a formal sample from one shop were artificial vinegar containing 3·4 per cent. of acetic acid. The shopkeeper declined the offer of the Inspector to take a sample in course of delivery from the maker, and was fined 10s. The jar in which it was supplied to the shopkeeper had an interesting label, "Acetic Vinegar. Unrivalled for pickling, salad, etc. This is an artificial product and must not be sold for pure malt vinegar." As far as I know, the phrase, "acetic vinegar," is a new one, and was probably intended as a declaration which could be pleaded in case of prosecution, but which would not be understood by the retailer selling it. The vinegar was probably labelled by the maker in this way to protect himself, as on a previous occasion one of his customers was fined in Birmingham for selling artificial vinegar.

J. F. LIVERSEEGE.

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.

AVAILABLE CARBON DIOXIDE IN BAKING POWDER.

ON January 8, a firm of manufacturing chemists was summoned at Sheffield for giving a false warranty to a Birmingham firm of tradesmen in respect of baking powder which yielded only 1·99 per cent. of available carbon dioxide, whereas a good baking powder should yield 8 per cent.

Mr. John Evans, F.I.C., Public Analyst for Sheffield, said that a good average baking powder should yield at least 8 per cent. of available carbon dioxide.

In cross-examination, he said that 10 per cent. was the commercial standard and the standard recognised by Public Analysts, and that it was the standard adopted by the Canadian Government, but he admitted that in this country there was no legal standard. He agreed that deterioration in baking powder could be set up by slight damp or warmth.

The solicitor for the defence contended that the defendants had complied with all the requirements of the Sale of Food and Drugs Acts. The baking powder had not been ordered with a specification as to its gas content although, in fact, when the baking powder was sent out it contained 8 per cent. of gas.

Mr. F. W. Richardson, F.I.C., Public Analyst for the West Riding, said that there was no standard for the amount of carbon dioxide in baking powder. In the main, however, he agreed with all that Mr. Evans had said. He had analysed some of the baking powder in question and had found the proportion of gas to vary in different makes.

The manager of the defendant's firm said that they made different baking powders, containing up to 13·5 per cent. of gas content; the lowest quality contained 8 per cent. Price had nothing to do with the matter.

The Chairman of the Bench said that they were satisfied that the defendant firm had discharged the liability upon them. They had proved to the satisfaction of the Court that, when they gave the warranty, they had reason to believe that the statements contained therein were true. The summons was dismissed.

SHREDDED SUET: LABEL OFFERED AFTER PURCHASE.

ON January 6, a tradesman and two assistants were summoned at Eastbourne for selling, to the prejudice of the purchaser, shredded suet which was not of the nature, substance and quality demanded.

It was stated that after the purchase was complete the assistant said: "Oh, I think I ought to have given you a label with the suet." The inspector declined to take the label (an explanatory slip issued by the manufacturers), as the transaction was closed. Subsequent analysis showed the sample to contain 89·62 per cent. of suet and 10·38 per cent. of flour. In cross-examination, the inspector maintained that he had a perfect right to refuse the slip.

The magistrates dismissed the summons.

FLAVOURED WATER AS BRANDY MINT.

ON February 1, a Marlow hawker was summoned by the Buckinghamshire County Council, at the Chesham Petty Sessions for selling brandy mint not of the nature, substance and quality demanded.

The Public Analyst's certificate showed that the sample contained no brandy, but was mainly water flavoured with peppermint. It was stated by the prosecution that a customer who asked for "Brandy Mint," and paid 1s. 3d. for a bottle of flavoured water, was deceived and prejudiced. In answer to the Chairman, who raised the question whether the purchaser was deceived any more than if he asked for brandy snaps, it was pointed out that in this case the bottle was labelled "Brandy Mint," which was stated to be recommended by doctors as a preventative of influenza.

The defendant said that he had sold such stuff for 40 years and had never been stopped. The drink was made from the small black-leaf mint and he sold it as peppermint.

The Bench dismissed the case upon payment of costs, and upon condition that the misleading statement that it was brandy mint was removed from the label.

Vitamin A in Cod-liver Oil.

REPORT* ON A COMPARISON BETWEEN THE COLORIMETRIC (ROSENHEIM, DRUMMOND) AND THE BIOLOGICAL METHOD OF DETERMINING VITAMIN A IN COD-LIVER OIL.

A SUB-COMMITTEE (Dr. H. Dale, England; Prof. Poulsson, Norway; Prof. Voegtlin, U.S.A.) was appointed at the International Conference to compare the colorimetric method of Rosenheim and Drummond (*Biochem. J.*, 1925, **19**, 753; ANALYST, 1926, **51**, 93) with the biological method of determining vitamin A. For this purpose 7 samples of cod-liver oil were provided. The vitamin A content was determined colorimetrically, and independent tests were applied to the same oils by the biological method in four laboratories.

COLORIMETRIC TEST FOR VITAMIN A ASSAY IN COD-LIVER OILS: 1. *Arsenic Chloride Method.*—The oil is measured from a Wright's capillary pipette,

* Report to the League of Nations Health Organisation by the Accessory Food Factors Committee (appointed jointly by the Lister Institute and the Medical Research Council. Published in *The Lancet*, 1928, **214**, No. 5447 (Jan. 21st).

graduated by means of mercury to hold 25 c.c. and delivering 20 mgrms. oil, into a test-tube of clear white glass of 10 mm. internal diameter. One c.c. of the reagent (pure $AsCl_3$) is delivered from a standard 10 c.c. burette into the test-tube, and a reading taken immediately (the time limit one minute) in a Lovibond's colorimeter. The results are expressed in standard units (blue) of the colorimeter. Five consecutive tests made in each case differed on the average by $\pm$ 0·10 unit.

2. *Antimony Chloride Method.*—By means of a standard pipette 2 c.c. of the oil are measured into a measuring flask of 10 c.c. capacity. The pipette is rinsed out three times with chloroform, and the solution made up to volume with the same solvent; 0·2 c.c. (= 40 c.mm. oil) of the solution are measured into a test-tube (10 mm. diameter) and mixed with 2 c.c. of a 30 per cent. antimony chloride solution in chloroform delivered from a standard burette. Readings are taken as above described. Limit of error as above.

The values obtained by the $AsCl_3$ method and its $SbCl_3$ modification agree within the limits of error of each method. The results obtained on the same oils by two independent observers agreed within $\pm$ 0·50 units—i.e., the usual difference in colorimetric work. The figures given in the table refer to the mean of the values obtained with the arsenic chloride and antimony chloride methods respectively.

Biological Method for Vitamin A Assay.—At a Conference held at the Lister Institute on December 18, 1925, it was agreed unanimously that the method for the biological assay of vitamin A, drawn up by Prof. Poulsson on behalf of the Permament Standards Committee of the League of Nations Health Organisation, and detailed in a memorandum of July, 1925, was defective in that no provision was made for an adequate supply of vitamin D (anti-rachitic factor) to the animals during the test.

The following general method was therefore recommended by the Accessory Food Factors Committee, and was adopted by the four laboratories undertaking the biological tests.—

(1) Young rats of weight 40–50 grms., 20–30 days old, to be used.

(2) The number of control animals to be equal to that in each group receiving oil.

(3) The animals to be fed on artificial diet devoid of fat-soluble vitamin until growth ceases, and excess of antirachitic vitamin (in form of irradiation, irradiated foodstuffs, or irradiated cholesterol) to be supplied during the whole or latter part of this pre-observation period.

(4) The material to be tested to be added to the diet when growth has ceased and the weight of the animal has become constant or is beginning to decline.

(5) The animals to be observed during a further period of four weeks, during which time the antirachitic vitamin should be supplied.

(6) Comparison to be instituted between the doses of the various oils required to restore the same rate of growth.

(7). Not less than three animals to be used for each dose of oil. The oil to be administered separately to each animal. The diluent to be some inert solvent whose inactivity should be controlled by the behaviour of control animals.

The comparative results obtained are summarised in the table. It was not always possible to make a comparison on the lines laid down in (6) above, and in two instances comparison was made between the *rate of growth* shown by rats *upon the same dose* of the different oils. By this method quantitative accuracy of comparison is impossible, seeing that the relation between size of dose and rate of growth has not been determined. But the oils can be graded in order of merit, provided that the dose selected for making the comparison does not exceed the minimum required for normal growth.

After the results had been submitted, Dr. Dale communicated the results

Oil 1.—An ordinary medicinal cod-liver oil. Details of preparation not available.

Oil 194.—Raw medicinal cod-liver oil prepared by the ancient "rotting" process. The liver remains in open barrels for many weeks, sometimes for several months. This oil is very strongly coloured.

Oils 202, 97, 149, 114.—Ordinary medicinal cod-liver oils, prepared by means of steam. Nos. 97, 140, and 114 have remained in half-filled bottles for two to three years and may have undergone alterations. No. 202 is a fresher oil and has been kept in filled bottles.

Oil 82.—Cod-liver oil prepared in a very primitive way by simply boiling the cod livers in an open pot. Such cod-liver oil is employed by the inhabitants for their own use.

Relative Values of Samples of Cod-liver Oil in Content of Vitamin A.

—	Laboratory.	Observer.	Method.	Vitamin. D. supplied as—	Cod-liver Oils. 1	194	202	97	140	114	82	Remarks.
1	Nat. Inst. for Med. Research.	Dr. Rosenheim.	C.	—	100	88	45	34	34	20	0	Expressed in units of blue (Lovibond) mean of values given by $AsCl_3$ and $SbCl_3$ reactions, using 1 c.cm. reagent and 20 mgms. of oil.
2	Univ. of Sheffield Pharmacolog. Dept.	Prof. E. Mellanby.	B.	Irradiated cholesterol	++++	+++	++	++	++	+	0	Graded by— Comparison of doses required to restore same rate of growth: 82 has toxic properties.
3	Univ. Coll. Lond. Biochem Dept.	Prof. J. C. Drummond	B.	,,		++	+++	++	+	±	0	Comparison of rate of growth on 10 mg. doses.
4	King's Coll. for Women, Physiol. Dept.	Prof. Mottram and Dr. G. Hartwell.	B.	,,		+++	++	++	++	+	0	Comparison of rate of growth, general condition and, where possible, postmortem exam. on 5 mgrms., 10 mgrms., 15 mgrms. and 20 mgrms. doses.
5	Lister Inst. Dept. of Exp. Pathology (Prof. Sir C. Martin).	Miss K. M. Soames and Miss J. Leigh Clare.	B.	Irradiated hardened cotton-seed oil.	+++	++	+++	++	++	+	±	Comparison of rate of growth on 20 mgrms. dose (Lister standard cod-liver oil = +++).
6	Univ. of Oslo.	Prof. Poulsson.	B.	Not supplied.		100 (0·5 to 0·75)	66 (0·75 to 1·0)	30 (2)	66 (0·5 to 1·25)	30 (2)		Comparison of smallest growth promoting dose (in mgrm.).

C. = Colorimetric. B. = Biological.

received from Prof. Poulsson (also included in the table), together with the following description of the various oils:—

RESULTS.—The grading of the seven oils for vitamin A value by the English workers using the biological tests is roughly the same, but there was a marked variation in the values obtained in different laboratories for the same oil. This variation in the results among themselves was at least as great as that existing between the latter and those obtained for the same oils by the colorimetric method. It was not possible to attach numerical values to the results obtained by the biological method. The colorimetric test gave oil No. 1 the first place and placed oil 194 not far behind. Oil No. 1 was also placed in the first rank by one of the two observers who examined it, using the biological method., Oil 194 was found next in value in two out of four biological tests; in the other two, oil 202 was found superior to oil 194. The results of the colorimetric test and of all four biological tests agreed (1) in assigning an intermediate position to oils 97 and 140, and (2) determining oil 114 to be inferior to these two, and (3) in finding oil 82 to be either very poor in vitamin A, or altogether devoid of it.

The Committee finds that the biological method does not, at present, permit of sufficient accuracy for the presentation of the above results in numerical form.

CONCLUSION.—In the examination of cod-liver oils for vitamin A the colorimetric method of Rosenheim and Drummond afforded information consistent with that derived from the biological tests.

