THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

A JOINT Meeting of the Society with the Food Group of the Society of Chemical Industry was held at the Chemical Society's Rooms, Burlington House, on Wednesday, February 2nd, 1938. The President, Dr. G. Roche Lynch, was in the chair, and was supported by Dr. E. B. Hughes, the Vice-Chairman of the Food Group.

Certificates were read in favour of:—Elmer Bruce Ashcraft, M.S., Ph.D., Alfred Ernest Cross, Frederick Raine Ennos, B.A., B.Sc., F.I.C., Reginald Lee Lord, M.Sc., Maison Gabriel de Navarre, Ph.C., B.S., Frank Arnold Robinson, M.Sc.Tech., A.I.C., William Henry Smith, Stanley Robert Thompson, Charles Edward Waterhouse, A.I.C.

The following were elected Members of the Society:—John Edward Byles, B.Sc., F.I.C., William Montague Dowson, B.Sc., A.I.C., Alfonso Matzas Fill, Joseph Frederick Hirst, B.Sc., F.I.C., Thomas Worthington Jackson, B.Sc., A.I.C., Robert Leopold Kenny, B.Sc., A.I.C., Arthur James Lindsey, M.Sc., Ph.D., A.I.C., Francis Arthur Lyne, B.Sc., A.I.C., Cecil Denis Bradley Moon, A.I.C., James Wilson Tullo, B.Sc., F.I.C., James Norman Vickers, B.Sc., A.I.C.

The following papers were read and discussed:—"The Influence of Feeding Stuffs on Meat," by V. C. Fishwick, N.D.A.; "Fat Absorption and Metabolism," by A. C. Frazer, M.B., B.S., M.R.C.S., L.R.C.P.; "The Concentration of Fruit Juices by Freezing," by P. L. Bilham, B.Sc., F.I.C.

NORTH OF ENGLAND SECTION

THE Thirteenth Annual General Meeting of the Section was held in Manchester on February 5th, 1938. The Chairman (Mr. A. R. Tankard) presided over an attendance of forty-four.

The Financial Statement and Secretary's Report were presented and adopted.

The following appointments for the coming year were made:—*Chairman*, Professor T. P. Hilditch; *Vice-Chairman*, J. R. Stubbs; *Honorary Secretary and Treasurer*, J. R. Stubbs; *Honorary Auditors*, J. W. H. Johnson and U. A. Coates;

Members of the Committee, W. F. Elvidge, H. Heap, E. G. Jones, A. Lees, C. R. Louden and A. R. Tankard.

An address was given by E. S. Hawkins, B.Sc., A.R.C.S., F.I.C., on "Side Lights on Analytical Practice in the Near East." A discussion was introduced by A. D. Powell, A.I.C., on "The Interpretation of Drug Standards."

The congratulations of the Section were offered to Professor W. H. Roberts on his nomination as President of the Society.

SCOTTISH SECTION

THE Third Annual General Meeting of the Section was held in Glasgow on January 27th, 1938.

The following office bearers were elected:—*Chairman*, Dr. J. F. Tocher; *Vice-Chairman*, T. Cockburn; *Committee*, T. W. Drinkwater, H. Dryerre, J. W. Hawley, H. C. Moir, A. Scott Dodd and R. T. Thomson; *Honorary Secretary and Treasurer*, J. B. McKean; *Honorary Auditors*, M. Herd and R. S. Watson.

The following papers were read and discussed:—"The Bakery Chemist's Point of View," by H. C. Moir, B.Sc., A.I.C.; "The Manufacture of Condensed Milk," by G. R. Howat, B.Sc., Ph.D.; "The Proportion of Copper present in Tomato Purée," by T. Cockburn, F.I.C., and M. Herd, B.Sc., F.I.C.

A Colorimetric Test for the Detection of Para-Hydroxybenzoic Acid in the Presence of Salicylic Acid

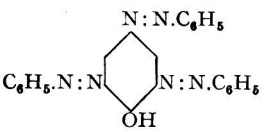
BY S. G. STEVENSON, M.Sc., B.PHARM., F.I.C., AND J. C. L. RESUGGAN

(*Read at the Meeting, December* 1, 1937)

EDWARDS, Nanji and Hassan (ANALYST, 1937, **62**, 178) have described a method for the extraction, detection and determination of *p*-hydroxybenzoic acid and its derivatives, with special reference to their distinction from salicylic and benzoic acids. A perusal of their paper indicated the large amount of work that they have recorded and the difficulties that they had in distinguishing between these compounds, particularly when more than one was present at the same time. We have tried to find a test which would distinguish more easily between *p*-hydroxybenzoic acid and salicylic acid, but beyond this we have made no attempt to modify the methods described by Edwards *et al.*, for we have found their method of extraction to be excellent.

Under certain conditions *p*-hydroxybenzoic acid couples with solutions of benzene diazonium salts to give a dark, red-brown mixture of mono-, bis- and tris-azophenols. These substances, which result from decarboxylation of the

p-hydroxy acid and subsequent coupling, are insoluble in solutions of alkali carbonates, whilst the product obtained by coupling salicylic acid with diazonium salts (namely, 4-hydroxy-azo-benzene-3-carboxylic acid) is readily soluble. Mono- and bis-azo substituted 4-hydroxyazo-benzene (azo derivatives of the para- acid) occur in forms which exhibit a colour reaction that can be utilised for the detection of *p*-hydroxybenzoic acid. If an ethereal solution of the products obtained from the coupling of benzene diazonium chloride and *p*-hydroxybenzoic acid is shaken with sodium hydroxide solution, a deep red colour immediately develops in the ethereal layer, and this colour remains so long as the ether is in contact with the alkali. The colour may be changed back to the original yellow-brown by washing the ethereal solution with water or dilute acid. No colour is produced in the alkali under these conditions. The essential difference between the two classes of azo compounds, *i.e.* those obtained from the para- acid and those obtained from salicylic acid, is shown by the formulae I and II.



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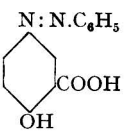

II

The diazo solution may be prepared in the usual way by dissolving 5 g. of aniline in a mixture of 13 ml. of conc. hydrochloric acid and 26 ml. of water. This solution is cooled to 5° C., and to it is added a solution of sodium nitrite (4·5 g. in 20 ml. of water), the mixture being slowly shaken until the presence of free nitrous acid is indicated by starch iodide paper. The solution is kept below 5° C. and used within one hour. In order to detect *p*-hydroxybenzoic acid alone, a small quantity is dissolved in a little sodium hydroxide solution and cooled to 5° C. An excess of the diazo solution is slowly added, and after standing for a short time the mixture is acidified and extracted with ether. If the ethereal solution is then shaken with a little sodium hydroxide solution, a deep red colour develops in the ether and the alkali solution remains practically colourless.

For a mixture containing the para- acid and salicylic acid, the same procedure for coupling is adopted, and the resulting solution is acidified and extracted with ether. The ethereal extract is then shaken with sodium carbonate solution, which removes all the salicylic acid derivative and leaves the para- acid derivative in the ether. The ethereal solution may then be tested with sodium hydroxide and the presence of the para- acid confirmed.

We have attempted to put this test on a quantitative basis, because the separation of the two azo derivatives, which might be weighed, seemed simple. Unfortunately, the proportions of the three (mono-, bis- and tris-) azo derivatives are not constant, so that it is not possible to work out either a theoretical or an empirical factor for converting the amounts of the azo derivatives back to the amounts of the respective acids. In some instances success seemed to be promised, but further work emphasised the fact that one cannot rely upon these three compounds being present in exactly the same amounts each time. Therefore, whilst we cannot put this method forward for the determination of the para- acid

in the presence of salicylic acid, we do suggest that it is a valuable test for the presence of the para- acid either by itself or in the presence of salicylic acid.

Normally, the acids will be present in foodstuffs and pharmaceutical preparations as the esters or as the sodium salts of the esters. After extraction the residue will usually consist of the free esters which will need hydrolysing before the test can be applied. The lower limit of the test is about 1 in 50,000, and the para- acid can be detected at this concentration in presence or absence of salicylic acid.

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December 9th, 1937

DISCUSSION

Mr. F. W. EDWARDS congratulated the authors on this piece of work, inasmuch as a very useful confirmatory test which would distinguish between the two isomeric hydroxybenzoic acids had been produced. The authors were very modest in their claims, and he thought that they might be persuaded to carry their investigations forward to the quantitative stage; he wished they had been successful there. The possibility of coupling in some other manner might lead, if they cared to explore the matter further, to a satisfactory quantitative method. He also thanked the authors for their kind references to the work of Dr. Nanji and himself, which had been carried out under very great pressure. A certain Port Authority had reported the presence of salicylic acid in a sample of smoked salmon, and they were required to investigate this allegation. In colorimetric tests on the acid isolated considerably less colour than they expected from the weight experimented upon was obtained, and this suggested the possibility that the acid might not be salicylic acid. For lack of time, they were only able to report the presence of so much of "a preparation of hydroxybenzoic acid," which left the matter in such a state that explanation could be given in Court later, if required. Their paper which followed represented the work of months, and, although they felt they had shown how certain reactions could be used to solve the problem of distinguishing between these preservative substances, they would like to have discovered one so definite as that just demonstrated. He wished to make one observation of a general nature. In such work as this a trouble frequently encountered was that the acids, as extracted from foodstuffs, usually contained traces of fatty substances and such products as vanillin and similar flavourings; it was always necessary to guard against interference by such substances in subsequent tests. If the authors went further, as he hoped they would, they might bear this point in mind.

