MAY, 1931. Vol. LVI., No. 662.

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, April 1st, the President, Dr. J. T. Dunn, being in the chair.

Certificates were read for the first time in favour of:—George Brown, A.I.C., Charles Louden, B.Sc., A.I.C., Charles Percy Money, B.Sc., F.I.C., Martin Priest, F.I.C., Arthur Goodyear Simpson, M.A., and Gerrish Smith.

Certificates were read for the second time in favour of:—K. N. Bagchi, B.Sc., M.B., D.T.M., William Nelson Bradshaw, B.Sc., Adrian Joseph Clifford Lickorish, F.I.C., Ernest Grenville Purser, B.Sc., A.I.C., and William Waddell Robson.

The following were elected Members of the Society:—Cecil Chilvers, B.Sc., F.I.C., Jack Hubert Hamence, M.Sc., A.I.C., Cecil John House, B.Sc., A.R.C.Sc., F.I.C., and Henry George Rees, B.Sc., A.R.C.Sc., A.I.C.

The following papers were read and discussed:—"Carbon Monoxide Poisoning: Its Detection and the Determination of the Percentage Saturation in Blood, by means of the Hartridge Reversion Spectroscope," by R. C. Frederick, A.I.C.; "Experiments on the Hardness of Fats," by H. M. Mason, M.Sc., F.I.C., and G. Walsh, B.Sc., A.I.C.; "A New Process for the Determination of Small Amounts of Bromide in Chloride," by B. S. Evans, M.C., Ph.D., F.I.C.; and "The Use of Bromine as a Reagent in the Determination of Alkaloids," by S. G. Walton and R. G. O'Brien.

NORTH OF ENGLAND SECTION.

A JOINT meeting of the Section with the Yorkshire Analysts' Association was held at Leeds on April 25th.

The following papers were read and discussed:—"Some Aspects of the Bacteriological Examination of Water," by W. G. Carey, F.I.C.; and "River Pollution Prevention Problems," by J. W. H. Johnson, M.Sc., F.I.C. A discussion on Sandalwood Oils was introduced by J. R. Walmsley, F.I.C.

There was an attendance of thirty, including the President (Dr. J. T. Dunn). The Chairman (Mr. C. J. H. Stock) presided.

NORTH OF ENGLAND SECTION.

Address of the Chairman (Mr. G. D. Elsdon),

Delivered at the Meeting held at Manchester, February 14th, 1931.

At the meeting of the Committee of this Section, held on December 6th, 1930, it was decided that the Annual Meeting should include among its agenda an address to be given by the Chairman. I was very strongly in favour of this suggestion being put into effect during succeeding years, but just as strongly opposed to it during the present session. There were two reasons, however, which caused me to consent. Firstly, I thought that it might be a very favourable opportunity to place on record the circumstances surrounding the formation of this section; and, secondly, that it would form a precedent for future holders of the office who would, from year to year, be able to give helpful and stimulating addresses to the members.

With the approval of the Council, a letter was sent on May 13th, 1924, by Mr. S. E. Melling, to all members of the Society living more than about 30 miles north of Birmingham, in order to see what demand there was for a North of England Section. The response to this letter was so encouraging that an extraordinary General Meeting of the Society was held in the rooms of the Manchester Literary and Philosophical Society on November 7th, 1924, at which very many London members were present. At this meeting it was resolved that a North of England Section should be formed, and I hope I may be forgiven for adding that I shall always remember with pride and pleasure that I acted as the first Hon. Secretary of the Section, although only in a temporary capacity. The first meeting of the Section was held on Saturday, February 14th, 1925, in the Milton Hall, Manchester, at which the rules of the Section were adopted, after full discussion, and Prof. W. H. Roberts, Messrs. J. Wood and H. T. Lea were appointed Chairman, Vice-Chairman and Secretary, respectively, together with a Committee consisting of Messrs. Elsdon, Hurst, Melling, Ross, and Stubbs.

The first ordinary meeting was held on Saturday, June 27th, 1925, at the Queen's Hotel, Leeds, and from that time the Section has continued to be successful. The meetings have always attracted an excellent attendance, considering the comparative smallness of our numbers and the very considerable distances which many of the members have to travel. This success has been due to two main reasons, the help and encouragement which has always been given by the Council of the Society, and the keenness of the members themselves. I feel that each one of those who have attended our meetings can take to himself some share of the success which has been attained. That this success has also been a source of advantage to the members themselves I think no one will deny. By mutual, helpful criticism, by debate, by opportunities of social intercourse, we have widened our outlook and been helped in the solution of our difficulties. I would here urge those of our younger members who may have such difficulties to bring them freely before the meetings or before other members privately, in the full knowledge that those who have special information and long experience will be glad to lend a helping hand to those not so happily placed.

The past session, which is brought to a close by this meeting to-day, has been one of the most successful of all. We have now held five meetings during which seven original papers have been presented and two discussions on general topics have been introduced, quite apart from a considerable number of smaller points which have been raised during the progress of the meetings. It is a most fitting

finish to an excellent session that our Secretary has been able to prevail upon Prof. T. P. Hilditch to give us the benefit of papers by himself and his co-workers, which we are shortly to have.

Apart from the general progress which has taken place in our profession during the year, there is one point of special interest both to Public Analysts and to works' chemists and manufacturers, on which perhaps I might say a few words. I refer to the publication of a series of Jam Standards by the Food Manufacturers' Federation. In certain quarters these standards have been subjected to a considerable amount of adverse criticism, particularly on the point that the Society has taken some part in the negotiations. This is not the place to engage in any controversy concerning the merits or demerits of the suggestions put forward. Scarcely anyone, I imagine, will claim that they are beyond criticism; but one can, at least, say that the decisions were reached after very full and careful examination of all the points which are at present being brought against them, and that they are the expression of a sincere desire to grapple with a most difficult situation.

The question of Food Standards is one which is surrounded by difficulties on every side. Only a few years ago the majority of Public Analysts and nearly all manufacturers were definitely opposed to them. More recently there has been a change in outlook, and the idea is gradually gaining ground. In my own opinion the institution of standards will do good. It should certainly remove from the market all those articles which are definitely inferior, whilst those makers who have gradually built up a trade in a high-class article, based upon a reputation gained over many years, are not likely to risk decrease in or loss of their trade by lowering their standard to any minimum which is proper. It may be argued that neither the Society nor a combination of manufacturers is suitable for such work, and this may be true, but until such time as our rulers find time to take this subject to themselves it would appear that our energies might more reasonably be given to the making of constructive proposals, than to the adverse criticism of those who are making every effort to improve the present state of our food supply.

Of special interest to many of our members was the Cheese Bill which was considered by Parliament during the year, but which was unfortunately crowded out owing to pressure of other business. Almost everyone approved of this Bill in principle, although some of the standards suggested were open to criticism. It is to be hoped that opportunity may be given during the coming year for a re-introduction of a similar Bill, and that it may have a more successful career than the former one.

The subject of milk continues to occupy a large proportion of the time of many of our members. It is now 30 years since the publication of the report of the Departmental Committee, but the passage of time has not served to settle the differences of opinion which the report induced. Among much that seems to be controversial there must be, at least, some points upon which even our most sceptical members are in agreement, and it seems to me to be of the utmost importance that these points of agreement should be thoroughly explored, so that each member may know exactly where he agrees with and differs from, the remainder of his colleagues.

In this connection there would appear to be a somewhat lamentable lack of desire upon the part of Government Departments to avail themselves of the assistance which could be afforded to them by our Society. Two important points have recently come to my knowledge. The Minister of Agriculture has intimated that an Inter-Departmental Committee has asked Dr. Tocher to deal with the available milk data along the lines of his "Variations in the composition of milk,"

and has asked certain persons to send any data which they have to Dr. Tocher. The Empire Marketing Board has apparently set up a committee dealing with the freezing-point of milk, and has a report ready for publication. They have also asked certain persons to use the apparatus which they have designed to determine the freezing-point of milks to be supplied. Neither the Ministry nor the Board has seen fit to approach the Society as a whole, and it would appear at least remarkable that the majority of those who are most intimately connected with these subjects should be in complete ignorance of the action which is being taken.

It would be impossible for me to close these few words without giving some expression of my appreciation of the honour which you have paid me in electing me as your Chairman for the past year. As far as I know I have only one qualification for the office, a great love for our profession together with a keen desire that the Society and our Section may prosper. In your kindness you have magnified this to such an extent that you have paid me this honour, an honour which I am not likely to forget. I feel that the year has been a most successful one, a fact of which I can speak without diffidence, as this success has been so largely due to the unremitting efforts of our most excellent Honorary Secretary, Mr. J. R. Stubbs, and the unqualified support which the members themselves have given in the orderly conduct of meetings.

I should further like to express the satisfaction with which the committee regard the support which the Section has had from its younger members. Its future must largely rest in their hands, but, judging by the enthusiasm which they are now showing, we need have no fear for its continued success.

Deaths.

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

G. J. Alderton, on March 10th, 1931.

M. Wynter Blyth, on March 23rd, 1931.

The Determination of Laevulose in Sweetened Condensed Milk.

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

For the purpose of finding the proportion of true milk constituents in condensed milk, it is desirable that satisfactory methods should be available for determining the amounts of any sugars other than sucrose or lactose. For example, the determination of any laevulose that might be present would be of value. Appreciable amounts of this sugar would come either from invert sugar intentionally added or from the inversion or breakdown of sucrose in the sample after manufacture; and in either case, the analysis of the sample upon ordinary lines, showing only lactose and sucrose, would lead to an erroneous interpretation of the results. The present

paper describes a rapid method for the direct determination of laevulose in con densed milk.

The method depends essentially upon a principle originally due to Kolthoff (*Chem. Weekblad*, 1922, **19**, 1; ANALYST, 1922, **47**, 301), and recently elaborated by Kruisheer (*Z. Unters. Lebensm.*, 1929, **58**, 268). This consists in the oxidation of aldose sugars—in this case lactose, and dextrose if present—with alkaline iodine solution, and subsequent determination of the unchanged laevulose by copper reduction. We have modified Kruisheer's procedure so as to secure the conditions most satisfactory for condensed milk. Other slight modifications would no doubt enable the method to be adapted for other products.

To avoid the interference of sucrose in the copper reduction which occurs with Fehling's solution, Kruisheer used the copper solution of Luff, a citrate-carbonate reagent, the use of which has been revived by Schoorl (*Z. Unters. Lebensm.*, 1929, **57**, 566; *Brit. Chem. Abst.*, 1929, B, 952). This solution is reduced by sucrose to a negligible extent.

In determining the amount of copper reduced, we have departed from Kruisheer's procedure, which depended on a volumetric determination of the unreduced copper. It seemed more desirable to determine the cuprous oxide itself, and for this purpose we have adopted the convenient and delicate process of Shaffer and Hartmann (*J. Biol. Chem.*, 1921, **45**, 349; *J. Chem. Soc.*, 1921, **120**, ii, 417), which does not require any separation of the cuprous oxide from the excess of cupric salt.

The stages of the process, then, are as follows:

(*a*) *Preparation of the serum.* This is carried out according to either of the methods described in the Society's "Report on the Determination of Sucrose" (ANALYST, 1930, **55**, 111).

(*b*) *Oxidation of the lactose* (and dextrose, if present) by treatment with alkaline iodine solution.

(*c*) *Reduction of copper (in Luff's solution) by the laevulose.*

(*d*) *Determination of reduced copper* by the iodimetric method of Shaffer and Hartmann.

The last three stages can be completed in 30 minutes.

We give below a description of the process in detail in its final form, and add a few notes describing certain matters that were dealt with in working it out.

SPECIAL SOLUTIONS REQUIRED.

Sucrose solution: approximately 9 grms. per 100 ml. (freshly prepared).

Normal iodine solution: 13 grms. of iodine and 15 grms. of potassium iodide per 100 ml.

Sodium carbonate and hydroxide solution: a mixture of approximately equal parts of 2 *N* sodium carbonate and 2 *N* sodium hydroxide solutions.

Sulphuric acid: approximately 5-normal.

Sodium sulphite solution: 20 per cent.

Sodium sulphite solution, 2 per cent.: freshly prepared or diluted from the stronger solution.

Luff's solution: dissolve 25 grms. of copper sulphate crystals in 100 ml. of water; 50 grms. citric acid in 50 ml. of water; 388 grms. $Na_2CO_3.10H_2O$ in 300 or 400 ml. of lukewarm water. Add the citric acid solution to the sodium carbonate solution, and then add the copper solution. Mix, cool, make up to 1 litre and filter.

Iodate-iodide solution: 2·7 grms. of potassium iodate, 30 grms. of potassium iodide, and 10 ml. of 0·5 *N* sodium hydroxide solution per litre.

Potassium oxalate solution: a saturated aqueous solution.

Sodium thiosulphate solution: approximately 0·05 *N*, accurately standardised (but see Note 5).

PROCEDURE. (*a*) *Preparation of the Serum.*—As mentioned above, this may be prepared by clarification with either zinc ferrocyanide or phosphotungstic acid as described in the "Report on Sucrose." If the latter method is used, the serum should be carried forward to its further treatment within thirty minutes of the clarification, in order to avoid significant inversion of the sucrose.

A control serum should also be prepared from fresh milk (100 ml. of milk with the same quantities of precipitants as for the condensed milk, made up to 200 ml. with water and filtered).

(*b*) *Oxidation of the Aldose Sugars.*—Place 10 ml. of each serum in 250 ml. conical flasks, taking care that the liquid does not flow on to the sides of the flask. To the fresh milk serum add 10 ml. of 9 per cent. sucrose solution, and to the other 10 ml. of water.

To each then add 5 ml. of *N* iodine solution and 6 ml. of the 2 *N* mixed alkali solution, shake round, and allow the flasks to stand for 10 minutes (in a bath at 15–20° C. if the room temperature is very low). Acidify with 1·6 ml. of 5 *N* sulphuric acid, and remove the liberated iodine first with 20 per cent. sodium sulphite solution, and finally, after adding five or six drops of starch solution, with 2 per cent. sodium sulphite solution. (This operation should have the precision of a titration, though the quantities need not be measured.) Immediately after wards add 1 drop of methyl orange solution and neutralise with 2 *N* sodium hydroxide solution (or with the mixed alkali solution).

(*c*) *Treatment with Luff's Solution.*—Add 20 ml. of Luff's solution to each flask, heat the contents to boiling in about 2 minutes on a plain wire gauze over a burner, then attach the flask to a reflux condenser, resting it on asbestos-covered gauze, and boil gently by heating with a Bunsen flame. (The burner, suitably regulated, should be already in position beneath the gauze when the flask of boiling solution is transferred to it.) After exactly 10 minutes' boiling, remove the flask and cool in running water for four or five minutes.

(*d*) *Titration of Reduced Copper.*—Add exactly 25 ml. of the iodate-iodide solution, and 20 ml. of saturated potassium oxalate solution. Acidify carefully, while swirling, with 20 ml. of 5 *N* sulphuric acid. Shake round (with some care, owing to frothing) until the precipitate of cuprous oxide (partly converted into white cuprous iodide) has dissolved, then titrate with 0·05 *N* thiosulphate solution. No further starch should be required. The end-point should be a sharp change to a fine light-blue.

CALCULATION OF THE LAEVULOSE.—The difference between the titrations of the sample and of the control, as ml. of 0·05 *N* thiosulphate, multiplied by 0·064, gives the percentage of laevulose in the sample, uncorrected for the effect of the volume of clarification precipitate. The volume of the precipitate can be calculated and allowed for as described in the "Report on the Determination of Sucrose."'

It is preferable to determine the exact value of the thiosulphate in terms of laevulose by making a test on 10 ml. of the fresh milk serum with a known amount of added invert sugar. (The latter may be used in the form of a solution of 0·5 per cent. or stronger, so that not more than a few ml. need be added to the serum.)

RESULTS OBTAINED ON KNOWN AMOUNTS OF LAEVULOSE.—A series of determinations was carried out, by the method described, on portions of a sample of condensed milk to which known amounts of invert sugar were added. The mixtures were clarified after the addition of the invert sugar. It will be seen that a small amount of laevulose was indicated in the condensed milk itself, when compared with the fresh milk control. The amounts of laevulose found have been corrected for the effect of the volume of precipitate.

Laevulose added. Per Cent.	Laevulose found. Total. Per Cent.	Laevulose found. Less amount in sample. Per Cent.
0	0·03	—
0·05	0·07	0·04
0·10	0·13	0·10
0·25	0·29	0·26
0·50	0·53	0·50
0·75	0·77	0·74
1·00	1·01	0·98

NOTES.—(1) At the end of stage (*b*), if the acidified solution, after removal of the iodine, is not neutralised at once, there is a risk of some inversion of the sucrose. Thus, in control tests on the fresh milk serum with added sucrose, one was neutralised within 2 minutes of acidification, another after standing for 8 minutes. The solutions were then carried through the remainder of the process as usual, and showed the following differences from a blank carried out with no sucrose present:

Neutralised within 2 minutes. Laevulose equiv. to 0·15 ml. *N*/20 thiosulphate.
,, after 8 ,, ,, ,, 0·7 ml. ,, ,,

An increase in the amount of acid above that specified will result in further risk of inversion. The combined effects can cause fairly large errors. When an extra 1·5 ml. of acid was added (*i.e.* double the amount necessary), and the mixture was left for 8 minutes before neutralising, laevulose equivalent to 6 ml. of *N*/20 thiosulphate was found. (This would correspond with an apparent 0·4 per cent. of laevulose in the sample.)

It is most important, therefore, that the procedure laid down should be closely followed, so as to avoid this source of error.

(2) The Luff's solution should be prepared carefully according to the formula given, otherwise the precipitation of the cuprous oxide is unsatisfactory. The titration of the reagent against standard acid is advisable as a check; 10 ml. should require about 45 ml. of 0·5 *N* acid, with methyl orange as indicator. The 20 ml. of Luff's solution specified in the method should not be varied, otherwise difficulties may be encountered in dissolving the cuprous oxide precipitate, or in securing a satisfactory end-point. This reagent is very sensitive, and should only be used under standard conditions.

(3) The alkalinity of the solution during the iodine oxidation of stage (*b*) was the cause of some difficulty at first. In the earlier experiments, 2 *N* sodium hydroxide alone was used as the alkali, and the amount necessary to ensure complete oxidation of the lactose had to be controlled very closely. Thus, in tests on fresh milk serum, with no sucrose or invert sugar added, the following series of results was obtained for varying amounts of added alkali:

Amount of 2*N* sodium hydroxide. ml.	Final thiosulphate titration. ml.	Difference from blank. ml.
Blank (reagents only)	34·5	
3·0	33·0	1·5
3·3	34·35	0·15
3·4	34·5	0·0
3·5	34·4	0·1
3·6	34·2	0·3
3·7	30·5	4·0

The differences represent unoxidised lactose, so that a variation of a fraction of a ml. of alkali solution might cause appreciable errors in estimations of laevulose. In later experiments, it was found that the optimum amount of alkali was not always the same. For one milk serum examined it was, for instance, in the neighbourhood of 3 ml., an amount which gave incomplete oxidation in the earlier case. Extending the time of oxidation was tried with excess of alkali present, but did not give complete oxidation.

Owing to these difficulties, plain sodium hydroxide solution was abandoned in favour of a weaker alkali, consisting of a mixture of sodium carbonate and sodium hydroxide. This gave much more satisfactory results, as the optimum range was less restricted. Thus, the following were the titrations obtained in a series of tests with varying amounts of the mixed alkali:

Amount of mixed alkali. ml.	Final thiosulphate titration. ml.
3	32·0
4	36·75
6	37·1
8	35·3

This and other tests showed that 6 ml. of the mixed alkali was a safe amount to adopt for general cases. The amount of acid for acidification was modified to correspond with the change in the amount of alkali.

(4) The milk is clarified by the zinc ferrocyanide method; the ammonia used prior to the clarification gives, on the addition of the iodine and alkali, a black precipitate of nitrogen iodide, which partly disappears during the subsequent standing. This phenomenon seems to have no effect, however, on the laevulose determination. In parallel experiments the same thiosulphate equivalent was found for the laevulose whether ammonia was used or not.

(5) The factor for converting the thiosulphate differences to laevulose is the mean of the values obtained in two series of experiments, in which known amounts of invert sugar solution were added in one case to fresh milk serum, in the other to condensed milk serum. Ammonia was used in preparing the serum.

The process was carried out as described in this paper, the invert sugar solution being added, in the form of a 0·50 per cent. solution (*i.e.* 0·25 per cent. laevulose) to the 10 ml. portions of serum taken for the test. The results are shown in the following table. The amounts of laevulose, shown as added to the fresh milk serum under I, are expressed as if they were the corresponding percentages present in a sample of condensed milk, a 50 per cent. serum from the fresh milk being taken to be approximately equivalent in composition to a 20 per cent. serum from the condensed milk.

	Laevulose added. Per Cent.	Titration $N/20$ thiosulphate. ml.	Difference, due to laevulose. ml.	Factor for converting to per cent. of laevulose.
I. Fresh milk serum.				
	0	36·8	—	—
	0·25	33·0	3·8	0·066
	0·5	29·0	7·8	0·064
	0·75	25·0	11·8	0·064
	1·0	21·3	15·5	0·065
			Mean	0·065
II. Condensed milk serum.				
	0	36·0	—	—
	0·25	32·0	4·0	0·063
	0·5	27·95	8·05	0·062
	0·75	24·1	11·9	0·063
	1·0	20·4	15·6	0·064
			Mean	0·063

From these data, a mean factor of 0·064 was taken. Clearly this gives the percentage as it would be indicated if there were no volume of precipitate correction. The latter, therefore, has to be allowed for in the usual way.

As before mentioned, it is preferable to establish the thiosulphate equivalent for the laevulose (added in the form of invert sugar solution) alongside the test on the sample, and its control, rather than to rely on the stated factor. This procedure automatically eliminates any errors due to slight differences in manipulation, and avoids the necessity for exact standardisation of the thiosulphate.

(6) It is important that the iodine and alkali solutions be reasonably close to the strength specified, otherwise the oxidation of the lactose may not proceed satisfactorily.

(7) Some doubt was felt at first as to the adequacy of the conditions for oxidising the lactose, if there should be appreciable amounts of dextrose present and if the room temperature at which the oxidation was carried out were too low. Experiments showed, however, that the laevulose could be determined correctly up to 1·5 per cent. when added as invert sugar (*i.e.* in conjunction with a like amount of dextrose), and at a room temperature as low as 10° C.

(8) Attempts were made to give added accuracy to the process by doubling the amount of serum worked with. This, however, was found to be definitely a disadvantage. The amounts of the various reagents used had to be correspondingly doubled, and this appeared to be responsible for cuprous deposits which adhered to the bottom of the flask, and were with difficulty dissolved by the iodine. The conditions given in the method as adopted seem to be the most satisfactory for securing a cuprous oxide precipitate which dissolves readily.

The above method was developed in connection with the work of the Milk Products Sub-Committee, at a time when it was considered that appreciable quantities of invert sugar might be found in sweetened condensed milks after fairly lengthy storage. As the result of applying this method to the analysis of some milks it has been discovered, however, that, while invert sugar was undoubtedly formed, the laevulose had been apparently converted simultaneously into laevan, which has no reducing action, only small amounts (about 0·5 per cent.) of laevulose remaining as such. No direct reduction method will therefore indicate the full percentage of sucrose which has been inverted. Further, the determination of sucrose by polarimetric methods is affected, as laevan has a specific rotation which is considerably less negative than that of laevulose, but it is hydrolysed to laevulose by the usual process of inversion.