In recording this conclusion, the Accessory Food Factors Committee, however, considers that before a conclusion is drawn as to the general validity of the colorimetric method for assay of vitamin A, tests should be made with substances containing vitamin A, other than cod-liver oil, such as butter, palm oil, cereal oils, etc.

F. GOWLAND HOPKINS, *Chairman.*

HARRIETTE CHICK, *Secretary.*

1*st September*, 1927.

The details of the basal diets used in the different laboratories are given in an appendix to this report.

Atomic Weights, 1928

(GERMAN COMMISSION).

ACCORDING to the eighth report of the German Atomic Weights Commission,* (consisting of Professors Bodenstein, Hahn, Hönigschmid and Meyer), the investigations published from December, 1926, to the end of November, 1927, necessitate some alterations in the table of atomic weights issued last year. The value for argon (39·88) is replaced by the more accurate value 39·94, that for titanium (48·1) by the value 49·0, and the value provisionally adopted for yttrium (89·0) is replaced by the now experimentally determined value 88·93. In the table for 1928, those atomic weights which are based more or less directly upon the basis of silver (107·880) have the second decimals placed as indices.

* *Chem. Ztg.*, 1928, **52**, 47.

PRACTICAL ATOMIC WEIGHTS, 1928.

Ag	Silver	107,88[0]	Ge	Germanium	72,60	Pt	Platinum	195,2
Al	Aluminium	26,97	H	Hydrogen	1,008	Ra	Radium	225,9[7]
Ar	Argon	39,94	He	Helium	4,00	Rb.	Rubidium	85,4[5]
As	Arsenic	74,96	Hf	Hafnium	178,6	Rh	Rhodium	102,9
Au	Gold	197,2	Hg	Mercury	200,6[1]	Ru	Ruthenium	101,7
B	Boron	10,82	Ho	Holmium	163,5	S	Sulphur	32,0[7]
Ba	Barium	137,3[7]	I	Iodine	126,92	Sb	Antimony	121,7[6]
Be	Beryllium	9,02	In	Indium	114,8	Sc	Scandium	45,10
Bi	Bismuth	209,0[0]	Ir	Iridium	193,1	Se	Selenium	79,2
Br	Bromine	79,91[6]	K	Potassium	39,10[4]	Si	Silicon	28,06
C	Carbon	12,00	Kr	Krypton	82,9	Sm	Samarium	150,4
Ca	Calcium	40,07	La	Lanthanum	138,9[0]	Sn	Tin	118,7[0]
Cd	Cadmium	112,4[0]	Li	Lithium	6,94	Sr	Strontium	87,6[3]
Ce	Cerium	140,2	Mg	Magnesium	24,32	Ta	Tantalum	181,5
Cl	Chlorine	35,45[7]	Mn	Manganese	54,93	Tb	Terbium	159,2
Co	Cobalt	58,97	Mo	Molybdenum	96,0	Te	Tellurium	127,5
Cp	Cassiopeium	175,0	N	Nitrogen	14,008	Th	Thorium	232,1[2]
Cr	Chromium	52,01	Na	Sodium	22,99[7]	Ti	Titanium	47,90
Cs	Caesium	132,8[1]	Nb	Niobium	93,5	Tl	Thallium	204,3[9]
Cu	Copper	63,57	Nb	Neodymium	144,2[7]	Tu	Thulium	169,4
Dy	Dysprosium	162,5	Ne	Neon	20,2	U	Uranium	238,1[3]
Em	Emanation	222	Ni	Nickel	58,68	V	Vanadium	51,0
Er	Erbium	167,7	O	Oxygen	16,000	W	Tungsten	184,0
Eu	Europium	152,0	Os	Osmium	190,9	X	Xenon	130,2
F	Fluorine	19,00	P	Phosphorus	31,04	Y	Yttrium	88,9[8]
Fe	Iron	55,84	Pb	Lead	207,2[0]	Yb	Ytterbium	173,5
Ga	Gallium	69,72	Pd	Palladium	106,7	Zn	Zinc	65,38
Gd	Gadolinium	157,3	Pr	Praseodymium	140,9[2]	Zr	Zirconium	91,2[5]

Connecticut Agricultural Experiment Station.

REPORT ON FOOD PRODUCTS AND DRUG PRODUCTS FOR THE YEAR 1926.

THE section of the Report dealing with Food Products gives 18 pages of analyses of common foods, on the lines of König's standard work, including meat and meat products, fish and fish products, eggs of various birds, dairy products, soups and broths, cereal products, vegetables, pickles and condiments, fruits, berries, etc. There are also 45 pages of analyses of special foods, such as gluten flours and breads, almond meal, soya bean meal, bran biscuits, diabetic biscuits, etc.

"DIABETIC" FOOD.—There is no longer any Federal definition of a "diabetic" food, the former definition having been revoked by U.S. Dept. Agr. Food Inspection Decision 199. Since such products are offered as dietetic aids in the treatment of disease, they are regarded by the food control officials as therapeutic agents rather than as foods, and more properly regulated under the provision of the Act referring to drugs.

The term "diabetic" as applied to this type of foods has been much abused in the past; many foods which differ but little from common foods of the same class have been designated by that term. Moreover, it may be true that some patients have been led to believe that foods bearing the qualification "diabetic" are curative or mitigative in themselves rather than merely dietetic adjuncts. For these reasons regulatory officials are inclined to discourage the use of the term "diabetic" as a part of the name of these special foods and in explanatory literature concerning them.

BAKING POWDER.—Seven samples of baking powder were examined for available carbon dioxide and metallic impurities. Baking powder should contain not less than 12 per cent. of available carbon dioxide. The samples contained from 7·2 to 13·4 per cent. of available carbon dioxide. None contained arsenic in excess of 1 part per million.

EGGS, DIPPED EGGS.—Forty samples of eggs were submitted by the Dairy and Food Commissioners. By "candling" and determining ammoniacal nitrogen 15 samples were passed as fresh, and 25 did not have the characteristics of fresh eggs.

One sample of *dipped eggs* (eggs dipped in oil) was also examined. A small quantity of oil with a refraction of about 72° at 25° C. was extracted from the shell. A sample suspected of being dipped yielded no oil when the shell was extracted. The dipped eggs showed a relatively high ammoniacal nitrogen content (2·7 mgrms. per 100 grms. of egg), and the yolks were settled in the shells. Air spaces, however, were generally less than 1 inch in diameter. The eggs were wholesome and edible, but did not have the characteristics of fresh eggs, excepting the fairly small air spaces.

CARBONATED BEVERAGES.—One hundred and seventy-nine samples of carbonated beverages were examined. The law requires a sugar content of not less than 5 per cent. in these products; saccharin is prohibited, and artificial colours and flavours must be declared, if used. Sodium benzoate is the only chemical preservative recognised in the regulations, and its presence requires label declaration.

Hydrogen peroxide as preservative.—Recently, hydrogen peroxide has been used, to some extent, as a preservative in bottled chocolate beverages. It is claimed that, owing to the fact that this substance readily decomposes into oxygen and water, the preservative, as such, will not be found in the beverages so treated. There is evidence, however, that the peroxide may persist for some time, particularly in beverages which are bottled without subsequent heating.

The apparently harmless nature of hydrogen peroxide, when used as a remedial agent or, according to older literature, as a preservative for certain foods, is not necessarily an argument in favour of its unrestricted use in foods, and control officials have generally adopted a conservative attitude with respect to its use for food preservation. One obvious objection to it, and to any other substance used for similar purposes, is the tendency it will have to create a disregard for those sanitary safeguards in manufacturing operations which food officials have emphasised and which manufacturers have so largely adopted. Again, commercial preparations of hydrogen peroxide are themselves preserved with mineral acids and other chemicals, and these "stabilisers," although in small amounts, are necessarily introduced into peroxide-treated beverages.

For the present, no objection is raised in this State to chocolate beverages so treated, provided the treatment is not in lieu of proper sanitary measures in

the plant; and provided that the peroxide, as such, is not present in the finished product; and further, provided that evidence of objectionable stabilisers is not found.*

All of the samples examined contained the required amount of sugar. Saccharin was found in seven samples, but they were all the product of one manufacturer. Five samples of chocolate soda were tested for hydrogen peroxide; four showed no trace of the preservative, and one showed the merest trace. Considerable laxity was noted in the matter of declaring artificial flavours and colours, 22 samples being deficient in this respect.

"COOKING FATS."—Two samples of "cooking fats" were examined. In composition they had the same resemblance to butter as certain other articles generally recognised as oleomargarines. They contained no milk or milk product, and were practically 100 per cent. fat. The so-called "cooking fats" are substitutes for butter and not for lard. By a Treasury Decision, No. 4006 (approved April 1, 1927) these so-called cooking compounds sufficiently resemble butter as to warrant their classification as oleomargarine.

ICE CREAM.—About two-thirds of the 288 samples examined contained over 12 per cent. of fat, the legal standard being 8 per cent. for plain ice cream and 6 per cent. for fruit and nut ice cream. Products resembling ice cream and sold under the name of "frozen pudding" have been held in the State of Connecticut to be subject to the ice cream regulations. If they contain less than 8 per cent. of milk fat, the percentage of fat must be declared by a suitable notice displayed at the time and place of sale.

PAPRIKA.—Paprika must not contain more than 8·5 per cent. of total ash, or more than 1 per cent. of insoluble ash. The iodine value of the extracted oil should not be more than 136 or less than 125. The iodine values 5 of 14 samples examined ranged from 105 to 122 and averaged 113. An old authentic sample of Hungarian paprika, including seeds but no stems, yielded 15·32 per cent. of ethereal extract having an iodine value of 122.

MEXICAN MAGUEY PLANT.—The concentrated sap of this plant (known also as agave and American aloe) is sold by a Mexican firm under the trade name of *Matamel.* Analysis of a sample gave the following results:—Total solids (at 60°, *in vacuo*), 72·6; ash, 2; invert sugar, 19·4; sucrose, 44·7; total nitrogen, 0·27; gums, pectins, etc. (precipitated by alcohol), 0·36; acidity as malic acid, 1·0 per cent.

According to the advertisement the preparation relieves bladder weakness. No scientific references to the medicinal uses of maguey were found, except that the juice is said to be laxative, diuretic and an emmenagogue, and in doses of 2 fl. ozs., useful in scurvy (*U.S. Dispensatory*, p. 1232).

COMPOSITION OF ACORNS.—The following table gives the composition of shelled acorns of various species, harvested in the autumn and at the time of germination. After storage in earth during the winter, starch was determined by the diastase method. By "soluble carbohydrates" is meant such as are soluble in 10 per cent. alcohol and reduce Fehling's solution after hydrolysis. It was found that the maximum reducing power of these soluble carbohydrates was reached after 30 minutes hydrolysis; thereafter reducing power diminished, probably owing to the destruction of laevulose.

* The revised rules and regulations will probably include hydrogen peroxide with those preservatives which are prohibited.

ANALYSES OF SHELLED ACORNS.

	White Oak		Red Oak.		Chestnut Oak.		Scarlet Oak.	
	Nov. 1925–Apr. 1926.		Nov. 1925–Apr. 1926.		Nov. 1925–Apr. 1926.		Nov. 1925–Apr. 1926.	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
	In the Fresh Material.							
Water	39·68	36·66	32·90	26·57	47·23	40·70	23·83	31·67
Ash	1·55	1·54	1·76	2·11	1·19	1·75	1·57	1·70
Protein (N x6·25)	4·48	4·93	4·80	5·06	4·49	5·27	5·90	5·10
Fibre	1·06	1·59	1·59	2·06	1·31	1·84	1·73	1·70
Carbohydrates:								
Starch	28·91	32·49	16·02	23·45	16·99	21·43	18·48	18·24
Soluble, as dextrose after hydrolysis 30 mins.	6·31 (4·83)[1]	5·95 (5·58)[1]	7·09 (4·30)[1]	4·60 (4·02)[1]	7·83 (7·07)[1]	7·71 (7·28)[1]	7·16 (4·05)[1]	4·48 (3·80)[1]
Undetermined	13·90	15·17	20·75	21·39	18·55	20·19	17·85	21·35
Fat	4·11	1·67	15·09	14·76	2·41	1·11	23·48	15·76
	In the Water-free Material.							
Ash	2·56	2·43	2·62	2·87	2·26	2·96	2·06	2·48
Protein	7·42	7·79	7·16	6·90	8·50	8·88	7·75	7·46
Fibre	1·77	2·51	2·37	2·81	2·48	3·11	2·28	2·49
Carbohydrates:								
Starch	47·93	51·27	23·89	31·94	32·20	36·14	24·26	26·69
Soluble, as dextrose after hydrolysis 30 mins.	10·47 (8·01)[1]	9·39 (8·80)[1]	10·58 (6·41)[1]	6·26 (5·47)[1]	14·83 (13·40)[1]	13·00 (12·27)[1]	9·41 (5·32)[1]	6·56 (5·56)[1]
Undetermined	23·04	23·97	30·88	29·12	35·16	34·04	23·41	31·27
Fat	6·81	2·64	22·50	20·10	4·57	1·87	30·83	23·05

[1] Direct Reduction.