Dr. H. R. NANJI said that when Mr. Edwards and he published their own paper they had actually considered the possibility of utilising the diazo-compounds for distinguishing the para- acid from salicylic acid, but their intention was to work on somewhat different lines. It was already known that some isomeric phenolic compounds showed distinct differences in their coupling with diazo-compounds derived from different amines, and they had anticipated that it might be possible to work out a simple colorimetric test. Their first problem, therefore, was to find a suitable aromatic amine the diazo-compound of which would couple with the para- acid but not with salicylic acid, or *vice-versa*, under given conditions. Their second difficulty was to find an amine that would not give mixed azo-derivatives. Unfortunately they could not make much headway in the time at their disposal. With regard to the chemistry of the azo-compounds involved in the test, there was a certain amount of confusion in his own mind. The authors stated that with the para- acid and diazobenzene chloride decarboxylation occurred

and that mono-, bis- and tris-azo-phenols were formed, but that with salicylic acid the only product shown was its mono-azo compound. Two German chemists, who had studied the action of diazobenzene chloride on the para- acid and salicylic acid in some detail, found that with excess of diazobenzene chloride, salicylic acid gave not only the mono-azo compound, but also the bis-azo compound and tris-azophenol, the last-named product being identical with that obtained from the para- acid. He did not know how the authors would reconcile that work with their own, but whatever might be the chemistry of the test, it seemed to be a very useful colorimetric confirmatory test for the para- acid. As regards the quantitative aspect, diazobenzene chloride was perhaps not altogether suitable, as it was one of those diazo-compounds which very readily gave mixed azo-derivatives. He did not know whether the authors had tried diazo-compounds derived from any other amines, but, on theoretical grounds, the diazo-compounds of some of the substituted anilines—particularly those containing negative substituents, such as chloroanilines or nitroanilines might possibly prove more satisfactory.

Mr. J. R. NICHOLLS said that this was a very interesting paper, since it utilised the fact that decarboxylation occurred when diazo compounds coupled with certain phenolic carboxylic acids. He had used the reaction as a qualitative test, but the authors had carried it considerably further, showing that it gave a product totally different from that produced with salicylic acid. With regard to adapting this test for quantitative colorimetric estimation, it was difficult to see how this could be done, as three products of probably varying tintorial power were formed. One of the main values of the test was that it could be carried out on a small quantity of material. He, personally, had found micro methods of identification very satisfactory, and the new method would be a very useful confirmatory test.

Mr. STEVENSON, replying to Dr. Nanji, said that they had not tried amines other than aniline. They had attempted assays on foodstuffs and pharmaceutical preparations, and it was then they had found that they could not put the test on a quantitative basis. If vanillin were present, it should be removed in the course of purifying the acid, because they had found that it did interfere with the test. He would like to make it clear that it was not only the colorimetric test they were trying to put on a quantitative basis; they had been trying to devise a method for isolating quantitatively and weighing an azo compound of fixed composition.

Mr. RESUGGAN replied to Dr. Nanji's reference to past work by German chemists and the fact that azo phenols had been produced in traces from salicylic acid. He believed that it was possible that impure salicylic acid was often used years ago, which would account for these results; pure salicylic acid yielded no azo-phenols under the conditions of the test.

The Gold Number in Analytical Practice

By JAMES FREDERICK MORSE

ALTHOUGH Zsigmondy's adoption of gold hydrosol to study the protective action of the common hydrophilic colloids has received considerable attention in clinical chemistry, notably in the Lange reaction of cerebrospinal fluid, comparatively little use of it has been made in general analytical practice. True, it has been applied by Elliott and Sheppard[1] in an attempt to grade gelatins, but they found that "the classification thus made possible is too rough, and moreover does not bear any simple relation to those properties of chief interest to users of gelatin." The Zsigmondy reaction has been observed to depend on *p*H value[2] and the degree of dispersion of the protective colloid, *e.g.* as affected by ageing, as well as on the mode of preparation of the gold sol.

That the method can have only limited application in biochemical analysis is obvious when the gold numbers of the usual protective colloids are compared. The gold number is the number of milligrams of protective colloid, added to 10 ml. of gold hydrosol, which just fails to prevent the change in colour from red to blue on the addition of 1 ml. of 10 per cent. sodium chloride solution. Whilst the gold number of potato starch is about 25 and that of soluble starch about 10 to 15, the value for proteins is very small, *e.g.* gelatin, 0·005 to 0·01; casein, 0·01; egg albumen, 0·08 to 0·10. Gum arabic occupies an intermediate position, *viz.* 0·15 to 0·5.

The gold number, therefore, should possess a special advantage in analytical practice in any clear-cut instance where differentiation between cereal (starchy) products and protein material is involved. I have investigated such an instance and the data were given in evidence in Court.

The problem was to prove the presence of pork stock in canned Danubian beans in tomato sauce. The usual estimation of creatinine was rendered extremely difficult owing to the development of interfering colour. Moreover, the amount of creatinine, even if accurately determinable, would not have provided a true basis for the evaluation of the pork initially employed in preparing stock, since salted pork of a very fatty character had been used. Finally, the presence of pork fat was not a possible source of evidence, owing to the use of a clarified pork stock.

A reasonable premise is that during the boiling of stock, hydrolysis of collagen would furnish gelatin and other degradation products, the presence of which might be proved by their high protecting power towards colloidal gold. As a control the same kind of beans in tomato sauce made without meat stock of any kind was used. All thermal conditions, including sterilisation (70 minutes at 117° C.), were maintained constant in both series.

The laboratory technique employed was as follows:—The sauce was separated from the beans by means of a sieve, and 25 ml. were diluted to 100 ml. with industrial methylated spirit. During this operation care was taken that the stirring was continuous and thorough, since the starch, bean protein and mucilage

are precipitated. After filtration the slightly turbid liquid was mixed with kieselguhr and rendered brilliant by re-filtration.

Four ml. of the extract (equivalent to 1 ml. of the original sauce) were diluted to 100 ml. with water, and 0·1 ml. of this solution was placed in the first of a series of ten tubes; subsequent additions were increased by 0·05 ml. In each tube 5 ml. of a gold sol, quite easily prepared according to the method of Borovskaya,[3]* were added and, after mixing, 1 ml. of *N* sodium chloride solution. When the sauce

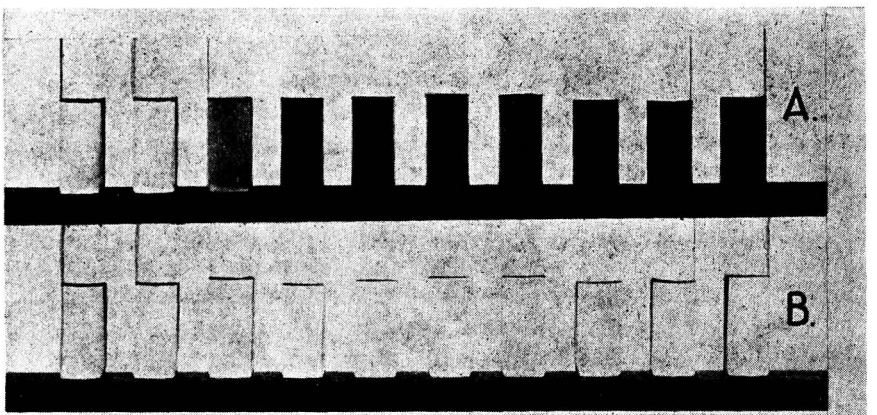

Fig. 1

Protective action of protein on gold hydrosol.
Series A. = sauce containing pork stock.
Series B. = sauce without pork stock.
(Concentrations increase from left to right.)

from a can of beans which had contained pork or pork extractives was treated by this method it was found that 0·25 ml. of the diluted sauce, equivalent to 0·0025 ml. of the original sauce, afforded complete protection to the gold sol (Fig. 1, A). The sauce from a can of beans which had not contained pork or its extractives failed to protect the gold sol in any concentration (Fig. 1, B). Whilst Fig. 1 conveys an accurate photographic record of the quantitative data, it cannot reproduce the true colour changes. Thus, in series A the red (unchanged) gold hydrosol shows as black, whilst in series B and tubes 1 and 2 of series A, the coagulated (blue) gold hydrosol shows as white.