The Detection of Small Quantities of Calcium.

By NORMAN EVERS, B.Sc., F.I.C.

(*Read at the Meeting, December* 3, 1930.)

The work described in the present paper was the outcome of an investigation into the possibility of including in the next edition of the British Pharmacopoeia a simple test which would be generally applicable for detecting traces of calcium in the salts described therein. It was desired that such a test should be capable of being used as a limit test, so as to lay down definite limits of calcium where this element was likely to occur.

Calcium is most likely to occur in magnesium carbonate and oxide, so that any method suggested must be capable of application to these compounds. Current methods for the detection of small quantities of calcium in magnesium salts are most unsatisfactory. For this reason the United States Pharmacopoeia (X) gives a long and tedious quantitative test for calcium in magnesium carbonate and oxide, depending on a double precipitation as oxalate. The present edition of the British Pharmacopoeia is content with stating that "no reaction" or "not more than the slightest reaction" for calcium should be obtained.

Precipitation as Oxalate.—Although complications were naturally expected when dealing with magnesium salts, it was thought that the oxalate precipitation would probably be applicable to other salts, and the first experiments were made to investigate this point. It soon became apparent that this test was quite useless for the purpose. The influence of salts on the precipitation was far too great.

The following experiments give an indication of the results obtained:

A control test was carried out with 2 mgrms. of calcium, 1 c.c. of dilute ammonia solution and 1 c.c. of 2·5 per cent. ammonium oxalate solution in 50 c.c. of solution. In the absence of salts a turbidity was produced almost immediately.

The experiment was repeated, adding 1 grm. of a number of salts, with the following results:

Adding 2 mgrms. of calcium.

Added Salts.	*Result.*
No added salt.	Almost immediate pptn.
Sodium chloride, 1 grm.	Slight ppt. after 3 hours.
Borax, 1 grm.	Slight ppt. after 3 hours.
Sodium potassium tartrate, 1 grm.	No ppt.
Potassium citrate, 1 grm.	No ppt.

Adding 5 mgrms. of calcium.

Added salts.	*Result.*
No added salt.	Immediate pptn.
Sodium chloride, 1 grm.	Almost immediate pptn.
Borax, 1 grm.	Slight ppt. after 30 minutes.
Sodium potassium tartrate, 1 grm.	Slight ppt. after 30 minutes.
Potassium citrate, 1 grm.	No ppt.

Variations in the concentration of the reagents did not appreciably improve matters. It was found that even 0·25 grm. of potassium citrate in 50 c.c. of solution prevented the precipitation of 2 mgrms. of calcium.

Further complications would be introduced if magnesium were also present in the salt as an impurity. This line of investigation was therefore abandoned.

Calcium Oleate Test.—The formation of an opalescence on the addition of sodium oleate solution to a solution is an extremely delicate test for calcium. Under the best conditions 0·01 mgrm. of calcium in 50 c.c. of solution, or 0·00002 per cent., can just be detected.

The test is also, of course, a test for magnesium, but is much less sensitive, 0·6 mgrm. in 50 c.c. of solution, or 0·0012 per cent., being the minimum quantity which can be detected. Further, within certain limits of concentration the precipitation of magnesium is entirely suppressed in the presence of potassium citrate, whilst the sensitiveness of the calcium test is actually increased.

The best conditions for the detection of calcium were found to be as follows: Take 50 c.c. of the solution containing calcium, which should be neutral or slightly alkaline. Dissolve in it 2 grms. of potassium citrate, and add 0·3 c.c. of a solution prepared by dissolving 10 grms. of oleic acid in 200 c.c. of 1 per cent. sodium hydroxide. Mix and allow the mixture to stand.

An excess of the reagent gives less opalescence. A certain excess of alkali is desirable for the best results. The test is only satisfactory between certain limits of calcium concentration. With quantities exceeding 1 mgrm. in 50 c.c. the opalescence is actually reduced. Under the above conditions quantities of magnesium up to 15 mgrms. give no opalescence.

Summarising the results, the oleate test is excellent for quantities of calcium varying from 0·01 mgrm. up to 1 mgrm. in the absence of more than 10 mgrms. of magnesium, and within these limits in the absence of other salts the opalescence appears proportional to the calcium present.

Further experiments showed, however, that, in spite of its delicacy, the oleate test is not suitable for the purpose in view. Possibly, if the test could be carried out, using standards containing the same concentration of the same salt, it would be satisfactory, but this is hardly practicable.

The addition of other salts, even in the absence of potassium citrate, caused the results to be erratic. This was partly due to their "salting out" effect on the soap, which sometimes caused flocculation, but this was not the whole explanation.

THE SULPHATE METHOD.—The differing solubilities of the sulphates, particularly in dilute alcohol, appeared to offer possibilities, and a search of the literature was made with this object in view.

Crookes ("Select Methods of Chemical Analysis," p. 52) states that, according to Scheerer, satisfactory results are obtained "by converting the alkaline earths into neutral sulphates, and adding alcohol to the aqueous solution until a persistent cloudiness is produced. After some hours all the calcium sulphate is deposited. When too much alcohol has been used some of the magnesium sulphate is deposited as well."

Hundeshagen (*Z. öffentl. Chem.*, 1909, **15**, 85), in a method for the analysis of magnesite, suggests that, after obtaining the mixed chlorides by evaporation with hydrochloric acid, the residue should be treated with 30 c.c. of warm water and 4 grms. of sodium sulphate, and the solution mixed with 40 c.c. of 90 per cent. alcohol. After standing for four hours the precipitated calcium sulphate is filtered off, washed with 50 per cent. alcohol, and dissolved in hydrochloric acid, being then precipitated as oxalate in the ordinary way.

Preliminary experiments were carried out with calcium alone in the presence of excess of dilute sulphuric acid adding twice the volume of 95 per cent. industrial methylated spirit.* The calcium was added as *N*/5 calcium chloride solution. As the test was primarily intended for testing magnesium oxide and carbonate, it was considered that it would be more convenient if it could be carried out in the presence of an excess of sulphuric acid.

A quantity containing 2 mgrms. of calcium with 25 c.c. of 10 per cent. sulphuric acid and 50 c.c. of 95 per cent. alcohol was found to become turbid after standing about 20 minutes, and after half-an-hour a flocculent precipitate separated. In the presence of 2 grms. of pure magnesium sulphate a similar precipitate was formed, but the turbidity appeared somewhat sooner.

More detailed tests were then carried out for the purpose of discovering the limits of the test and the best conditions.

Limit of Magnesium Concentration.—Five grms. of magnesium sulphate or 1 grm. of pure magnesium oxide deposited crystals of $MgSO_4.7H_2O$, but 3 grms. of magnesium sulphate and 0·5 grm. of magnesium oxide remained clear. These latter quantities or their equivalents in other magnesium salts should, therefore, not be exceeded.

Concentration of Sulphuric Acid.—Increase of concentration of sulphuric acid was found to make the test more sensitive up to 20 per cent., but above this concentration the turbidity was reduced.

Concentration of Alcohol.—Reduction of the amount of alcohol below double the volume of dilute sulphuric acid reduced the sensitiveness of the test. Increasing quantities of alcohol were inadvisable owing to crystallisation of magnesium sulphate.

* Referred to subsequently as alcohol.

Sensitiveness of the Test.—Two grms. of pure magnesium sulphate, with the required amount of calcium as $N/5$ calcium chloride solution, were dissolved in 25 c.c. of 20 per cent. sulphuric acid, and 50 c.c. alcohol were added.

Calcium. Mgrms.	Time of precipitation.
0	No ppt. in 24 hours
0·1	Faint trace of ppt. in 24 hours
0·2	Trace of ppt. in 24 hours
0·4	Slight ppt. in 24 hours
1	Turbidity in 25 minutes
2	Turbidity in 6 minutes
4	Turbidity in 2 minutes
8	Turbidity immediately

The test therefore appears capable of detecting 0·1 mgrm. of calcium in the presence of 0·2 mgrm. of magnesium, or a Mg : Ca ratio of 2000:1.

Effect of Magnesium Concentration.—Differing quantities of magnesium sulphate were taken, 1 mgrm. of calcium being added to each.

Magnesium sulphate. Grms.	Calcium. Mgrms.	Turbidity time. Minutes.
3	1	15
2	1	20
1	1	30
0·5	1	45
0	1	60

A sample of calcium-free magnesium oxide gave similar results.

It is desirable, therefore, to keep the magnesium concentration within narrow limits.

The Qualitative Test.—The following is the final form of test adopted:—Dissolve the required weight of magnesium salt in 25 c.c. of 20 per cent. (by weight) sulphuric acid, and add 50 c.c. of 95 per cent. alcohol. Note the time at which a definite turbidity first appears. If none appears in half-an-hour, less than 1 mgrm. of calcium is present.

Commercial Samples.—A sample of light magnesium oxide gave the following results:

Magnesium oxide. Grm.	Turbidity time.
0·25	Immediate
0·2	5 minutes
0·15	23 minutes
0·1	60 minutes

This sample, therefore, contained about 1 mgrm. of calcium in 0·15 grm.=0·66 per cent. of calcium.

The results on other commercial samples are shown in the following table:

Samples of.	Number tested.	Weight taken. Grm.	Number clear after 30 mins.	Number turbid after 30 mins.
Magnesium oxide, light	6	0·2	3	3
		0·1	6	0
		0·4	6	0
Magnesium oxide, heavy	2	0·2	2	0
Magnesium carbonate, light	8	0·5	2	6
Magnesium carbonate, heavy	7	0·25	8	0
		0·5	6	1
		0·25	7	0

These samples were from three different manufacturers in this country. With one exception, the "heavy" varieties contained very little calcium, but the "light" varieties were much more frequently contaminated.

Quantitative Method.—The above test has the disadvantage that it depends on individual judgment as to whether a solution is turbid or not. As a rough test, it may be regarded as satisfactory, but more definite results may be obtained by weighing the calcium sulphate after allowing the precipitate to stand overnight. The results obtained are slightly low, as calcium sulphate appears to possess a small solubility in the solution. The test was carried out in the same way as before, taking 2 grms. of magnesium sulphate and adding definite amounts of calcium, but experience showed that the use of 25 per cent. sulphuric acid, instead of 20 per cent., gave slightly higher results. After standing overnight the precipitate was filtered off on a Gooch crucible previously washed with alcoholic sulphuric acid and ignited. The residue was washed with 200 c.c. of a mixture of 2 volumes of alcohol and 1 volume of 25 per cent. sulphuric acid, ignited, and weighed as calcium sulphate. The following results were obtained in the presence of 2 grms. of magnesium sulphate in each case.

Calcium taken. Mgrms.	Calcium found. Mgrms.	Error. Mgrm.
0·4	0·3	−0·1
1·0	0·8	−0·2
2·0	1·5	−0·5
3·0	2·6	−0·4
5·0	4·5	−0·5
10·0	9·2	−0·8
20·0	18·9	−1·1

The agreement between duplicate determinations was within 0·1 mgrm. in each case. The results are obviously somewhat low, but, considering the convenience of the method, its use as a limit test for calcium in magnesium carbonate and oxide should be quite satisfactory.

Effect of Chlorides.—One and a half grm. of calcium-free magnesium chloride, to which 2 mgrms. of calcium had been added, gave 5·2 mgrms. of calcium sulphate = 1·5 mgrm. of calcium, so that the presence of chlorides has little effect on the result.

Commercial samples of magnesium oxide and carbonate from three British manufacturers gave the following results:

		Taken. Grm.	Calcium sulphate. Mgrms.	= Calcium oxide. Per Cent.
Magnesium carbonate, light ..	A	0·5	6·6	0·54
	B	0·5	5·0	0·41
	C	0·5	7·2	0·59
	D	0·25	3·2	0·53
Magnesium oxide, light ..	A	0·2	4·0	0·82
	B	0·2	10·6	2·18
	C	0·2	3·4	0·70
	D	0·1	2·2	0·91
Magnesium carbonate, heavy	A	0·5	Nil	—
	B	0·5	Nil	—
	C	0·5	Nil	—
	D	0·5	1·8	0·15
Magnesium oxide, heavy ..	A	0·2	Nil	—
	B	0·2	Nil	—
	C	0·2	Nil	—

Three samples of light magnesium carbonate containing stated amounts of calcium were kindly supplied by the Washington Chemical Company. The results were:

Calcium oxide stated. Per Cent.	Taken. Grm.	Calcium sulphate weighed. Grms.	= Calcium oxide. Per Cent.
Less than 0·1	0·5	0·1	0·01
0·2	0·5	1·8	0·15
0·6	0·5	7·2	0·59

A reasonable standard would appear to be that not more than 10 mgrms. of calcium sulphate should be obtained from 0·5 grm. of magnesium carbonate or 0·2 grm. of magnesium oxide, corresponding with a maximum of 1·9 per cent. of calcium oxide in the oxide and 0·8 per cent. in the carbonate.

The method has also been tried tentatively in other cases where the oxalate method presents difficulties. It has been found that the results are unaffected by the presence of iron and phosphates, and the method has been used without any difficulty for the determination of calcium in such a preparation as compound syrup of iron phosphate or chemical food, in which the calcium determination is otherwise a troublesome business.

I wish to acknowledge the assistance of Mr. C. E. Davis in the experimental work.

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The Detection of Benzoic Acid.

By ALFRED NORMAN LEATHER, B.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, December* 6, 1930.)

The following method for the detection of benzoic acid (and, incidentally, salicylic acid) is especially applicable to jams, sauces, cordials, mineral waters and milks, but is of fairly general application to foodstuffs and beverages. A slight modification supplies a means of detecting with certainty the presence of a benzoyl radicle in an organic compound when only a very small quantity (1–2 mgrms.) of the compound is available. The method depends on the distillation of benzoic acid with steam, in the apparatus described, into a solution of alkali in such a way that the volume of the latter is not materially increased. Benzoic acid is detected by an application of an observation by Hinks (Analyst, 1913, **38**, 555), that an ethereal solution of benzoic acid becomes cloudy on adding a drop of strong ammonia solution. As steam-volatile acids other than benzoic yield a turbidity in this reaction, the presence of benzoic acid is confirmed by the formation of basic ferric benzoate, or, in some cases, of characteristic crystals of silver benzoate.

The process may be completed in twenty minutes, and, in the form described, will detect 100 parts of benzoic acid per million.

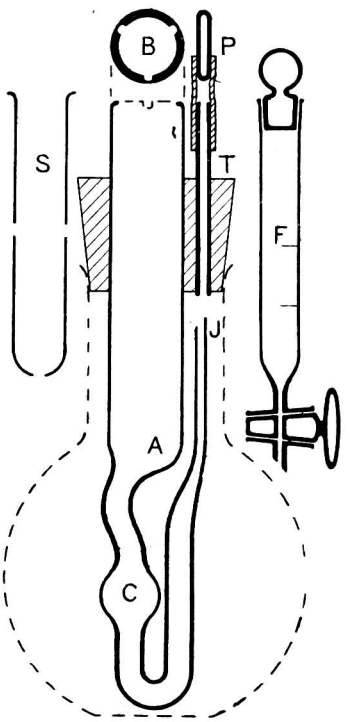
Apparatus.* The apparatus shown in the diagram (half the actual size) consists of a 250 ml. round, flat-bottomed, wide-mouthed flask ("CO_2" flask), fitted with a rubber stopper carrying a special U-tube (A). The rubber stopper must be easily removable. It has two holes, one to take a tube 2 cm., and the other a tube 4 mm. in diameter. Through the larger hole passes the widened limb of the U-tube, which reaches almost to the bottom of the flask. The widened portion is 10 cm. long, and at its upper end has a slight rim turned inwards with three indentations in it. A plan-sketch of this end is shown at (B). The U-bend itself is made from glass tubing having an internal diameter of 5·5 mm. Between the wide limb and the U-bend is a bulb (C), 1·5 cm. in diameter, the centre of which is 3 cm. above the bottom of the U-bend. Above the bulb the tube has a slight outward curve. The other limb of the U-tube is drawn out, about 5 cm. above the U-bend, to an internal diameter of 2 mm., and this drawn-out limb reaches up to within 6 mm. of the stopper, where it is cut off at an angle of 45° (J). The volume of liquid required to fill the U-tube up to the level of the bottom of the bulb is approximately 1 ml., while 0·5 ml. of liquid is sufficient to "seal" the U-bend.

A thin-walled tube (S), 7·5 cm. long and 1·4 cm. in external diameter, and having a number of holes (3 mm. in diameter) in the bottom and sides, passes down inside the wide limb of the U-tube, and rests with its rim on the inward-turning rim of the latter. This perforated tube acts as a splash-guard, and must hang clear of the walls of the U-tube.

* The Scientific Glass-Blowing Co., 12, Wright Street, Burlington Street, Manchester, can supply the complete apparatus for 7s. 6d.

Through the other hole of the rubber stopper passes a glass tube (T) flush with the lower surface of the stopper, and extending about 2 cm. above the upper surface. This tube carries at the upper end a short piece of rubber tubing which may be closed by a glass plug (P).

A small cylindrical separator (F) has a capacity of 4 ml., and is fitted with a glass stopper and capillary tap (1·5 mm. internal diameter). The capillary tube



above and below the tap should be short. Marks are made on the separator indicating a content of 1 ml. and 2 ml. above the tap.

Description of the Test.—Transfer 10 grms. of the sample to the flask, add 75 ml. of saturated brine, 1 ml. of 10 per cent. sulphuric acid, and about 0·5 grm. of coarsely powdered pumice. Fit the rubber stopper (carrying the U-tube) into the flask. Drop 0·5 ml. of approximately *N* sodium hydroxide solution into the mouth of the tube so that it runs down into the U-bend, pass the splash-guard (S) down into position, and close the rubber tube with the glass plug (P). Place the flask on a thin iron gauze over an ordinary Bunsen flame and boil for three minutes. The weight of steam driven out of the apparatus should be about 10 to 12 grms.

The brine aids the distillation of benzoic acid (*cf.* Monier-Williams, *Public Health Reports*, No. 39, Ministry of Health). The steam passes through the U-tube and comes into intimate contact with the sodium hydroxide solution. The

upper part of the tube is designed to allow the steam to pass out and return the splashings to the bulb. Since a large portion of the U-tube is immersed in steam or boiling liquid, little condensation occurs. (The volume of liquid in the U-tube is somewhat increased by condensation just as boiling is commencing; afterwards some evaporation occurs and the volume slowly diminishes.)

Remove the apparatus from the flame and take out the glass plug (P). Remove the rubber stopper and U-tube from the flask, and rinse the outside of the U-tube with a jet of water from a wash-bottle. Lift out the splash-guard (S), allowing the drop of liquid adhering to it to drain back into the U-tube. Incline the U-tube in such a way that the contents run out of the end (J) of the drawn-out limb, and collect the liquid as completely as possible in the small separator (F).

To the liquid in the small separator add two drops of 50 per cent. sulphuric acid and about 1 ml. of ether (using the marks on the sides as a guide). Shake thoroughly and run off the lower layer. Wash the ether by shaking with an equal volume of water. After washing, the volume of ether is slightly reduced. Again wash the ether with a correspondingly reduced volume of water, and repeat the washing a third time. Run off the water as completely as possible. Add one drop of strong ammonia solution (from a "quill" tube). If benzoic acid is present in the sample to the extent of 100 parts per million, the ether becomes turbid.

If a turbidity forms, it is necessary to apply the following confirmatory test:—Shake the separator thoroughly, and run off as completely as possible the small aqueous layer into a hollow microscope-slide and evaporate just to dryness by warming on a steam-heated plate (*e.g.* by putting the slide across a corner of a covered water-bath). Cool the slide and dissolve the residue in a drop of water (conveniently added by means of a platinum wire loop about 5 mm. in diameter). Add at the edge of the drop (by means of a loop about 3 mm. in diameter) a small drop of ferric alum solution (7·5 per cent., filtered). The presence of benzoic acid is confirmed by the formation of a zone of the opaque buff basic ferric benzoate precipitate.

Salicylic and Cinnamic Acids.—If these substances are present in the sample, they distil in the same way as benzoic acid. They are extracted by ether in the small separator, and cause a turbidity when the drop of strong ammonia solution is added, provided that they are present in the sample to the extent of 100 parts per million. They yield residues of ammonium salicylate and cinnamate, respectively, when the drop of ammoniacal extract is evaporated on the hollow slide, On testing the residue with ferric alum, as described, ammonium salicylate yields an intense blue-violet zone. The ammonium cinnamate residue is not completely soluble in water (probably owing to partial hydrolysis during evaporation). The drop, however, containing some few undissolved particles, yields a precipitate with ferric alum of ferric cinnamate resembling the benzoate in texture, but yellow instead of buff in colour. If to the same drop a further addition is made in the cold of a small drop of purple alkaline permanganate (2·5 per cent. sodium hydroxide, 2·5 per cent. potassium permanganate) on a 5 mm. loop, immediate

reduction to a green colour occurs, and an odour of benzaldehyde is noticeable. (*Distinction from benzoic acid.*)

SULPHUR DIOXIDE.—If sulphur dioxide is present in the sample it distils in the same way as benzoic acid, and is transferred to the small separator. It should here be oxidised by the addition of slight excess of potassium dichromate solution (one or two drops of a concentrated solution), after acidification, and before extraction with ether. If not removed, it dissolves in the ether, from which it is not all removed by washing, and it yields a turbidity with ammonia.

OTHER ACIDS GIVING THE TURBIDITY REACTION.—I have found that an ethereal solution of almost any ether-soluble acid yields a turbidity on adding a drop of strong ammonia solution. In order to interfere with the test an acid must fulfil the following conditions:—It must be volatile with steam; it must be soluble in ether; it must not be removed from ether by washing with water under the conditions of the test.

These conditions are fulfilled by the whole series of volatile fatty acids from butyric upwards. However, these acids do not usually occur in foodstuffs in the free state in sufficient quantity to give a turbidity in the test. Some exceptions are: Rancid butter, very sour milk, certain vinegars and preparations therefrom.

When the drop of the ammoniacal solution of the turbidity due to these acids is evaporated on the hollow slide almost to dryness, the odour of the free acids is noticeable. The residue does not usually completely re-dissolve on adding the drop of water. On adding the drop of ferric alum a turbidity may be produced, but this may be seen to be due to the separation of oily drops, and is readily distinguishable from the benzoate precipitate.

Slight modifications are recommended when applying the test to the following:

(*a*) *Vinegar, Pickles and Sauces.*—It is necessary to increase the amount of caustic soda solution in the U-tube to prevent the liquid becoming acid before the end of the three minutes' boiling. It may be necessary to use 1 ml. of 10 per cent. caustic soda solution.