(Cf. Baker and Hulton, ANALYST, 1917, **42**, 351, 383.)

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Nature of the Protein Surrounding the Fat Globules in Milk. R. W. Titus, H. H. Sommer and E. B. Hart. (*J. Biol. Chem.*, 1928, **76**, 237–250).—No theory has been generally accepted regarding the chemical nature of the protein substance which immediately surrounds the fat-globules in milk, but diverse views have been propounded at different times as to its nature and whether or not it constitutes a protein distinct from casein, lactalbumin or lactoglobulin. In order to compare the fat envelope with the different milk proteins the latter were prepared in as pure a form as possible, the casein and lactalbumin from skim milk and lactoglobulin from colostrum milk. From an examination of the nitrogen distribution of the fat envelope and comparisons, it is quite evident that this particular protein is very closely related to, if not identical with, casein.

The sulphur, phosphorus and tryptophane content of the envelope, as determined on the original material, agree almost exactly with the sulphur, phosphorus and tryptophane content of casein. The specific rotation of the fat envelope, as compared with that of casein, agrees very well, yet the difficulty in getting a clear solution renders this determination of limited value. The precipitin test shows no distinction between the fat envelope and casein, but points to their identity. The most outstanding distinction between the fat envelope protein and casein is its lower solubility and darkening of the solution when dissolved in sodium hydroxide. This suggests a possible contamination of the fat envelope with some unknown substance. P. H. P.

Determination of Lactic Acid in Sugar Solutions Decomposed by Alkali. T. E. Friedemann. (*J. Biol. Chem.*, 1928, **76**, 75–87.)—Lactic acid, one of the main products resulting from the decomposition of sugars by alkali, is difficult to determine in the mixture of other products which accompany it in such solutions. The applicability and reliability have been tested in these cases of an oxidation method for the determination of lactic acid recently described by Friedemann, Cotonio and Shaffer (*J. Biol. Chem.*, 1927, **73**, 335 ; ANALYST, 1927, **52**, 418–419), and the method can be used with solutions of such mixed sugar derivatives. Only small amounts of solution are required, and the rate and amount of lactic acid production under various conditions may be followed. It was necessary to determine whether other saccharinic acids present in the solution interfere with the oxidation of lactic acid to acetaldehyde, and whether they are themselves oxidised to volatile sulphite-binding, or iodine-reacting, products. The sugars themselves, various saccharinic acids, and sugar alcohols yield, on oxidation, only small amounts of interfering substances. From analysis of artificial mixtures it is concluded that the combined error from the other substances in untreated solutions of sugar derivatives probably does not exceed 5 or 10 per cent. This error is somewhat reduced by preliminary extraction of the acids by ether or by removal of other derivatives by copper-lime precipitation. The results for lactic acid in sugar solutions by the oxidation method are in approximate agreement with the yield of zinc lactate which may be isolated from the same solutions by more laborious procedure, and are probably more reliable.

P. H. P.

Detection of Virgin Olive Oils in Refined Olive Oils. Baud and Courtois. (*Ann. Chim. anal.*, 1928, **10**, 11–14.)—Pure refined olive oils have a characteristic tint and fluorescence which distinguishes them from virgin oils when viewed by ultra-violet light. Two or 3 c.c. of the sample, in a small quartz tube, are placed in a dark chamber before the screen in a Wood's light apparatus, *i.e.* in the 3650 Å rays, and the colour and fluorescence noted; in order to accentuate the colour, the tube is then turned so that the oil is spread over the whole surface. Viewed by transmitted light, virgin oils assume a yellow-brown coloration with no fluorescence, whilst refined oils appear blue. In very thin layers the yellow colour is not apparent, and only the blue fluorescence of the treated oils appears.

By reflected light the treated oils show a milky fluorescence which masks the blue colour. Intensity of coloration seems to depend on the extraction process. Thus a stronger fluorescence is shown by refined pulp oils than by refined second-pressure oils or those extracted by solvents. An addition of 10 per cent. of pulp oil may be certainly detected in a mixture with virgin oil, whilst 10 per cent. of second-pressure oil in such a mixture gives a doubtful result. Soya and grape-seed oils show a blue to indigo fluorescence. Prolonged heating causes fluorescence to develop in virgin olive oils. D. G. H.

Examination of Cod-Liver Oil in Wood's Light. H. Marcelet. (*Compt. rend.*, 1928, **186**, 226–228.)—The best containers for cod-liver oils which are to be examined by means of the mercury vapour lamp are special non-fluorescent quartz crucibles. As these are expensive and difficult to obtain, a drop of oil may be placed on a vertical sheet of non-fluorescent glass or paper, and the streak examined against a background of cardboard which has been lightly glued, and over which a non-fluorescent animal charcoal has been sifted. The light should be filtered through a nickel screen so as to allow the passage of the rays 3340 to 3906 Å., and the carbon screen should be 10 cm. behind the oil. The 24 samples of commercial and pharmaceutical oils examined showed a fluorescence which varied from very pale yellow to brown or golden yellow, according to the quality of the oil, and which persisted after the oils had been heated to 150 to 200° C. The drops themselves often appeared chestnut-brown. J. G.

Chemical Investigation of Muttonbird Oil. Part II—Comparison of Stomach Oil and Body Fat. C. L. Carter. (*J. Soc. Chem. Ind.*, 1928, **47**, 26T–30T ; *cf.* ANALYST, 1921, **46**, 458.)—The *Stomach Oil* of the muttonbird (*Austrebata lessoni*) is a pale yellow or orange oil of low sp. gr. (0·881-885), giving the marked colour tests of liver oils, and containing at least 25 per cent. of cetyl oleate. Of the liquid esters, oleyl oleate was found to be the chief constituent; it was isolated after hydrogenation as octadecyl stearate. The unsaponifiable matter (38·4 per cent. of the saponification products) consisted of cetyl alcohol, 65; oleyl alcohol, 28; and cholesterol, 7 per cent.; the mixed acids (only 5 per cent. saturated) were chiefly oleic, together with linolic and more unsaturated acids, at least 12 per cent. of which had a composition agreeing with the formula $C_{22}H_{36}O_2$.

Body Fat.—The extracted body fat is a fairly firm, white crystalline mass melting at 34–38° C., with sp. gr., 0·9123–0·9175 ; n_D, 1·4712 ; saponification value, 196·8–200 ; acid value (oleic) 3·41 ; iodine value (Wijs) 73. On saponification, the mean molecular weight of the fatty acids was 282, their m.pt. 30–32° C., iodine value (Wijs) 73. No unsaponifiable matter was obtained and no ether-insoluble bromides. The fat consisted of glycerides of stearic and palmitic acids in nearly equal amounts, with about 25 per cent. of oleic acid. The stomach oil and body fat have acids and alcohols of the same number of carbon atoms, and it is possible that by means of biochemical oxidases and reductases, or by glutathione, the

body fat (a deposit fat) may be converted into the stomach oil, excreted in the preen gland, and swallowed for immediate use. D. G. H.

Titre of New Zealand Mutton Tallows. A. M. Wright and I. Thompson. (*J. Soc. Chem. Ind.*, 1928, **47**, 13–14T.)—Summarised results are given of several thousand titre determinations made during a period of seven years on mutton tallows, manufactured in the North and South Islands of New Zealand. The A.O.A.C. method was used, the preliminary saponification being effected by glycerin and potassium hydroxide solution, and the solidifying points of the mixed fatty acids being expressed in degrees centigrade. As the stock yielding the tallow becomes older and more mature, the titre mostly increases gradually to a maximum and then falls slightly, the fall being more or less coincident with the onset of winter. The following figures, giving the seasonal average of the titre over seven years for stock grown in various mean latitudes, indicate a definite relationship between the titre and the latitude :—

TITRE OF TALLOW.

Mean latitude S.	Caul and Kidney fats	Intestinal and visceral fats.
40° C.	47·9° C.	44·1° C.
41·5	46·1	43·8
43·5	45·8	43·0
44·5	45·1	42·8
46	44·7	42·7

Probably such differences are due to climatic variations, as the different latitudes vary as to rainfall, temperature, humidity, and sunshine, but there are many anomalies incapable of simple explanation. T. H. P.

Pseudo-ephedrine from *Ephedra alata*. O. F. Black and J. W. Kelly. (*Amer. J. Pharm.*, 1927, **99**, 748–751.)—Dried twigs of *Ephedra alata* yielded about 1 per cent. of crude pseudo-ephedrine, $C_{11}H_{17}ON_3$, whereas the Chinese variety, known as Ma Huang, gives only 0·26 per cent. Pseudo-ephedrine can be readily converted into ephedrine, from which it differs in having two methyl groups, instead of one, attached to the single nitrogen atom. The two isomers may be differentiated by the behaviour of their oxalates, that of ephedrine being insoluble in water, whilst that of the pseudo modification is readily soluble. Pseudo-ephedrine melts at 116° C., and its hydrochloride (colourless needles) melts at 180° C. T. H. P.

Studies on the Analysis and Chemistry of Neoarsphenamine. A. E. Jurist and W. G. Christiansen. (*J. Amer. Chem. Soc.*, 1928, **50**, 191–196.)—Neoarsphenamine (a complex mixture of varying composition) is a condensation product of 3,3:-diamino–4,4:-dihydroxyarsenobenzene. A fairly complete knowledge of the composition may be arrived at by means of the arsenite method, whereby the neoarsphenamine is oxidised with an excess of iodine, the excess

reduced with sodium arsenite, the solution acidified, and sulphur precipitated as barium sulphate. Free sodium formaldehyde sulphoxylate reduces 4 atoms of iodine, whereas the combined compound (of the *N*-methylene type) reduces only 2 atoms. The sulpharsphenamine sulphur of Elvove is shown to be nuclear sulphur, whilst two types of combined sulphoxylate appear to be present, the second of which reduces iodine in the same way as the free compound, and is probably to be explained on the basis of a double salt of arsphenamine base and sulphoxylate similar to metallic compounds of arsphenamine. There is a type of sulphur present in neoarsphenamine arising from some reaction or decomposition of sodium formaldehyde sulphoxylate, but it is no longer present as sulphoxylate.

D. G. H.

Determination of Hexamine. J. Rae. (*Pharm. J.*, 1928, **120**, 71.)—The following modification of the B.P. method for determining hexamine was found satisfactory. One grm. of hexamine is dissolved in water, and the solution made up to 100 c.c.; to 10 c.c. are added 25 c.c. of *N* potassium dichromate solution and 10 c.c. of concentrated sulphuric acid, the mixture heated on a water bath for 1 hour, with occasional shaking, cooled and made up to 250 c.c. To 25 c.c. of the solution, 1 grm. of potassium iodide is added, and the liberated iodine titrated with 0·1 *N* sodium thiosulphate solution ; the number of c.c. used deducted from 25, and the figure, multiplied by 5·833, gives the percentage of hexamine in the sample.

D. G. H.

Biochemical, etc.