It is suggested that analysts may find this method of value in special instances in which protein change could be a major factor. Thus, it might serve to follow the course of bacterial activity and thereby possess a diagnostic value, *e.g.* for

* BOROVSKAYA'S GOLD HYDROSOL.—Add 1 ml. of 1 per cent. auric chloride solution to 95 ml. of distilled water contained in a flask of resistance glassware. Heat to 90–95° C., add 5 ml. of 1 per cent. sodium citrate solution, heat to boiling, and boil until the correct red colour is obtained. According to Borovskaya only 1 to 3 minutes' boiling is required, but I have consistently found that up to 10 minutes is necessary for the colour sequence:—bluish purple→purple→deep crimson→red. (Thereafter the colour changes to orange-red.) A red colour is required, the sensitivity of the preparation appearing to be greatest at this point.—J. F. M.

mastitis milk. In certain preliminary experiments in this laboratory concerning protein denaturation the gold number has yielded interesting and unexpected results. For instance, the gold number of milk (as supplied to the locality) is not influenced by air/liquid interface denaturation (air-blowing or exposing the milk with a large surface), and it is only slightly increased in milk boiled for 5 minutes. Again, the gold number of the whey resulting from the rennet treatment of the milk to make junket is practically that of the original milk. Even more striking are the data obtained for the gold number of egg white. Solutions of egg white—1 per cent. by volume—were tested after being heated for 5 minutes at different temperatures. Up to 50° C. the number remained constant, but it increased between 50° C. and 70° C., indicating reduced protective action. However, from 70° C. to 90° C. the gold number decreased, and at 100° C. the protective action was in excess of the original value.

On the assumption that hydrolysis of egg white was yielding products possessing high protective effect for gold hydrosol, it was argued that water-soluble protective material should be extractable from heat-coagulated egg white. In fact, when the white of an egg which was boiled for 15 minutes was heated with distilled water for 5 minutes at 100° C., there resulted a clear solution which possessed double the protective action of a similar cold water extract of the coagulated egg white.

SUMMARY.—(1) Attention is drawn to the possibility of utilising the gold number in investigations where proteins and carbohydrates require differentiation, or where changes in protein structure are involved.

(2) Data are given relating to an examination of canned beans with meat stock.

(3) Data are instanced from preliminary investigations into protein denaturation, in which milk and egg white were employed.

This work was carried out under the supervision of Dr. William Clayton, whom the author thanks for his interest and advice.

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November 30th, 1937

The Micro-Electrolytic Determination of Copper in the Presence of Other Metals by Controlled Potential

By A. J. LINDSEY, Ph.D., M.Sc., A.I.C.

Although considerable attention has been paid to the micro-electrolytic determination of copper, no procedure has yet been described for its separation from other metals in chloride solutions, by the method of controlled potential.[1,13] A hydrochloric acid electrolyte has the advantages that it can be prepared readily from an alloy (or other substance) by the action of conc. hydrochloric acid and a chlorate, and that in such a solution copper may be determined in the presence of tin, antimony and lead.

The Determination of Copper.—Analyses attempted in Pregl's apparatus[2] with chloride solutions containing anodic depolarisers were unsuccessful. The voltage could not be held constant, and, even after prolonged electrolysis, deposition was not complete. Further, when tin also was present, it was deposited together with copper towards the end of the electrolysis.

Table I

Determination of Copper in Chloride Solution

Experiment	HCl present (sp.gr. 1·16) Drops	Voltage	Copper found mg.
1	5	0·8	4·99
2	5	0·8	4·99
3	5	1·0	4·97
4	5	1·0	5·03
5	5	1·0	5·00

With the apparatus designed for potential control[14] successful determinations were made. The method is an adaptation of that already described for normal-scale determinations,[15] and the manipulative details were as recommended in the former paper.[14] The electrode and deposits were prepared for drying by dipping, first into distilled water, and then successively into two quantities of acetone. The high purity, easy volatility and complete miscibility with water of this solvent, make it an excellent substitute for the more costly alcohol and ether previously recommended. Table I shows results obtained with accurately measured quantities of 5 ml. of copper chloride solution containing 5·00 mg. of copper. As depolariser 10 drops of 2 per cent. hydroxylamine hydrochloride solution were used, and in each experiment the current strength fell from an initial value of 100 milliamperes to about 10 milliamperes during the electrolysis time of 15 minutes. Hydrogen or carbon dioxide stirring was employed. No copper could be detected in the residual liquid upon making it alkaline with ammonia and adding hydrogen sulphide.

Hydrazine may also be used as the anodic depolariser; the anode to cathode potential difference then necessary for quantitative deposition is 0·7 volt. The quantity of depolariser used is not critical.*

THE DETERMINATION OF COPPER IN CHLORIDE SOLUTIONS CONTAINING ANTIMONY, TIN, LEAD, ZINC, ALUMINIUM, OR NICKEL.—An examination of the deposition potentials of these metals shows that copper cannot be separated from antimony by potential control, but that careful control of potential should give an easy separation from tin or lead. Such separations have already been effected in macro-electrolyses. Accurate adjustment of potential should not be necessary in the separation from zinc, aluminium or nickel. The following methods are based upon these considerations.

Antimony present.—The procedure closely follows the method described by Lassieur for normal-scale determinations.[16] The two metals are deposited together from hydrochloric acid solution, and the mixed deposit is re-dissolved in a mixture of hydrofluoric acid and nitric acid, from which solution, in the presence of chromate ions, copper alone is deposited. The antimony remains in solution in the quinquevalent form, as fluoride.

To the solution containing the two metals as chlorides were added 1 ml. of hydrochloric acid (sp.gr. 1·16) and 0·1 g. of hydroxylamine hydrochloride. The solution was diluted to about 15 ml. and electrolysed at 60 to 70° C. and an anode to cathode potential of 1·2 volt. The copper first deposited was quickly covered with a dark layer of antimony-copper alloy. The vessel was washed down after 10 minutes, and in another 10 minutes the electrolysis was terminated by rapidly replacing the solution by a beaker of water. The mixed deposit was not weighed in this series of experiments, as the micro-electrolytic determination of antimony is to be the subject of further investigation. The two metals were removed from the electrode with a mixture of 1 ml. of conc. nitric acid and 1 ml. of hydrofluoric acid (40 per cent.) in an electrolysis tube, and the solution was immediately diluted to about 15 ml. After further addition of three drops of 5 per cent. potassium dichromate solution the liquid was electrolysed for 20 minutes at room temperature. During this time the potential was kept at 1·2 volts until the current strength had fallen to 50 milliamperes, after which the potential was raised sufficiently to maintain the current at 50 milliamperes. The deposit was washed and dried in the usual manner.

Tin present.—Quantities of stannous chloride solution were measured, acidified with hydrochloric acid, and oxidised by warming with a few mg. of potassium chlorate. To the solutions thus obtained quantities of copper chloride solution were added from a pipette, and electrolysis was carried out in the presence of a depolariser, as described for copper solutions.

Lead present.—Experiments were made with a solution of lead chloride in water. The procedure was exactly as described for tin.

Zinc, Aluminium or Nickel present.—No difficulty was experienced in determining copper in solutions containing these metals. The solutions of the chlorides of the metals were treated by the method given above for simple copper solutions. Accurate potential control was not necessary, but was considered desirable in order

* With controlled potential the anode is not attacked (*cf.* ANALYST, 1938, **63**, 105, footnote).

to maintain constant conditions for the copper depositions. The results demonstrate that zinc, aluminium and nickel do not interfere with the quantitative determination of copper.

TABLE II

DETERMINATION OF COPPER IN THE PRESENCE OF OTHER METALS

Experiment	Metal taken mg.	Copper taken mg.	Copper found mg.
6	Sb. 10·0	5·80	5·83
7	10·0	5·80	5·88
8	5·0	5·80	5·80
9	2·5	5·80	5·80
10	Sn. 10·0	5·00	4·96
11	8·0	5·00	4·95
12	6·0	5·00	4·99
13	2·0	5·00	4·99
14	Pb. 5·6	5·80	5·79
15	5·6	2·25	2·25
16	2·8	5·80	5·80
17	1·1	5·80	5·81
18	Zn. 10·0	5·00	4·96
19	8·0	5·00	4·96
20	6·0	5·00	4·97
21	4·0	5·00	4·97
22	2·0	5·00	4·96
23	Al. 6·0	5·05	5·02
24	4·0	5·05	5·04
25	2·0	5·05	5·05
26	Ni. 10·0	5·80	5·80
27	8·0	5·80	5·76
28	5·0	5·80	5·80
29	2·0	5·80	5·77

The methods tested as described above for mixtures of pure metals have been applied to the determination of copper in its common alloys, only a few mg. of the alloy being used for each analysis. Some typical results of such analyses are given in Table III. The specimen was dissolved by warming with a mixture of

TABLE III

DETERMINATION OF COPPER IN ALLOYS

Alloy	Taken mg.	Copper (calc.) mg.	Copper found mg.
Brass (57·8 per cent. Cu.)	6·495	3·76	3·80
	5·11	2·96	3·00
Brass (67·7 per cent. Cu.)	6·18	4·19	4·22
	8·47	5·73	5·79
Bronze (95·4 per cent. Cu.)	5·87	5·61	5·66
	3·39	3·24	3·27
Gunmetal (82·5 per cent.)	5·45	4·50	4·53
	4·66	3·84	3·85

5 drops of conc. hydrochloric acid and either a few mg. of potassium chlorate or 1 drop of conc. nitric acid. The solution was prepared in an electrolysis tube and, when nitric acid was used to aid solution, the tube was heated in a water-bath to expel most of the oxidising gases before diluting for electrolysis. Two drops of 50 per cent. hydrazine hydrate solution were added as depolariser, and the deposition of copper was effected as described earlier.

The method should be useful for rapid analysis of mixtures containing copper when only a few mg. of material are available, and is particularly recommended on account of the short time necessary for each determination.

I wish to express my thanks to Dr. H. J. S. Sand for his interest in this work.