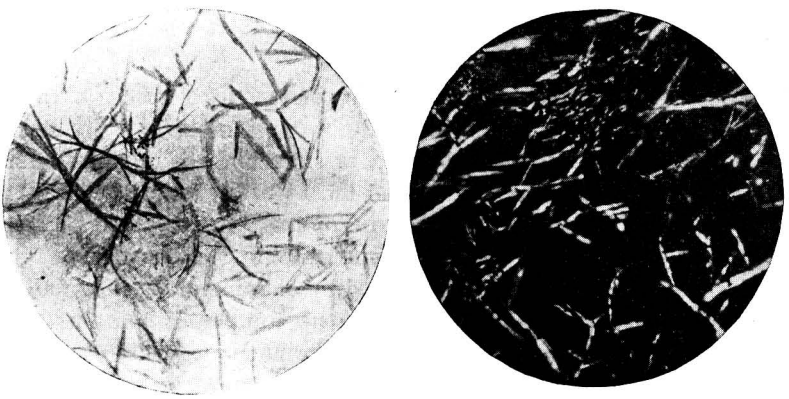
(*b*) *Mineral Waters and Wines.*—Twenty ml. of the sample may be used, in which case the turbidity reaction is obtained if the sample contains 50 parts per million of benzoic acid. If it is desired to detect 10 parts per million, proceed as follows:—Shake 200 ml. of wine, acidified with 1 ml. of 10 per cent. sulphuric acid, with 100 ml. of ether. Run off the wine and shake the ether with 10 ml. of 2 per cent. sodium hydroxide solution. Run off the alkaline layer, acidify with sulphuric acid, transfer to the apparatus and complete the test as described.

(*c*) *Fats.*—Fats tend to retard the distillation of benzoic acid with steam. If the time of boiling is increased to six minutes, the turbidity reaction may be obtained if the sample contains 100 parts per million of benzoic acid.

(*d*) *Flour.*—Benzoic acid in the proportion of 20 parts per million has been detected as follows:—Shake thoroughly 50 grms. of flour with 150 ml. of ether, and filter into a separator. Shake the ether with 10 ml. of 2 per cent. sodium

hydroxide solution containing 20 per cent. of alcohol. Run off the alkaline layer, acidify with sulphuric acid, transfer to the apparatus, and complete the test as usual, but increase the time of boiling to six minutes.

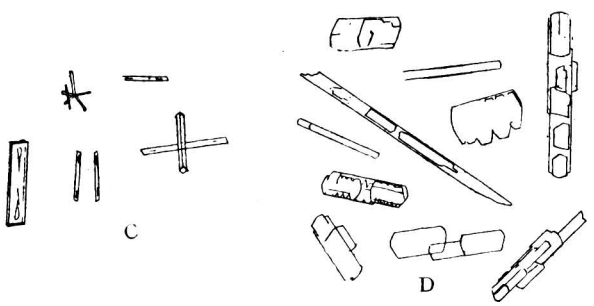
A MICRO-REACTION FOR BENZOIC ACID.—Instead of testing the residue of ammonium benzoate on the hollow slide with ferric alum as described above, a very sensitive and distinctive reaction may in most cases be obtained with



SILVER BENZOATE × 20.

A. Ordinary light. B. Polarised light.

silver nitrate. The residue on the slide is dissolved in a small drop of water in the cold, and a minute particle of solid silver nitrate is added to the centre of the drop on the tip of a platinum wire. Very small crystals are formed at first,



TYPICAL FORMS × 40.

C. Silver benzoate. D. Silver salicylate.

close to the place where the silver nitrate was added. After a minute or two, larger and more characteristic crystals appear (see photographs and sketch). These are best observed by polarised light. Where a crystal is free from superimposed crystals, it may be shown to exhibit parallel extinction. The crystals are very thin and appear chiefly gray and white between crossed Nicols. Under

similar conditions ammonium salicylate yields well-formed and readily distinguishable crystals of its silver salt (see sketch). These consist of long, comparatively thick, four-sided prisms, which exhibit brilliant colours between crossed Nicols.

The presence of volatile fatty acids interferes with the formation of the characteristic crystals described. The ammonium benzoate residue recovered from jams, cordials and mineral waters readily gives characteristic crystals of silver benzoate, but that from pickles and sauces containing vinegar (which contains traces of butyric and higher acids) and from coffee extract and rancid butter may fail to give them.

A TEST FOR THE BENZOYLRADICLE, USING ONLY 1 TO 2 MGRMS. OF THE COMPOUND.—Hydrolyse the compound by suitable treatment (*e.g.* by heating in a small test-tube with a drop of alcoholic potassium hydroxide) and transfer to the flask of the apparatus described. Add 25 ml. of brine and 1 ml. of 10 per cent. sulphuric acid, together with about 0·5 grm. of coarsely powdered pumice. Complete the test as usual, but increase the time of boiling to 5 minutes. In general, no noticeable turbidity occurs on adding the drop of ammonia to the small separator. A small residue is obtained on the slide if the compound contains the benzoyl radicle. Dissolve the residue in a very small quantity of water, and confirm by adding a particle of silver nitrate and observing the characteristic crystals of silver benzoate.

PUBLIC ANALYST'S DEPARTMENT,
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Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates.

XIX. Laboratory Notes on Analytical Technique.

BY W. R. SCHOELLER, Ph.D.

(*Work done under the Analytical Investigation Scheme.*)

THIS Section should be grouped with Section VI (ANALYST, 1926, **51**, 613), as it deals with another phase of the specialised technique gradually evolved in the course of this research. Whilst the earlier paper discusses processes for dissolving the earth acids after *alkali* fusion and recovering them from such solutions, the present one describes the treatment of solutions resulting from fusion with an *acid* flux (*i.e.* bisulphate). This brief laboratory companion should assist those interested in the subject; at the same time, avoidance of repetition will simplify the text of subsequent Sections.

Certain improvements of recent date are here given for the first time. The manipulations will be discussed in the following order: *A*, Bisulphate fusion. *B*, Solution of bisulphate melt; destruction of tartaric acid. *C*, Recovery of earth acid from tartrate solution. *D*, Recovery from oxalate solution. *E*, Filtration and washing of precipitates. *F*, Ignition and purification of precipitates. *G*, Micro-tests for earth acids.

A. Bisulphate Fusion.—A platinum crucible should not be used for this operation, for two reasons. First, the fusion is a protracted one, because any attempt to hasten it by increasing the heat results in considerable foaming, with dissipation of sulphur trioxide and risk of loss. Secondly, the fused mass becomes contaminated with platinum, which interferes in subsequent separations. A silica glass or vitreosil crucible is free from these objections. In contact with the non-metallic surface, the bisulphate does not foam at all readily when rapidly heated to the dissociation temperature; hence the fusion can generally be accomplished in less than ten minutes, the crucible being manipulated with the tongs throughout.

Potassium bisulphate is more convenient and effective than the sodium salt, which loses sulphur trioxide at a lower temperature. If the flux becomes pasty before the attack is complete, it is regenerated by heating with about 0·5 c.c. of strong sulphuric acid. The attack on the silica crucible is practically negligible: thus, one crucible of silica glass, which had already been in use for a long time before being put under observation, lost 0·0052 grm. after 32 fusions, an average of 0·16 mgrm. per fusion. Another crucible of the same make suffered no loss in weight after the first three fusions.

Procedure.—The empty silica crucible is weighed before and after fusion; an allowance for silica can then be made, if necessary. The proportion of flux is about 3 grms. for 0·25, 4 for 0·5, 6 for 1 grm. of material. The bisulphate need not necessarily be dehydrated by a preliminary fusion before the material is added: when an ignited oxide is fused for re-treatment, the flux is added to it and gently heated on an asbestos mat till fused; any loss by dusting during the transfer of the oxide is thus obviated. The crucible is then held over the free flame, gently rotated from time to time, and the heat raised till the fused mass is clear. The mass is made to solidify in a thin layer around the sides of the crucible; 0·5 c.c. (or more) of strong sulphuric acid is added, and the fusion repeated. The melt is allowed to set clear of the bottom, the crucible being supported in an inclined position.

B. Solution of Bisulphate Melt; Destruction of Tartaric Acid.—Two solvents are in use: a saturated solution of ammonium oxalate, and 20 per cent. tartaric acid (roughly the same weight of solid reagent as the bisulphate taken).

To remove the cake from the crucible, the latter is partly filled with the solvent, placed on a pipeclay triangle, and gently heated with a moving flame at the point where the melt adheres; as a rule the lumps slide off the side of the crucible almost at once. The crucible contents are transferred to a beaker; the crucible is thoroughly rinsed, first with hot solvent, then distilled water, heated, and weighed.

The liquid in the beaker is stirred and warmed till the cake is dissolved. With ammonium oxalate no difficulty will be experienced, but tartaric acid lixiviation may prove troublesome with mixed oxides in which tantalum largely preponderates; no doubt the solution of tantalic oxide is assisted by mineral associates such as niobium, titanium, and iron. If they are absent or very subordinate, a certain amount of hydrolytic precipitation of tantalic acid often takes place, with formation of cloudy or opalescent colloidal solutions. Now it is essential, at least for the precipitation of members of the hydrogen sulphide group, to secure a clear solution of the fused mass. To achieve this when dealing with materials of high tantalum content, the operator has the choice of two procedures.

(1) The bisulphate melt is leached in the crucible (capacity, 50 c.c.) with cold 20 per cent. tartaric acid solution with the assistance of air agitation. The melt disintegrates, leaving a pulverulent residue, which dissolves when the liquid is heated on the water-bath.

(2) The bisulphate melt is extracted with ammoniacal ammonium tartrate (a 20 per cent. solution of tartaric acid containing an excess of 10 c.c. of strong ammonia). The tartaric earth-acid complexes being more stable in ammoniacal than in acid solution, ammonium tartrate is a better solvent for tantalic oxide than is tartaric acid. The alkaline solution remains clear on acidification; in fact, it often is slightly turbid after the lixiviation, and, if so, a small excess of sulphuric acid removes the turbidity.

If from any cause a clear tartrate solution has not been obtained, the liquid is evaporated with a few c.c. of sulphuric acid till practically all the water is expelled. This may produce the desired effect; if not, a maximum concentration of sulphuric acid must be attained, which means destruction of the tartaric acid. That operation is not nearly so tedious as it is reputed to be. The tartrate liquor, containing about 5 c.c. of sulphuric acid, is evaporated on a hot plate till it blackens and foams. Strong nitric acid is then slowly dropped into the covered beaker from a tube inserted through the spout. The black colour is discharged, with copious evolution of red fumes. When this ceases, the beaker is uncovered and heated to the appearance of white fumes; if the liquid now remains colourless, all the organic matter has been destroyed; but if darkening again occurs, the treatment with nitric acid is to be repeated. During such treatment the sulphuric acid should not actually boil, but just fume. Finally, all the nitric acid is expelled in the usual manner. The cold residual acid mass, upon dilution with 20 per cent. tartaric acid, yields a clear solution.

Filter paper, tannin, oxalic and citric acids also are destroyed by the above procedure. Ammonium chloride is entirely removed by evaporation with a large excess of nitric acid; ammonium sulphate with *aqua regia*.

C. Recovery of Earth Acid from Tartrate Solution.—The subject has been very fully discussed under XVI and XVII (Analyst, 1929, **54**, 704, 709). It may be recalled that the bulk of earth acid is precipitated by hydrochloric acid added to the boiling tartrate solution ("tartaric hydrolysis") as *HP*, the balance

being recovered from the filtrate as the tannin precipitate *TP*. This mode of working has stood the test of numerous applications. One slight change has been made, which constitutes an improvement of practical importance. In Section XVII it was found necessary to re-treat all the weighed tannin precipitates and determine the impurities (chiefly Fe_2O_3), the net weight of M_2O_5 being obtained by difference. That procedure proved to have two disadvantages:

(1) The tannin precipitate is once more in solution, whereas it is required in the solid state for further treatment. (2) Any impurities that find their way into the solution of the tannin precipitate after it has been weighed, will cause a low result, since they will be deducted from the gross weight; as a matter of fact, the errors in the majority of test analyses under XVII are slightly negative. The following short description of the complete recovery procedure embodies the slightly modified purification method by which the drawbacks of the original process are obviated:

Procedure.—The boiling acid tartrate solution of the bisulphate melt (200 c.c.) is treated with 25 to 30 c.c. of strong hydrochloric acid, and the boiling continued for 10 minutes. The precipitate, *HP*, is collected, washed, ignited, and weighed. The combined filtrate and washings are nearly neutralised with fresh (silica-free) ammonia, boiled down to less than 150 c.c., and treated with ammonia, ammonium sulphide and acetate (5 grms.); the precipitated ferrous sulphide, if any, is filtered off after complete flocculation. The filtrate (200 c.c.) is slightly acidified with acetic acid, the hydrogen sulphide boiled off, and the boiling solution treated with a fresh solution of tannin (1 grm.). The precipitate, *TP*, is free from iron and silica; after ignition it only requires lixiviation (see *E* and *F*).

The distinctive feature of the modified procedure is, that the elimination of the impurities *precedes* the precipitation of *TP*. $(HP+TP)=(Ta,Nb)_2O_5$.

D. Recovery from Oxalate Solution.—The behaviour of the earth acids and certain mineral associates in tartrate solution differs from that in oxalate solution. (1) Precipitation of earth acid with strong mineral acid ("tartaric hydrolysis") is not feasible in oxalate solution; at least, the precipitation is very incomplete (XVI, *loc. cit.*).

(2) The tartrate solutions are not precipitated by ammonia; hence they can be freed from iron by precipitation with ammonium sulphide. This method is not applicable to oxalate solutions, from which ammonia precipitates the earth acids.

(3) Tannin precipitates titanium, zirconium, thorium, iron, aluminium, and uranium, together with the earth acids, from the neutralised tartrate solution (XVII, *loc. cit.*). From almost neutral oxalate solution half-saturated with ammonium chloride, tannin precipitates the earth acids and titanium, but not zirconium, thorium, aluminium, and iron (XVIII, Analyst, 1930, **55**, 612). Quantitative separations based on this differential precipitation are under investigation.

(4) The common accidental impurity co-precipitated by tannin from tartrate solution is iron, which is eliminated as has been described under *C*; in the case of

oxalate solutions, the common contaminant is calcium, the oxalate of which should be filtered off prior to the precipitation of the earth acids by tannin.

Procedure.—The distilled water, dilute ammonia, and strong ammonium chloride solution used should be lime-free, which is ensured by the addition of ammonium oxalate in the proportion of 1 grm. per litre and filtration after some days' standing.

The oxalate solution of the bisulphate melt is left to settle, and any calcium oxalate removed by filtration and washing with water. The clear solution is boiled, cautiously neutralised with *N* ammonia, treated with an equal volume of saturated ammonium chloride solution, and treated with tannin as described in Section XVIII for the precipitation of titania (*loc. cit.*, p. 608).

E. FILTRATION AND WASHING OF PRECIPITATES.—*Use of Filter Pulp.*—It should by now be almost unnecessary to recommend the addition of filter pulp in the filtration of amorphous and gelatinous precipitates. It is one of the most valuable expedients ever introduced into analytical practice. Apart from accelerating filtration and facilitating the washing, it imparts porosity to the ignited precipitate, and thus renders it easily soluble in fused bisulphate. Another advantage of filter pulp is its strong scouring action; after completing the transfer of earth-acid or tannin precipitates to the filter, we remove the last of the precipitate adhering to the glass by rubbing a little pulp round the inside of the beaker by means of a rubber-tipped glass rod. The beaker is thus easily and thoroughly cleaned.

Hydrolysis Precipitate HP.—The precipitate is collected on a No. 40 Whatman or No. 0 Swedish filter (11 cm.). The clear supernatant liquor may first be decanted into another beaker, filtered, and the beaker rinsed and discarded. This facilitates the incorporation of filter pulp with the precipitate in the original beaker; the mixture is then transferred to the filter. After draining, it is returned (if large) to the beaker, well stirred up with the wash-liquor, collected on the filter, and the washing completed. The wash-liquor is 2 per cent. ammonium chloride or hydrochloric acid. A slight opalescence sometimes seen in the filtrates from niobium precipitates is of no consequence, as the addition of ammonia prior to the iron precipitation has the effect of clearing the solution. The ferrous sulphide may be tested for M_2O_5 by ignition and solution in hydrochloric acid; any slight white residue is added to *TP*.

Tannin Precipitates are very voluminous. That is their one disadvantage, in spite of which tannin has become an indispensable, and even the most important, reagent in earth-acid analysis. Fortunately, the ordinary facilities have proved adequate to overcome the difficulty. We apply suction filtration, using a platinum cone and No. 40 Whatman paper. The precipitates shrink considerably under suction; we use nothing larger than 12·5 cm. filters. In exceptional cases (*e.g.* when dealing with 0·25 grm. of titania), we divide the precipitate between two such papers. The precipitate should be returned to the beaker by a stream from the wash-bottle *before* it has become compressed and furrowed by the effect

of suction; it is thus removed without difficulty. It is churned up with the wash-liquor, and mixed with a little filter pulp, after which it is again transferred to the filter, and the washing completed. A 2 per cent. ammonium chloride solution is used for washing; in the case of precipitations from tartrate solution, it should contain a little tannin (about 0·5 grm. per litre).

For small tannin precipitates, filtration under atmospheric pressure is convenient; a loose-textured paper (No. 41 Whatman) is quite safe and ensures rapid filtration. The bulkiness of tannin precipitates increases in the order Ta–Nb–Ti–Al, *i.e.* with decrease in atomic weight.

F. IGNITION AND PURIFICATION OF PRECIPITATES.—A platinum crucible is as unnecessary for the ignition of the precipitates under discussion as it is undesirable for bisulphate fusions. When Weiss and Landecker assert that earth-acid and titania precipitates may be reduced by ignition in contact with filter paper to "blue-black" or "deep-black" oxides (*Z. anorg. Chem.*, 1909, **64**, 80), we are forced to assume that their products were contaminated with undetected reducible impurities such as stannic or tungstic oxide. Whether they used platinum crucibles or not is not stated; at any rate, the permeability of platinum to reducing gases at high temperatures is an argument against its use.

Porcelain crucibles are very satisfactory, while the use of silica crucibles enables the operator to proceed at once with a bisulphate fusion of the weighed oxides. Having conducted some thousands of ignitions of earth-acid and titania precipitates in contact with filter paper in silica and porcelain crucibles, we can definitely state that we have never observed any perceptible discoloration to take place.

The time-honoured, tedious process of igniting hard, lumpy precipitates with addition of ammonium carbonate in a platinum crucible to constant weight is now out of date. The oxides obtained by ignition of precipitates, prepared as prescribed above, are soft, light powders which readily attain constant weight after application of the following simple process:

Procedure.—The moist precipitate (*HP* or *TP*) is heated in a tared porcelain or silica crucible on an asbestos mat until the paper is quite charred. The ignition is completed on a triangle; the crucible may be weighed as a check.

The ignited oxide is cautiously transferred to a 50 c.c. beaker, which is covered while a little 5 per cent. hydrochloric acid is added. If any oxide or filter ash adheres to the crucible, it is cleaned with the same acid, which is added to that in the beaker. After half-an-hour's hot digestion, the liquid is rendered slightly ammoniacal, the precipitate collected, washed with 2 per cent. ammonium nitrate, and ignited in the same crucible on an asbestos mat, then over a strong burner for 15 minutes. The crucible is weighed, and the net weight found by subtraction of the filter ash.

The lixiviation process removes small quantities of alkali and sulphur trioxide, the usual loss being of the order of 0·001 grm. The positive errors recorded in two of our earliest experiments on tartaric hydrolysis (IX, ANALYST, 1927, **52**, 634,

Exps. 1 and 3) could only be due to incomplete washing uncorrected by leaching, which was adopted at a later date.

G. MICRO-TEST FOR EARTH ACIDS.—The tannin precipitates, on account of their bulky nature and characteristic colour, are invaluable in micro-work, all the more so as other earth-acid reactions are not sufficiently sensitive or specific for the purpose.

On many occasions we have searched the filtrates from *TP* for minute amounts of earth acids, so as to satisfy ourselves that the recovery was complete. After standing for a day or more, these solutions generally deposit a dark, flocculent alteration product of tannin, which is almost ash-free, and has not been found to contain earth acid.

Our procedure for the detection of earth acid in the tannin filtrates may serve as an example of micro-work. The liquor is evaporated with 100 c.c. of nitric, and 5 to 10 c.c. of sulphuric acid for the destruction of the ammonium salts, tannin, and tartaric (oxalic) acid. When colourless, the acid liquid is transferred to a silica dish in which the evaporation is pushed to complete dryness. The residue, consisting of the bisulphate originally used as a flux, is dissolved in hot water, the solution rendered slightly ammoniacal, and the small precipitate collected, washed, and ignited.

The constituents of the precipitate may be silica, earth acid, alumina, and ferric oxide; the possible presence of titania should always be taken into account in earth-acid work. The precipitate is treated in the usual manner with hydrofluoric acid and a drop of sulphuric acid in a small platinum cup made of foil; the residue is fused with a speck of bisulphate, and the mass dissolved in a c.c. or so of ammonium oxalate solution. The liquid—filtered, if turbid, through a tiny pad of filter pulp—is boiled in a 20 c.c. beaker and treated with a few mgrms. of tannin, an equal bulk of saturated ammonium chloride solution, and 0·2 *N* ammonia added, drop by drop, from the fine jet of a burette. Near the neutral point, the earth acids (and titania) will be precipitated as characteristic, yellow to red complexes, whilst iron and alumina remain in solution (*cf. D*). If a faint excess of ammonia is added, they will be precipitated, iron as a mauve, aluminium as a dirty-white complex, soluble on re-acidification. The earth-acid precipitate is collected on a 4 to 5 cm. filter, washed, ignited, and weighed; it is once more fused with bisulphate, dissolved in a little ammonium oxalate, and the liquid tested colorimetrically for titania with hydrogen peroxide and sulphuric acid.

Working in this manner, we have occasionally found a fraction of a mgrm. of earth acid in the liquors.

SUMMARY.—The following manipulations of fundamental importance in earth-acid analysis are discussed and described: bisulphate fusion, solution of the melt in oxalate or tartrate solution; tannin precipitation of the earth acids from tartrate and from oxalate solution; filtration, washing, ignition, and purification of precipitates; a micro-test for earth acids.

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Notes.

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

A COLOUR TEST FOR *o*-DIHYDROXY-PHENOLS.

If to an aqueous solution of catechol or related *o*-dihydroxy-phenol, there are added acetic acid and ammonium molybdate, an intense reddish-brown colour is developed. The depth of the colour depends upon the concentration of the phenol.

The colour is doubtless associated with the formation of a molybdenum-polyphenol complex. Compounds of catechol and various metals have been described by Weinland and Sperl (*Z. anorg. Chem.*, 1925, **150**, 69), and Weinland and Maier (*Z. anorg. Chem.*, **150**, 217); Weinland, Babel, Gross and Mai (*Z. anorg. Chem.*, **150**, 177) have also shown that molybdic acid forms complex anions containing 1 and 2 molecules of pyrogallol or gallic acid. Martini has described a micro test for molybdenum by the use of catechol (*Anal. Assoc. Quím. Argentina*, 1926, **14**, 177; *Mikrochem.*, 1928, **6**, 63), and recently Paget (*Bull. Sci. Pharmacol.*, 1930, **37**, 537) has shown that adrenaline hydrochloride in 0·5 per cent. solution gives with ammonium molybdate solution a reddish-brown colour which changes to a greenish fluorescence after addition of sodium hydroxide.*

The test, as I use it, seems to be fairly specific for the *o*-dihydroxy-phenols; it is carried out as follows: To 2 c.c. of an aqueous solution of the phenol are added 0·5 c.c. of glacial acetic acid and 1 c.c. of a concentrated (14 per cent.) solution of ammonium molybdate. There appears immediately a reddish-brown coloration which is stable.