Improved Method for the Determination of Methaemoglobin. J. B. Conant, N. D. Scott and W. F. Douglass. (*J. Biol. Chem.*, **76**, 223–227.)—The method of Conant and Fieser (*J. Biol. Chem.*, 1924–25, **62**, 623) has been improved, and a convenient and reliable procedure has been developed for the determination of methaemoglobin in the presence of its cleavage products. Titanous tartrate has been substituted for anthrahydroquinone sulphonate, since it reduces methaemoglobin to haemoglobin and does not interfere with the subsequent formation of a stable oxyhaemoglobin. This eliminates the necessity of a rapid manipulation during the saturation with oxygen, which was the chief drawback of the former method. The titanous tartrate is extremely sensitive to oxygen and is best prepared for each determination by the addition of titanous chloride to a mixture of sodium borate and sodium tartrate in a tonometer filled with nitrogen. The method may be applied to salt-free protein solutions or those which contain phosphates or borates. Some typical results are summarised. Three solutions are required :—(1) A 20 per cent. solution of titanous chloride ; (2) a 0·2 *M* solution of borax saturated with sodium tartrate ; and (3) solution 2 containing enough sodium hydroxide to neutralise the free hydrochloric acid present in quarter the volume of solution 1. As a rule, the borax and tartrate mixture must be about 2*M* in sodium hydroxide solution, but it is decided by titration. The procedure is as follows :—A tonometer is filled with oxygen-free nitrogen by being thrice evacuated and filled, and 1·60 c.c. of solution 3 are run in.

(The solutions are added through the capillary attached to the stop-cock in such a way that no air is introduced). The tonometer is turned so that the solution wets the walls, and 0·40 c.c. of the 20 per cent. titanous chloride is run in. The titanous chloride and the alkaline borax-tartrate solutions are completely mixed by rotation of the tonometer, and 0·50 c.c. of solution 2 is run in to rinse the bore of the stop-cock. There is no need to wait for the green precipitate to dissolve. Ten c.c. of the haemoglobin solution are now added through the stop-cock, and the last portion is forced in by means of nitrogen. The tonometer is shaken for 5 minutes, or longer, while the precipitate dissolves and the solution becomes dark purple ; then the nitrogen is removed by evacuation and air is admitted. The tonometer is again shaken for at least 5 minutes to insure saturation of the reduced haemoglobin with oxygen, a sample is withdrawn, and the combined oxygen is determined in the Van Slyke apparatus (Van Slyke and Neill, *J. Biol. Chem.*, 1924, **61**, 523).

Absorption Spectra of Oils and Oil Constituents, with Special Reference to Pro-Vitamin D. I. M. Heilbron, E. D. Kamon and R. A. Morton. (*Biochem. J.*, 1927, **21**, 1279-1283.)—An investigation has been made to determine whether ergosterol can be detected in vegetable oils by means of the spectroscope, since the oils also acquire antirachitic potency on irradiation. The detection would depend only on (*a*) the chance occurrence of substances peculiar to a particular oil, or particular process of extraction, and (*b*) the capacity of small amounts of the selectively absorbing ergosterol to show themselves in the presence of the general absorption of the other constituents. The three absorption bands of ergosterol, 293·5, 281·5 and 270 $\mu\mu$ were detectable with certainty for 0·2 per cent. ergosterol in kapok seed oil, sometimes for less. The sensitiveness of the direct spectrographic method depends primarily on the transparency of the oil under investigation, and in cases of clear samples of high purity, percentages as low as 0·01–0·02 have been detected, *e.g.* in cottonseed oil. A "negative" test does not, therefore, *exclude* a concentration of ergosterol less than 0·2 per cent. A large number of oils and oil extracts have been examined, and their absorption curves have been obtained. The results are given in a table and graphs. Yeast fat gave by far the most pronounced absorption of all the oils examined. Cottonseed oil, linseed oil, maize oil and some samples of arachis oil were rich sources of this compound. Cod-liver oil does not exhibit the pro-vitamin bands, although it contains the precursor substance. The method only makes it possible to discriminate between oils which contain relatively little ergosterol and those which contain quite material amounts. P. H. P.

The Relative Content of the Fat-Soluble Vitamins *A* and *D* in a series of Cod-Liver Oils. J. L. L. Clare and K. M. Soames. (*Lancet*, 1928, **214**, 150–182.)—Biological tests were applied to the same series of Cod-liver oils as were described in the Report of the Accessory Food Factors Committee (p. 156).

The experiments described have demonstrated how small is the degree of accuracy which it would seem possible to attain with the biological methods at

present available for assay of vitamins *A* and *D*, unless a prohibitive number of animals is used. Notwithstanding this drawback, the results have convinced the authors that the content of vitamin A in cod-liver oil bears no necessary relationship to that of vitamin *D*. This lack of parallelism between the content of these vitamins may be explained, in part, by the fact that vitamin A is less stable than vitamin *D* and, therefore, more likely to be affected adversely by methods of preparation and storage which involve heat and oxidation. Oil 202, one of the oils poorest in vitamin *D*, while richest in vitamin *A*, was also one of the freshest of the oils and had been kept in filled bottles. The medicinal value of cod-liver oil depends more upon its antirachitic value than upon its content of vitamin *A*, for the latter is readily and more conveniently obtained from foodstuffs. If the amount of one of these vitamins in a particular oil bears no necessary relationship to the other, as from the experiments cited appears to be the case, the biological method of testing cod-liver oil laid down in the United States Pharmacopoeia, which aims at the assay of vitamin *A* only, is open to criticism.

Biochemical and Spectroscopic Studies on Purified Cholesterol. C. E. Bills, E. M. Honeywell and W. A. MacNair. (*J. Biol. Chem.*, 1928, **76**, 251–261). The purification of sterols is beset with difficulties, and, although cholesterol is said to be freed from " provitamin "—a sterol indistinguishable from ergosterol—by treatment with charcoal or permanganate, over-irradiation, or purification via allocholesterol, cholesteryl chloride, or cholesterol dibromide, yet a further study has been made of its purification and activation. The activation of cholesterol has been studied by means of biological tests and absorption spectra. Details are given for the quantitative application of the Shipley line test. The positions of the three absorption bands of ordinary cholesterol, and ergosterol, were confirmed—293·5, 282 and 270 $m\mu$. By means of an especially appropriate light source a fourth band common to each was discovered at 260 $m\mu$. By a comparison of destruction rates it has been established that the activatable, ergosterol-like contaminant in cholesterol actually is ergosterol. It is remarkable that ergosterol, so highly unstable by itself, should be sufficiently resistant when admixed with cholesterol to withstand years of ageing. Cholesterol specially treated with charcoal or bromine for the removal of ergosterol was found to be activatable by ultra-violet rays. The activatability is due either to cholesterol itself, or to a hitherto undiscovered impurity which persists after three purifications with bromine. The limit of purification by bromine is reached by a single treatment. In either case the activatability is associated with absorption bands at 315 and 304 $m\mu$. The authors consider that the view of Jendrassik and Keményffi (*Biochem. Z.*, 1927, 1927, **180**, 180), that the activatability is attributable to an equilibrium existing between cholesterol and provitamin is open to dispute. T. H. P.

Bacteriological.

Formation of Hydrogen Sulphide by Natural Reduction of Sulphates. L. Elion. (*Ind. Eng. Chem.*, 1928, **19**, 1368.)—The number of true sulphate-reducing bacteria as yet isolated is very small. *Microspira desulphuricans* is a

non-sporogenic, anaerobic bacterium which has been isolated from ditch mud and closely resembles *M. aestuareii*, the latter, however, requiring the presence of sodium chloride for its development. The author has also proved the existence of a third member of this species, *Vibrio thermodesulphuricans*, which needs a temperature of 55° C. for its optimum action. W. P. S.

Viscous Fermentation of Mineral Waters. R. Gayot. (*J. Pharm. Chim.*, 1927, VIII, **7**, 69–70.)—Beverages of low acidity containing tartaric acid are rendered viscous by the action of a *Torula*, which produces a colloidal dextran capable of swelling in contact with water. The sugars attacked the most readily by the organism are different according as the conditions are aerobic or anaerobic. T. H. P.

Germicidal Efficiency of Sodium Hydroxide, Sodium Carbonate and Trisodium Phosphate at the same Hydrogen Ion Concentration. M. Levine, E. E. Petersen and J. G. Buchanan. (*Ind. Eng. Chem.*, 1928, **19**, 1328, 1340.)—When the alkalis are studied individually, their germicidal efficiency appears to be a direct function of the hydrogen ion concentration, but the hydrogen ion concentration is not a reliable index of the relative efficiencies of different alkalis. Variations of over 500 per cent. are found in the time required to kill bacteria by solutions of sodium hydroxide, carbonate and phosphate at the same hydrogen-ion concentration. W. P. S.

Toxicological and Forensic.

Studies on Gossypol. II. Nature of Carruth's D Gossypol. E. P. Clark. (*J. Biol. Chem.*, 1928, **76**, 229–235.)—After cottonseed meal has been prepared it contains many times less gossypol than the untreated seeds, although little or no gossypol is found in the expelled oil. The change was at first thought to be due to oxidation, but later to hydrolysis. Carruth (*J. Biol. Chem.*, 1917, **32**, 87) called the change gossypol "D gossypol," but it has never been isolated. Aniline D gossypol, obtained by hot aniline extraction of cottonseed meal, has been found to be identical with dianiline gossypol obtained by the condensation of gossypol with aniline, as shown by melting points, optical properties and molecular weights. Upon hydrolysis of aniline D gossypol a substance has been obtained and shown to be identical both chemically and physiologically with analytically pure gossypol. These facts, therefore, render untenable the hypothesis that D gossypol is an oxidation or hydrolytic product of gossypol. To explain the mechanism of the transformation of gossypol in D gossypol, it has been suggested that in the cooking and pressing process to which cotton seeds are subjected in the manufacture of cottonseed oil the gossypol present in the seeds is bound by condensation with free amino groups of the seed proteins, and substances *similar in type* to dianiline gossypol are formed. It would seem desirable to substitute the term *bound* gossypol for D gossypol (*cf.* ANALYST, 1928, 107). P. H. P.

Water Analysis.

Direct Nesslerisation after Kjeldahl Digestions. H. M. Chiles. (*J. Amer. Chem. Soc.*, 1928, **50**, 217–221.)—Ammonia in the presence of alkali sulphates (and in higher concentration than by previous methods) may be satisfactorily Nesslerised by the use of a protective colloid (gum arabic) to prevent precipitation of the colouring substance. The limit of accuracy appears to be the accuracy of the colorimeter readings. The colloid solution is prepared by adding 10 grms. of powdered gum arabic, with vigorous stirring, to 190 c.c. of ammonia-free water. After complete dispersion, 4 grms. of Permutit powder (as prepared for ammonia determinations) are added, and the mixture shaken at intervals for 10 minutes, after which the slightly turbid supernatant liquid is decanted. This should only give a faint coloration with Nessler solution, and, if necessary, the Permutit treatment is repeated. One-tenth of its volume of Nessler solution is then added, the whole left to stand, and the clear solution decanted as required. Addition of 3 c.c. of solution is usually a suitable quantity. The perchloric acid decomposition method is used, with omission of perchloric acid for urine. For micro-determinations the proportions suggested are :—Conc. sulphuric acid, 70 c.c. ; water, 50 c.c. ; 20 per cent. perchloric acid, 20 c.c. ; anhydrous sodium sulphate, 15 grms. ; and copper sulphate, 1 grm. D. G. H.

Dissolved Oxygen Absorption-Time Relation of Activated Sludge Effluents. P. Gaunt and W. E. Abbott. (*J. Soc. Chem. Ind.*, 1928, **47**, 14–16T.)—The course of the absorption of dissolved oxygen by sewage or polluted water at 21° C. is usually represented, during the progress of the carbonaceous fermentation, occupying from 5 to 19 days, by Phelps's equation, $\log L\alpha/L + Kt$, where $L\alpha$ indicates the oxygen absorbed during such stage of the fermentation, L the oxygen requirement of the liquid at time t (days) and K a constant. The value of K may, however, sometimes vary from the average value, 0·11, to a greater extent than has been previously recognised. The above equation cannot safely be applied to reasonably purified effluents, in which nitrification, resulting in rapidly accelerated absorption of different character from that due to the earlier carbonaceous fermentation, normally commences before the third day; the rate of this accelerated absorption may be represented by a logarithmic equation. If certain simple assumptions are made, the rate of acceleration of this oxygen-absorption due to nitrification is such as might be anticipated from the action of nitrite-producing organisms developing by binary fission; the time elapsing between two successive fissions is found to vary from one to three days. T. H. P.