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A Contribution to Water Analysis

PART I

SPECIFIC CONDUCTIVITY AS A MEASURE OF TOTAL DISSOLVED SOLIDS

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IN some laboratories rapid analytical methods for the examination of water are in use, such as the Kubel-Tieman oxygen absorption determination, which has largely replaced the old four-hour process, and Winkler's persulphate method, superseding the standard distillation method for free and albuminoid ammonia. If, in a few instances, there should be a slight sacrifice of accuracy, this is usually compensated for by the saving of chemicals, time and labour.

DETERMINATION OF TOTAL SOLIDS BY EVAPORATION.—In most text-books the only method given for determining the total dissolved salines in water is evaporation and weighing. Although this method appears simple, closer examination shows that it may be tedious and associated with certain difficulties. It is the custom to

dry the residue for one or two hours in the air-oven after evaporation, at temperatures varying from 100° to 180° C.

At 110° C. at atmospheric pressure the salines may still contain water; for instance, $CaSO_4.2H_2O$, $MgSO_4.H_2O$, $MgCl_2.6H_2O$, $K_2CO_3.2H_2O$, $Na_2CO_3.H_2O$, $CaCl_2.2H_2O$, $Ca(NO_3)_2.4H_2O$, $Mg(NO_3)_2.6H_2O$. Even at 180° C. some salts will still retain water of crystallisation.

Many waters contain dissolved organic matter, and this must be removed before a true figure for the total salines can be obtained. To remove this organic matter the usual practice is to ignite the salts at a very low temperature, then to add ammonium carbonate solution, and finally to dry and weigh. Great care is necessary in burning off the carbon if easily decomposable salts are present. In the ignition there is a tendency for calcium and magnesium carbonates, especially the latter, to be converted into oxides. But, contrary to the accepted belief that moistening with ammonium carbonate effects complete recarbonation of any oxide formed, I have found unconverted oxide to remain after repeated additions of ammonium carbonate and subsequent drying. In waters containing only small amounts of bicarbonate the error with recarbonation will not be great.

All the salts present in water may be converted into anhydrous sulphates by moistening them with dilute sulphuric acid and then igniting quite strongly; the resulting sulphates are stable, and this method gives very accurate results. But if a water contains no sulphate, or only a trace, it is misleading and unsatisfactory to express all the basic constituents in terms of their sulphates.

Electrical Conductivity as a Measure of Dissolved Salines

Electrical conductivity has frequently been mentioned in connection with water analysis, but hitherto it appears to have been looked on as, at best, no more than an approximate method of measuring the amount of dissolved salines in a water. However, solutions of the order of $N/100$ to $N/1000$, as found in natural waters, are very well suited to conductivity measurements, and such determinations can be rapidly and accurately made.

The chief objections to applying conductivity to the analysis of water are: (1) that equal concentrations of the various salts found in waters have rather different specific conductivities; (2) that α, the degree of dissociation of a salt, varies considerably with concentration, even at this great dilution; (3) that the temperature coefficient is very large.

It was decided to make practical conductivity/concentration measurements for the various salines found in waters, and also for mixtures of these salines, from zero concentration to about 100 parts per 100,000 (covering the range of ordinary waters), to measure the temperature coefficients for the salts, and to find the effect of dissolved free carbon dioxide on the conductivity measurements.

Apparatus Used.—The slide wire and bridge outfit was made by the Cambridge Instrument Co. (Gallenkamp's Catalogue, 9th Ed., *d* 3762). The slide wire is 10 metres long and is wound in 50 turns on a screw-threaded cylinder. The buzzer comprises an electro-magnetic interrupter and a transformer, the secondary of which is connected with the bridge. The frequency is about 500 periods per second. Resistances of 1, 100 and 1000 ohms are incorporated.

The most satisfactory type of conductivity cell is that having a ground-in thermometer-stopper and fixed platinum electrodes, the latter preferably about 1 cm. apart. The cell-constant is found in the ordinary way, $N/100$ and $N/50$ solutions of pure potassium chloride being used.

EFFECT OF DISSOLVED FREE CARBON DIOXIDE ON CONDUCTIVITY MEASUREMENTS.—As many natural waters, especially well waters, contain free carbon dioxide in solution, the effect of such dissolved gas on the conductivity was investigated, and it was found, in complete agreement with Bordas and Touplain,[1] that the effect is appreciable only in waters that are very low in dissolved salines. Waters rich in bicarbonate ions repress the dissociation of dissolved carbon dioxide into $H^{\cdot}$ and HCO'_3 ions, and thus the conductivity is not affected. Even in distilled water, with which the maximum effect is experienced, a *saturated* solution of carbon dioxide (100–150 parts per 100,000) would only give a specific conductivity corresponding with an apparent saline-content of about 2 parts per 100,000. Hence, for all practical purposes the influence of free carbon dioxide may be regarded as negligible.

CONDUCTIVITY/CONCENTRATION CURVES FOR THE SALINES FOUND IN NATURAL WATERS.—The salines usually met with in waters are the bicarbonates, chlorides, sulphates and nitrates of calcium, magnesium and sodium, with occasional traces of the carbonates.

Solutions of these salts in a pure form were prepared, and the specific conductivity of each was measured at concentrations varying from zero to about 100 parts per 100,000, 18° C. being chosen as the standard temperature for measurement. Calcium bicarbonate solution was prepared by bubbling pure carbon dioxide through lime-water and eventually filtering. Magnesium bicarbonate was obtained by bubbling carbon dioxide through a suspension of magnesium carbonate, and then filtering, and sodium bicarbonate solution by passing carbon dioxide through a solution of sodium bicarbonate of analytical reagent quality. Each bicarbonate solution was standardised by titration against $N/10$ sulphuric acid, a blank test being made on distilled water, with methyl orange as indicator, and allowance being made for any free carbon dioxide present. All the curves were plotted—Specific Conductivity at 18° C. against Total Dissolved Salines (bicarbonates were expressed as carbonates in the total solids). From stock solutions of these salines a large number of artificial waters of various types were prepared, each containing definite known amounts of dissolved salines and covering every likely natural type, and the specific conductivity of various dilutions of each, down to zero concentration, was measured at 18° C.

From a study of the curves for all these artificial waters and of the "single salt" curves obtained previously, it was discovered that nitrate and sulphate curves of the three metals fell together, as did also the chloride and carbonate curves, with the bicarbonate and mixed saline water curves occupying an intermediate position on the graph.

Consideration of all the factors and of the conditions usually obtaining in natural waters showed that three empirical "type" curves could be drawn (see Fig. 1), representing, respectively, sulphate or nitrate waters, bicarbonate or mixed saline waters, and chloride or carbonate waters. The specific conductivity is measured or calculated at 18° C., and in the total solids all bicarbonates are

represented as carbonates, as previously explained. The points on the curves have been joined by straight lines. This is justifiable, as the small error introduced is within the limits of error of the method.

TEMPERATURE CORRECTION FOR SPECIFIC CONDUCTIVITY.—By actual measurements on solutions of the salts and on natural waters, at different concentrations, it was found that a universal temperature correction factor for the specific conductivity could be applied to all waters. The specific conductivity was increased or decreased by 2·4 per cent. of the value at 18° C. for each 1° C. above or below this standard temperature, respectively. This correction factor may be applied between 10° C. and 30° C., with an error of not more than 1 per cent. in the corrected specific conductivity.

Thus, measurement may always be made at ordinary room temperature, and the corrected specific conductivity at 18° C. read from a specially constructed table giving the conversion factor for, say, each 0·2° C. difference of temperature.

EVALUATION OF TOTAL SALINES BY MEASUREMENT OF SPECIFIC CONDUCTIVITY AND REFERENCE TO "TYPE" CURVES.—A simple measurement of the electrical conductivity will, of course, not suffice to show with any accuracy the amount of dissolved salines that a water contains, but if a water is to be analysed there are certain determinations that are nearly always made.

By far the greater number of natural waters are chiefly bicarbonate waters The ordinary alkalinity titration to methyl orange gives total carbonate + bicarbonate (usually expressed as $CaCO_3$). A differential titration, with phenolphthalein and methyl orange as indicators, will give each separately. Chloride is determined on the same solution immediately after the alkalinity titration. Sulphate is determined by a turbidimetric method and nitrate colorimetrically.

A measurement of specific conductivity will give the total saline-content of a water with considerable accuracy if the approximate proportions of bicarbonate, carbonate, chloride, sulphate and nitrate are known. Carbonate and chloride are added together, also sulphate and nitrate (all reckoned as molecular compounds, not as ions*). This gives three groups corresponding with the three curves: Types (1), (2) and (3), and enables the correct point to be fixed, either on one of the curves or at some definite distance between two of them, for reading the amount of total salines (*cf.* Fig. 1). The method of calculation is illustrated by the following example.

* The conventional method of expressing saline combinations of the individual ions found by chemical analysis of a water sample is combination of the metals with the acid radicles in the order in which the salts would separate out on evaporation of the water to dryness. Thus calcium is expressed as calcium carbonate and, if any remains, as sulphate, chloride and nitrate, in that order. If carbonate remains over after all calcium ion has been accounted for, it is combined with magnesium and then with sodium.