The limits of sensitivity of the test are as follows:

Pyrocatechol	1 in 75,000
Pyrogallol	1 in 100,000
Protocatechuic acid	1 in 75,000
Protocatechuic aldehyde	1 in 75,000
Gallic acid	1 in 200,000
Adrenaline	1 in 60,000

The following phenols give little or no coloration: Guaiacol, resorcinol, quinol, phloroglucinol, orcinol, phenol. Salicylic acid gives a coloration in strong solution, the limit being 1 in 3000.

J. H. Quastel.

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Cardiff City Mental Hospital.

* Since this was written my attention has been drawn to the fact that Kedesdy (*Mitt. Kgl. Materialsprüfungsamt*, 1907, **25**, 268) has used a nitric acid solution of ammonium molybdate for the colorimetric determination of gallotannin and gallic acid.

THE *p*H VALUE OF CULTURE MEDIA.

IN describing "The Testing of Admiralty Disinfectant Fluid" in the February number of THE ANALYST, Messrs. Patterson and Frederick emphasise the importance of the *p*H value of the broth used in the test. They state that the method of preparing the broth in their laboratory is that of McIntosh and Smart (*Brit. J. Exp. Path.*, 1920, **1**, No. 1, February).

The reaction specified for Admiralty broth is *p*H 7·6, but considerable variation from this figure may be obtained if McIntosh and Smart's method of control is used. It is our experience that a broth showing no coloration with phenolphthalein (and, therefore, conforming to McIntosh and Smart's technique) may have a reaction as high as *p*H 8·2.

The exact point at which indicator colour changes occur will always remain a matter of individual observation. McIntosh and Smart state that phenolphthalein first shows a pink colour at *p*H 7·9, but the generally accepted figure is *p*H 8·3.

In any case, a more rigid method of controlling the reaction of the broth seems desirable, and, as the use of comparators for *p*H control is now recognised to be quite satisfactory, it would appear to be much simpler and more accurate to specify a reaction of *p*H 7·6, using a reliable comparator with phenol red as indicator.

JAS. GIBSON.

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PLAISTOW, E.13.

Erratum: In the Note by Messrs. Rideal and Sciver (April issue, p. 250, line 21): *For* "2 per cent. *read* "10 per cent."

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, 1930.

OF the 1127 samples examined, 1052 were informal, and 75 formal.

NITRATES IN WATERED MILK.—Nine samples of milk from one farm showed evidence of tampering, although only two contained less than 8·5 per cent. of solids-not-fat. In every case but one nitrates (derived from the water supply at the farm) were present in the milk. It was significant that from the time the

farmer knew that his milk was being sampled, there was a steady improvement in the quality of successive samples, but even in samples taken on the last day nitrates were still present in small amount, showing that water was still being added.

TABLE VINEGAR.—In two cases the bottle was definitely labelled "Table Vinegar," but the contents consisted entirely of artificial vinegar. In a case taken in Birmingham in 1926 (ANALYST, 1927, **52**, 29) the magistrates decided that table vinegar should consist of malt vinegar. Both the vendors concerned were communicated with, and in both cases they agreed not to use the offending label in future.

SAUSAGES.—When a formal sample (containing 600 parts of sulphur dioxide per million) was bought, no label was given to the inspector, and there was no notice visible in the shop, but while the sample was being divided a card in the window, advertising some New Zealand mutton, was removed, showing the preservative notice underneath. Obviously, that could not be said to have been "conspicuously visible," and the vendor was prosecuted and fined £1.

DYED MURCIA ORANGES.—These were bought from a street barrow and were small oranges of a rich colour. When examined, they were found to be artificially coloured with a coal-tar dye. Similar oranges were bought in Birmingham some years ago (*cf.* ANALYST, 1925, **50**, 183), and apparently the practice has been carried on for a considerable time. The Town Clerk's Department, however, considered that it would be inadvisable to prosecute as, in their opinion, it was impossible to prove by analysis that the sample did not consist of Murcia oranges. The fruit was of inferior quality, but, after dyeing, was an excellent imitation of a Tangerine orange. Incidentally, the fraud may be detected by examination of the calyx which, in the genuine orange, is green, and in the dyed article was coloured red.

COFFEE EXTRACT.—This was a proprietary article, and was shown, on analysis, to consist of dried aqueous extract of coffee. In the description on the label, however, a statement was made that the contents (weighing 1 ounce) were equivalent to more than half-a-pound of coffee. Coffee, however, yields about 25 per cent. of its weight of extract when treated with water, so that, at the most, 1 ounce would be equivalent to only four ounces of coffee, quite apart from the fact that the flavour and aroma of the original coffee are altered and partly lost. The firm was communicated with, and their explanation was to the effect that the average person does not extract everything out of ordinary coffee, and that 1 ounce of the extract will give as much usable beverage as is generally obtained from half-a-pound of ordinary coffee. This is obviously not what the ordinary purchaser would imagine the statement to mean, and the firm finally agreed to omit the sentence from the description both on the wrapper and on the tin.

BEEF SUET.—A sample contained 85 per cent. of fat, and the label stated that "8 oz. would go as far as 12 oz. of ordinary suet." This kind of statement is very misleading, and simply means that the housewife is careless enough to waste over one-third of every pound of raw suet she buys. Shredded suet certainly is prepared in a convenient form for use, but there is no need to exaggerate its qualities in this way. No satisfactory settlement has yet been made with the packers of this article.

H. H. BAGNALL.

CITY OF SALFORD.

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1930.

OF the 3290 samples examined during the year, 1556 were bought under the Food and Drugs Act, and of these 50 (3·2 per cent.) were adulterated.

CHEESE.—The necessity for a Cheese Bill is shown by a number of Salford cases in past years, and the wide variation in the product is brought out by 20 samples purchased in April and May, the inspector in each case asking for "cheese." Arranged in order of fat content on the dry substance, the samples ranged from 69·0 per cent. to 33·8 per cent. of fat, while the prices varied from 1s. 4d. to 10d. per lb. While one may pay 1s. 4d. for a cheese containing only 23 per cent. of fat, it is yet possible to purchase one with 40 per cent. at 10d. per lb. Under present conditions all these cheeses must be classed as genuine.

SULPHUR DIOXIDE IN DRIED APRICOTS.—Two samples (formal and informal) from the same dealer contained 3000 and 2700 parts per million, respectively. During the past two years the average amount of sulphites found in dried apricots has been about 500 parts per million. There is no doubt that such excessive quantities of "preservative" are really the result of attempting to improve the appearance of an inferior article by bleaching. An interesting experiment was made to see how much sulphite remained after the fruit had been prepared for the table in the ordinary way (soaking overnight and boiling for 45 minutes with water and sugar). After such treatment 70 per cent. of the original amount still remained. On the instructions of the Health Committee, the London agents of the packers were communicated with. They agreed to withdraw all the consignment from sale, and to recall any portions of it that had already reached the hands of retailers.

CASTOR OIL PILLS.—These pills, though bought as "Castor Oil Pills," were actually labelled "Compound Castor Oil Pills," the word "compound" being in comparatively small type. They contained various vegetable laxatives, chiefly aloes, with, at most, 5 per cent. of castor oil. A deputation was received from the Wholesale Association, and finally it was agreed that the pills should be described as "Compound Laxative Pills," "Laxative Pills," "Compound Aperient Pills," or "Aperient Pills," to be followed in each case by the statement: "Each pill contains (the appropriate amount) of castor oil." It was further agreed that the description used should be in type at least as prominent as the words "Castor Oil" on the label and in the descriptive matter.

STRENGTH OF SUNLIGHT.—In general, the monthly figures showed that the active amount of sunlight received in the centre of the City is considerably less than the amounts received at the outlying stations.

Influence of the Purity of the Potassium Iodide.—During the year it has been discovered that the purity of the potassium iodide used affects the results obtained by the method previously described (ANALYST, 1927, **52**, 641; 1929, **54**, 101) to a considerable extent. During one week in July the determinations at the Regent Road Station were made in quadruplicate as follows:

Two qualities each of sulphuric acid and potassium iodide were used, the first being ordinary "pure" chemical reagents (which were of excellent quality), and the second being the finest quality obtainable from the manufacturers of fine

chemicals. From these, four test solutions were prepared each day and exposed, side by side, with the following results:—

		Iodine in a week. Mgrms.
1.	Purest potassium iodide and purest acid ..	33·2
2.	Ordinary potassium iodide and purest acid ..	39·7
3.	Ordinary potassium iodide and ordinary acid ..	40·3
4.	Purest potassium iodide and ordinary acid ..	34·6

In this experiment it will be seen that the greatest variation is caused by the quality of the potassium iodide, the results of Nos. 1 and 4 falling in one class, and those of Nos. 2 and 3 in another.

Chemical examination of the potassium iodide revealed practically no difference, each sample being of high quality. Titration of the "ordinary" sample pointed to the presence of a little potassium chloride (about 0·5 per cent.), though this was not indicated by qualitative test. The lesson to be learned is that only potassium iodide of the highest purity should be used in this test. There is no doubt, however, that the figures taken for a period represent a good comparative measure of the sunlight received at the different stations.

H. E. MONK.

Department of Scientific and Industrial Research.

FOOD INVESTIGATION. Special Report No. 40.

THE CORROSION OF THE TIN-PLATE CONTAINER BY FOOD PRODUCTS.*

AFTER a review of work already done in connection with corrosion of tins by the contained foods, the apparatus used in connection with the experiments at the Low Temperature Research Station is described. The preliminary experiments indicate that the treatment of the steel may have a considerable effect on the rate of corrosion, and the value of the cold rolling process is emphasised. Further, the value of films of oxide is discussed, and the need for soundly constructed cans emphasised. The influence of the hydrogen-ion concentration on the corrosion of steel was studied in detail, and it was found that differences in the concentration at different points result in localisation of attack of the corroding medium, so that at high acidities exposed portions of the metal are particularly liable, and at low acidities the attack is directed towards pits, seams and other less exposed portions. Efficient exhaustion of the tins is specially important with low acidities. In the case of tin, elimination of air and other oxidising agents is very important, and corrosion of tin in the presence of the ferric salt is much more rapid than when free oxygen is present but iron absent. With a tin-iron couple the

* Obtainable at H.M. Stationery Office, Adastral House, W.C.2. Price 1s. 6d. net.

corrosion of the iron is remarkably decreased by contact with the tin; contact with iron increases the rate of corrosion of tin; total corrosion of the couple is less than that of a similar area of iron; corrosion of the tin increases as the pH of the corroding medium decreases in the presence or absence of air, and any hydrogen liberated is always from the iron. Experiments with tin plate bore out these conclusions. A study of inhibitors and accelerators of corrosion showed that sugars, particularly beet sugar, colloids such as agar and gelatin, and tin salts are among the former, whilst sulphides are accelerators. The results of adding these substances are, however, not foregone conclusions, but involve several simultaneously operating factors. Discoloration of canned foods by tin occurs in the presence of anthocyanin pigments, and double lacquering of the tins is necessary in these cases for a first-class pack, or cool storage. Iron may cause blackening, by combination with tannin, and the conditions governing the formation of sulphides in various classes of food were investigated in detail, particularly for marine products, corn, meat, and fruit. The end part of the Report deals with practical experiments and considerations; the conditions found favourable for the formation of hydrogen swells are low acidity, lacquer on the inside of tin, presence of substances (*e.g.* sulphides) which accelerate corrosion with products of high acidity, storage at high temperatures, and inefficient cooling after processing, the presence of absorbers of tin salts, inefficient exhausting and insufficient headspace. Conditions favouring perforations are low acidity, lacquering, presence of oxygen (due to inefficient exhausting or minute pores in the tins), presence of anthocyanin pigments or other oxidising agents, presence of substances which render tin salts insoluble, and inefficient cooling and storage at high temperatures. It is recommended that attention should be paid to technical and mechanical details, including the adjustment of acidity in canning fruits by the addition of 0·3 to 0·5 per cent. of citric acid, care in selecting sugar free from sulphur compounds, and the use of beet sugar as an inhibitor of corrosion, or possibly the addition of agar. The appendix deals with the examination of canned fruits for factory control.

D. G. H.

Standardisation of the Method of Presenting Results of the Analysis of Foods and Feeding Stuffs.

CONVENTION INTERNATIONALE POUR L'UNIFICATION DE LA PRÉSENTATION DES RESULTATS D'ANALYSE DES MATIÈRES DESTINÉES A L'ALIMENTATION DE L'HOMME ET DES ANIMAUX.*

RESOLUTIONS for unification in the presentation of results of the analysis of food materials concern the expression of notation, quantities of material, volume, temperature, calorimetric determinations, pressure, specific mass, density, refractive index, polarimeter readings, acidity, alkalinity, reducing sugars, iodine and bromine values, and the factor for protein. In the case of brandies the special

* *Ann. Falsificat.*, 1931, **24**, 69–75.

regulations enact that esters should be expressed as ethyl acetate; aldehydes as acetaldehyde; higher alcohols as isobutyl or isoamyl alcohol, and volatile acids as acetic acid. They are to be expressed as mgrms. per litre, and as mgrms. per 100 c.c. of absolute alcohol contained in the brandy analysed; extractives and fixed acidity as grms. per litre, and the letters "C.I." indicate conformity with these expressions. The Convention is to be ratified at Paris as soon as possible, and the Governments concerned are to append their signatures up to July, 1931.

D. G. H.

Ministry of Agriculture and Fisheries.

STATUTORY RULES AND ORDERS, 1931, No. 168.

AGRICULTURAL PRODUCE (GRADING AND MARKING), ENGLAND.

THE AGRICULTURAL PRODUCE (GRADING AND MARKING) (CIDER) REGULATIONS, 1931, DATED MARCH 23, 1931, MADE BY THE MINISTER OF AGRICULTURE AND FISHERIES AS TO GRADE DESIGNATIONS AND GRADE DESIGNATION MARKS FOR CIDER.*

In exercise of the powers conferred on him by the Agricultural Produce (Grading and Marking) Act, 1928, the Minister of Agriculture and Fisheries hereby makes the following regulations:—

1. Grade designations to indicate the quality of cider produced from apples and pears grown in England and Wales shall be as follows:—

SELECT CIDER (CHAMPAGNE PROCESS) or
SELECT CYDER (CHAMPAGNE PROCESS)
SELECT CIDER or SELECT CYDER

and the quality indicated by such grade designations shall be deemed to be as described in columns (2) and (3) of the First Schedule hereto.

2. A grade designation mark shall be any one of the grade designations specified in regulation 1 associated with the words "Empire Buying Begins at Home" and with the following mark, namely, a map of England and Wales in silhouette with the words "Produce of England and Wales" inscribed in a circle placed centrally in the map within which circle is a design representing the Union Jack, and which is more particularly described in the Second Schedule hereto.

3. These regulations shall come into operation on the 23rd March, 1931.

4. These regulations may be cited as the Agricultural Produce (Grading and Marking) (Cider) Regulations, 1931.

In Witness whereof the Official Seal of the Minister of Agriculture and Fisheries is hereunto affixed this twenty-third day of March, 1931.—CHARLES J. H. THOMAS.

* H.M. Stationery Office, Adastral House, London, W.C.2. 1931. Price 1d. net.

SCHEDULE I.

Cider made from Apples and Pears grown in England and Wales.

GRADE DESIGNATIONS AND CHARACTERISTICS.

Grade designation. 1.	General characteristics. 2.	Special characteristics. 3.
SELECT CIDER (CHAMPAGNE PROCESS) or SELECT CYDER (CHAMPAGNE PROCESS).	Produced from clean and reasonably sound cider apples only, or from a suitable blend of clean and reasonably sound high acid and sweet and/or bitter sweet apples and/or of clean and reasonably sound pears only; no concentrated apple juice or other fruit juices to be used; no foreign acids to be permitted; no sweetening substances to be used other than pure beet or pure cane sugar; acetic acid must not be present in such quantities that it is discernible to the palate; and the total volatile acids of the acetic type present must not exceed 0·15 per cent., expressed as acetic acid; to be free from preservatives and/or artificial colouring agents prohibited by the Public Health (Preservatives, etc., in Food) Regulations in force for the time being; to be free from artificial bouquets and essences; to be free from disorders such as ropiness and sickness.	In the process of manufacture (1) the late stages of fermentation must take place in bottle, and (2) the deposit must be removed and the removal of deposit must be by the disgorging process after a suitable period of storing. Artificial carbonation is not permitted. To the pure, *i.e.* undiluted juice or battery diffusion juice of similar gravity, may be added not more than 25 per cent. of its own volume of a syrup made from pure cane or pure beet sugar (the syrup or its constituents may be added at any stage of manufacture). The original gravity of the finished product, whether pure juice cider or a cider to which syrup has been added, must not be less than 1·040 at 60° F.
SELECT CIDER or SELECT CYDER	Produced from clean and reasonably sound cider apples only, or from a suitable blend of clean and reasonably sound high acid and sweet and/or bitter sweet apples and/or of clean and reasonably sound pears only; no concentrated apple juice or other fruit juices to be used; no foreign acids to be permitted other than a *maximum* proportion of 1·0 gramme per litre (equivalent to 0·16 ounce per imperial gallon) of either tartaric or citric acid; no sweetening substances to be used other than pure beet or pure cane sugar; acetic acid must not be present in such quantities that it is discernible to the palate, and the total volatile acids of the acetic type present must not exceed 0·15 per cent. expressed as acetic acid; to be free from preservative and/or artificial colouring agents, prohibited by the Public Health (Preservatives, etc., in Food) Regulations, in force for the time being; to be free from artificial bouquets and essences; to be free from disorders such as ropiness and sickness.	To the pure, *i.e.* undiluted juice or battery diffusion juice of similar gravity, may be added not more than 25 per cent. of its own volume of a syrup made from pure cane or pure beet sugar (the syrup or its constituents may be added at any stage of manufacture). The original gravity of the finished product, whether pure juice cider or a cider to which syrup has been added, must not be less than 1·040 at 60° F.

SCHEDULE II. This gives the Grade Designation Mark.

AGRICULTURAL PRODUCE (GRADING AND MARKING) ACT, 1928.

THE following Circular (S.C. 12234) has been sent to the Local Authorities administering the Act:

SIR,—It has been brought to the notice of the Ministry of Agriculture and Fisheries that many of the Officers who have been instructed by Local Authorities to execute the above-mentioned Act are in some doubt as to the extent of their duties. The following observations are intended for their guidance:

The Act is primarily an amendment of the Civil Law, but it also contains certain criminal provisions which are of considerable importance. The Act may accordingly be considered under two headings—Civil Provisions and Criminal Provisions.

CIVIL PROVISIONS.—Under Sections 1 and 2, the Minister of Agriculture and Fisheries may make regulations prescribing grade designations for any kind of agricultural produce, and defining the quality indicated by such designations. Any person may use these designations, no special authority being required. The Minister has also prescribed a mark, generally known as the National Mark, which, when used in association with a grade designation, constitutes a grade designation mark. The Minister may authorise or empower a person or committee to authorise the application of grade designation marks, and persons thus authorised are known as "authorised packers."

Grade designations and definitions of quality and also grade designation marks are prescribed by regulations (Statutory Rules and Orders). A purchaser of produce to which a grade designation or National Mark is applied has a definite contract that the produce accords with the definition implied by the designation, and if it does not do so he has his remedy in respect of the breach of contract.

It may happen that where the definition includes a reference to the number, quantity, measure, gauge or weight of the goods, a seller, whether the original packer or subsequent handler who fails to fulfil the contract, may also fall under suspicion of having committed an offence against Section 2 (2) of the Merchandise Marks Act, 1887. As regards prosecutions under this last-mentioned Act, the Ministry is, under the Merchandise Marks (Prosecutions) Act, 1894, and the Regulations (S.R.O., No. 49 of 1914), made under that Act, the authority charged with this duty in all matters relating to agricultural and horticultural produce. Where, therefore, any suspicion of an offence against the Act of 1887 arises, the Ministry desires that the question of prosecution should be referred to it with a full report of the circumstances for decision as to the steps to be taken.

The use of grade designations and the National Mark is entirely voluntary, and the object of the Ministry is to encourage their use in order to secure the widest possible measure of standardisation of product, pack and package throughout the trade in home produce. For this reason, the Ministry wishes to dispel any idea that the adoption of the statutory grade designations and authorisation to apply the National Mark involve increased risk of incurring criminal liability. So far as the National Mark is concerned, it is believed that the machinery provided for its administration is sufficient to prevent the authorisation of fraudulent persons, or at least to ensure their expulsion from the select body of authorised packers before they have time to commit fraud in connection with the Mark. The use of the statutory grade designations without the concurrent use of the National Mark is, as yet, uncommon, and accordingly of no commercial significance.

Officers of Local Authorities are not, therefore, required to undertake any duties in connection with questions arising under Sections 1 and 2(1) and (2) of the Act.

CRIMINAL PROVISIONS.—It comes within the province of Local Authorities to deal with offences under Section 2 (3) (forgery or representation of the National Mark) and Section 2 (4) (the unauthorised application of the National Mark). Offences under Section 2 (3) are of a very serious character, and if they were committed it would be most desirable that the criminal should be brought to justice.

Local Authorities are also concerned with Sections 3 and 4 of the Act.

Examination of Eggs.—Section 3 requires that all eggs, whether of English, foreign, or Empire origin—that have been preserved in any way shall be marked before sale or exposure for sale. The manner in which such eggs must be marked is prescribed in the Agricultural Produce (Grading and Marking) (Eggs) Regulations, 1930. In the case of imported eggs which have been preserved, the marking is in addition to that prescribed in the Merchandise Marks (Imported Goods) No. 5 Order, 1928, as an indication of origin. Cold-stored and chemically-stored eggs

are exempted from this provision, and are dealt with under Section 4. At the moment, therefore, Section 3 applies only to eggs preserved in lime water, water-glass, or oil.

It can usually be proved by analysis when these methods of preservation have been employed, but as it is always possible that individual eggs may fail to afford the proof required, it may be necessary to take a series of samples in cases where there is reason to suspect that such eggs are being sold unmarked.

In a prosecution under Section 3 of the Act, it is not necessary to prove the method of preservation. It is sufficient to show that the eggs have been subjected to a process of preservation other than cold storage or chemical storage.

The Government Chemist has been investigating tests by which the fact that eggs have been preserved in oil, water-glass or lime may in certain cases be detected, and the Ministry understands that, in any case, where a Public Analyst desires information as to these methods in connection with samples which have been submitted to him under the Act, the Government Chemist will be glad to communicate to him the latest results. Communications on this subject should be addressed to the Secretary, Ministry of Agriculture and Fisheries.

Section 4 requires that all premises used by way of trade or for purposes of gain for the cold storage or chemical storage of eggs, of whatever origin, must be registered, and that all *British* eggs which have been kept in cold storage or chemical storage must be marked before being removed from the storage premises. The manner of marking is prescribed in the Agricultural Produce (Grading and Marking) (Eggs) Regulations, 1930.