Organic Analysis.

Volumetric Determination of Organic Compounds completely oxidisable by Sulphuric and Chromic Acids. H. Cordebard and V. Michl. (*Bull. Soc. Chim.*, 1928, **43**, 97.)—Compounds containing acetic acid, or forming acetic acid on oxidation, which otherwise would be oxidised only with difficulty,

are completely oxidised, in the presence of silver nitrate, to carbon dioxide and water. The substance under examination (equivalent to 10 c.c. of 0·1 *N* acetic acid) is placed in a 250 c.c. flask provided with a reflux condenser, together with 10 c.c. of *N* potassium dichromate solution and 0·455 grm. of silver nitrate. This weight of silver nitrate is equivalent to 8 c.c. of *N* potassium dichromate, the amount theoretically required for 10 c.c. of 0·1 *N* acetic acid. Through the top of the condenser are now added 20 c.c. of concentrated sulphuric acid. Oxidation is complete after boiling for 30 minutes. The amount of chromium left is determined by titration with ferrous sulphate after precipitating the excess of silver with a solution of common salt, and from this the amount of chromium reduced (oxygen consumed) is readily obtained. The amount of oxygen used to oxidise all the carbon to carbon dioxide serves as a basis for determining the substance oxidised. Numerous substances have been examined by the method, and a table is given showing the theoretical amount of potassium dichromate and silver nitrate required, and the time necessary for complete oxidation. Among the compounds given are aspirin, acetanilide, phenacetin, veronal, antipyrine and urotropine. R. F. I.

Determination of Nitrogen Bases in Petroleum Oils. R. H. McKee and H. H. Parker. (*Ind. Eng. Chem.*, 1927, **19**, 1343-1344.)—Nitrogen bases are present to the extent of up to 15 per cent. in shale petroleum products. Comparative determinations with sulphuric acid, hydrochloric acid, and acetic acid, respectively, showed that acetic acid is the most suitable reagent for the absorption of nitrogen bases in petroleum distillates; it gives clearer solutions, dissolves more of the bases, and causes less polymerisation than does hydrochloric acid. Five c.c. of the oil should be mixed with 10 c.c. of glacial acid in a Babcock test bottle, the mixture then diluted with water to reduce the acid to 25 per cent. strength, and submitted to centrifugal action. Twenty-five per cent. acetic acid is then added so as to bring the oily layer into the graduated neck of the bottle, the mixture again submitted to centrifugal action, and the decrease in the volume of the oil read. Portions of the saturated and unsaturated hydrocarbons dissolve in the glacial acetic acid but are precipitated when the water is added. W. P. S.

Acid Values of Fats and Oils. A New Method for determining the Barium Values of Fats and Oils. W. L. Davies. (*J. Soc. Chem. Ind.*, 1928, **47**, 24T–26T.)—Acid values are preferably determined by a method whereby aqueous dilution has least effect on the titratability of the free acids, *i.e.* the acids may be titrated in alcoholic solution with an alkaline earth hydroxide (specially suitable for coloured fats), or in ethereal solution with any alkali after addition of excess of alkaline earth salt solution. The total and insoluble barium values of fats and oils were determined by a quick method, in which 5 grms. of fat are saponified as usual, an aliquot portion of the alcoholic solution is used for determining the saponification value of the fat, and this figure then used to calculate the total barium value (× 1·367). The alcohol is driven off from another portion, 800 c.c. of water added, and then standard acid to neutralise

free alkali and alkali formed by hydrolysis. After addition of 1 c.c. of 0·1*N* barium chloride solution, the excess of acid is back-titrated with 0·1*N* sodium hydroxide, successive c.c. of barium chloride solution added, and the liquid titrated until no further acidity is apparent on adding the barium chloride. The relation between acidity and barium chloride is plotted. The curve obtained demonstrates the conditions where hydrolysis of soluble barium soaps comes into action and the titration value of the excess alkali used for saponification, which is about 8 per cent. smaller than that found by titration in alcoholic medium. By producing the curves, the barium chloride value is obtained.

Fat or Oil.	Total barium value (A).	Insoluble barium value (B).	Soluble barium value (C).	B – (200 + C).
Linseed	262	239	23	+16
Cottonseed	262	255	7	+48
Rapeseed	243	223	20	+ 3
Coconut	347	338	9	+129
Palmnut	272	256	16	+40
Cod-liver oil	253	240	13	+27
Butter fat (1)	308	238	70	−32
Butter fat (2)	312	241	71	−30
Beef tallow (1)	267	195	72	−77
Beef tallow (2)	269	185	84	−99
Margarine fat	261	251	10	+41

The conditions for titrating the free alkali when determining the saponification value are also discussed. D. G. H.

Analysis of Brominated Cresols. J. Buxton and H. J. Lucas. (*J. Amer. Chem. Soc.*, 1928, **50**, 249–252.)—The bromide-bromate titration method of Francis and Hill (*J. Amer. Chem. Soc.*, 1924, **46**, 2499) was modified by substituting glacial acetic acid for alcohol. About 0·1–0·15 grm. of the phenol or substituted phenol is dissolved in 25 c.c. of glacial acetic acid, diluted with 50 c.c. of water, and standard bromide-bromate solution slowly introduced to give an excess of 2–4 c.c. ; after shaking and standing for 1 minute, 0·5 grm. of potassium iodide is added, and the liberated iodine titrated. In Robertson's total bromine method (*J. Chem. Soc.*, 1912, **107**, 902) a better end-point may be obtained by boiling the solution, to remove hydrogen peroxide, while still alkaline, with some of the iron salt needed for the end-point. Complete decomposition of the hydrogen peroxide ensues, and if more than 1 c.c. of *N* ferric nitrate solution is added, the ferric hydroxide dissolves very slowly after acidifying. Thirty c.c. of cold concentrated sulphuric acid are added to enough sample to give the equivalent of 9 c.c. of 0·1 *N* silver nitrate, the mixture being kept cold, and, after solution, 10 grms. of chromic anhydride are added at 0° C., and the flask connected with the absorption flask, containing 40 c.c. of *N* sodium hydroxide solution and 20 c.c. of 3 per cent. hydrogen peroxide, and the reaction flask carefully heated. After disconnection, 1 c.c. of *N* ferric nitrate is added, the mixture boiled, cooled,

acidified with 20 c.c. of 6 *N* nitric acid, 9 c.c. more of ferric nitrate added, and the titration carried out by adding 10 c.c. of 0·1 *N* silver nitrate, filtering, washing the precipitate and back-titrating precipitate and washings with 0·1 *N* potassium thiocyanate solution. D. G. H.

Quantitative Determination of Aromatic Aldehydes by Titration with a Solution of Benzidine. P. N. Van Eck. (*Pharm. Weekblad*, 1928, **65**, 82–84 ; *cf.* ANALYST, 1924, **49**, 105.)—A 0·1 *N* solution of benzidine is prepared from a solution of the required amount of reagent in 3 *N* acetic acid, by the addition of water. For the standardisation, benzidine sulphate is precipitated from 5 c.c. of the solution, after neutralisation to phenolphthalein with sodium hydroxide, by the addition of 10 c.c. of 0·1 *N* sulphuric acid. After it has stood for 1 hour, it is filtered off, washed and titrated with 0·1 *N* sodium hydroxide solution (phenolphthalein as indicator). Cinnamic aldehyde (in cinnamon oil), anisaldehyde, benzaldehyde, vanillin and heliotropine have been determined successfully as follows. To 200 to 300 mgrms. of oil, dissolved in 5 c.c. of glacial acetic acid (or 100 mgrms. in 5 drops of acid, in the case of vanillin), are added 1 c.c. of a solution of 1 c.c. of blood in 5 c.c. of glacial acetic acid. The solution is titrated with benzidene till a drop gives a blue colour when placed on filter-paper soaked in hydrogen peroxide (*cf.* ANALYST, 1922, **47**, 528). The coloured compounds produced during the titration of benzaldehyde or of vanillin may be taken as indicators of the respective end-points. J. G.

Colorimetric Determination of Nitrotoluene in Nitrobenzene. H. Muraour. (*Bull. Soc. Chim.*, 1928, **43**, 71.)—Five c.c. of the nitrobenzene are mixed with 20 c.c. of sulphuric acid. A mixture of 20 c.c. of sulphuric acid at 60° Bé, and 12 c.c. of nitric acid at 40° Bé is added to this, the temperature being maintained at about 40° C. After a few minutes the mixture is cooled in water to precipitate the *m*-dinitrobenzene and the dinitrotoluenes, and then extracted with ether. The ethereal extract is washed with water, then with sodium carbonate solution, and again with water, after which it is diluted to 200 c.c. with alcohol. Ten c.c. of this diluted extract, to which are added a few c.c. of a solution of *m*-dinitrobenzene, are treated with 10 c.c. of a saturated alcoholic solution of sodium hydroxide. The blue coloration obtained is compared with that produced by treating in the same manner a mixture of nitrobenzene and nitrotoluene of known composition. The test will detect less than 0·3 per cent. of nitrotoluene in nitrobenzene. The method is applicable to the determination of monoitrotoluene in the mononitrobenzene prepared from coal-tar. The red colour produced by the alcoholic soda solution with dinitrothiophene disappears in presence of the excess of soda. (The nitrobenzene prepared from Borneo oil contains no dinitrothiophene). R. F. I.

Volumetric Determination of Amino Nitrogen. K. Linderström-Lang. (*Comptes. rend. Trav. Lab. Carlsberg*, 1927, 17, No. 4, 1–17.)—In a mixture of pure amino acids, titration with hydrochloric acid in the presence of acetone

determines the number of strongly basic nitrogen-containing groups, but not those which are weakly basic or are exceptional in other respects. A list of the latter type (*e.g.* taurine and other amino-sulphonic acids) is given, and the theoretical basis of the above conclusion is discussed from a consideration of the relationship between the activity coefficients of the ions concerned. The preparation of naphthyl red (benzeneazo-α-naphthylamine), the indicator used in these experiments, is described for the first time. A mixture of 5 grms. of α-naphthylamine, 100 c.c. of absolute alcohol and 10 c.c. of 5 *N* hydrochloric acid was well shaken for 1 hour, 10 c.c. more of 5 *N* acid added, and the solution warmed to 60° C. After 1 hour a further 10 c.c. of 5 *N* acid and 200 c.c. of water were added, the mixture steam-distilled, and the green precipitate filtered off, washed with cold water and added to 100 c.c. of water and 20 c.c. of 5 *N* ammonia. The solution was shaken, warmed to 75° C., and the red precipitate filtered off, washed with cold water and recrystallised three times from 75 per cent. alcohol (large reddish-brown crystals, m.pt. 124° C.). The titrations were carried out for two colours of the indicator, orange and red (P_H, 5·1 and 4·8, respectively), and with 100, 150 or 200 c.c. of pure acetone for each 10 c.c. of liquid investigated. The control consisted of the acetone with 10 c.c. of water and 10 drops of a 0·1 per cent. solution of indicator in 96 per cent. alcohol, whilst 0·53 c.c. and 1·10 c.c. of 0·1 *N* hydrochloric acid were required to produce the two colours, respectively. The acid was then added to 10 c.c. of the solution to be examined till a red colour was produced. Acetone was then added gradually and titration continued in the clear solution till the colour of the control was obtained. All the amino acids examined (except lysine and histidine dichlorides, which crystallised out in all solutions except those which contained least acetone and most acid) remained in solution. Twenty mono-amino and di-amino acids and oxyacids, dipetides and amides were examined, and 100 per cent. of the total nitrogen was titrated in all cases except histidine (66·6 per cent.), asparagine, arginine, dipeptides and tryptophane (50 per cent.), creatine and guanidine (33·3 per cent.), urea (incomplete titration), and taurine (zero titration). The best results were usually obtained for the highest acetone concentration and the most acid control. Solutions of ammoniacal salts and buffers commonly used in enzyme reactions do not disturb the titration, but allowance must be made if hydrochloric acid is used to dissolve the amino acid originally. J. G.