The following table will make this clear:

Ca^{++}	CO_3''	SO_4''	Cl'	NO_3'
Mg^{++}	,,	,,	,,	,,
Na^{+}	,,	,,	,,	,,
K^{+}	SO_4''	Cl'	NO_3'	CO_3''

The order of precedence is from top to bottom and from left to right. It should be noted that the sequence accepted for potassium is different from that of the other metals.

The total salines are expressed in the form of the *anhydrous* salts and in the state in which these would exist at the temperature of evaporation. By this convention all bicarbonates are expressed as carbonates, and an endeavour is made to put the sum of individual determinations and the result of direct determination of total solids by evaporation on a comparable basis.

The analysis of a water gave:—Specific conductivity at 18° C., $6{\cdot}49 \times 10^{-4}$ r.o.; alkalinity (bicarb.), 25·2 as $CaCO_3$; carbonate, none; sulphate, negligible; chloride, 12·7; nitrate, 1·6 parts per 100,000.

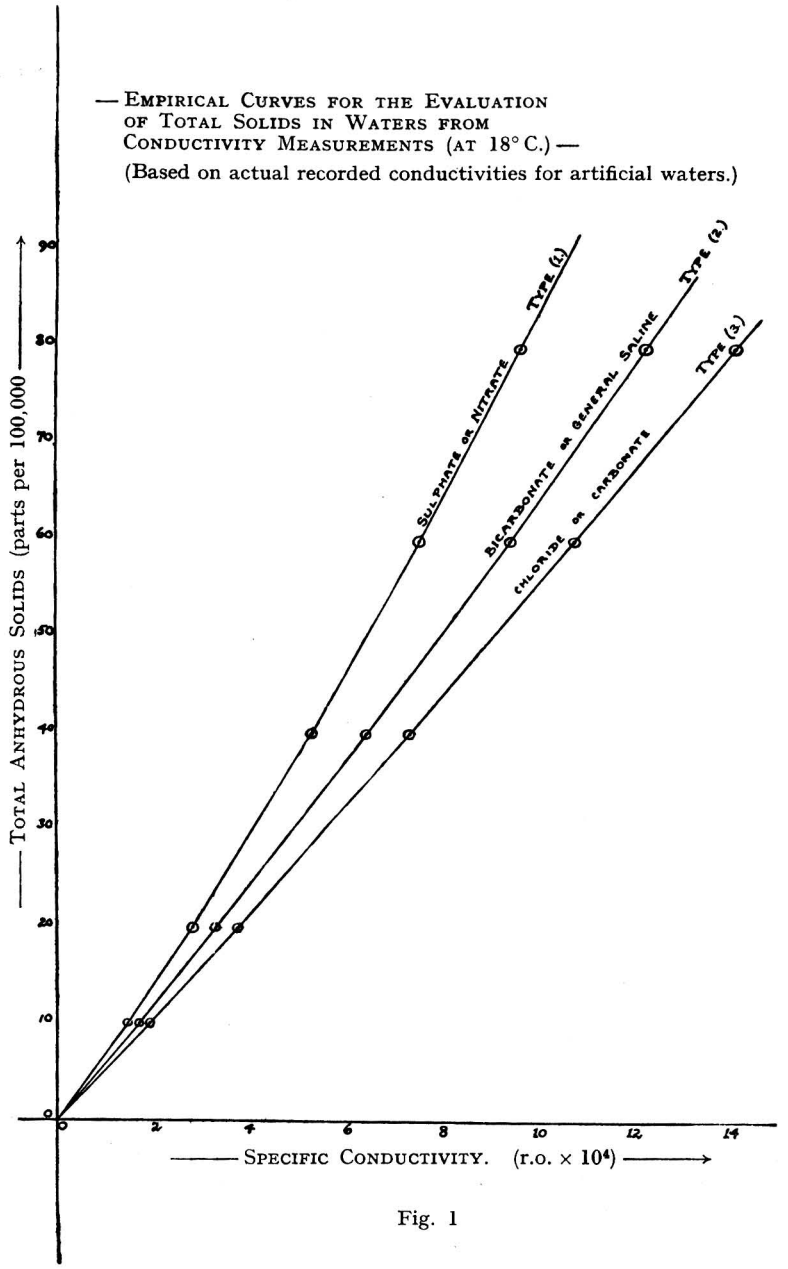

Fig. 1

This was a mixed water. Nitrate (Type 1) and an equal amount of chloride (Type 3) complemented each other and acted as though there were an additional 3·2 parts per 100,000 of bicarbonate. There were, therefore, 28·4 parts of

"bicarbonate," obtained by adding 1·6 (nitrate) and 1·6 (chloride) to the 25·2 parts of carbonate obtained by titration, together with 11·1 parts of chloride (obtained by subtracting 1·6 complement for nitrate from 12·7 of chloride found by titration). This means there were, roughly, 70 per cent.

$$\frac{28{\cdot}4}{28{\cdot}4 + 11{\cdot}1} \text{ of Type 2 and 30 per cent. } \frac{11{\cdot}1}{28{\cdot}4 + 11{\cdot}1}$$

of Type 3 waters. The specific conductivity corresponds with a value of 40·5 parts per 100,000 of total solids on Type 2 curve, or with 35·5 parts on Type 3 curve. Hence, the final evaluation of the total salines was

$$\frac{70}{100} \times 40{\cdot}5 + \frac{30}{100} \times 35{\cdot}5 = 39{\cdot}0 \text{ parts per } 100{,}000.$$

(The actual known saline-content was 39·4 parts per 100,000.)

NOTE.—With calcium as the dominant metal, the total solids tend to be slightly higher, and with magnesium they are usually slightly lower for the same specific conductivity.

ACCURACY OF THE CONDUCTIVITY METHOD.—The following table selected from a long series of actual experimental results will give an idea of the accuracy that may be expected from the conductivity method. All figures represent parts per 100,000.

Water	Total solids by evaporation	Ignited recarbonated solids	Sulphated ignited total solids	Calculated sulphated solids	Total solids from sp. conductivity
1	80	72·8	90·7	90·9	79
2	25	23·8	30·0	30·0	25
3*	6·9 (without SiO_2)	7·2	—	8·2 (without SiO_2)	7
4†	109·2	—	109	108·6	110
5	240	240·4	—	284·4	244 (on 1 in 4 dilution)
6‡	20·5	18·7	—	25·8	16
7§	1092	986	—	1341	1100 (on 1 in 20 dilution)

* Contained about 0·5 parts of SiO_2 per 100,000.
† Highly nitrated water; decomposition on ignition; 6 parts of SiO_2 per 100,000.
‡ Contained 5·0 parts of SiO_2 per 100,000.
§ Very saline borehole water; 4·7 parts of SiO_2 per 100,000.

From the analysis of borehole and hot-spring waters it would appear that silica in such waters is usually in the molecular form and practically non-conducting. When silica is likely to be present a rapid colorimetric estimation should always be made and the value for silica so obtained added to the total solids evaluated by specific conductivity.

SPECIAL APPLICATIONS OF THE METHOD.—Specific conductivity measurements are particularly useful in testing samples of distilled water (*e.g.* for batteries), in the regular analytical control of town water supply systems (when seasonal variations in the saline content of the water or changes due to clarification and purification treatment may be easily followed), in the analysis of waters for use in boilers, and so forth.

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PART II

THE DETERMINATION OF HARDNESS

Numerous methods have been proposed for the determination of the hardness of water. Of these, the four best known are perhaps those of Clark, Hehner, Wartha-Pfeifer and Blacher.

Hehner's titration method at best can give but a very rough approximation to the true result. The old standard procedure of Clark is tedious and often inaccurate, as the factors for calcium hardness and magnesium hardness are different. Contrary to the statement in Thorpe[1] and the investigation of Leick,[2] no difficulty was experienced with the determination of magnesium solutions by Clark's method. The approximate ratio of calcium to magnesium in a water will be fairly well indicated when using the process by the appearance of a false foam or scum at the "calcium end-point." It was found that with solutions of average hardness calcium salts required from 10 to 20 per cent. less soap solution than magnesium salts of a corresponding hardness.

Adsorption errors may be very great in the soap method, and it was found (in agreement with Leick) that sodium chloride and sulphate lowered the apparent hardness, as found by this titration.

The Wartha-Pfeifer method makes use of the insolubility of calcium carbonate and magnesium hydroxide, but with soft waters a relatively larger error is introduced because of the slight solubilities of these two substances. Sodium chloride and sulphate do not interfere, but the procedure is long and rather tedious, and with soft waters results are only approximate.

Blacher's method, using a standard solution (usually $N/20$) of pure potassium palmitate in glycerin and alcohol, has found considerable favour, and his titration method has other applications. Most authorities agree that the method is inaccurate with small degrees of hardness, and Leick[2] observed errors of 150 to 300 per cent. when the hardness fell below 1°. As the usually accepted technique for the Blacher titration was found to be rather unsatisfactory, an attempt was made to evolve a more scientific procedure, with refinements that would eliminate great errors even with very soft water.

PREPARATION OF THE POTASSIUM PALMITATE SOLUTION.—The potassium palmitate solution used was made as follows:—Pure palmitic acid (26·5 g.) was dissolved in 800 ml. of warm 90 per cent. alcohol, and 500 g. of glycerin and 0·2 g. of solid phenolphthalein were added. Approximately 100 ml. of a 4 per cent. solution of potassium hydroxide in 20 per cent. alcohol were added, and a further quantity was run in gradually from a burette until there was a very faint but definite pink colour. This neutralised solution was finally made up to 2 litres with neutral 90 per cent. alcohol.