Section 4 also makes it an offence for any person to remove, alter, or obliterate any mark which was borne by an egg at the time it was stored in cold storage or chemical storage premises, or for anybody to sell or expose for sale any eggs from which such a mark has been removed or on which the mark has been altered or obliterated.

As a result of the foregoing provisions, the only *unmarked* eggs that may be lawfully offered for sale in the home market are fresh eggs (*i.e.* eggs not preserved, cold-stored, or chemically stored) produced in Great Britain and Northern Ireland.

The Ministry has its own inspection service in connection with the grading of produce and the administration of the National Mark Schemes, and should the Ministry's Inspectors, in the course of their duties, obtain any information as to contraventions of Section 2 (3), Section 2 (4), Section 3, or Section 4 of the Act, they will communicate the evidence to the appropriate officer of the Local Authority, with a view to the taking of such further action as the Local Authority may think fit.

I am, Sir, your obedient servant,

(*Signed*) CHARLES J. H. THOMAS.

March 31st, 1931.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Determination of Lactic Acid in Milk and Milk Products. L. H. Lampitt and M. Bogod. (*Compt. rend. du Neuvième Congrès de Chimie Industrielle ; Chim. et Ind.*, Special No., 510–5 (March, 1930).)—The method depends upon the oxidation of lactic acid to acetaldehyde by means of potassium permanganate, as suggested by Boas (*Deutsch. Med. Wochenschr.*, 1893, **19**, 340) and later developed by von Furth and Charnass (*Biochem. Z.*, 1910, **26**, 199) and Embden (*Abderhalden's Handbuch der biochemischen Arbeitsmethoden*, 1912, **5**, 12, 55). For the determination the following reagents are required:—Sodium hydroxide, 0·1 *N*; sulphuric acid, 0·1 *N*; phosphotungstic acid reagent (Hinton and Macara, ANALYST, 1927, **52**, 677); saturated solution of copper sulphate; pure

powdered calcium hydroxide; sulphuric acid, 5 *N*; potassium permanganate, 0·004 *N*; standardised (0·1 *N*) iodine solution; sodium bisulphite, approx. 0·02 *N*.

Procedure.—To 10 grms. of milk, 4 grms. of condensed milk or 1 grm. of dried milk are added 10 ml. of 0·1 *N* sodium hydroxide and about 30 ml. of water. The mixture is stirred, heated to boiling, and the liquid transferred to a 100 ml. measuring flask and cooled, and to it are added 10 ml. of 0·1 *N* sulphuric acid. This is followed by 5 ml. of phosphotungstic acid, and water is added to the mark; the mixture is well shaken and filtered, the first 10 ml. of filtrate being rejected. Twenty ml. of the filtrate are accurately measured into a 50 ml. flask, and 2 ml. of saturated copper sulphate added, followed by 3 grms. of calcium hydroxide. The whole is mixed, and water is added to the mark; the flask is shaken and allowed to stand for 15 minutes, with occasional shaking, and the contents are transferred to a centrifuge tube. After centrifuging for 5 minutes at 2000 to 2500 R.P.M. the supernatant liquid is filtered through a fine filter paper. Twenty-five ml. of this filtrate are accurately measured into a 250 ml. distillation flask which contains a little talc and 10 ml. of water; 1 ml. of 5 *N* sulphuric acid is added, and the flask is attached to a condenser; a dropping funnel is attached, and 100 ml. of 0·004 *N* potassium permanganate are poured into the funnel. The adaptor at the end of the condenser is made to fit into a flask of 100 to 110 ml. capacity, containing 10 ml. of sodium bisulphite solution; the end of the adaptor dips below the level of the bisulphite solution. A narrow tube from the flask extends to a U-tube containing 1·0 ml. of 0·01 *N* iodine solution to which 10 ml. of cold water have been added; both the receiving flask and the U-tube are immersed in ice. The distillation flask is now heated with the tip of a Bunsen flame just touching the bottom of the flask; when boiling begins, the permanganate solution is allowed to run, drop by drop, into the boiling liquid. The dropping is so regulated that 100 ml. may be added in 50 to 60 minutes. In this period, from 80 to 100 ml. of liquid are distilled. The receiving flask is now removed, the distillate and contents of the U-tube are rinsed into a titration flask, and the excess of bisulphite titrated with standard 0·01 *N* iodine solution; allowance is made for the iodine in the U-tube. Ten ml. of the bisulphite solution are titrated at about the same time. The difference between the titrations, multiplied by 0·45, gives the amount of lactic acid in mgrms. Determinations on known quantities of lactic acid added to milk powder showed a loss of acid due to the clarification of approximately 10 per cent.; a more accurate result for the lactic acid present is, therefore, obtained by multiplying the amount found by 10/9. Determinations have been carried out on milk, condensed milk and dried milk of different degrees of acidity, with and without added alkali. It has been shown that the total lactic acid content of normal milk is less than the equivalent of the acidity determined by titration, and that this difference diminishes or changes in sign if added alkali is present.

The Fat of Sow's Milk. O. Laxa. (*Ann. Falsificat.*, **1931, 24**, 87–88.)—Sow's milk was dried with sand, the residue extracted with ether, and the fat dried in a current of carbon dioxide. The granular, clear, brown-yellow fat had

the following characteristics:—Solidif. pt., 17–18·5° C.; m.pt., 28° C.; butyro refractometer reading at 40° C., 52; saponification value, 193·9; iodine value, 58·2; Hehner value, 93·7; Reichert–Meissl value, 2·1; Polenske value, 1·2; solidif. pt. of insoluble acids, 36·5–37·5° C.; m.pt., 39–40° C.; iodine value, 61·9; molecular weight, 276·9. The melting point of the saturated acids was 60·5, and their molecular weight 256, and the composition of the fat is deduced as oleic acid, 64·5; palmitic, 26·6; myristic, 2·6; volatile acids (caprylic and capric), 1·4; and glycerol, 4·9 per cent. D. G. H.

Determination of Starch in Flour by Diastase and Acid Hydrolysis. B. G. Hartmann and F. Hillig. (*J. Assoc. Off. Agr. Chem.*, 1931, **14**, 112–116.)—The results of further work on peptic digestion of starch-containing materials prior to diastatic conversion of the starch (ANALYST, 1927, **52**, 160) show that the yield of starch is materially increased by this procedure. In the peptic digestion the acidity is adjusted to correspond with 5 c.c. of *N* hydrochloric acid per 100 c.c. of substrate. After this digestion the mixture is carefully neutralised with alkali, then slightly acidified with hydrochloric acid, and, finally, treated with calcium carbonate to ensure the virtual neutrality required for the proper function of the diastase. It is shown that the action of the pepsin consists solely of digestion of the proteins, the starch being thereby rendered accessible to diastatic conversion. In addition to this modification of the official method (*Assoc. Off. Agr. Chem., Methods of Analysis*, 1925, 119), the preliminary treatment of flour, etc., with ether and alcohol to free it from sugars and fat is simplified and rendered more reliable. Full details of the procedure are given. The percentages of starch found in this way in four commercial starches and in wheaten flour are slightly lower than those obtained by subtracting from 100 the sum of the percentages of moisture, fat, protein (N × 5·7) and ash; the undetermined matter, probably crude fibre, etc., amounted to 0·5 per cent. with the wheaten flour, and varied from 0·1 to 0·9 per cent. with the commercial starches examined. T. H. P.

Increase in the *p*H Value of White and Yolk of Hens' Eggs. P. F. Sharp and C. K. Powell. (*Ind. Eng. Chem.*, 1931, **23**, 196–199.)—The *p*H value of the white of untreated eggs rises very rapidly after the eggs are laid owing to the escape of carbon dioxide, and increases more rapidly as the temperature rises. For instance, from an initial value of 7·60, a *p*H value of 9·25 will be reached in two days at 37° C., in five days at 16° C., and in ten days at 2° C. After long periods of storage, particularly at the higher temperatures, the value begins to decrease. In the case of the yolks, the *p*H value increases at a slower rate. Dilution of the white and yolk has but little effect on the increase of the *p*H value. W. P. S.

Determination of Small Proportions of Invert Sugar in Raw Sugars. L. Eynon and J. H. Lane. (*J. Soc. Chem. Ind.*, 1931, **50**, 85–86T.)—In the determination of invert sugar in unclarified solutions of sugar products (ANALYST, 1923, **48**, 277; 1924, **49**, 90), the errors due to reducing non-sugars and to calcium salts act in opposite senses. With low-grade products, such as molasses, the nett

effect of these two errors may be serious, but with raw sugars such effect is negligible. The invert sugar Table I (ANALYST, 1923, **48**, 221) does not make provision for sugar samples containing less than 0·3 per cent. of invert sugar, but these cases are met by dissolving the material (25 grms.) with such quantity of neutralised invert sugar solution that the whole, after being made up to 100 c.c., contains 0·1 per cent. of added invert sugar. The titration is then carried out as accurately as possible, the percentage of invert sugar in the sample being obtained by deducting 0·1 from the percentage found and multiplying the remainder by 4. This procedure renders possible the determination of 0·01 per cent. or even less of invert sugar, and is useful also for testing the purity of sucrose preparations intended for purposes of standardisation. The acid, standard 1 per cent. invert sugar solution, prepared as already described (*J. Soc. Chem. Ind.*, 1923, **42**, 34T), is remarkably stable, its titre remaining practically unchanged for many months, despite the formation of a small quantity of mould mycelium.

The following table, referring to 10 c.c. of Fehling solution, gives the burette readings for solutions containing 25 grms. of sugar sample, plus 0·1 grm. of added invert sugar per 100 c.c. It applies strictly to solutions containing 25 grms. of sucrose per 100 c.c., but the less amount given by 25 grms. of raw sugar introduces an error negligible in ordinary work.

Volume of solution required. c.c.	Invert sugar in sugar sample. Per Cent.	Volume of solution required. c.c.	Invert sugar in sugar sample. Per Cent.	Volume of solution required. c.c.	Invert sugar in sugar sample. Per Cent.
20	0·464	28	0·209	36	0·066
21	0·423	29	0·188	37	0·052
22	0·384	30	0·168	38	0·040
23	0·348	31	0·148	39	0·028
24	0·315	32	0·128	40	0·017
25	0·284	33	0·111	41	0·008
26	0·257	34	0·095	41·7	0·000
27	0·232	35	0·080		

T. H. P.

Isolation of Quinic Acid from Fruits. E. F. Kohman and H. H. Sanborn. (*Ind. Eng. Chem.*, 1931, **23**, 126.)—Quinic acid may be isolated from prunes and cranberries by a process depending on the solubility of the lead and calcium salts of the acid, compared with the relative insolubility of the same salts of other inorganic acids. Although the separation is not strictly quantitative, there are indications that prunes and cranberries contain about 1 per cent. of quinic acid; the acid is also present in grapes. W. P. S.

Determination of Rancidity in Oils and Fats. A. Taffel and C. Revis. (*J. Soc. Chem. Ind.*, 1931, **50**, 87–91T.)—In order to eliminate the disturbing effect of the presence of peroxides in the ethyl ether used in the Kreis test for rancidity, and also the emulsification due to ether, a few drops of a 5 per cent. solution of phloroglucinol in alcohol are used in place of the 10 c.c. of 0·1 per cent. ethereal solution of the original test. Ten c.c. of oil (or 5 c.c. of a very rancid oil) are shaken

with 10 c.c. of concentrated hydrochloric acid for 30 seconds, 10 drops of 5 per cent. alcoholic phloroglucinol then added, the mixture shaken for 30 seconds, and set aside for 1 or 2 minutes, and the colour noted. The test, as thus used, was found more satisfactory, and in some cases more delicate than the usual Kreis test. Oils which have become rancid or have been air blown at fairly moderate temperatures contain (*a*) certain peroxides easily reducible by hydriodic acid, and those which have become rancid or been blown at higher temperatures such as 120° C. contain, in addition to a large proportion of these substances, other peroxides (*b*) which offer more resistance to reduction by hydriodic acid. The amount of each type of oxidation product may be determined, and the method depends on the fact that the amount of iodine set free by a rancid oil in the presence of barium iodide may be considered a measure of the peroxides or reducible oxygen in the oil. (*a*) Oils with a slight degree of rancidity, as shown by the Kreis test. Ten grms. of the oil are added to 40 c.c. of glacial acetic acid, followed by 2 grms. of anhydrous barium iodide (or 2 c.c. of 50 per cent. potassium iodide solution). After shaking, the mixture is poured into 100 c.c. of water, the bottle rinsed with 20 c.c. of water, and the liquid titrated with 0·1 *N* thiosulphate solution in the presence of starch. A blank is carried out without oil, and the titration gives a measure of the easily reducible peroxides. If the oil is strongly rancid the same ingredients are put in a 60 c.c. bottle, the remaining air displaced with carbon dioxide, and the stoppered bottle left in boiling water for 2 minutes, after which it is shaken, put back for 2 minutes, and again shaken, the hot contents poured into 150 c.c. of water, and the titration carried out as before. (*b*) The proportions of oil, barium iodide and acetic acid necessary to give the maximum thiosulphate titration must be found by experiment, but 1·25 to 2·5 grms. of oil, 10 to 20 grms. of barium iodide, and 100 c.c. of acetic acid are usually suitable. The mixed reagents are placed in a 150 c.c. distilling flask, air is displaced with carbon dioxide, and the whole heated to the b.pt. and kept just boiling for 30 minutes in a current of carbon dioxide. The flask is cooled, the contents poured into 400 c.c. of water containing starch solution and dilute sulphuric acid, and titrated, the titration giving the measure of all the difficultly reducible oxides. These methods were tested on B.P. liquid paraffin containing benzoyl peroxide, and satisfactory agreement with the calculated figures was obtained. The procedure has been worked out in detail for arachis oil, but the methods are apparently of universal application to all types of rancidity, and give definite and reproducible figures distinguishing between the two types of rancidity. D. G. H.

Oil from the Seeds of *Ribes rubrum* L. (Red Currant). A. Jermstad. (*J. Pharm. Chim.*, 1931, **123**, 243–244.)—The hard dried seeds of the red currant cultivated in Norway, yielded to ether 20·4 per cent. of a yellow oil of bland taste, and having the following characteristics: Sp. gr. at 20° C., 0·9311; $n_D^{20°}$, 1·4801; acid value, 3·1; saponification value, 193·3; and iodine value, 176·3. These figures agree with those for the oil obtained from fruit grown in other countries. D. G. H

Solubility of Tea-seed Oil in Alcohol of Varying Concentrations. K. Hashi. (*J. Soc. Chem. Ind., Japan*, 1931, **34**, 64B.)—A purified and decolorised sample of tea-seed oil having the following properties was used: Sp. gr. at 25°/25° C., 0·9125; n_D^{25}, 1·4650; acid value, 0·53; iodine value (Wijs), 77·7. The solubility of the oil in alcohol and water mixture was measured by Alexejeff's method. Known quantities of oil and solvent were placed in a closed glass tube, heated with shaking, and the temperature noted at which both phases merged into one. The clouding point on slow cooling with shaking was also determined. The results are expressed in the following table:

Alcohol per cent., by weight.	Critical temp. °C.	Critical concentration (oil per cent.).
99·75	71·0	40·8
95·50	99·8	41·5
90·45	129·8	44·0
85·50	155·0	48·0

The results are also given in graph form. R. F. I.

Solubility of Rape Oil in Alcohol of Varying Concentrations. K. Hashi. (*J. Soc. Chem. Ind., Japan*, 1931, **34**, 66B.)—Purified and decolorised rape oil was used, having the following constants: Sp. gr. at 25°/25° C., 0·9117; n_D^{25}, 1·4690; acid value, 0·09; iodine value (Wijs), 99·5. The same technique was employed as in the preceding abstract. The results are given in tabular and graphical form:

Alcohol per cent., by weight.	Critical temp. °C.	Critical concentration.
99·75	86·3	38·5
95·50	113·0	40·3
90·45	140·3	43·0

R. F. I.

Use of Acridine Dyestuffs for the Determination of Nitrites. W. M. Rubel. (*Z. Unters. Lebensm.*, 1930, **60**, 588–592.)—"Rivanol" (Koremann), 2-ethoxy-6.9-diamino-acridine hydrochloride, $C_2H_5O.C_6H_3CN(NH_2).C_6H_3NH_2.HCl$, $3H_2O$ is a yellow-green antiseptic, which has a solubility of 1:260 and is fairly stable in the dark. If 0·5 c.c. of a 0·1 per cent. solution and 0·5 c.c. of hydrochloric acid (sp. gr. 1·06) are added to 10 c.c. of a 2- to 100-fold dilution of the liquid to be investigated, a yellow-green to orange or red colour is obtained, depending on the amount of nitrite present. This may be matched against a scale of standard solutions containing (*e.g.*) 0·1 (yellow) to 0·001 mgrm. (red) of N_2O_3 (as sodium nitrite) in 10 c.c., and treated in the same way, the final comparison being made in a colorimeter of Duboscq type. The colour, which results from diazotisation of the amino-group, changes to yellow on heating, and is stable in the light for 1 hour, when a brown precipitate appears, but for longer in the dark. Its sensitiveness (0·001 mgrm./10 c.c.) is greater than that of the *m*-phenylenediamine reaction, and equal to that of the Griess reaction, but the colour is stabler than that of the latter and, unlike it, is unaffected by phenol and

ammonium salts, and is only slightly suppressed by thymol. Amino-acids, less than 10 per cent. of sodium chloride, nitrates, glucose and lactic acid have no effect, aldehydes weaken the colours, and free iodine produces a green-blue colour. Free ammonia, which interferes with the colour by alteration of the *p*H value, must be neutralised. Satisfactory results were obtained with sugars and extracts from meats. J. G.

New Lead Iodide Double Salt of Trigonelline. K. Lendrich and F. Mayer. (*Z. Unters. Lebensm.*, 1930, **60**, 569–575.)—Raw, whole coffee beans were boiled beneath a reflux condenser with 70 per cent. alcohol, caffetannic acid separated, and caffeine (simultaneously extracted with the trigonelline) was removed from the alcoholic extract by means of chloroform, the alcohol then expelled by evaporation under reduced pressure, and the aqueous solution cleared with lead acetate and treated with solutions of bismuth and potassium iodides. A suspension in water of the resulting brick-red precipitate was treated with hydrogen sulphide and a slight excess of hydriodic acid, and lead acetate added to the filtered liquid, which was then again filtered immediately to remove the bulk of the free lead iodide. Trigonelline lead iodide was deposited, on standing over-night, in dense golden needles, $C_7H_7NO_2,PbI_2$ (m.pt. 217° C., with decomposition), and was freed from lead iodide by recrystallisation from warm water, and dried at 105° C. This salt was also prepared from the free base by addition of a mixture of lead acetate and iodide solutions containing 1/3 of the calculated equivalent quantity of the latter. The base itself was prepared from the coffee-extract by separation as the mercuric chloride salt; the chloride was then produced by the action of hydrogen sulphide and treated with silver oxide. J. G.

Assay of Pyramidon by the Silver Cyanide Method. R. Machtou. (*J. Pharm. Chim.*, 1931, **123**, 329–333.)—One grm. of the pyramidon is dissolved in water and the solution made up to 100 c.c. To 50 c.c. of this solution are added 50 c.c. of a 5 per cent. solution of mercuric chloride, and the solution is vigorously shaken and filtered. The mercury in 10 c.c. of filtrate is determined by the silver cyanide method, using a solution made by pouring 0·05 *N* silver nitrate solution into 100 c.c. of water, to which have been added 10 c.c. of ammonium hydroxide and 1 c.c. of 10 per cent. potassium iodide solution, adding this until a distinct opalescence persists. If "*n*" is the quantity of 0·05 *N* silver solution used, *n*/2 subtracted from 10 (*a*) (the amount of silver solution corresponding with the mercury in the solution) is the quantity equivalent to the cyanogen combined with the mercury. This value may be greater or less than 5·5. In the latter case the Denigès formula $A=a\times 0{\cdot}192$ is used. In the former case the mercuric filtrate is diluted to twice the volume, and the factor multiplied by 2. In order to determine the amount of mercury fixed by the pyramidon, the percentage of mercury in the 50 c.c. of the solution used for precipitating the pyramidon must be known; it is determined on 10 c.c. of the solution made up to 50 c.c., 10 c.c. of this being used. The method breaks down if the pyramidon is adulterated with antipyrin but was otherwise found very accurate for varying quantities of pyramidon. D. G. H.

Direct Determination of Available Carbon Dioxide in Baking Powder. M. R. Coe. (*J. Assoc. Off. Agr. Chem.*, 1931, **14**, 99–102.)—The two separate determinations required by the gasometric method for ascertaining the available carbon dioxide in baking powder (*ibid.*, 1923, **6**, 453; *A.O.A.C., Methods of Analysis*, 1925, 305) may be reduced to a single determination by use of the following procedure: 25 c.c. of 5 per cent. ammonium sulphate solution are run into the 250 c.c. decomposition flask containing 1·7 grm. of the baking powder, the liquid being then kept at the boiling point until evolution of gas ceases and afterwards cooled to room temperature. When equilibrium is established, usually in about 15 minutes, the volume of the available carbon dioxide is read on the graduated tube and suitably corrected for temperature and pressure. If the total carbon dioxide in the sample is also required, this may be determined on the same portion of material without detaching the flask from the apparatus: The burette containing a few c.c. of the ammonium sulphate solution is filled with dilute sulphuric acid (1+5), 25 c.c. of which is run into the flask. The liquid is heated almost to boiling point and allowed to cool as before. The volume of gas then read is diminished by the volume of acid used; the remainder, corrected for temperature and pressure, represents the total carbon dioxide. The use of ammonium sulphate solution in this process ensures satisfactory evolution of carbon dioxide from baking powders of all varieties, acts as a protein-coagulant with powders containing egg-albumin, and thus destroys foam, and obviates the low results given by phosphatic or egg-albumin powders when distilled water is employed. The details of the operations are described.

T. H. P.

Biochemical.

Studies on Arginine. I. Rate of Catabolism of Arginine in Rats, including Method for Determination of Arginine in Biological Material. V. C. Kiech, J. M. Luck and A. E. Smith. (*J. Biol. Chem.*, 1931, **90**, 677–696.)—A volumetric method is described in detail for the determination of arginine in protein-free tissue extracts. The arginine is converted in the presence of arginase to ornithine and urea, and the latter is determined as dixanthydryl urea by oxidation with potassium dichromate and sulphuric acid. An alternative and more rapid method was devised, the principle of which was heat coagulation for removal of the tissue proteins and the use of urease for destruction of the pre-formed urea, and this was compared with the first (tungstic acid) method. However, the arginine values obtained by the heat coagulation method were too low, and added arginine was unsatisfactorily recovered, but with the tungstic acid method the extra arginine was recovered fairly well. In fasting female rats the arginine content was found to average 26·1 mgrms. per 100 grms. of muscle, and 27·5 mgrms. per 100 grms. of liver-free carcase. The values for liver were omitted because of fluctuations, probably due to the great activity of the arginase in the macerated organ, which gave to the liver values an uncertain significance. An arginine content of 25 or 30 mgrms. per 100 grms. of tissue corresponds with 2 or 2·5 mgrms.

of arginine α-amino nitrogen. This in turn represents 4 or 5 per cent. of the non-protein amino nitrogen content of rat muscle, liver, or carcase. On the assumption that all of the non-protein amino nitrogen is present in the form of amino acids with a mean molecular weight of 120, the content of the latter would be about 390 mgrms. per 100 grms. of tissue. Thus arginine would account for about 6 or 7 per cent. of the non-protein amino acids of rat muscle and carcase. These analyses demonstrate clearly the existence of arginine as a constituent of vertebrate muscle. This is not in harmony with the conclusions of Kutscher and Ackermann (*Z. Biol.*, 1926, **84**, 181), who, in summarising their extensive investigations on the extractions of muscle expressed the generalisation that arginine, though a characteristic constituent of invertebrate muscle, was absent from the vertebrates. Arginine, administered to fasting rats by subcutaneous injection, was rapidly catabolised. Less than 12 per cent. of the injected nitrogen was present at any time in substances other than urea and arginine. Ornithine, which presumably would be formed, must have been catabolised almost as rapidly as arginine. It is proposed to correlate these and related observations on the metabolism of amino acids with data on oxygen consumption and carbon dioxide production.