Inorganic Analysis.

Detection and Determination of Metals by means of Ortho-hydroxyquinoline (Oxin). I. M. Kolthoff. (*Chem. Weekblad*, 1927, **24**, 606–610.)—The preparation and properties of *o*-hydroxy-quinoline (oxin) are briefly described. For use in the following determinations the commercial product is recrystallised from 50 per cent. alcohol. Its m.pt. is 75° C. and its solubility is a minimum at P_H 7·2, the iso-electric point. The methods described by Berg (ANALYST, 1927, **52**, 302, 431, 494, 611) and by Hahn and Vieweg (*id.*, 431) are criticised, and improvements suggested. For qualitative purposes copper, cadmium, zinc and

magnesium are best detected in the presence of an alkaline solution of Rochelle salt, whilst for nickel and cobalt the presence of acetic acid and ammonium acetate is recommended. Silver, mercury, bismuth, lead, aluminium, ferric iron, manganese and calcium have also been detected qualitatively. *Gravimetric determination.*—To about 150 mgrms. of alum in 150 c.c. of water are added 2 to 5 c.c. of 4 *N* acetic acid, and a slight excess of a 5 per cent. solution of oxin in alcohol (less than a week old). One c.c. of a 10 per cent. solution of ammonium acetate is then added, and, after 15 minutes on the water-bath, the solution is filtered on a weighed sintered-glass filter (G. 5–7). The precipitate of $Al(C_9H_6NO)_3$ is washed with water when cold, and dried at 110° to 120° C. until constant in weight. The maximum recorded error is 0·03 per cent. for 0·4 grm. of alum taken. The volumetric determinations are based on those of Berg (*loc. cit.*). *Zinc.*—To 50 c.c. of a solution of about 0·01 *M* zinc sulphate are added 5 c.c. of a 4 *N* acetic acid, 5 c.c. of 2 *N* sodium acetate solution and a slight excess of oxin solution. The solution is boiled, and filtered after 25 minutes, the washed precipitate dissolved in 10 to 15 c.c. of boiling *N* acetic acid, and the solution cooled and titrated with potassium bromate solution by Berg's method after the addition of methyl red and potassium bromide. The maximum error was −1·5 per cent. for 100 c.c. of a 0·0002 *M* solution of zinc. *Magnesium.*—To 50 c.c. of solution are added 2 c.c. of 2 *N* ammonium chloride solution and 0·5 to 1·0 c.c. of 6 *N* ammonia. It is important to add the oxin to the boiling solution, and the error is thereby reduced from +6 per cent. to less than −3 per cent. for a 0·00025 *M* solution of magnesium. The remainder of the procedure is similar to that described for zinc. In the presence of calcium the method of Hahn and Hartleb (ANALYST, 1927, **52**, 495) is recommended. *Calcium*—Fifty c.c. of a 0·005 *M* solution are boiled with 1 to 2 c.c. of 6 *N* ammonia, and the procedure described for zinc then followed. This involves an error of −1 per cent., but, if less than the stated amount of calcium is present, the precipitate should stand for an hour before filtration. Strontium interferes with this determination, but barium does not (*cf.* Hahn and Hartleb, *loc. cit.*). *Aluminium.*—Precipitation is carried out in the presence of 2 to 5 c.c. of 4 *N* acetic acid at 90° C., and the solution then boiled, and 10 c.c. of 2 *N* sodium acetate solution added. The washed precipitate is dissolved in 20 c.c. of 4 *N* hydrochloric acid and titrated. The error is −1 per cent. for 0·002 *M* solutions of alum, but for more dilute solutions the precipitate should be allowed to stand before filtration. J. G.

Solution of Sulphide Precipitates in acidified Hydrogen Peroxide. A. S. Komarowsky. (*Z. anal. Chem.*, 1927, **72**, 293–295.)—Salkowski's observation (ANALYST, 1916, **41**, 257) that metals dissolve more or less easily in acidified hydrogen peroxide, has been applied to sulphide precipitates, with a view to avoiding the fumes from nitric acid or *aqua regia* and the elimination of the excess of nitric acid from the solution. Mercuric sulphide is readily soluble in warm 4 *N* hydrochloric acid when 6 per cent. hydrogen peroxide is added, drop by drop. The sulphides of cobalt and nickel dissolve easily in 0·5 *N* mineral acids, and

even in acetic acid, with a few drops of 3 per cent. peroxide on warming. Calomel also is soluble in 2 *N* hydrochloric acid and hydrogen peroxide. W. R. S.

Gravimetric Determination of Copper as Thiocyanate. J. M. Kolthoff and G. H. P. v. d. Meene. (*Z. anal. Chem.*, 1927, **72**, 337-345.)—The method was found to yield very good results, either in cold solutions or at the boiling point. Neither hydrochloric nor sulphuric acid interferes at concentrations below 0·5 *N*. The excess of precipitant in the solution should be less than 0·5 *N*, otherwise a soluble copper complex is formed. Considerable ferric or ferrous salt may be present without interfering with the accuracy; with ferric salt, the bisulphite or sulphurous acid reduction is expedited by warming. Neither cobalt, nickel, manganese, zinc, nor arsenic interferes. Bismuth, antimony, or tin may contaminate the precipitate through hydrolytic dissociation; this is effectively counteracted by addition of tartaric acid. The authors collect the precipitate on a porous crucible, wash with small amounts of water until the disappearance of the thiocyanate reaction, and weigh after heating to constant weight at 110° to 120° C. W. R. S.

Titrimetric Determination of Trivalent Arsenic by Oxidation. F. G. Germuth. (*Amer. J. Pharm.*, 1927, **99**, 751-754.)—The following method is easily carried out, gives highly accurate results, and avoids the use of an unstable indicator. Of the substance containing arsenic in the arsenious state, 0·5 grm. is dissolved in warm 1 : 2 hydrochloric or, preferably, sulphuric acid; alkali arsenites, however, are best dissolved in 15 per cent. potassium hydroxide solution. The solution is diluted with 100 c.c. of water and then rendered slightly alkaline to methyl red by careful addition of 2 *N* potassium hydroxide solution; 4 c.c. of 5 *N* sulphuric acid and 2 drops of 0·2 per cent. potassium iodide solution are then introduced. The mixed liquid is diluted to about 200 c.c. and titrated with 0·1 *N* potassium permanganate, 1 c.c. of which corresponds with 0·00495 grm. of As_2O_3; the result is corrected for the minute amount of permanganate required to oxidise the potassium iodide used as catalyst. The potassium permanganate solution used is best standardised by means of Sörensen's sodium oxalate.

T. H. P.

Spectroscopic Determination of Platinum in Silver Alloys. H. de Laszlo. (*Ind. Eng. Chem.*, 1927, **19**, 1366–1368.)—Small quantities of platinum in silver beads may be determined by means of the spectrograph; standard pairs of silver-platinum electrodes are prepared, each containing a definite amount of platinum, ranging from 5 to 0·1 per cent., and a condensed spark between each set of electrodes is photographed with a quartz spectrograph under identical conditions for a definite time. The spectra so obtained and the number and wave length of the platinum lines visible in the spectrum are noted. A table is given showing the platinum lines in silver-platinum alloys, and reference is made to this table when dealing with an alloy of unknown composition. The accuracy of the method is about ±20 per cent. W. P. S.

Precipitation of the Ammonium Sulphide Group. J. Röll. (*Z. anal. Chem.*, 1927, **72**, 298–301).—The disadvantages of the use of a stock solution of ammonium sulphide are discussed. They are obviated if the filtrate from the ammonia precipitate is treated with a current of hydrogen sulphide for a few minutes. The precipitate may be filtered off after settling, and the filtrate is free from nickel. W. R. S.

Elimination of Phosphoric Acid by Lead Acetate in Qualitative Analysis. G. G. Kandilarow. (*Z. anal. Chem.*, 1927, **72**, 263–264.)—The ammonia and ammonium sulphide group precipitate is dissolved in hydrochloric acid, the solution (200 c.c.) freed from hydrogen sulphide by boiling, and dilute lead acetate solution stirred in, drop by drop, till no further precipitate forms; a slight excess is then added. This procedure precipitates all the phosphoric acid along with the lead chloride. The liquid is allowed to clear completely before filtration; the filtrate, containing iron, zinc, manganese, and alkaline earths is treated with ammonium sulphide. The sulphide precipitate is then dissolved in sulphuric acid, whereby lead is eliminated. The phosphate precipitate may contain some iron and aluminium, and possibly the whole of the chromium; hence it is advisable to carry out the test for chromium in a small separate portion before proceeding to remove the phosphoric acid. W. R. S.

Detection of Traces of Soluble Bromides. H. Baines. (*J. Soc. Chem. Ind.*, 1928, **47**, 11–13T.)—The following procedure is more rapid and sensitive than any previously suggested:—Two solutions are required:—(1) 30 c.c. of 10 per cent. sodium hydroxide, 20 c.c. of glacial acetic acid and 1 c.c. of 0·25 per cent. aqueous solution of the sodium salt of fluorescein are mixed and diluted to 100 c.c.; (2) an approximately 0·001 *N* aqueous solution of chlorine or sodium hypochlorite. To about 1 c.c. of the solution to be tested, containing 5 or 6 drops of solution (1), the chlorine solution is added, drop by drop, with shaking after each addition; if bromine is present, a pink colour appears, but excess of chlorine bleaches the liquid. If comparison is made with a blank test in which distilled water is used, potassium bromide in about 0·000002 *N* concentration gives a positive result. A modification of this procedure, in which a single solution is employed, is also described. The above method, which may be made roughly quantitative by colorimetric comparison, cannot be applied directly to solutions containing a large excess of reducing substances. T. H. P.

Potentiometric Titration of Boric Acid in the Presence of Certain Inorganic Salts. M. G. Mellon and F. R. Swim. (*Ind. Eng. Chem.*, 1927, **19**, 1354–1355.)—Whilst the presence of sodium, lithium, and calcium chlorides has some influence on the titration curve of boric acid, the most marked effect being produced by calcium chloride, a good end-point cannot be obtained, and, in view of the satisfactory results given by the addition of certain polyhydroxy organic compounds to the boric acid solution, the use of inorganic salts appears to be of no value. W. P. S.

Titration of Ammonium Molybdate. G. Hammarsten. (*Compt. rend. Trav. Lab. Carlsberg*, 1927, **17**, No. 5, 1–8; *cf.* Abstract, Linderström-Lang, p. 174).—The determination of phosphorus after precipitation asammonium phosphomolybdate according to Sörensen (*id.*, 1925, **15**, No. 10) may be shortened by means of the following method :—A clear, approximately 0·1 *N* alcoholic solution of potassium hydroxide was standardised by titration against 0·1 *N* hydrochloric acid by means of a control which consisted of 25 c.c. of carbon dioxide-free water and 50 c.c. of acetone (the usual " pure " commercial product) with thymolphthalein (1 c.c. of a 0·5 per cent. alcoholic solution) as indicator. The precipitated ammonium phosphomolybdate was well washed (to remove ammonium nitrate which titrates as nitric acid in the presence of acetone), dissolved in 5 c.c. of 1·0 *N* ammonia, and titrated immediately with the alkali. Care was taken to exclude atmospheric carbon dioxide. The presence of acetone displaces the indicator towards the basic side, and the ammonia is not titrated. The theoretical factor 0·111 is used for the conversion of c.c. of alkali to mgrms. of phosphorus for from 0·1 to 2·0 mgrms. of phosphorus, but for larger quantities the empirical factor 0·112 is used. Comparison with Scheffer's formol-titration method (back-titration with 0·1 *N* hydrochloric acid 1 hour after the addition of a known excess of 0·1 *N* sodium hydroxide solution and 10 c.c. of formalin to the ammoniacal solution) showed that the latter method was less rapid and less accurate, though cheaper. J. G.

Physical Methods, Apparatus, etc.