Blacher recommends a clear solution of lime-water, neutralised to phenolphthalein with $N/10$ hydrochloric acid, for standardising the palmitate, but it was found more satisfactory to use accurately standardised neutral solutions of calcium chloride and magnesium sulphate.

BLACHER'S PROCEDURE FOR ESTIMATING HARDNESS.—One hundred ml. of the water are neutralised to methyl orange with $N/10$ hydrochloric acid, carbon dioxide is removed by aeration, and 0·5 ml. of a 1 per cent. solution of phenolphthalein in neutral alcohol is added. Sodium hydroxide solution ($N/10$) is added drop by drop until there is a faint permanent pink colour (usually one drop), then one drop of $N/10$ hydrochloric acid is added to decolorise the liquid, and finally one drop more. Palmitate is run in "to a faint but definite pink." A blank of 0·3 ml. is usually subtracted, and the number of ml. remaining is multiplied by the standardisation factor previously determined. The titration is supposed to be carried out in a slightly acid medium, so that a pink colour due to hydrolysis of magnesium palmitate will not occur before the end-point.

It was found, however, that magnesium salts *did* give a faint pink long before the end-point, and this gradual colour-deepening made accurate work most difficult, and obscured the true end-point of the reaction.

PROCEDURE RECOMMENDED.—Owing to several objections to the method recommended by Blacher, experiments were made, and the following procedure is proposed:

A blank test on 100 ml. of distilled water should always be made. Except for neutralisation and aeration, which are unnecessary, this blank solution is treated in exactly the same way as the test solution (*supra*). Potassium palmitate is then run in until a strong red colour (0·6 to 0·8 ml.) results, so that "faint pinks" from magnesium salts will not interfere, and the test solution is titrated to this shade, the "blank" being eventually subtracted from the test reading. Two similar 350-ml. Erlenmeyer flasks should be used.

There is always a very slight difference in shade between the "blank" and test solutions, but this is not noticeable if the two flasks are rested on a white background at some distance from the eye and tilted slightly forward, so that comparison and colour matching are done at an angle, by reflected, not transmitted, light.

It is not possible to match colours accurately unless the "blank" is given approximately the same turbidity as the test solution. Kaolin, washed free from acid, was found most suitable for this purpose. A pinch is added from the end of a small spatula. The addition of a little kaolin also to the test solution facilitates matching.

As the addition of 0·05 ml. of palmitate solution at the end-point produces a noticeable difference in the depth of the phenolphthalein colour, a high degree of accuracy is attainable by this procedure.

STANDARDISATION OF THE POTASSIUM PALMITATE SOLUTION.—The solution was standardised, as described, against accurately prepared solutions of calcium chloride, barium chloride, and magnesium sulphate.

Three series of "waters" were prepared, which in each series covered a hardness range from 0 to about 25 degrees, the hardness being due to calcium chloride, barium chloride and magnesium sulphate, respectively. All were treated in exactly the same way. None was aerated, as free carbon dioxide was absent. From the volume of palmitate used with each solution of known hardness the corresponding factor to convert the results into degrees of hardness was found.

The following results were obtained:

CALCIUM CHLORIDE SOLUTION

Hardness	Palmitate used (after deduction of blank) ml.	Factor for hardness
0·5	0·15	3·3
1	0·34	2·9
2	0·67	3·0
5	2·00	2·50
10	4·30	2·33
15	6·73	2·23
20	9·15	2·19
25	11·54	2·17

MAGNESIUM SULPHATE SOLUTION

0·83	0·29	2·9
1·664	0·60	2·8
4·16	1·60	2·6
8·32	3·47	2·40
12·48	5·42	2·30
16·64	7·41	2·24
20·80	9·43	2·21

BARIUM CHLORIDE SOLUTION

2·5	0·96	2·6
5·0	2·05	2·44
12·5	5·62	2·22
25·0	11·73	2·14

As calcium and magnesium are the metals that give rise to hardness in natural waters, barium chloride was disregarded in calculating the average factors for converting ml. of palmitate solution into hardness.

Palmitate used ml.	Factor	Palmitate used ml.	Factor
0·05	3·3	4	2·35
0·1	3·2	5	2·30
0·2	3·0	6	2·27
0·5	2·82	7	2·24
1·0	2·67	8	2·22
1·5	2·58	9	2·20
2·0	2·52	10	2·20
2·5	2·47	Above 10	2·19
3·0	2·42		

The standard solution of potassium palmitate will keep unchanged for years, but each fresh lot must be standardised as described above, and a "standardisation curve" may be drawn. It is suggested that the cause of the decreasing factor with increasing hardness is the increase in the adsorption of potassium palmitate owing to the increasing amount of finely divided precipitate of the palmitates of calcium, magnesium, and so on.

Note.—With very soft waters the degree of acidity just prior to titration with palmitate must be exactly the same as that of the "blank" if large errors are to be avoided. After addition of phenolphthalein and $N/10$ sodium hydroxide solution to give a faint pink colour, the shade is matched in the "blank" and test solution by adding very dilute (say $N/100$) sodium hydroxide solution to one or the other and comparing the colours. Then with the same small, graduated pipette (held vertically), two drops (0·10 ml.) of $N/10$ hydrochloric acid are added to each, and the solutions are titrated in the ordinary way. This small refinement

of technique gives satisfactory results even with solutions of less than 1 degree of hardness.

The following results are typical of those obtained:

Actual hardness	Palmitate solution added ml.	Factor	Hardness found
0·5 ($CaCo_3$)	0·21	3·0	0·6
0·2 ,,	0·05	3·3	0·17
0·42 ($MgSO_4$)	0·11	3·2	0·35

The maximum error here is 20 per cent., whereas in this range the usual method gives errors of anything from 100 to 300 per cent.[2]

EFFECT OF SODIUM CHLORIDE AND SULPHATE.—It is only with highly mineralised waters that the salt-content will cause errors, and for such waters the necessary corrections can be made by titrating a solution of known hardness containing the same amount of salines as the water under investigation. Sodium sulphate and sodium chloride are highly ionised in solution and they affect the nature of the palmitate precipitate, which also encloses unchanged potassium palmitate solution, giving rise to the high results obtained. Weissenberger[3] attempted to repress the hydrolysis of magnesium palmitate by adding NaCl, but he found that the results were inaccurate.

INFLUENCE OF IRON, ALUMINIUM AND ZINC.—These three metals are occasionally present in small amounts in waters, and if actually in solution they all contribute to the hardness.

In the palmitate method all three will be precipitated if the solution is made neutral to phenolphthalein, so that the titration must be carried out in a more acid medium, and the "blank" must be given an acidity corresponding with that of the test solution. Under these conditions the iron and zinc titrations were found satisfactory, but solutions of aluminium gave consistently high results, probably owing to the formation of some complex with the potassium palmitate.

CONCLUSIONS.—A comparative study of the three most favoured hardness methods for determining hardness has shown that, if certain refinements of technique are adopted, the palmitate method is the simplest and most reliable of all. It has been shown that when a "blank" is used for comparison (so that there is no need to titrate to any definite shade of colour), and when the correct standardisation factor is employed, the hardness of even soft waters may be accurately determined.

Clark's method, besides being tedious, is somewhat unreliable, and Wartha–Pfeiffer's method is useful only with fairly hard waters, and even then gives slightly low results.

When the method of procedure suggested above is employed the accuracy of the palmitate titration is such that, with all ordinary waters containing no interfering substances, magnesium may be satisfactorily calculated from the difference between total hardness and the lime (determined by volumetric permanganate titration of the precipitated oxalate); this is shown by the following results obtained with three natural waters.

	Water (1)	(2)	(3)
Total hardness (palmitate solution)	72·5	11·8	16·5
Calcium (expressed as $CaCO_3$) (vol. method)	46·5	3·2	9·4
Hardness due to Mg (by diff.)	26·0	8·6	7·1
Actual $Mg_2P_2O_7$ (weighed)	28·9	9·4	7·8
Hardness due to Mg (calculated from $Mg_2P_2O_7$ above)	26·0	8·5	7·0

Iron, aluminium and zinc will not interfere if the titration is performed in the usual manner.

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PART III

COMPARISON OF DISTILLATION AND DIRECT METHODS OF ESTIMATING FREE AND ALBUMINOID AMMONIA IN WATERS

Distillation after addition of sodium carbonate and then further distillation after addition of "alkaline permanganate" solution has long been the accepted standard English method for determining free and albuminoid ammonia in waters.

But in Germany and elsewhere on the Continent the "direct" method of Winkler[1] has found great favour. The free ammonia is estimated by direct nesslerisation and the total ammonia (free+albuminoid) by nesslerisation after the water has been treated with potassium persulphate to convert nitrogenous organic matter into ammonia.

With a view to ascertaining if the tedious distillation method could, with advantage, be replaced by the rapid direct method, a comparison of the two processes was made on a large number of natural waters, and for solutions and suspensions of a number of organic substances.

For the distillation process 500 ml. were used and the free and albuminoid ammonia in the distillates were estimated by nesslerisation with the use of a Hellige comparator with standard ammonia discs. The comparison troughs for use with ordinary waters are 250 mm. in length, so that as little as 0·001 parts of ammonia per 100,000 can be accurately evaluated.