P. H. P.

Effect of Heat upon the Biological Value of Cereal Proteins and Casein. A. F. Morgan. (*J. Biol. Chem.*, 1931, **90**, 771–792.)—A brief summary of recent literature on studies on the heat denaturation of proteins is given, and the experiments of the author are described in detail. Preliminary growth experiments with young rats showed that the protein of cereals subjected to dry heat or toasting at approximately 200° C. for 45 minutes or to similar procedures during manufacture is not well utilised for growth. Cooking with water had but little similar effect, and caramel formation during toasting was found to account for only a small part of the injury. The addition of 5 per cent. of casein to these toasted diets very nearly made up the discrepancy between the latter and correspondingly supplemented raw diets, thus indicating that the deficiency observed lay in the protein fraction of the toasted diet. When young rats were given diets which contained raw and toasted (heated at 150° C. for 30 minutes) wheat gluten as source of protein at 9, 12, 15, 18, 21 and 24 per cent. levels (crude protein), in a diet otherwise adequate, the growth in 56 days per grm. of protein eaten was found to be 1·29 to 1·40 for raw gluten at all levels up to 18 per cent., and to fall to 1·15 and 0·98 at 21 and 24 per cent. The corresponding figures for the toasted gluten were 0·94 to 1·09, 1·12 and 0·86. The maximum growth rate on both raw and toasted diets was seen at the 18 per cent. level, but the toasted gluten supported less growth than the raw, both absolutely and relatively to the amount eaten at all levels. Male and female animals were used in about equal numbers in all groups, and the factors were averaged, since differences in the rates of growth per grm. of protein eaten for the two sexes appeared to be insignificant. The biological values of raw, water-cooked and toasted whole wheat protein, alone and supplemented by 5 per cent. of casein, as determined by nitrogen balance on young rats

according to the modified Mitchell method, were found to be 64, 67 and 52 for wheat alone, and 67, 75 and 69 when supplemented by the casein, and in a similar comparison of biological values of raw and toasted wheat gluten at an approximately 12 per cent. level the figures obtained were 66 and 54. Large mature rats used for a similar study of raw and toasted wheat gluten gave values of 83 and 64, another test with raw and toasted casein at an 8 per cent. level gave values 66 and 53. In all cases the differences between the biological values of raw and toasted proteins were found to be more than 6 times as great as their probable errors. It is emphasised that the *digestibility of the toasted proteins was but little different from that of the raw*, particularly in the older animals, and the unexplainable loss of nitrogen occurred chiefly in the urine; thus the change produced by the heat treatment lies probably in the assortment or availability of the amino acids absorbed.

P. H. P.

Effect of Drying and Sulphuring on Vitamin *C* Content of Prunes and Apricots. A. F. Morgan, A. Field and P. F. Nicholls. (*J. Agric. Res.*, 1931, **42**, 35–45.)—In a study of the antiscorbutic property of peaches by Morgan and Field (*J. Biol. Chem.*, 1929, **82**, 579; ANALYST, 1929, **54**, 483) all of the fruit was from the same orchard, and the fresh fruit was tested along with the sun-dried and dehydrated products, sulphured and unsulphured. The sulphured peaches, both sun-dried and dehydrated, were found to have retained the full antiscorbutic value of the fresh fruit, but the unsulphured apparently retained none. Similar tests with prunes and apricots, involving a larger variety of drying conditions, were also reported to have been made, but were not then described in detail. The questions were raised: (1) Does sulphur dioxide protect other fruits equally well? (2) If so, how much is required for such protection? (3) How is the protective effect achieved? Each of these questions is now answered, in part at least. The vitamin *C* content of frozen fresh prunes and apricots and of prunes and apricots dried by various methods has been determined by biological technique; this is described. The fruit was prepared as described by Morgan and Field (*J. Biol. Chem.*, 1929, **82**, 579; ANALYST, 1929, **54**, 483; and *J. Biol. Chem.*, 1930, **88**, 9; ANALYST, 1930, **55**, 643). Doses of the different fruit products were given to guinea pigs for 60 and 90 days, and the rates of growth of the animals receiving the various doses were compared. Examinations were also made for symptoms of scurvy, and in cases where animals died because of insufficient protection from scurvy the length of the survival period was determined. The 60-day period is shown to be as effective for assay of vitamin *C* as the 90-day period. Frozen fresh prunes of two crops retained the vitamin *C* satisfactorily, but frozen fresh apricots packed in cases which were not evacuated, lost all of this property. A second lot packed in cases which were evacuated and filled with nitrogen before the fruit was frozen, retained the vitamin. The difference is ascribed to retention of tissue respiratory oxygen in the unevacuated lot. Sulphured, dehydrated and sun-dried prune products retained the vitamin *C* of the fresh fruit satisfactorily only when the fruit was dipped in lye in the usual commercial fashion before the sulphur dioxide treatment. This is ascribed to better penetration by the protecting

sulphur dioxide after the lye dipping. All unsulphured products of both fruits, whether sun-dried or dehydrated, were without antiscorbutic value. The dehydrated products, both prune and apricot, retained the vitamin *C* more completely than did the corresponding sun-dried fruit. The dehydrated and sun-dried apricots, containing 450 to 500 or more parts of sulphur dioxide per million, retained the antiscorbutic property more or less completely. With less than this amount, all products lost this property completely. The tendency to loss of vitamin *C* in frozen, sun-dried and dehydrated apricots appears to be greater than in peaches or prunes; the tendency is even greater in the case of vitamin *A*, and points to the probable presence of powerful oxidative catalysts as well as of tissue oxygen in apricots. P. H. P.

Bacteriological.

Limitations of Phenol Coefficients of Coal-Tar Disinfectants. C. M. Brewer and G. L. A. Ruehle. (*Ind. Eng. Chem.*, 1931, **23**, 150–152.)—Experiments with a considerable number of samples of coal-tar disinfectants lead the authors to conclude that it is impossible to calculate the *Staphylococcus aureus* phenol coefficient from the *B. typhosus* coefficient, and that the phenol coefficient is limited in usefulness to interpretations based on comparisons of different disinfectants against test organisms alone and only under prescribed conditions. Any attempt to estimate the efficiency of a disinfectant against other species of pathogenic bacteria from the *B. typhosus* phenol coefficient is unreliable and unsafe. (See ANALYST, 1930, **55**, 594.) W. P. S.

Inter-relationships of Plankton and Bacteria in Natural Purification of Polluted Water. C. T. Butterfield and W. C. Purdy. (*Ind. Eng. Chem.*, 1931, **23**, 213–218.)—Results of biological and chemical experiments indicate that the chief function of certain plankton in the biochemical oxidation process is to keep the bacterial population of the water below the saturation point, and thus provide conditions suitable for continuous bacterial multiplication, and, as a result, provide for more complete oxidation. This theory of the function of the plankton is supported by the results obtained when the limiting numbers of bacteria were reduced by physical and chemical means. Such reductions were followed invariably by renewed bacterial multiplication and oxidation.

W. P. S.

Toxicological.

Hydrogen Sulphide Poisoning. L. B. Allyn. (*Ind. Eng. Chem.*, 1931, **23**, 234.)—A boy who broke off the valve of a cylinder he found on a waste-heap at the bottom of a deep valley was killed almost immediately by the gas which escaped from the cylinder; a rescuer dropped dead as he picked up the body. Other persons were partially overcome by the gas, which was discovered subsequently to be hydrogen sulphide. This tragedy emphasises the poisonous

qualities of hydrogen sulphide in high concentrations; 2000 parts per million cause almost immediate cessation of breathing, and death by acute poisoning is as rapid as in poisoning by cyanides. Hydrogen sulphide is, however, a non-cumulative poison and, if a victim can be revived, there are no systemic sequelae. W. P. S.

Poisoning by Chloroform during Narcosis. A. Sartori. (*Chem. Ztg.*, 1931, **55**, 222.)—The various organs of a child who died while under the influence of chloroform were examined in the following way:—Of each of the separate organs or mixtures of organs submitted for analysis, either an aliquot part or the whole was mixed with water, and the mixture acidified with tartaric acid and distilled in a current of steam. An aliquot part of each distillate was heated with alcoholic potassium hydroxide and aniline. All gave the odour of isonitrile, which was especially distinct for the brain, stomach, and kidneys. For quantitative purposes, each distillate was heated at 50–60° C., and a stream of air passed through it, the air being then led over glowing glass beads to convert any chloroform present into hydrochloric acid, and afterwards through silver nitrate solution acidified with nitric acid. In no case was any appreciable turbidity thus produced, this result being explained by the interval of 13 days between the death of the patient and the examination of the organs.

The wide variation of the fatal dose of chloroform with different individuals, with the age, with the state of the heart, etc., is emphasised. Whereas many people are able to inhale 50 or 100 grms. of chloroform without suffering harm, as little as 1·5 or 2·5 grms. has sometimes caused death. T. H. P.

Behaviour of Lead in the Animal Organism. II. Lead Tetraethyl. R. A. Kehoe and F. Thamann. (*Amer. J. Hygiene*, 1931, **13**, 478–498.)—The authors have investigated the rate of absorption of tetraethyl lead through the skin of rabbits, its fate in the tissues over a prolonged period of time, and the rate of its excretion. Full details are given of the manner of applying the lead tetraethyl to the skin of the animals and the collection of the urine, faeces, etc. Lead tetraethyl was extracted from the tissues by distilling in a current of steam in an apparatus permitting bromine to be mixed with the vapour just before it passes into the cooling condenser; the liquid in the receiver then contains the lead as bromide. The residue remaining after the extraction process, and also the urine, etc., was prepared for the lead determination by the usual method of wet oxidation. The actual method of determination of the lead is not described, that given in *J. Amer. Med. Assn.*, 1929, **92**, 4, being used. It is shown that lead tetraethyl is absorbed through the skin, but that it is rapidly decomposed by the skin and other tissues, so that only a small portion of the lead found later in the blood is in the form of lead tetraethyl, and no lead remains in this form after from 3 to 14 days. It is concluded that poisoning by lead tetraethyl is not different from lead poisoning by other lead compounds. S. G. C.

Organic Analysis.

Saponification Values of Highly Coloured Oils. H. S. Jois, B. L. Manjunath and S. Venkata Rao. (*J. of Mysore Univ.*, 1930, **4**, 241–242.)—The saponification value of highly coloured oils is determined by saponifying 1 to 1·5 grm. of the oil with 0·5 *N* alcoholic potassium hydroxide as usual, and after refluxing for half an hour, adding 50 c.c. of toluene, 25 c.c. of neutral saturated sodium chloride solution, 5 grms. of solid sodium chloride (to prevent dilution of the salt solution during addition of the acid), and lastly, 1 c.c. of phenolphthalein. The liquid is then titrated with 0·5 *N* hydrochloric acid, the mixture being heated on a water-bath towards the end. Since the colouring matter is dissolved in the toluene layer, the end-point is sharp. A blank experiment is made simultaneously and the necessary correction applied. Results obtained by this method with ordinary oils agreed very closely with those obtained by the usual method. The principle has also been applied to the determination of acid values. D. G. H.

Fluorescence Reaction of β-Naphthol. N. Schoorl. (*Pharm. Weekblad*, 1931, **68**, 279–280.)—A reaction having a sensitiveness of 1:100,000 is obtained if 1 c.c. of a solution containing the β-naphthol is mixed with 5 c.c. of glacial acetic acid, and 5 c.c. of concentrated sulphuric acid added as a layer. The immediate formation of a yellow-green zone, which, on mixing, imparts a green fluorescence to the solution, is a positive reaction (*cf.* Groll, *id.*, 1931, **68**, 236). The use of an alcoholic solution of β-naphthol (*cf.* De Haas, ANALYST, 1930, **55**, 202) is not essential for solutions containing less than 1 part in 2000 (the solubility of β-naphthol in water), but it is necessary to use "ordinary" glacial acetic acid, since acid specially purified by treatment with chromic acid produces a reaction only after some interval (1 to 24 hours). It has been found (*cf.* Zwikker, *Chem. Weekblad*, 1931, **68**, 63, 147) that a trace of acetaldehyde increases the rate of reaction with the purified acid, probably in a manner analogous to the Denigès test for aldehydes. J. G.

Determination of Cellulose. K. Kürschner and A. Hoffer. (*Chem. Ztg.*, 1931, **55**, 161–163, 182–184.)—The results of a number of experiments demonstrate the advantages of a mixture of alcohol and nitric acid as a reagent for obtaining the cellulose of wood free from lignin. The procedure recommended is as follows:—One grm. of the wood (borings) is well mixed with 25 c.c. of the reagent (20 c.c. of 96 per cent. alcohol and 5 c.c. of concentrated nitric acid) in a 250 c.c. flask, which is heated under a reflux condenser on a boiling water-bath for an hour. The liquid is then decanted on to a porcelain or glass filter-crucible, any small quantity of the solid reaching the crucible being rinsed with alcohol-acid mixture into the flask again. The treatment with a total of 25 c.c. of the reagent is repeated, and the mass subsequently filtered; the residue is washed with alcohol and water and very gradually dried, the final temperature being 108° C. The raw cellulose thus obtained is tested for lignins and for pentosans by means of phloroglucinol and hydrochloric acid. If lignins are present, the material is coloured cherry-red

by the cold reagent, which itself remains colourless; if pentosans also are present, subsequent heating colours the reagent red. If, however, as is usually the case, pentosans only are present, no reaction occurs in the cold, whereas, on being heated, the liquid turns red, whilst the solid particles remain practically uncoloured. When lignin is detected in this way, the cellulose is subjected to a third treatment with the alcohol-nitric acid mixture. Of 27 woods of different kinds, none required more than the three treatments. T. H. P.

Studies in the Composition of Coal. Methods for the Rational Analysis of Coal. W. Francis and R. V. Wheeler. (*J. Chem. Soc.*, 1931, 586–593.)—The rational analysis of coal involves the determination of the quantities of free hydrocarbons and resinous compounds, organised plant entities, and ulmin compounds of which the coal is composed, together with a measure of the reactivity of its ulmin compounds (*cf. J. Chem. Soc.*, 1928, 2967). The methods described are used for the routine examination of coals in the Fuel Technology Laboratories of Sheffield University. *Preparation of the Sample.*—The sample of coal is ground, dried, and sieved through a 60-mesh sieve and then on a 120-mesh sieve (I.M.M. standard). Fifteen grms., in a round-bottomed flask, fitted with a ground-in reflux condenser, are boiled in a glycerin-bath with pyridine (225 c.c.) for 8 hours. After cooling, the mixture is filtered through a sintered-glass filter (Schott and Gen., type 17 G.3), and the residue, the amount of which must be determined, washed with a little pyridine; the filtrate is reserved. The extracted coal is transferred to a beaker, boiled for a short time with dilute hydrochloric acid, filtered off, washed, and dried at 105° C.; it is then carefully ground, with frequent sieving, so as just to pass through a 120-mesh sieve; any dust passing through a 150-mesh sieve, the formation of which must be avoided, is discarded. The object of this preliminary treatment is to remove soluble hydrocarbons and resins, and to obtain the same physical condition for all samples. *Hydrocarbons and Resins.*—As much as possible of the pyridine from the above reserved filtrate is removed by distillation, and the residue is boiled for ¼ hour with an excess of dilute hydrochloric acid, cooled, and filtered through a coarse filter paper. The residue, after washing with water, is dried and extracted with ethyl alcohol in a Soxhlet extraction apparatus, the weight of the extracted material giving the combined amount of hydrocarbons and resins in the coal. *Resistant Residue.*—The coal, prepared as described above (0·5 grm.), is boiled for 7 hours under reflux with an oxidising solution, chosen from the following table (p. 334), appropriate to the carbon content of the coal.

The mixture is cooled and filtered through a weighed sintered-glass crucible (2 G.3). The oxidised coal is washed from the filter into a beaker, the volume made up to 100 c.c., 20 c.c. of *N* sodium hydroxide are added, and the mixture gently boiled for 1¼ hours. [The appearance under the microscope of a small sample of the residue remaining after this treatment will indicate whether the correct oxidising solution has been used; a practical trial of possible oxidising solutions may be necessary; if the oxidising solution used is too weak, the resistant residue

Carbon content of coal.*	Oxidising solution. HNO_3, c.c. *N*-acid.	*2N*-acid.	Water, c.c.	ClO_3, grm.
78	37·5	—	12·5	Nil
79	40	—	10	Nil
80	42·5	—	7·5	Nil
81	45	—	5	Nil
82	47·5	—	2·5	Nil
83	50	—	Nil	Nil
84	46 and	4	Nil	Nil
85	—	28	22	0·2
86	—	29	21	0·35
87	—	30	20	0·5
88	—	32·5	17·5	0·625
89	—	35	15	0·75
90	—	40	10	1·0
91	—	50	Nil	1·5

* On "pure coal" basis, *i.e.*, after making allowance for the fact that the "ash" of a coal is not of the same composition or quantity as the original mineral matter (see Tideswell and Wheeler, *Amer. Inst. Min. Met. Tech. Paper*, No. 104, 1928).

will be opaque; if too strong, the residue will consist of bleached and macerated fragments, whilst the correct oxidising solution should yield transparent particles of a yellow, orange, or red colour (except those of fusainised wood tracheids), and the larger particles will usually be portions of macrospore exines, and may not be quite transparent.] The solution is filtered through the crucible previously used, with gentle suction, if necessary, and the residue, after having been washed successively with hot water, dilute hydrochloric acid and hot water (3 or 4 times), is dried and weighed. The weight (P) represents the resistant plant entities together with insoluble ash. Further work is necessary to establish the amount of resistant residue in the case of durain coal, for which reference should be made to the original paper. *Reactivity Index of the Ulmins.*—The prepared coal (0·5 grm.), with 0·9 grm. of potassium chlorate and 50 c.c. of *N* hydrochloric acid, is placed in a 300 c.c. pressure bottle (screw-stoppered, or, for research purposes, a sealed-off flask), which is immersed in a water-bath which is then quickly heated to boiling; the boiling is continued for 7 hours, the flask is allowed to cool overnight, and its contents are filtered through a sintered glass crucible (1 G.3). After washing, the residue is rinsed into a beaker with 100 c.c. of water, 20 c.c. of *N* potassium hydroxide are added, and the mixture boiled gently for $1\frac{1}{4}$ hours. The solution is filtered through the same crucible, and the residue washed successively with hot water, dilute hydrochloric acid, and hot water, slight suction being used only if unavoidable. The weight (R) of the residue, after drying at 105° C., and its ash content (A) are determined. The weight of ash (A) in 0·5 grm. of the prepared coal is also determined from the data found above.

$$\text{Reactivity Index} = \frac{(0{\cdot}5 - \text{A}) - (\text{R} - \text{A}_1)}{(0{\cdot}5 - \text{A}) - (\text{P} - \text{A}_1)} \times 100$$

A table is given of typical rational analyses of British coals. S. G. C.

Determination of Water in Vegetable-tanned Leather. R. F. Innes and J. G. M. Coste. (*J. Inter. Soc. Leather Trades Chem.*, 1931, **15**, 126.)—It is shown that when leathers are dried in an air oven or vacuum oven the consequent loss in weight does not represent water alone With heavily greased leathers any method of determining the water content based on loss of weight on heating gives results much higher than those obtained by prolonged desiccation over calcium chloride or sulphuric acid at laboratory temperature, and it is shown that certain constituents of the grease are lost. Other volatile materials lost on heating are sulphur and essential oils. The official method for the determination of water in leather is unsound, and should be replaced as soon as possible by a method which will distinguish between water and other volatile constituents of leather. R. F. I.

Determination of Copper in Tanning Extracts. D. Burton. (*J. Inter. Soc. Leather Trades Chem.*, 1931, **15**, 126; *British Section Committee.*)—The Committee has studied three methods for the determination of copper in chestnut extracts, (*a*) dissolving the ash in acid and depositing the copper on a weighed electrode; (*b*) comparing the tint produced by adding hydrogen sulphide to a solution of the copper with standard copper solutions; (*c*) similar to (*b*), but using sodium diethyl dithiocarbamate instead of hydrogen sulphide. Of these, method (*a*) is recommended. The ash of 50 grms. of the extract is heated with a few drops of sulphuric acid until it fumes strongly, then with 10 c.c. of 2*N* sulphuric acid. The solution is diluted to 100 c.c., and electrolysed over-night with a current from a 2-volt accumulator, a weighed cathode of platinum foil being used. After washing in water and immersing for five minutes in absolute alcohol, the cathode is dried in an oven and weighed. Results by six analysts varied from 0·0034 to 0·0050 per cent. of copper. R. F. I.

Identification in Small Samples of Leather of the Different Minerals used in Tanning. K. Kamfer. (*Mikrochem.*, 1931, **9**, 34–37.)—Salts of iron, chromium or aluminium, or mixtures of these, are most commonly used in tanning. *Chromium* is detected, after conversion into chromate, by the diphenylcarbazide reaction. A sample of less than 1 mgrm. is sufficient for the test. The sample is ashed in a porcelain micro-crucible, and then melted with a particle of sodium peroxide to oxidise the chromium to chromate. The mixture is then dissolved in a drop of sulphuric acid (1:5), and 1 to 2 drops of a 2 per cent. alcoholic solution of diphenylcarboxylic acid are added. In the presence of chromium an intense violet colour appears. As only mercury and molybdenum give the same reaction, and these elements are not used for tanning, the reaction is specific for chromium in leather. *Iron* is detected by the thiocyanate reaction after conversion into the ferric state. About 1 mgrm. of leather is ashed and the ash is evaporated with a drop of nitric acid, heated, and a crystal of potassium bisulphate is added. After dissolving in a drop of dilute hydrochloric acid a drop of potassium thiocyanate solution is added. The characteristic red colour indicates the presence of iron. *Aluminium* is detected by the alizarine reaction, or the fluorescent reaction with morin. The sample is ashed, and, as described above, is fused with potassium

bisulphate, then dissolved in a drop of hot water. For the alizarine test a drop of the test solution is placed on a piece of filter paper which has previously been impregnated with potassium ferrocyanide, and dried. Any iron or chromium is retained in the central zone of the drop, whilst the aluminium moves through the capillaries of the paper to an outer circle. A drop of a saturated alcoholic solution of alizarine is placed on the paper, which is held over a bottle of ammonia, and the violet colour of the ammonium alizarinate is visible. When much aluminium is present the red colour of the aluminium alizarinate is also visible, and when less aluminium is present the red colour is visible only after heating, which volatilises the ammonia. For the morin test a drop of the test solution is mixed with two drops of 2 *N* sodium hydroxide solution in a micro-test tube, and centrifuged. The clear solution is acidified with a few drops of 2 *N* acetic acid, and one drop of a saturated solution of morin in methyl alcohol is added. In the presence of aluminium there is a green fluorescence. J. W. B.