New Colorimeter Based on the Lovibond Colour System, and its Application to the testing of Cod-liver Oil, and other purposes. O. Rosenheim and E. Schuster. (*Biochem. J.*, 1927, **21**, 1329–1334.)—A new colorimeter is described in detail. The need for its construction arose during work on the colorimetric determination, by means of the trichloride of arsenic or antimony reaction, of the chromogen contained in cod-liver oil and other fats, which is assumed to be identical with vitamin *A*. Lovibond's tintometer was not suitable for the rapid matching necessary, owing to the transient nature of the blue colour developed, although it could be used to match the various shades of blue. Standard glasses are arranged in frames containing 10 each of the red, yellow and blue units, inside a wooden box, in such a way that, by means of knobs, they can be rapidly moved horizontally behind a window and below the cell (or test-tube) which contains the coloured solution to be matched. The frames contain units of each colour and tenths of units; thus there are 6 frames, of which, 2 contain blue glasses, one frame with a scale of blueness rising by increments of whole units from 0 to 9, and the second by tenths of units from 0 to 0·9 ; similarly 2 frames for units and tenths of units, respectively, of yellow and 2 for red. The seventh frame holds a blank space and 3 glasses, each having a tint of 10 units, and being blue, yellow and red respectively. There is a scale attached by which the tint of the matching glasses may be read. The application of the colorimeter to the testing of cod-liver oil is described. The apparatus should be useful in

colorimetric work generally and in biochemistry in particular. The differences in concentrations and thicknesses of layers of solutions is eliminated by this ; also the preparing of fresh standard solutions for comparisons. The variable accidental colour admixtures can be matched, but only the essential colour value of the reaction itself need be read. P. H. P.

Radio-Elements as Indicators. F. Paneth. (*Nature*, 1927, **120**, 884–886.)—The extreme sensitiveness of measurements of radioactivity by means of the electroscope may be used in the employment of radioactive substances as indicators. In general, such a substance is mixed with its non-active isotope, and, since isotopes have identical chemical properties, the non-active isotope may be determined in small quantities. The method is limited by the half-value period of the indicator, since elements detectable in small quantities have short half-value periods, and a list is given of suitable indicators for use with thallium, lead, bismuth, polonium, radon, radium, actinium, thorium and protactinium. For example, the solubility of lead chromate may be determined by activating the salt with a known quantity of thorium *B*, when 0·001 mgrm. of lead may be measured electroscopically. Thorium *C* is used in conjunction with bismuth. The method has been applied to the proof of electrolytic dissociation, to the measurement of the surface of powdered adsorbents and the proof that adsorption occurs in a unimolecular layer, to the detection of volatile metallic hydrides, and the determination of alloy formation, rates of evaporation, solution and diffusion, and the storing up of certain substances (*e.g.* bismuth) in the organs of the body. J. G.

Protective Tubes for Thermo-couples for Determining Heat Penetration in Processed Foods. K. L. Ford and A. G. Osborne. (*Ind. Eng. Chem.*, 1927, **19**, 1345–1346.)—When thermo-couples are used for heat penetration determinations, with the end of the couple exposed to the heating medium, the conductivity of the protective tube affects the accuracy of the readings. It is shown that bakelite is a good substitute for glass or metal tubing, since it possesses a lower heat conductivity than metal and a greater resistance to failure than glass. W. P. S.

Porcelain Hot Water Funnel. (*Chem. Ztg.*, 1928, **52**, 103.)—The porcelain funnel described is similar in form to the usual laboratory article made of copper, except that the stem is longer. The walls of the funnel are hollow and provided with outlets through which steam or hot water at any desired temperature can be circulated. The angle of the funnel is exactly 66°, to ensure that a glass funnel shall be in close contact with the hot porcelain. It can be obtained in three sizes from Messrs. Rosenthal & Co., Werk Marktredwitz. R. F. I.

Colour Glass Standardisation. D. B. Judd and G. K. Walker. (*Oil and Fat Ind.*, 1928, **5**, 16–26.)—Examination of 129 Lovibond red glasses, with scale markings between 7 and 8, has shown that two of these glasses having the same engraved number may differ in depth of colour by an amount corresponding with more than one Lovibond red unit. The mean degree of inaccuracy for all the glasses amounts to 0·205 unit. T. H. P.

Reviews.

A DICTIONARY OF APPLIED CHEMISTRY. By Sir EDWARD THORPE and eminent contributors. Vol. VII. Thalenite–Z, with index to the complete work. London: Longmans, Green & Co., Ltd. Pp. 765. Price 60s. net.

The publication of the seventh volume of "Thorpe" brings to completion the new edition of this great work, which embraces the whole field of applied chemistry, and the comprehensive nature of the Dictionary renders it indispensable to chemists in every sphere. To the chemist seeking information on his own particular subject a work of this kind makes, possibly, small appeal, as he will have access to literature dealing with the subject in greater detail than is possible in the book under review. Few libraries, however, are sufficiently well equipped to supply information on applied chemistry in all its branches, and herein lies the unique virtue of *Thorpe's Dictionary*, as the chemist requiring information on a subject outside his own sphere will find here an authoritative article written by an expert, and in the event of fuller details being required the references to the original literature will suffice to supply the necessary clue.

The article in the volume under review which is of the greatest general interest is that on Water, and this subject is treated at considerable length, the whole occupying a space of over 100 pages. To Dr. Briscoe has been allotted the difficult task of dealing with the chemical and physical properties, and in the space at his disposal he has written an admirable article describing the more important physical properties of water, a notable feature being the excellent collection of tables giving the most trustworthy determinations of the constants involved.

To write fully on the chemical properties of water would require a volume in itself; so the author gives only a brief outline of the theories of solution and their various modifications, and wisely refrains from expressing any view as to the theory which he personally favours; under "Hydrolysis," however (p. 364), the statement that "The neutrality of such a solution (say, potassium chloride) is quite compatible with extensive hydrolysis to yield equivalent amounts of acidic and basic solutes of the same type" will not meet with universal approval.

"Water in its Economic and Sanitary Relations" is treated by Professor P. F. Frankland, who discusses the characteristics of the various categories of water used for drinking purposes, their liability to contamination, and the significance to be attached to the analytical data obtained in their examination.

The chemical and bacteriological methods employed in the analysis of water are described in detail, and due attention is paid to the beneficial effects of storage, sterilisation, and filtration on the organic purity of drinking supplies. The factors influencing the action of water on lead are adequately treated, but one would have liked to learn the views of the writer with regard to its action on zinc, and the consequent effect of zinc on the health of the consumer, a subject which has hardly received the attention which it deserves. The statement occurs on p. 374,

that, "It has been estimated that about twelve millions of the inhabitants of Great Britain are supplied with water for domestic purposes from shallow wells," an estimate which appears to the reviewer to be somewhat high. The subject of "Water" is concluded by an excellent summary on "Water Softening" containing a description of the various plants in use for this purpose.

Under "Toxins and Anti-Toxins" Professor Hewlett discusses the nature of the poisonous substances elaborated by bacterial agency, and describes the modern investigations made to determine the precise composition of the toxins produced by the diphtheria, tetanus, anthrax, and tubercle bacilli, respectively.

The nature and mechanism of action of snake venoms is briefly outlined, and the article is concluded by an exceedingly able review of the remarkable reactions occurring in the animal organism when small doses of foreign proteins are introduced into the blood.

Sir Frederick Gowland Hopkins gives an account of the present state of knowledge of the vitamins. The chemical constitution of these elusive compounds is not discussed, as, to quote the author's own words, "To deal seriously from a standpoint strictly chemical with substances which have never been isolated in a pure condition is, of course, impossible."

The article furnishes an excellent summary of the distribution in nature of the known vitamins and their significance in animal nutrition, whilst the various methods employed in their concentration are outlined. The article is written in a most lucid and interesting manner, and the only criticism which can be made is that the subject could well have been treated at greater length, in view of the supreme importance of the vitamins to the welfare of mankind. As, however, the subject is necessarily treated from a chemical standpoint, the critic is disarmed by the author's opening statement, and the remedy for our lack of precise knowledge lies with the chemist.

Professor Turner contributes the sections on tin and zinc, which deal with the occurrence in nature of these metals, their extraction from their ores, and the use of the metals and their compounds in the arts, whilst adequate attention is paid to the chemistry of the elements and their compounds. The author has used wise discretion in condensing into a reasonable compass the vast amount of information available without omitting anything of fundamental importance, which is perhaps the most difficult part of the task involved.

Toluene and Xylenes occupy, respectively, 83 and 38 pages of the volume under review, and the writers, Drs. Rowe and Davies, have included an enormous number of the known derivatives of these compounds in the respective sections, with copious references to the original literature. The labour involved in the compilation of these articles must have been very large, and the writers, in bringing together this most imposing array of compounds, have rendered useful service to research workers in certain branches of organic chemistry. The reviewer considers, however, that many will share his opinion that the relative importance of these compounds is incommensurate with the space allotted to them. In making this criticism a great deal of sympathy is felt for the editor and contributors,

as the task of selecting certain organic compounds for inclusion and rejecting others is one of extreme difficulty, but, at the same time, it would appear that if all compounds of equal importance to those of toluene and the xylenes were to be treated at similar length the bulk of this publication would be unduly great, and the continual increase in the number of known organic compounds renders the more necessary a judicious elimination, analogous to the modern vogue of "slimming," if this work is to be kept within reasonable dimensions.

The volume is concluded by an index to the whole work by Miss Micklethwait, which greatly enhances the utility as a work of reference, as many of the articles in the dictionary are of sufficient length to require an index, and, moreover, many subjects are treated under different headings in various parts of the work. The indexing appears to have been excellently done, and bears evidence of having been carried out with meticulous care by an experienced hand.

It has been the privilege of the writer to review each volume of the new "Thorpe" as it appeared, which has involved a careful study of a considerable proportion of the contents, and, as a result, one cannot fail to appreciate the very great value of the work as a whole, which constitutes a library in itself and is unique in the literature of chemistry.

GEO. R. THOMPSON.

ATOMIC FORM, WITH SPECIAL REFERENCE TO THE CONFIGURATION OF THE CARBON ATOM. By EDWARD E. PRICE. 2nd edition. 217 pp. Appendix and index. London: Longmans, Green & Co., Ltd. Price 7s. 6d.

In this interesting volume the author sets forth his views for correlating the actual crystalline forms of molecular substances with the atoms of which they are composed, based on the assumption that the atoms themselves have geometric, *i.e.* crystalline, forms.

He submits that all the elements may assume crystalline form, that there are those who believe that all matter is crystalline, even gases and such substances as rubber, cellulose, soaps and even organised materials like bamboo, and that therefore it would be expected that crystalline compounds had been built up from crystalline atoms.

His views are, at the moment at all events, unorthodox, but he points out that it is not easy to reconcile modern theories involving negatively charged electrons revolving round a central nucleus with the power of forming sharp-edged smooth-faced stable crystal masses, especially as electricity is not known to play any part in their formation.

Further, if, as is generally assumed, all the atoms are made up of one general basic material, it is difficult to account for the diversity in character of the different elements, especially in the case of those elements having nearly similar atomic weights. If, however, the form of the atom enters into the problem, a more obvious explanation is at hand.

Mr. Price suggests that the geometrical form and the size of the atoms are mainly responsible for their characteristic properties. Valency is explained by

the number of available faces for stable attachment between atoms which are brought into contact; variable valency to "atomic movements and ethereal pulses"; monovalent monatomic atoms of the Helion-Argon type would have faces so numerous, and therefore so small, compared with the mass of the atoms, that stable attachment would be impossible, whilst, on the other hand, multivalent atoms would have larger faces and therefore be more capable of stronger combination.

The application of these principles to the forms of carbon itself and to a number of mainly organic compounds occupies the greater part of the book, as the structure of these is so much better known than is the case with inorganic substances.

It was his first study to envisage a geometrical solid which would represent the carbon atom. Carbon, being tetravalent and having four equal valencies, suggests a tetragonal form with four equal faces—the "carbonoid." The great stability of the benzene ring makes it essential that six such carbon atoms could combine to form a figure having the needed stability and symmetry—the "benzenoid." Two carbon atoms conjoined form the "ethyloid" which would satisfy the requirements of the paraffin series.