DIRECT METHOD.—One hundred ml. of the water is made slightly acid with (usually) one drop of concentrated sulphuric acid in a 250-ml. boiling flask. Then approximately 0·05 g. of finely powdered ammonia-free potassium persulphate is added, the neck of the flask is covered with a small beaker, and the flask is suspended in boiling water for 15 to 20 minutes. The treated water is then cooled to room temperature and nesslerised direct for total ammonia. The free ammonia is estimated on another 100 ml. portion without the persulphate treatment.

As hard waters yield a precipitate with Nessler's reagent, calcium and magnesium are held in solution in this direct method by the addition of 2·5 ml. (very occasionally 5 ml.) of a 50 per cent. w/v solution of Rochelle salt to each 100 ml. of water to be nesslerised; 2·5 ml. of Nessler's reagent is then added drop by drop. In the distillation method 2 ml. of Nessler's reagent is used for each 100 ml. of distillate nesslerised.

STANDARDISATION OF THE HELLIGE AMMONIA DISCS.—The three discs were standardised for the 250-mm. troughs by means of accurately made solutions of ammonium chloride and ammonium sulphate in ammonia-free distilled water. Curves were drawn and a table was prepared giving the amount of ammonia (in mg.) in 100 ml. of solution nesslerised (*i.e.* parts of ammonia per 100,000) for every reading of the discs.

It was found that one drop of conc. sulphuric acid+2·5 ml. of Rochelle salt solution+2·5 ml. of Nessler's reagent added to a standard ammonia solution gave the same reading on the disc as was given by the standard ammonia solution+2 ml. of Nessler's reagent only, so that the tables prepared were equally suitable for evaluation of the free and albuminoid ammonia by the distillation and direct methods.

THE PERCENTAGE OF TOTAL ORGANIC NITROGEN IN VARIOUS FORMS WHICH IS CONVERTIBLE INTO AMMONIA.—Solutions of known strength of a number of nitrogenous organic substances, most of which are commonly found in traces in waters, were prepared, and the free and albuminoid ammonias estimated by both processes.

With the solutions of all the substances listed the "theoretical ammonia," where given, has been calculated from the total nitrogen in solution (estimated on the original substance by a micro-Kjeldahl method).[3]

The results given in the following table are expressed in parts of ammonia per 100,000 of solution.

Solution	"Theoretical ammonia"		Distillation method		Direct method	
	Free	Alb.	Free	Alb.	Free	Alb.
Urea	0	0·0500	0·005	0·002	0	0·0200
Uric acid	0	0·0500	0·0035	0·003	0	0·013
Ox-blood serum ..	0·0645 total		0·003	0·031	0	0·030
,, ,, ..	0·1290 ,,		0·009	0·062	0	0·061
Milk serum*	0·0645 ,,		0·007?	0·022	0·001?	0·0335?
,, ,, *	0·1290 ,,		0·018?	0·042	0·003?	0·070?
Urine (A)†	—	—	0·015	0·012	0·017	0·065
,, (B)†	—	—	0·017	0·027	0·025	0·064
Faeces (A) (suspension)	—	—	0·089	0·049	0·097	0·050
,, ,, (suspension 1 in 5 diln.)	—	—	0·020	0·015	0·019	0·014
,, (B) (suspension)	—	—	0·006	0·032	0·006	0·022
,, ,, (filtered suspension)	—	—	0·008	0·013	0·003	0·011
Sewage fluid (A) ..	—	—	0·449	0·160	0·470	—
,, ,, (B) ..	—	—	0·370	0·089	0·390	0·070
,, effluent (C) ..	—	—	0·232	0·028	0·225	0·035
Casein‡	0	0·100	0·001	0·049	0·001	0·049
Indole	0	0·100	yellow, milky turb.	0·0250	yellow, milky turb.	0·0685 (tot.)
Skatole	0	0·100	0·001	0·008	0·002	0·066
Indole (1 in 2 diln.) ..	0	0·050	yellow, milky	0·013	yellow, milky	0·0345 (tot.)
Skatole (1 in 2 diln.) ..	0	0·050	0·001	0·004	—	0·033

* The milk serum gave a curious yellow colour, and matching was difficult.

† The large difference between the albuminoid ammonia obtained by distillation and by the direct method is explained by the fact that urine contains urea, which yields considerable nitrogen on treatment with potassium persulphate, but very little with alkaline permanganate.

‡ The albuminoid ammonia distilled over very slowly with casein (standard method). Almost 1 litre of distillate had to be collected before a colour was no longer given with Nessler's reagent.

It will be noted that the results are strongly opposed to the suggestion of Purvis and Hodgson,[4] that with substances such as indole and skatole the standard distillation method results in a quantitative conversion of the organically combined nitrogen into an ammoniacal form.

It will be further observed that where considerable differences exist between the values obtained for albuminoid ammonia by the distillation and direct methods,

those from the latter tend to be distinctly the greater, and do, in fact, give a more rational indication of the extent of "pollution" by the foreign substances which were introduced.

The following solutions gave reasonably good agreement between the two methods:—Ox-blood serum, faeces, sewage fluids, casein. The following solutions showed no agreement:—Urea, uric acid, urine, indole, skatole.

TURBID WATERS.—When the free and albuminoid ammonia are being estimated in a turbid water by the direct method, a blank of the actual water under examination must be used in the left-hand trough of the Hellige comparator. The plain water may be used as a "blank" for the free ammonia, but for the total ammonia the water should be boiled with sulphuric acid and potassium persulphate, as in the test, before being used as a "blank," because often this boiling either precipitates all turbidity or alters its character considerably.

A drop of concentrated sulphuric acid should always be added in the direct method of estimating free ammonia, as is done for the total ammonia.

One of the chief advantages of the Hellige comparator is that it enables compensation to be readily made for turbidity, which in the ordinary way would preclude all possibility of direct colorimetric assessment.

COMPARISON OF THE METHODS WITH NATURAL WATERS.—In order to learn what degree of agreement there might be between the amounts of free and albuminoid ammonias as estimated by the "standard" method and the corresponding values obtained by the "direct" method in general water analysis, a large number of samples of varying origin and nature were analysed.

Typical results are presented in the following table:

	Water	Free ammonia		Albuminoid ammonia	
		Distillation	Direct	Distillation	Direct
(1)	Town supply	0·002	0·002	0·0125	0·0125
(2)	,, ,, ...	0·002	0·002	0·016	0·013
(3)	Swimming bath	0·008	—	0·071	0·106
(4)	Town supply	0·002	—	0·013	0·015
(5)	Swimming bath	0·0075	0·0075	0·014	0·028
(6)	,, ,, ...	0·061	0·057	0·041	0·092
(7)	Borehole	0·0075	0·011	0·016	0·017
(8)	Dam water	0·009	0·009	0·034	0·023
(9)	Swimming bath	0·036	0·039	0·034	0·065
(10)	Crude sewage (1 in 25 diln.) ..	0·331	0·332	0·058	0·058
(11)	Sewage after sedimentation ..	0·292	0·294	0·035	0·032
(12)	River water	0·004	0·005	0·0155	0·0165
(13)	Swimming bath*	0·070	0·078	0·096	0·1125
(14)	Dam water	0·046	—	0·032	0·034
(15)	Country stream	0·002	0·003	0·046	0·047
(16)	Swimming bath	0·008	0·014	0·067	0·100
(17)	River water	0·0025	—	0·017	0·015
(18)	Swimming bath	0·013	0·013	0·022	0·044

NOTE.—With some waters (direct method) the maximum possible colour after nesslerisation took considerably longer than ten minutes (half-an-hour, or even more) to develop. With others the "standard" procedure yielded albuminoid ammonia very slowly; for example, in one sample (Swimming bath*) ammonia was still coming off after 1 litre of distillate had been collected.

A study and comparison of the results obtained will show that there is generally quite reasonable agreement between the two methods—except with the swimming bath waters.

A possible explanation of the difference here is that bath waters may contain traces of urea, uric acid, etc., which, as has been shown, are not readily acted on by alkaline permanganate, but are broken down by potassium persulphate.

With none of the other waters listed would a different interpretation be put on the result of analysis by using the rapid direct method for free and albuminoid ammonia in place of the standard method, so that the persulphate method can be recommended for all natural waters whenever the physical condition of the water itself will allow of its employment.

It has been shown by continued distillation of a swimming bath water that albuminoid ammonia may continue to come over in small quantities even after as many as five lots of 200 ml. have been distilled, and the sum of the values for the albuminoid ammonia then approaches the total found by the direct method. This raises the question if it would not be advisable always to employ the direct method and so get a rapid and pronounced indication of urinary and similar contamination.

Neither of the methods investigated gives a quantitative measure of the organic nitrogen present under all conditions, but in this respect treatment with potassium persulphate is better than with alkaline permanganate, and usually shows 50 per cent. or more of the total nitrogen.

Some of the solutions were boiled for 30 minutes or longer, and with twice the quantity of potassium persulphate, but this made no difference to the result.