Inorganic Analysis.

Simultaneous Volumetric Determination of Lead and Bismuth. H. T. Bucherer and F. W. Meier. (*Z. anal. Chem.*, 1931, **83**, 351–361.)—The volumetric application of several precipitation reactions of lead was studied, the end-point being ascertained by filtration of a small quantity of solution and addition of the precipitant. The most sensitive reaction was found to be the formation of lead selenite, a white crystalline precipitate. The weakly acid lead acetate solution is treated with a standard solution of selenious acid at 80° to 90° C., and the filtered portions are tested with the standard solution after addition of a little alcohol. Bismuth is precipitated as selenite in 0·05 to 0·08 *N* nitric acid solution at 70° C.; towards the end the solution is boiled. The two metals can be determined in the same solution by selenious acid precipitation without an intervening filtration; the bismuth is precipitated first from feebly nitric acid solution. When the precipitation is complete, as shown by a filtered test portion, the solution is treated with an excess of sodium acetate and titrated for lead. W. R. S.

Volumetric Determination of Iridium. S. C. Woo and D. M. Yost. (*J. Amer. Chem. Soc.*, 1931, **53**, 884–888.)—Chloriridic acid was titrated in 0·1 to 0·2 *N* hydrochloric acid solution with thiosulphate after addition of potassium iodide, benzene being used as indicator; the operation was conducted in conical flasks, and the volume of solution was such that the benzene layer rose into the upper narrow part of the flask, where its colour could be easily observed against a white background. A potentiometric method also was studied. Standardised titanous chloride solution is added very slowly to the 0·1 to 0·2 *N* hydrochloric acid solutions containing 2 to 3 grms. of sodium chloride in a total volume of 50 c.c. At the end-point the potential changes abruptly from 0·65 to 0·4 volt. The results given show a maximum deviation of 0·3 per cent. from the calculated average. W. R. S.

Separation of Iron, Titanium, and Aluminium. E. Schwarz von Bergkampf. (*Z. anal. Chem.*, 1931, **83**, 345–350.)—The precipitation of these metals from tartrate solution and their direct determination are described. The weakly acid solution containing 1 grm. of tartaric acid is saturated with hydrogen sulphide, which reduces the iron to the ferrous state. The solution is made ammoniacal and again treated with hydrogen sulphide, the precipitate collected and washed as usual, and converted into ferric oxide by at least half-an-hour's ignition at 850° C. The filtrate is cooled in running water after addition of 40 c.c. of sulphuric acid (1:1); not more than 10 c.c. of the acid should be required to neutralise the ammonia present. The titanium is precipitated in a bulk of 400 c.c. by 6 per cent. aqueous cupferron solution; the precipitate is collected, washed with 10 per cent. hydrochloric acid, and ignited in the usual manner. The filtrate in an 800 c.c. beaker is made ammoniacal, heated to 70° C. (it should remain clear), and precipitated with a 6 per cent. solution of *o*-hydroxyquinoline (5 grms. of base dissolved in 12 grms. of glacial acetic acid and diluted to 100 c.c.). The solution is stirred and kept at 70° C. for some minutes, the precipitate collected in a porous glass crucible, washed with hot water, dried for 2 to 3 hours at 140° C., and weighed (Al_2O_3 factor, 0·1110). Vanadium interferes in this process. W. R. S.

Volumetric Determination of Selenium. B. Ormont. (*Z. anal. Chem.*, 1931, **83**, 338–339.)—The author questions the reliability of the method proposed by Benesch (ANALYST, 1929, **54**, 63). W. R. S.

Determination of Zirconium by means of Selenious Acid. S. G. Simpson and W. C. Schumb. (*J. Amer. Chem. Soc.*, 1931, **53**, 921–933.)—The quantitative precipitation of zirconium by selenious acid, first described by Smith and James (*J. Amer. Chem. Soc.*, 1910, **42**, 1764), was submitted to a thorough investigation. A 10 per cent. solution of selenious acid is used as the precipitant; the recovery of zirconium as basic selenite is complete from hydrochloric acid (less than 0·6 *N*) solutions. In presence of sulphuric acid the precipitation is very slow. Alkali chlorides and nitrates do not, but alkali sulphate does, interfere. Sulphate causes incomplete precipitation at the above acidity. Other quadrivalent elements (hafnium, titanium, thorium, ceric cerium) are precipitated like zirconium. Manganese, zinc, cobalt, copper, lead, bismuth, iron, aluminium, and rare earth metals do not interfere; uranium oxide and vanadic acid are adsorbed, but can be eliminated by re-precipitation, the freshly-precipitated zirconium selenite being soluble in 6 *N* hydrochloric acid, which incidentally forms non-adsorbed vanadyl salt by reduction. The effect of titanium and cerium is eliminated by double precipitation from a solution containing hydrogen peroxide, which peroxidises the former and reduces the latter to cerous salt. Thoria, if present, must be eliminated as oxalate, which necessitates the following sequence of operations: solution of the selenite precipitate in 6 *N* hydrochloric acid, treatment with 40 c.c. of hot 10 per cent. oxalic acid filtration, evaporation of the filtrate with strong sulphuric acid to destroy oxalate, precipitation of the zirconia with ammonia, solution of the precipitate in 15 c.c. of hot 12 *N* hydrochloric acid, re-precipitation with selenious acid in presence of hydrogen peroxide. It is recommended

to re-treat the thorium oxalate, *i.e.* by decomposition by heating with strong sulphuric acid, precipitation of thorium hydroxide with ammonia, solution in hydrochloric acid, re-precipitation of the oxalate, and addition of the last filtrate to that from the first oxalate precipitate.

The following procedure separates zirconium from other elements prior to selenite precipitation: the nearly neutral solution (150 c.c.) containing 20 c.c. of 12 *N* hydrochloric acid and 20 of alcohol is heated, diluted to 500 c.c., boiled, and treated with 20 c.c. of 10 per cent. selenious acid. After standing hot for 2 hours, the precipitate is collected, lightly washed, returned with a minimum of hot water, and dissolved by heating with 15 c.c. of 12 *N* hydrochloric acid; hydrogen peroxide (20 c.c. of 3 per cent.), and water to 500 c.c. are added, the solution boiled and precipitated with selenious acid, and the precipitate collected, washed, and returned, as before. The two filters previously used are digested with 40 c.c. of hot 10 per cent. oxalic acid; the pulp is filtered off and washed, the filtrate and washings being added to the zirconium precipitate. The liquid (200 c.c.) is boiled, treated with 12 c.c. of 6 *N* hydrochloric acid, and left in the cold for at least 10 hours, the thorium oxalate filtered off and washed with a solution containing 40 c.c. of 6 *N* hydrochloric, and 25 grms. of oxalic acid per litre. The filtrate is evaporated with 30 c.c. of sulphuric acid. If the oxalate precipitate is large it should be re-treated as prescribed above, and the second filtrate added to the first. Any precipitated selenium is filtered off; small amounts of colloidal selenium in the filtrate may be disregarded. The solution is precipitated with ammonia, the precipitate collected, lightly washed, returned to the beaker, and dissolved by heating with 15 c.c. of 12 *N* hydrochloric acid. Hydrogen peroxide (as before) is added, and the boiling solution diluted to 500 c.c., again precipitated with the same amount of selenious acid. The precipitate is collected, washed with hot water, ignited (finally over a Meker burner), and weighed as ZrO_2. If thoria is known to be absent, the first selenite precipitate is simply treated by double re-precipitation in presence of hydrogen peroxide, the filter papers used being ignited and added to the final zirconia.

For the determination of zirconium in its minerals, use is made of a flux consisting of 15 parts of fine sodium peroxide and one of powdered sugar carbon. Twenty-five grms. of the mixture is placed in a 50 c.c. nickel crucible, and 1 grm. of the fine ore powder thoroughly stirred in. A cover of flux is applied, the crucible placed in running water, and ignition started with a glowing fragment of cotton twine, the crucible being immediately covered. The cold mass is transferred to a 1000 c.c. beaker, 300 c.c. of cold water added, which is then heated to boiling; the crucible is rinsed with water. The liquid is diluted to 900 c.c. and heated till clear enough for filtration. The residue is collected and washed, and the filtrate rejected. If much phosphate is present the residue is rinsed back, treated with hydrochloric acid, then ammonia, again collected, ignited, and the fusion repeated. The residue is then dissolved in hydrochloric acid, the solution evaporated with sulphuric acid till it fumes, diluted, filtered, the filtrate precipitated with ammonia, and the precipitate dissolved in 15 c.c. of 12 *N* hydrochloric acid. This solution is ready for selenious acid precipitation.

If earth acids are present, the re-fusion is carried out with potassium carbonate (ANALYST, 1928, **53**, 518). The fusion residue is ignited, fused with bisulphate, the sulphate solution precipitated with ammonia, and the precipitate dissolved in hydrochloric acid for selenious acid precipitation. W. R. S.

Revision of the New Iodimetric Determination of Vanadium in Alloy Steels and Ferrovanadium. W. Werz. (*Z. anal. Chem.*, 1931, **83**, 161–164.)—Certain weaknesses in the author's method (ANALYST, 1930, **55**, 769) have come to light, and the following revised process is proposed: *Steel.*—From 1 to 3 grms. of steel drillings are heated with 25 c.c. of phosphoric acid (sp. gr. 1·70), and 200 c.c. of water in a 500 c.c. Erlenmeyer flask until dissolved; this takes normally 10 to 15 minutes. The solution is oxidised with nitric acid (sp. gr. 1·4), an excess of 5 c.c. of this acid being added, and boiled for a few minutes to drive out nitrogen oxides. Any insoluble residue of chromium carbide is filtered off and rejected. Ten c.c. of ammonium persulphate solution (5 per cent.) are added, and the solution is boiled for 35 minutes; 25 c.c. of phosphoric acid (sp. gr. 1·70) are then added, and the solution is cooled. From 2 to 10 c.c. of potassium iodide solution (0·2 *N*) are added (6 c.c. are required for a 3 grm. sample containing about 1 per cent. of vanadium). The solution is kept for 5 minutes, and the liberated iodine is titrated with 0·05 *N* sodium thiosulphate (1 c.c.=0·00255 grm. V) starch being used as indicator. The volume of the solution titrated should be roughly 200 c.c., corresponding with a phosphoric acid concentration of 1:3; the optimum temperature is 19° to 22° C. *Ferrovanadium.*—One grm. is dissolved in 50 c.c. of nitric acid (sp. gr. 1·2). The solution is diluted to 500 c.c., and 50 c.c. of this are withdrawn into a 500 c.c. Erlenmeyer flask, 50 c.c. of phosphoric acid, 150 c.c. of water and 5 c.c. of nitric acid (sp. gr. 1·4) are added, and the process carried out as for steel. S. G. C.

Determination of Magnesium in Portland Cement and Similar Materials by 8-Hydroxyquinoline. J. C. Redmond and H. A. Bright. (*Bureau of Stds. J. Research*, 1931, **6**, 113–120.)—The authors have thoroughly investigated the 8-hydroxyquinoline method for the determination of magnesium and its application to the analysis of Portland cement, and propose the following process as an equally accurate rapid alternative to the more usual pyrophosphate method.—The sample (0·5 grm.) is decomposed by gentle heating with a mixture of 10 c.c. of water and 10 c.c. of concentrated hydrochloric acid in a 400 c.c. beaker. Three drops of methyl red indicator (0·2 per cent. in alcohol) are added, and then ammonia solution (sp. gr. 0·9), until the solution is distinctly yellow; some macerated filter paper is added, the solution is boiled for 1 or 2 minutes and the precipitate of alumina, etc., allowed to settle. The precipitate is filtered, without further delay, and washed with hot ammonium chloride solution (2 per cent.). The calcium in the filtrate is precipitated by adding 1 c.c. of ammonia solution (sp. gr. 0·9), heating to boiling, adding 25 c.c. of hot ammonium oxalate solution (4 per cent.) and continuing the boiling for 2 to 3 minutes. The liquid is digested on a steam-bath for $\frac{1}{2}$ to 1 hour, filtered, and the calcium oxalate washed 5 or 6 times with warm

water. The volume of the filtrate at this point should be about 350 c.c. The filtrate is heated to 60° to 70° C., and 20 c.c. of 8-hydroxyquinoline solution are added (prepared by dissolving 25 grms. of the compound in 60 c.c. of glacial acetic acid and diluting to 2 litres with cold water; 1 c.c. is equivalent to 0·0016 grm. of MgO); this is followed by the addition of 4 c.c. of ammonia solution (sp. gr. 0·9) for each 100 c.c. of solution; the whole is stirred mechanically for 10 to 15 minutes, and then kept until the precipitate has settled. The alternative to be adopted if no mechanical stirrer is available is to heat the solution to 60° to 70° C., and add 4 c.c. of the ammonia solution for each 100 c.c. of solution, and then add 40 c.c. of the 8-hydroxyquinoline solution and heat to boiling, when the beaker is at once set aside until the precipitate has settled. The precipitate, magnesium hydroxyquinolate, $Mg(C_9H_6ON)_2.2H_2O$, is filtered, washed with hot dil. ammonia (1:40) and dissolved in 50 to 75 c.c. of hot dilute hydrochloric acid (1:9); this solution is diluted to 200 c.c., 15 c.c. of concentrated hydrochloric acid added, and cooled to 25° C. The magnesium is now determined by the volumetric determination of the 8-hydroxyquinoline in the solution by the bromate-bromide method as follows:—Twenty-five c.c. of 0·2 *N* bromate-bromide solution (prepared by dissolving 20·00 grms. of potassium bromide and 5·57 grms. of potassium bromate in 1 litre of water) are added, followed immediately by 10 c.c. of potassium iodide solution (25 per cent.); the liberated iodine is titrated with 0·1 *N* sodium thiosulphate solution (standardised against 0·1 *N* iodine solution, which, in turn, has been standardised with arsenious acid), with 2 c.c. of starch solution (0·5 per cent. in 0·25 per cent. aqueous salicylic acid) as indicator. The ratio of the bromide-bromate solution to the standard thiosulphate solution is obtained by adding 25 c.c. of the former to 200 c.c. of water and 20 c.c. of conc. hydrochloric acid, followed by 10 c.c. of the potassium iodide solution and titration of the liberated iodine with the thiosulphate solution. One c.c. of 0·1 *N* thiosulphate is equivalent to 0·000504 grm. of MgO. S. G. C.

Determination of Small Quantities of Boric Acid by a Flame Test. W. Stahl. (*Z. anal. Chem.*, 1931, **83**, 268–289, 340–344.)—Boric acid in quantities of a few mgrms. cannot be determined accurately by the ordinary volumetric or gravimetric processes. Traces may be determined by Bertrand and Agulhon's colorimetric procedure employing turmeric paper (*Bull. Soc. Chim.*, 1914, **15**, 292). For quantities of the order of 0·3 mgrm., the following process involves errors not exceeding 15 per cent. The vapour of methyl borate is introduced through the air hole of a Bunsen burner, and the intensity of the green coloration compared with that produced by a known amount of boric acid. The apparatus required consists of a set of standard alcoholic solutions of boric oxide, three Bunsen burners of equal size with special fittings, and means for simultaneously passing equal amounts of air through the unknown and two standard solutions. The strongest flame effect is given by a mixture of 100 volumes of methyl alcohol and 20 of strong sulphuric acid. The boric acid to be determined need not be previously separated. The smallest quantity of boric acid which can be detected

by the method by means of a set of micro-burners is 0·005 mgrm. The original papers should be consulted for full details. W. R. S.

Microchemical.

Micro-combustion of Carbon and Hydrogen in Mercury Compounds. M. Furter. (*Mikrochem.*, 1931, **9**, 27–30.)—Verdino (*Pregl's Quantitative Organic Micro-analysis*, 1930) found that satisfactory determinations of mercury compounds could be made by using Pregl's universal filling. When Pregl's filling (with lead peroxide asbestos to absorb oxides of nitrogen) was used for the combustion of compounds containing not only carbon, hydrogen and mercury, but also sulphur and nitrogen, the tube, after the combustion, was found to be "poisoned," and although correct hydrogen results could be obtained subsequently with the tube, carbon results were invariably low by 1 to 2 per cent., and continued heating of the tube had no beneficial effect. J. W. B.

New Sensitive Reaction of Ammonia. K. G. Makris. (*Z. anal. Chem.*, 1930, **81**, 212, 213.)—The addition of a slight trace of ammonia to a solution of silver nitrate and tannin causes the reduction of the silver nitrate to silver. A fragment of cotton-wool is moistened with a few drops of the freshly prepared reagent (5 c.c. of 20 per cent. silver nitrate solution and 1 c.c. of a 5 per cent. solution of tannin), and placed in the mouth of a test tube containing about 1 c.c. of the unknown solution and a few drops of potassium hydroxide solution. The tube is then slowly heated, and in the presence of as little as 5γ of ammonia a reduction of silver is apparent soon after boiling. J. W. B.

Micro-Determination of Iodine in Common Salt. H. Werner. (*Z Unters. Lebensm.*, 1930, **60**, 495–500.)—The method described by Winkler (*Pharm. Zentralh.*, 1923, **64**, 512; Leitch and Henderson, *Biochem. J.*, 1926, **20**, 1003) has been adapted by the author. The salt (50 grms.) is dissolved in water, filtered, 1 c.c. of *N* hydrochloric acid added, and the iodide oxidised to iodate by 1 c.c. of chlorine water. After removal of the excess of chlorine by prolonged evaporation, any insoluble salt is redissolved, the mixture cooled and 5 c.c. of 25 per cent. phosphoric acid added with 0·1 grm. of potassium iodide and 1 c.c. of 1 per cent. starch solution. The resulting iodine ($KIO_3+5KI+6HCl=6KCl+3I_2+3H_2O$) is titrated immediately with 0·002 *N* sodium thiosulphate solution, 1 c.c. of which is equivalent to 0·042 mgrm. of iodine. The maximum recorded error is $\mp 3\gamma$ ($1\gamma = 0{\cdot}001$ mgrm.) for 50 grms. of salt containing from 5 to 27γ of iodine. In the presence of more than 1·4 mgrms. of manganese as manganous sulphate, or more than 0·01 mgrm. of iron as ferrous sulphate, a blue colour due to liberation of iodine from the potassium oxide by these salts is obtained immediately, but if 4 drops of 10 per cent. oxalic acid solution are added, the reaction with the manganese is inhibited for 10 minutes, while a similar retardation is obtained for iron if the original solution is acidified with phosphoric instead of with hydrochloric acid. The normal degree of accuracy is, therefore, obtainable by these means in

the presence of either or both of these compounds if the solution is titrated immediately after addition of the reagents, when the iodine from the iodate only is liberated. J. G.

Physical Methods, Apparatus, etc.

New Micro-Balance. J. Donau. (*Mikrochem.*, 1931, **9**, 1–14.)—Certain disadvantages of the Nernst torsion balance, such as the lack of proportionality of the swings, the time taken to come to rest, and the fact that the Nernst balance is built for a fixed tare, have been overcome in the construction of a somewhat similar type of torsion balance. The balance is simple to construct, and can be made of glass or metal (magnalium or duralumin). The balance differs from the Nernst balance in that it has two arms of approximately equal length and the pointer in the centre. The pointer is attached just below the position where the two arms join it, to a fine quartz or tungsten thread, by means of shellac or selenium. The thread is stretched between the ends of an arc-shaped support made of metal, or, better, of quartz or glass, since these are less affected by temperature variations. The weight of the balance is usually 300 to 400 mgrms.; heavier models weighing more than 750 mgrm. show more variation in the zero point, while that of the lighter models stays very constant. The advantage of having two arms is that varying tares may be used, the load ranging from 150 to 400 mgrm. In the glass model both the arms are bent downwards near the point where the pans are to be suspended. The arms of the metal balance are straight, but small screws are placed on the ends, by means of which the centre of gravity may be lowered or raised. By suitably adjusting the angle of bend of the glass model, or the screws of the metal model, by empirically testing the different positions, the balance can be adjusted so that it maintains the same sensitiveness throughout its whole range, and no calibration table is necessary.

Three different models of the balance were used for a number of determinations. The first weighed about 400 mgrms. and one scale division represented 0·059 mgrm. (readings are taken to 1/100 of a scale division). The pointer came to rest in about 6 seconds. The second model weighed about 0·300 mgrm., and one scale division represented 0·0247 mgrm.; readings could be taken after 4 seconds. The third model weighed 800 mgrm., 0·03 mgrm. represented one scale division, and the swinging came to rest in 10 seconds. Excellent results were obtained in test determinations with each of the balances. The same type of balance was used for determinations of small amounts of the heavy metals (*cf.* ANALYST, 1930, **55**, 598). J. W. B.

Some Applications of Ultra-Violet Light. L. Colombier. (*Ann. Falsificat.*, 1931, **24**, 89–96.)—An unsuccessful attempt was made to determine *p*H values with certain substances, such as eosin, quinine and acridine, by means of the fluorescence under ultra-violet light. It was found, however, that umbelliferone, in particular, and its derivatives, were excellent indicators with strong acids and bases up to dilutions of 0·001 *N*, also with acetic acid, and with ammonia

to 0·01 *N*. At a *p*H about 6·5 the blue fluorescence suddenly disappears in passing from alkalinity to acidity. Ultra-violet rays, in combination with umbelliferone, allow of the titration of 1 c.c. of acid solution diluted to 250 c.c. with 0·01 *N* alkali, but results are lower than with phenolphthalein, which changes at a *p*H of 9 to 10. Malic acid may be detected by placing a few c.c. of the solution, or particles of the solid, on a watch glass with 1 c.c. of a 0·1 per cent. solution of resorcinol, evaporating the liquid, and taking up the residue with 1 c.c. of sulphuric acid (1 vol. of concentrated sulphuric acid and 1 vol. water). After 5 minutes on a water-bath, 10 c.c. of water are added, and just enough sodium hydroxide to neutralise the acid. If malic acid is present, a blue fluorescence appears when viewed by ultra-violet light. The reaction takes place with all β-ketonic acids, and an analagous and specific reaction occurs with citric acid after oxidation with permanganate. The permanganate is added to the boiling solution until a light yellow colour results, the solution then poured into a crystallising dish with resorcinol, and the procedure carried on as for malic acid, when a violet fluorescence indicates the presence of citric acid. The violet fluorescence produced with resorcinol is specific, but ethyl aceto-acetate is more satisfactory than malic acid in this reaction. A few mgrms. of β-naphthol, dissolved in concentrated sulphuric acid, warmed for 2 minutes and examined by ultra-violet light show a blue-violet fluorescence, and the reaction is specific. A fraction of a mgrm. of orcinol may be detected if Crump's reaction (with chloroform and potassium hydroxide) is observed under ultra-violet light. D. G. H.

Reviews.

MONOGRAPHS ON BIOCHEMISTRY. ENZYMES. By J. B. S. HALDANE, M.A. Pp. vi+235. London: Longmans, Green & Co. 1930. Price 14s. net.