Space does not permit of going further into details, but it is enough to say that Mr. Price, with great ingenuity, shows how aggregates of carbonoids and benzenoids might square with the actual structure of the allotropic forms of carbon; how strings of carbonoids would fit in with the series—C_nH_{2n+2}; how his theory throws light on the phenomenon of steric hindrance, on the connection between isomerism and optical activity, and on the condensed ring formation of substances like anthracene, naphthalene, etc.

The appendix contains a short history of the early theories of atomic form; also full directions for making models of the *carbonoid* so that those interested can visualise, in three dimensions, the structural formation which the ordinary constitutional formulae are meant to express.

The modern theories of the constitution of matter are so abstruse and so largely derived from mathematical considerations that the common man can hardly grasp the connection with the solid things around him.

Mr. Price's ideas are, in comparison, delightfully simple and concrete, make less demand on the imagination, and leave us still with a comfortable and stable earth on which to live, and move, and have our being.

CECIL H. CRIBB.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By A. F. HOLLEMAN (issued in English in co-operation with HERMON CHARLES COOPER). 7th edition. Pp. x + 541. London: Chapman & Hall. 1927. Price 17s. 6d. net.

The preceding edition of this well-known text-book was reviewed in THE ANALYST (1922, 47, 413) by Professor Allmand, with whose estimate, broadly speaking, the present writer agrees. The preface states that important new chapters have been added on catalysis, colloids, acidimetry, isotopes, definition of elements, atomic structure, and the iron-carbon system. These chapters give

a concise, readable *résumé* of the progress of discovery to within the past year. Whilst particular attention is paid in nearly every text-book to a presentation of the newest important facts and theories of physical chemistry, the same cannot always be said of the progress of metallurgical knowledge. In the present work (p. 368) the smelting of oxidised copper ores is stated to be "very simple," but the metallurgy of sulphide ores is "much more complicated." Such was the case until matte-smelting, either in the blast or reverberatory furnace, coupled with the production of blister copper from the matte in the converter, revolutionised copper smelting. As a matter of fact, the text-matter is limited to a very brief account of the now defunct Welsh process. For the precipitation of gold from cyanide liquors (p. 382), electrolysis is stated to be employed. Unless the writer is quite mistaken, zinc dust precipitation is still almost universally applied.

The book contains a number of misprints, mostly of the obvious type. Perhaps the most serious is the adjective "non-sulphurous" (p. 368) applied to copper ores amenable to flotation; evidently "sulphurous" was intended.

As is often the case with works by American authors or translators, the text is apt to suffer from a certain vagueness, ambiguity, or lack of precision caused by laxity in the application of grammatical rules or by careless construction of the sentence. Such style the experienced professional man may tolerate for the sake of information by an authority on some special subject; on the other hand, a college text-book, such as this, intended to help the student in acquiring accurate fundamental ideas on any branch of science should be written with the utmost regard to clearness and logic.

W. R. SCHOELLER.

THE THEORY OF EMULSIONS AND THEIR TECHNICAL TREATMENT. By WILLIAM CLAYTON, D.Sc., F.I.C. Foreword by Professor F. G. DONNAN, C.B.E., M.A., Ph.D., D.Sc., F.R.S. 2nd edition. Pp. x + 283, with 42 illustrations. London: J. & A. Churchill. 1928. Price 15s.

The present volume is a new, enlarged, and completely revised edition of the earlier work by Dr. Clayton, entitled: *The Theory of Emulsions and Emulsification*, which appeared in 1923. In addition to modifications in the theoretical treatment which have been rendered necessary by the amount of new and important work which has been published in the last five years, the author has likewise recast certain of the later portions so as to lay greater stress upon the scientific applications of emulsions and emulsification to numerous technical and industrial operations, many of which are of first-rate importance. To workers in such diverse fields as petroleum technology, rubber, soap manufacture, dairy chemistry, the margarine industry, and edible and medicinal food preparations, the new edition of this work will be of inestimable advantage and profit.

Besides the changes referred to, the author has laid all interested in this wide field under an obligation by bringing up to date and systematising an extensive bibliography, as well as by his inclusion, as a third appendix, of the principal publications dealing with the separation of technical emulsions particularly

crude oil-field emulsions. Dr. Clayton has been fortunate in being able to include an account by Professor Ramsden—to whom the book as a whole is dedicated—of the "theory of emulsions stabilised by solid particles," a contribution to science which has been long awaited, and of which only very partial and inadequate accounts had hitherto been available.

The first edition of Dr. Clayton's work was soon recognised as the most authoritative account which had up to that time appeared in any language upon the field of emulsions, and it was obvious from the first that further editions would be called for. In welcoming the present volume, one can hardly say more than that it is a worthy successor to the first. In fact, it is *the* standard work on the subject and is likely to retain this enviable position for many years. It represents one of the happiest combinations of the purely scientific and the technical with which the writer is acquainted. It is a book which without exaggeration must be recognised as really indispensable alike to the academic and to the industrial chemist—whatsoever his field may be.

W. C. M. LEWIS.

REAGENZIEN UND NÄHRBODEN. Eine Zusammenstellung der wichtigsten und zweckmässigsten Vorschriften für die Laboratoriumspraxis. By E. BÖHM and K. R. DIETRICH. Pp. 375 + vii. 1927. Berlin: Urban und Schwarzenberg. Price 18*m*.

This book is a collection of over two thousand formulae for reagents and culture media. Without entirely neglecting the requirements of other practice it, in effect, selects bacteriology, general microscopy and pathological chemistry for preferential treatment. The relative attention to different interests is evident from the numbers of recipes in each section: general purposes 190, alkaloids 68, food analysis 53, alcohols and alcoholic liquids 52, water analysis 47, paper, wood and cork 22, clothing fabrics 6, turpentine, gums and essential oils 18, volumetric and gas analysis 134, urine 318, faeces 11, blood 18, gastric contents 24, stains for microscopical (bacteriological, botanical and physiological) investigations 600, fixing liquids 132, impregnating, embedding and clearing agents 68, preservatives and mounting media 33, culture media 185, cleaning preparations, disinfectants, varnishes, frigorifics, metal-plating and battery fluids 49.

The subjects most productive of devices appear to be glucose and albumin in urine, for which there are, respectively, 107 and 81 tests. Among stains for microscopy, there are 57 containing carmine and the same number with haematoxylin, while as many as 15 eosin-methylene blue "double stains" are described.

To so great an extent are reagents identified with authors that an index of the latter contains 1,138 names. There are several instances of the same reagent recurring under different names.

Food chemistry gets scant notice. Eleven formulae differentiate between raw and heated milk, 5 distinguish cows' and human milk, 7 detect formalin, 5 identify sesame oil, and 25 others populate sparsely a huge field.

Errors are very few and arise from misconceptions rather than want of care.

Thresh's reagent is given the composition: potassium iodide 1·8 grammes; hydrochloric acid 45 c.c.; *Liq. Bismuthi B.P.* 30 c.c. English text-books differ greatly in their versions of this, and wide variations do not destroy the effect; but, as given in *Year Book of Pharmacy*, 1880, p. 50, the true one is:—Liq. Bismuthi, B.P. j Pot. Iodid. 3iss.; Acid. Hydrochlor. 3iss.; mix.

The effect of another potassium bismuth iodide reagent for alkaloids, that of Mangini, is given as "brown precipitates." It is claimed (ANALYST, **7**, 180) for this test that it distinguishes many of the alkaloids, one from the other, by the gradations of red and yellow colours.

"Allen's Reagent" proves to be a device of A. H. Allen for discriminating between glucose and most of the other Fehling-reducing substances found in urine, and is valuable in the extreme, but too little known. It consists in boiling 7 to 8 c.c. of urine, adding 5 c.c. of the copper sulphate part of Fehling's solution, followed, when partly cooled, by 1 to 2 c.c. of a saturated solution of sodium acetate rendered feebly acid with acetic acid. Then (to quote from the original paper (ANALYST, 1894; **19**, 180), and also from A. H. Allen's *Chemistry of Urine*, 1895, where the same words are used) "the liquid is next filtered. To the filtrate, which will have a bluish-green colour, 5 c.c. of the alkaline tartrate mixture used for preparing Fehling's solution is next added, and the liquid boiled for fifteen to twenty seconds." The book under notice substitutes, in place of the final addition, 5 c.c. of concentrated aqueous Rochelle salt solution.

The section on culture media is well arranged and supplies the requirements of many special branches of bacteriology. Media specially devised for colon, typhoid, dysentery, diphtheria and tubercle bacilli, and for yeasts, soil bacteria, acetic and lactic bacteria, cholera vibrio, sarcinae, gonococci, streptococci, pneumococci and spirochaetes, are included. The only noticed difference in formula to what we are accustomed is that "peptone water" contains exsiccated sodium carbonate (0·2 per cent.) and potassium nitrate (0·01 per cent.) in addition to peptone and salt. Such further ingredients would make the article unsuitable for some purposes for which it is customarily used.

Three indexes, devoted respectively to the ingredients, the authors, and the objects of the tests, are well arranged.

So many types of peculiarly specialised work are represented in this book that its compilation must have entailed much hard work combined with exceptional knowledge. The authors have done this with generous effort and have produced a volume of great utility.

WILLIAM PARTRIDGE.

THE ELEMENTS OF VEGETABLE HISTOLOGY. By C. W. BALLARD. 2nd edition. London: Chapman & Hall. 1927. Price 16s. net.

The aim of the author of this book, originally published in 1921, is to provide an introduction to the study of plant histology for students whose future work will include the microscopic examination of foods and drugs. Introductory chapters deal with methods of preparing, staining, and mounting specimens, with the use

of the microscope and with the chemical reactions of plant tissues. The main part of the book is devoted to descriptions of the cell, of plant tissues, and of the structure of root, stem, leaf, flower, fruit, and seed. An appendix includes formulas for reagents, data of microscopic objectives, etc.

It cannot be said that the arrangement is satisfactory. The chapter on microscopic accessories, which includes the use of micrometers and the camera lucida, is placed at the end of the book, whilst the chapter on the microscope is at the beginning. The occurrence and appearance of starch grains, fats, crystals, and so on, are described in Chap. XII, and one has to turn to Chap. IV to find the chemical tests for them. The descriptions of the cells in various tissues must be sought, not only under the appropriate headings, but also in the chapters dealing with the structure of the various organs.

Nor is the information imparted always satisfactory. An elementary student would find it difficult to make satisfactory stained sections from the instructions given here. There is no hint, for example, of the necessity of straightening paraffin sections after they have been floated on water; the statement is made that "Melting of the paraffin during this operation (that of drying the slide after the section has been floated on) is of no consequence." After removing the paraffin with xylol the student is directed to get rid of the xylol by evaporation and then to place the slide in 95 per cent. alcohol. Apart from a note in the appendix on Schulze's reagent, no instructions seem to be given for maceration.

In the chapters on reactions and staining there are some important omissions. Sudan III is given neither as a reagent for oil nor as a cuticular stain. Ruthenium red is not mentioned as a pectin reagent. Aniline hydrochloride is not given as a wood reagent, though it is the most convenient. No mention is made of the methods which have been worked out by Senft and Mangham for the application of the osazone reactions to sections of plant tissues.

Apart from this, the systematic portion is, for the most part, written in a concise fashion and may serve to give the student a general idea of plant structure. But there are inaccuracies. "Hydrocarbons—This group includes the vegetable fats and oils"; "The nourishing material or endosperm is stored within the embryo, and these are termed exalbuminous seeds"—are examples.

The illustrations, except those borrowed from another text-book, are too often crude. Despite a note that in drawing cells, they should be surrounded by a wall of definite thickness, the use of a single line—which may of course be quite legitimate—is frequent in diagrams, to which it gives a grotesque appearance, as in transverse sections of epiderms, where the cells are represented by isolated outlines of their cavities. Page 128 is entirely taken up with diagrams of collenchyma, not one of which is characteristic. A diagram of a plant cell is given in which the nuclear, vacuolar membranes and the cell wall are represented each by a single line of the same thickness.

The price for a small 8vo volume of 289 pages and of an elementary nature seems excessive.

MACGREGOR SKENE.