The present volume is, according to the author, not intended to supersede the previous one of this series, entitled "The Nature of Enzyme Action," by the late Sir Wm. Bayliss. If we understand the author aright, each of these books—the old and the new—is written from the particular point of view of its author.

An enzyme is defined as a soluble colloidal, organic catalyst, produced by living organisms, a definition which rules out crystalloidal catalysts and active surfaces, which appear to be responsible for many oxidations and reductions. Whilst not denying the views of Bayliss and others, that a catalyst can merely accelerate a reaction which occurs slowly in its absence, the author puts forward the less comprehensive idea that a catalyst can promote a reaction only provided that a loss of free energy results. This conception is consistent with the fact that many reactions promoted by enzymes are reversible, for it must be the energy liberated that causes the reversion. The directive power of enzymes is recognised by the author.

A very useful table is given showing the optimum pH value of the best known enzymes and their sources. The conception that an enzyme unites with its substrate is discussed with the aid of mathematics, and a list of substrate concentrations at which half the maximum initial velocity is reached is given for different enzymes. The value in many cases is identical with the constant of Michaelis.

The course of enzymatic reactions is discussed from the mathematical standpoint. Very comprehensive chapters are those on Specificity, Co-enzymes, Activators, Kinases and Complements, and on the Poisoning of Enzymes.

Due attention is paid to the work of Willstätter and others on the purification of enzymes, and the concluding chapter deals with "The Classification of Enzymes and on Theories of Enzyme Action."

The Bibliography has been carefully prepared, and is comprehensive.

The book is in many respects unique, in that it deals with the subject from a different point of view from that of any other book in the English language, and doubtless it will supply a want.

ARTHUR R. LING.

(1) UNTERSUCHUNG DER NAHRUNGS-UND GENUSSMITTEL, ALLGEMEINE METHODEN. Dr. WILHELM PLÜCKER. Urban & Schwarzenberg, Berlin. 1931. Pp. 1046. Price 55 R.M. (59 R.M. bound).

(2) TABELLEN-UND RECHENBUCH FUR NAHRUNGSMITTELCHEMIKER. Dr. WILHELM PLÜCKER. Pp. 231. Price 20 R.M. 22 R.M. (bound).

(1) This is an important—and weighty—volume, which is of considerable interest because there is no English work (so far as the reviewer is aware) which covers quite the same ground. It is essentially a treatise on analytical methods applicable to foodstuffs, including oils and all substances coming within the purview of the food chemist; there is no discussion of the composition of particular foods or of limiting values for various constants, but there is a really valuable collection of methods, reactions and processes, together with numerous references. The methods treated of include such matters as sampling, with a simple mathematical treatment of its probable errors, and grinding, and a discussion on the volume corrections for precipitates. There is, too, a useful chapter on biological methods, including the precipitin reactions and fermentation processes as applied to the analysis of sugars and honey.

At the other end of the volume there are working details of physical methods, including cryoscopy, spectroscopy, viscosimetry, pH, electrometric titrations, and conductivity, in addition to the well-known fundamental operations such as weighing with the microbalance and the usual measurements.

The bulk of the volume consists of a collection of the qualitative reactions of nearly all the various substances which occur in foodstuffs, followed by details of quantitative methods, with many alternative processes suggested for special purposes or applicable to particular commodities. There are useful indications of which method is best for a given purpose, or its limitations in the presence of

possible interfering substances, and methods are given for a wide range of determinations which are not of everyday occurrence, and for which reference to books is likely to be made by the analyst before starting; one can turn to Dr. Plücker and save laborious study of journals.

There are two defects, from the point of view of the English reader, arising mainly from the fact that the subject is treated largely from a biological aspect. The volume appears complementary to part of Abderhalden's *Handbuch der biologischen Arbeitsmethoden*, which is the reason for a number of cross references to alternative processes or details not contained in these covers. The second defect is less excusable—the omission of many valuable methods which have been published in THE ANALYST and other English journals and of mention of processes of great importance in this country. A few examples may be cited in the hope that such omissions may be rectified in a future edition. There is no adequate treatment of the subject of preservatives; sulphur dioxide is not given at all, nor benzoic acid, though there is much information on succinic, malic and other acids. For the determination of fibre, *N* nitric acid is prescribed, whereas in England one must generally use 1·25 per cent. sulphuric acid for official tests. The determination of lactose in milk is given, and of total solids in such products as condensed milk, but no mention is made of the work of the Committee of this Society, nor of Dr. Monier-Williams' contributions. Methods are given for starch determination, but not that by Rask. The alcohols are discussed, but the useful methods given by Adams and Nichols (ANALYST, 1929) are omitted. The acetin method for glycerin assay is mentioned, but not described, though it is used very widely in England and America, much more so than the bichromate method. Truly, Fachini and Somazzi's method is more modern, but it is open to serious criticism. This list might be much extended, but will suffice to indicate that the author has not adequately followed non-German publications, if his work is intended to appeal widely to non-German readers.

Subject to these limitations, the book is to be warmly commended because of what it does include—and that is a vast amount.

(2) This is a companion volume, adding much to the utility of the former. It is not an ordinary book of tables, though it does include most of the usual data, numerical and otherwise. The particular features are detailed tables of special values, such as those of phloroglucides of the less common carbohydrates forming pentosans, Lane and Eynon's and other sugar tables, tables of refractive indexes of solutions of different alcohols, butyric acid values of butter and of coconut-oil mixtures, A. and B. values (Kuhlmann and Grossfeld), and a host of useful matter otherwise only available in the original memoirs.

Although the list of contents is well detailed, an index should be added.

It seems strange to English minds that such valuable—and expensive—books should be sent out in paper covers; anyone purchasing them would do well to buy the bound volumes. The weight is such that, with paper covers, the books would soon fall to pieces.

H. E. COX.

THE PRINCIPLES OF PLANT BIOCHEMISTRY. Part I. By MURIEL WHELDALE ONSLOW, M.A. Pp. 326. Cambridge: At the University Press. 1931. 16s. net.

As stated in the preface, the book deals only with the higher plants, a limitation, which, it is true, keeps the book within reasonable proportions, but, on the other hand, leads to a distorted view of the subject it purports to deal with; in practice it has, however, not been found possible strictly to adhere to this, since the subject of respiration has of necessity required some reference to the behaviour of yeast. The subject-matter is divided into six chapters, devoted respectively to The Sugars, The Cell Wall, Oxidising and Reducing Systems, The Plant Proteins, Nitrogen Metabolism, and Respiration. It is claimed that, as far as possible, each section has been treated comprehensively, and it must be conceded that the author has exhibited remarkable industry in abstracting a very formidable mass of literature and attempting to present the reader with an intelligible account of all this. Each chapter is provided with a useful bibliography which will be welcomed by those in search of first-hand information. The author has throughout endeavoured to stimulate interest by criticising or appraising the value of the researches described, and suggesting in which direction further work is indicated. The criticism is, perhaps, not always quite justified, as in the case of the implied stricture upon the methods of certain authors who "estimate pentoses and pentosans in leaves, without taking into account the presence of uronic acids in pectins, etc. . . ." and this in an alcoholic extract (of leaves) which was subsequently treated with basic lead acetate before analysis. P. HAAS.

CHEMICAL METHODS IN CLINICAL MEDICINE. First Edition. By G. A. HARRISON, B.A., M.D., B.Ch. Pp. ix+534. London: J. & A. Churchill. 1930. Price 18s.

Dr. Harrison is to be congratulated on producing a book greatly wanted in the English language, dealing with the application of chemistry to pathological states.

Many books have been written which deal with sections of this subject, but the comprehensive way in which Dr. Harrison has attacked and successfully carried out his task is worthy of admiration. His aim has been to discuss the chemical nature of pathological states, to equip us with reliable methods of analysis, both qualitative and quantitative, to teach us the deductions to be drawn, and to illustrate his conclusions with typical analyses and case records.

Apart from the value of the book to the medical profession, it should prove of great service to those analysts who are called on to make pathological investigations. They will find full details of chemical processes, and ample references should they desire to consult original publications.

The author, in his experience of teaching, refers very truly to the mystery which surrounds the term pH in the medical student's mind, and suggests the use, instead, of CH, *i.e.* the concentration of hydrogen in ionised form. For those whose time only permits of the acquiring of a limited knowledge of chemistry and mathematics, there is a good deal to be said for the employment of this term.

It is pleasing to recognise the caution of the author in his claims for the values of pathological chemistry in diagnosis and treatment; *e.g.*, to quote two instances, the disappointing results of the Van den Bergh reaction in the diagnosis of the nature of jaundice; and the futility, except in one or two special conditions, of the determination of blood calcium. On the other hand, however, it may be suggested that the proved value of the colloidal gold reaction on cerebrospinal fluid renders it worthy of a more detailed exposition.

Although throughout the book very full and valuable tables of the results of analyses are given, they can be misleading. For instance, on page 390, results of analyses of test meals are given in summarised form. To quote one item as an example, the free hydrochloric acid in cases of duodenal ulcer is given as varying from 0·00 to 0·35 per cent. In this condition the typical feature is hyperacidity, and values of 0·2 per cent. and over will be found in 90 per cent. of the cases, whilst values of 0·00 per cent. will occur about once in 1000 patients suffering from this disease. Thus the bald statement cited above, although strictly accurate, does not stress the characteristic hyperacidity, and will mislead the inexperienced. Similar criticism may be directed to other items.

In the chapter on "Miscellanea and Conundrums" it would have been far better to deal with the detection of blood stains fully or omit the section. It is not in keeping with the thoroughness which characterises the rest of the book. The apology for its inclusion is that the chemical pathologist is occasionally asked to examine blood stains, but surely he is asked more often to make analyses of vomit to determine the nature of the poison in cases admitted to hospital in an urgent state. So far as the commoner poisons are concerned, the author may well consider this inclusion in a future edition.

The book is well printed and bound, and a number of helpful illustrations are included. The book has a satisfactory index. G. ROCHE LYNCH.

ELEMENTS OF WATER BACTERIOLOGY. Fifth Edition. By S. C. PRESCOTT, S.B., Sc.D., and C. A. WINSLOW, S.M., Dr.P.H. Pp. viii+219. New York: John Wiley & Sons; London: Chapman & Hall. 1931. Price 12s. 6d.

The first edition of this American work was issued in 1904, and was a little book of 162 pages of small size; the present edition has 219 much larger pages, a fairly representative increase for a subject which has not shown any very extensive developments of recent years. Sewage and shell-fish were not, however, included in the first edition.

In this space the authors have well covered their subject. After a short chapter on the bacteria in natural waters, follow three chapters on the quantitative examination and its interpretation. Counts on both gelatin and agar are recommended, but no reference is made to the use of agar for both low and blood temperature counts, a procedure of value. As regards the composition of the media the authors take the sound view that the aim is not media which yield the maximum numbers, but rather that the object is to bring out the quantitative differences

between potable and polluted waters. Throughout, the recommendations of the Standard Methods Committee of America are quoted and generally accepted. The English Standardisation Committee's Report of 1904 is mentioned, but not their second report.

Two chapters are devoted to the colon group, and the significance to be attached to the presence of these strains. While the value of the test is emphasised, the important question of permissible standards is not clearly treated, and the directions are difficult to follow and to use. The greatest divergence from English methods is in regard to the failure to recommend bile salt media for the estimation and isolation of this group. Experiments, using bile itself, are given at some length, and their value recognised, but the authors apparently acquiesce in the views of the Standards Committee, which make no mention of bile, and recommend ordinary lactose broth as the enrichment medium. Lactose bile salt neutral red agar is not even mentioned, and there is considerable discussion as to the relative value of Endo agar and eosin methylene blue agar. English bacteriologists are so satisfied with the use of the bile salts broth and agar that there is no need to try others, and most of them gave up Endo agar many years ago. There is an interesting discussion on the relative value of the *B. coli* and *B. aerogenes* groups, the authors taking a rather non-committal attitude as to the value of their differentiation in judging the potable qualities of a water.

The utility of *B. enteritidis sporogenes* and streptococci determinations are discussed, but little value is placed upon their estimation. The former is stated to be now called *B. sporogenes*, but the usual view is that the characteristic milk change is due to *B. welchii*, Klein's original strain being a mixture of anaerobes.

It is refreshing to note that, unlike so many recent American books, credit is given to English work, much of which was pioneer work, although some important English investigations are omitted. For example, Wilson's recent work on the isolation of *B. typhosus* and *B. paratyphosus* from sewage is not mentioned, while standard English methods for examining shell-fish are ignored.

The book is clearly written, well printed, and contains a great deal of valuable information, while the teaching is mostly in line with English experience. With a few reservations, some of which have been indicated, it can be recommended as a reliable guide to the subject and as a most useful book of reference.

W. G. SAVAGE.

PERFUMES, COSMETICS AND SOAPS, WITH SPECIAL REFERENCE TO SYNTHETICS. By W. A. POUCHER. Third Edition. Vol. I. Pp. xxix+394, with 30 illustrations. Vol. II, pp. xiv+521, with 66 illustrations. London: Chapman & Hall. 1930. Price 21s. and 25s. net, respectively.

The popularity of this work is shown by the fact that though only first published in 1923, a third edition is already called for.

Vol. I, which maintains its character as a dictionary of raw materials of value and interest to the chemist-perfumer, has been expanded by the inclusion of some

30 more natural products, and about 250 new synthetics, making, in all, a total of over 1000 substances dealt with. The value of the volume to the analyst is much increased by the inclusion of the chemical formulae and physical constants for nearly all the synthetics, and the very large number of formulae for the reproduction of natural perfumes by mixtures of synthetics is still a very useful feature of the book.

It is a pity that advantage has not been taken of the issue of a new edition to correct some of the errors referred to in the review of the second edition (ANALYST, 1926, **51**, 275), but except for the corrected spelling of safrole, these all remain. Under zinc stearate it is interesting to note a warning that powders containing this salt have been reported in the U.S.A. to have caused illness and even death in children, and the use of magnesium stearate instead is recommended.

Vol. II has been enlarged by the inclusion of four new chapters dealing with (1) the Purchase and Use of Flower Absolutes, (2) Odour Classification, (3) Sachets and Solid Perfumes, and (4) Hair Dyes. Among the last-named, paraphenylene-diamine is said to be the most important, and the dangers attending its use are pointed out.

In this volume, also, no attempt has been made to correct the defects referred to in the review of the second edition (ANALYST, 1927, **52**, 109), except that the subject of transparent soap manufacture has now been much expanded; but here, however, there is another mis-statement, namely, that in the process of dissolving soap in alcohol and distilling off the solvent, the soap should be "a first class milling base," whereas it is customary to use a tallow-rosin (primrose) soap, the rosin playing an important part in securing transparency.

Most of the very large number of formulae included have been revised, and brought into accord with present-day practice.

The work is written in a concise but interesting manner, and is well illustrated, and this edition will doubtless prove as popular as the earlier ones have done.

W. H. SIMMONS.

ANALYTICAL CHEMISTRY. Vol. I. QUALITATIVE ANALYSIS, BASED ON THE GERMAN TEXT OF F. P. TREADWELL. Translated and Revised by WILLIAM T. HALL. Seventh English Edition, Revised. Pp. ix+610. New York: John Wiley & Sons, Inc.; London: Chapman and Hall, Ltd. Price 23s.

The new edition of Treadwell–Hall's Qualitative Analysis has undergone a few changes, some of which will be discussed below; the text-matter on the Rare Earths has been altered with the help and advice of Mr. H. F. V. Little, author of the scholarly treatise on Aluminium and its Congeners, in Newton Friend's Series of Text-books.

The book is so well known that a general survey of its contents has become superfluous. I can, therefore, confine my attention to certain parts, dealing mostly with rarer elements.

An example of how errors are perpetuated in text-books is furnished by the familiar chart showing the spectra of a number of metals. While still at school I was an assiduous reader of Wislicenus's Treatise, published about 1875. The old book and the one under review contain the same chart, in which the wrong symbol, "Ka" for potassium occurs three times.

On account of the high price of platinum, if for no other reason, it would be advisable to mention the use of silica crucibles for pyrosulphate fusions (p. 138). On the same page, we find that the destruction of tartaric acid, etc., is regarded as necessary prior to the detection of aluminium in solution. This is no longer true, as tannin precipitates the metal quantitatively from tartrate solution. Though not specific for aluminium, the reaction might be with advantage described, as it is very delicate, and forms part of a useful and convenient method for the separation of aluminium from iron (ANALYST, 1929, **54**, 712).

An unfortunate mistake has spoiled the description of the method for the separation of the earth acids from titania and zirconia (ANALYST, 1929, **54**, 454). The colour of the tannin complexes of tantalum and niobium is given as "sulfur-yellow" (p. 168B); actually the colours are sulphur-yellow for tantalum and red for niobium, as stated in the original. As to the application of the procedure, the book directs the operator to "repeat the treatment if the residue is not light yellow in color." Nothing could be more unlike the original text, which gives unconditional directions for a single treatment, while the colour of the residue is given as "buff to bright scarlet." As they stand, the directions are altogether misleading.

A drastic revision of the pages on tantalum and niobium (527 to 531) is badly needed. Much of the text-matter is out of date; some of the reactions are of no diagnostic value; and several statements are erroneous. Sodium hexaniobate has not been isolated; the stable salt is $7Na_2O.6Nb_2O_5$. Of the tantalum reactions cited, the first consists in the precipitation of tantalic acid by mineral acids from alkaline solution; yet reactions 2, 3, 4, and 8 are described as taking place in acid solution. The following is a glaring instance of careless proof reading coupled with inadequate treatment of the tannin reaction, the most important one in earth-acid analysis. Under Tantalum, we read that "Tincture of nutgalls produces no precipitate (difference from niobic acid)." Turning to niobium, we find that "Tincture of nutgalls produces no precipitate"!

In view of the minute quantities in which rubidium and caesium are met with, the spectroscope is likely to remain the analytical weapon of paramount importance for their detection. It is, therefore, disappointing to find that the spectroscopic examination of the alkali group has been discarded in favour of a wet separation method of Noyes and Bray. The advisability of this change is more than questionable. The wet process represents an achievement involving a disproportionate expenditure of time and labour, and requiring a number of unusual reagents. One may be permitted to question its practical value; it may, no doubt, serve as an exercise for college students working with artificial mixtures

of high rare-alkali content. But no chemist in actual practice, I venture to say, would engage in work of this kind without a spectroscope.

The concluding 20 pages of the book consist of a tabulated outline of Noyes and Bray's comprehensive scheme for the detection of all the known metals. It would be of interest to the profession to know whether the scheme has found practical application outside those colleges where it forms part of the laboratory discipline. I believe, rightly or wrongly, that it suffers from over-elaboration, because it sets out to solve an artificially created problem. Fortunately for the analyst, there is such a thing as paragenetic incompatibility, by virtue of which *substantial* amounts of certain metals (such as would respond to the tests when one grm. of substance is taken as directed) are not met with in association with certain other metals. For example, it is unnecessary to look for metals of the platinum group as major constituents of silicates or titanoniobates. For the detection of traces of an element, on the other hand, it will still be necessary to isolate it from a larger amount of material by a special procedure.

The number of misprints noticed in the book indicates rather superficial proof-reading. A bad slip occurs on p. 168B, line 4 of paragraph 9*a*, where "tantalum" should be substituted for "zirconium" in the sentence "differs from zirconium and columbium." On p. 499, rubidium chloroplatinate is described as a white crystalline precipitate, and "cerium" occurs twice as a mis-spelling for "cesium."

W. R. SCHOELLER.

IMPURITIES IN METALS. THEIR INFLUENCE ON STRUCTURE AND PROPERTIES. By COLIN J. SMITHELLS, M.C., D.Sc. Second Edition. Roy. 8vo. Pp. xiii+190, with 181 illustrations. London: Chapman & Hall, Ltd. 1930. Price 18s. net.

The fact that a second edition of this work has been called for within the short space of two years indicates that a very real demand existed for a book which at the time of its first appearance was somewhat novel in conception. The new edition has given the author an opportunity of carrying out a thorough revision of the data presented, and of bringing the whole up-to-date.

An exact knowledge of the influence of impurities, or, as they may preferably be called, "minor constituents" (for they include both accidental and intentional additions), is of interest, not only to the metallurgist and engineer, but also to the physicist engaged on the measurement of fundamental constants of materials, and to the analytical chemist. The subject is here treated as a natural development of metallography. To those who make no special claim to metallographic knowledge the first four chapters will be found to be of considerable value. They deal with methods of studying the Structure of Metals, *X*-rays and the Structure of Metals, the Structure of pure Metals and the Structure of Alloys.

The general arrangement of the book remains unchanged. The minor constituents are grouped together and classified as metallic, non-metallic and gaseous, with a further sub-division according to their solubility in the metal or alloy.

This method adds to the lucidity of the treatment and stimulates interest by revealing the scientific principles governing the wealth of information presented. It has the effect, however, of scattering the references to the "major constituent" from one end of the book to the other. Thus the chemist, using the book as a work of reference, will find that the effect of impurities on copper is dealt with at frequent intervals between page 3 and page 156. It must be added that this unavoidable inconvenience is compensated for by a useful index; though here, as in the text, the author occasionally trips over names, *e.g.* Andrews for Andrew, Beckinsdale for Beckinsale, Langenburg for Langenberg, Stoke's law for Stokes' law. There still remain a few discrepancies which, however, are not likely to be seriously misleading; for example, the solid solubility of copper in silver is given on p. 44 as 4 per cent. and on p. 116 as 6 per cent., whereas it is actually about 1·7 per cent. (Hansen).

Special attention has been devoted to the revision of the sections on the effect of gases on metals and on the influence of minor constituents on the mechanical properties of metals, as the results of many new researches in these fields have become available since the date of original publication of the book. The production of an exhaustive account of these subjects in the space available would be impossible, but the author has made a well-balanced choice of material, and covers a wide field with commendable accuracy.

The book is amply illustrated, and the excellence of the printing and of the reproduction of the photomicrographs reflect great credit on the publishers.

R. H. GREAVES.

DIE SCHLÄMMANALYSE. By Dr. HERMANN GESSNER. (Kolloidforschung in Einzeldarstellungen, Bd. X.) Pp. vii+244. Leipzig: Akademische Verlagsgesellschaft. 1931. Price: Stitched, M.16.50; bound, M.18.

This well-produced monograph deals with the subject of analysis by elutriation, *i.e.* the determination of grain-size of muds, slimes, soils and fine suspensions generally. To the student of soil physics it has special appeal, but it deserves the attention of all interested in the wider field of colloid physics.

Size-frequency analysis is becoming increasingly important, and Dr. Gessner's treatment can readily be adapted to emulsions.

The author commences with Stokes' formula and its recent modifications, following then with an excellent account of modern work on coagulation. The various methods suggested and applied in analysis by elutriation are next examined in considerable detail, with a remarkable array of illustrations of apparatus. These, with graphs, total 103 figures. A critical examination of the value of such analyses closes the volume.

The German is unusually easy to follow, and the printing and binding are excellent. Altogether the book can be heartily recommended to all interested in this special field. The well-known authority, Professor Georg Wiegner, has contributed an appreciative foreword.

WILLIAM CLAYTON.

Erratum.—In the review on "Practical Physical Chemistry" (p. 276, line 34) *for* "27·30" *read* "27·83."