CONCLUSIONS.—The rapid direct method for the estimation of ammonia has been compared critically with the generally adopted standard method. The limitations of each, when employed as a measure of total organic nitrogen, have been demonstrated, and it has been shown that for natural waters, whenever the physical condition of the water itself makes it possible, the direct method may be employed in place of the standard method. By the use of the Hellige comparator the turbidity found in most natural waters may be compensated for, the water itself being made the "blank." The direct method effects considerable saving in reagents, etc., and requires only about half-an-hour for an estimation.

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I wish to acknowledge the assistance given to me in these investigations by Mr. A. W. Facer, Government Analyst of Southern Rhodesia.

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The Complete Analysis of Chromite

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According to Dittler,[1] Treadwell and Hall,[2] and Hillebrand and Lundell,[3] when the complete analysis of chromite is undertaken the mineral must be fused with sodium carbonate or sodium carbonate plus potassium nitrate.[3] In my experience, however, these methods are not as straightforward as they appear. In the first place the mineral must be extremely finely powdered. Secondly, the chromite must be heated with the flux in a platinum crucible for some hours, and it usually happens that the first fusion does not decompose the mineral, so that a second and even a third fusion are necessary, with the result that the process becomes very tedious. Lastly, the platinum crucible suffers considerably, especially when sodium carbonate is used together with potassium nitrate, and the platinum must be removed from the solution with hydrogen sulphide before proceeding with the analysis.

Fusion with Potassium Pyrosulphate.—It was found that potassium pyrosulphate ($K_2S_2O_7$) readily decomposed chromite, and its use gave excellent results. On decomposition the metals are converted into the sulphates, which are dissolved in boiling dilute hydrochloric acid. The insoluble residue, which consists of only part of the silicates present in the sample, is fused with a little sodium carbonate and dissolved in dilute acid. In this way the whole of the sample is easily brought into solution. It is not necessary that the mineral should be powdered very finely, because material passing through a 100-mesh sieve is decomposed within a very short time. The fusion can be done in a platinum or a silica crucible, but I prefer to use a silica crucible because the molten mass does not tend to froth, as when platinum is used.

Procedure.—Fuse 0·5 g. of the powdered mineral with 15 g. of potassium pyrosulphate in a 50-ml. silica crucible, preferably first fusing the pyrosulphate in the crucible until copious fumes of sulphur trioxide are given off, then cooling and adding the sample. The fusion is best accomplished over a Bunsen burner, the crucible being rotated from time to time and the flame kept small at first and gradually increased to full heat. The decomposition should be complete after 30 minutes. It is not advisable to complete the fusion over a Méker burner, because when the temperature is raised too high, it is very difficult to dissolve the resulting sulphates.

After decomposition is complete, cool the melt, add 5 ml. of dilute hydrochloric acid and heat gently to loosen the cake. Transfer the cake with hot water to a beaker which contains 20 ml. of conc. hydrochloric acid, heat until the melt has disintegrated, add 200 ml. of water, and boil until solution is complete. Filter and wash with hot water. Fuse the residue with a little sodium carbonate in a platinum crucible, take up the carbonate melt with water and hydrochloric acid and add it to the main solution.

Evaporate the solution to dryness in a platinum dish on a water-bath, stirring it during the latter part of the evaporation. (Difficulty in evaporation to dryness may arise when too much potassium pyrosulphate is used for the fusion. In

such event the basin is removed from the water-bath when the mass becomes syrupy, cooled, and the residue is broken up; the evaporation is then completed.) Finally, dry in an air-oven at 105° C. for two hours. After cooling, add 10 ml. of conc. hydrochloric acid and 75 ml. of hot water, heat on the water-bath, and stir until all the salts have dissolved. Filter and wash with hot dilute hydrofluoric acid. All the silica remains behind on the filter; it is determined in the usual way. Fuse the small amount of residue, left after treatment with hydrofluoric acid, with a little potassium pyrosulphate and add it to the filtrate, which now contains the chromium, iron, aluminium, magnesium, etc. Make up this solution to 200 ml., and use aliquot portions (50 ml.) for the determination of the various constituents as follows:

In one portion the following are determined:—the combined chromic, ferric and aluminium oxides; calcium oxide; magnesium oxide. In the second portion iron (calculated as ferrous oxide), and, in the third, chromium (calculated as chromic oxide) is determined. Alumina is found by subtracting the sum of the ferric and chromic oxides from the combined oxides determined in the first portion after recalculating the ferrous oxide to ferric oxide.

The analyst can, of course, determine the various constituents by separate fusions, instead of using aliquot portions from one fusion.

(1) (*a*) Dilute to 200 ml., heat to boiling, and add ammonia in slight excess. Boil for a minute. Filter while hot and wash with hot water containing a little ammonium chloride. Dissolve the precipitate in hot dilute hydrochloric acid and repeat the precipitation, etc. Add a little filter-paper pulp before the second filtration, and stir well. Ignite the precipitate and weigh as the combined oxides, *i.e.* $Cr_2O_3 + Fe_2O_3 + Al_2O_3 + TiO_2$.

(*b*) Concentrate the combined filtrates by evaporation and destroy the ammonium salts as described by Hillebrand and Lundell[3] (p. 119). Dissolve in 50 ml. of hot water and 1 ml. of hydrochloric acid. Add 1 ml. of acetic acid, 5 ml. of saturated oxalic acid solution and 10 drops of 1 per cent. bromocresol green solution. Heat to boiling and add ammonia until the solution assumes a blue colour. Leave overnight, filter, and wash with dilute ammonium acetate solution. Dissolve the precipitate of calcium oxalate in dilute sulphuric acid, and titrate with $N/50$ potassium permanganate solution.

(*c*) To the filtrate add excess of ammonium phosphate and 10 per cent. (by vol.) ammonia solution, and stir well. Leave overnight. Filter and wash with dilute ammonia. Dissolve the precipitate in hot dilute hydrochloric acid and repeat the precipitation. Leave overnight, filter, ignite the precipitate and weigh as $Mg_2P_2O_7$.

(2) *Ferrous Oxide.*—Dilute the second aliquot portion to 200 ml., heat to boiling and add ammonia solution in slight excess. Boil for a minute. Filter and wash with hot dilute ammonium chloride solution. Dissolve the precipitate in dilute hydrochloric acid. (This step is necessary, to convert the iron into chloride, and to remove all traces of platinum, which interferes in the reduction.)

Evaporate the solution, reduce with stannous chloride, etc., and titrate with $N/10$ potassium permanganate solution, as described by Hillebrand and Lundell[3] (p. 305).

(3) *Chromic Oxide.*—For this determination it is essential to remove all the chloride. Dilute the solution to 300 ml., and precipitate the hydroxides as described above. Filter and wash thoroughly with dilute ammonium sulphate solution. (One precipitation, when properly done, is usually sufficient for the removal of the chlorides.) Dissolve the precipitate in dilute sulphuric acid, oxidise with potassium or ammonium persulphate and silver nitrate to dichromate; add an excess of ferrous ammonium sulphate and titrate back with permanganate. (See Hillebrand and Lundell,[3] p. 410.)

Titanium may be determined colorimetrically after separation from the green chromium salts as follows:—Oxidise the chromium to chromate in a solution which must not be too acid, and precipitate the iron, titanium, etc., with ammonia. Wash the precipitate well, dissolve it in sulphuric acid, and determine titanium by the well-known hydrogen peroxide method.

Manganese may also be determined colorimetrically by the periodate method after removal of the chromium. For this purpose oxidise the chromium as described under titanium, and precipitate the manganese, iron, etc., with bromine water and ammonia. Dissolve in sulphuric acid, and proceed as usual.

THE BEHAVIOUR OF CERTAIN SILICATES IN THE PYROSULPHATE FUSION.—Schoeller[4,5] states, in connection with the analysis of tantalite, that silica is not converted into a soluble silicate when an acid flux is used for the decomposition of the mineral. Apparently he has considered only the case when quartz alone is present in the sample. I have therefore investigated the effect of the pyrosulphate fusion on the silicates present in the samples of chromite analysed by me.

The silicates in the chromite samples were chiefly pyroxenes and a hydrated silicate of iron and magnesium known as bowlingite.

The silica-contents were determined both in the insoluble residue and in the solution, and the total silica on a separate sample by the method described above. The following results were obtained:

No.	A. Per Cent.	B. Per Cent.	C Per Cent.	D. Per Cent.
1 (*a*)	0·24	0·48	0·72	0·66
1 (*b*)	0·22	0·48	0·70	—
2 (*a*)	0·38	0·62	1·00	—
2 (*b*)	0·38	0·60	0·98	1·06
3	0·36	0·60	0·96	1·00
4	0·20	0·44	0·64	0·58
5	0·70	0·78	1·48	1·58
6	3·66	1·38	5·04	5·10
7 (*a*)	3·64	0·96	4·60	—
7 (*b*)	3·74	0·92	4·66	—

A, silica in insoluble residue; B, silica in solution; C, sum of A + B; D, total silica in the sample.

From these figures it is evident that part of the silicates in the sample is decomposed by the fusion, and that the liberated silica is not rendered insoluble. Microscopic examination shows that the insoluble residue consists largely of pyroxenes, with only a small percentage of the hydrated mineral. The latter becomes porous and shows other signs of the action of the flux, whilst the pyroxenes

apparently remain absolutely intact, even their refractive index not changing appreciably. It therefore appears that the pyroxenes are not acted on by the pyrosulphate, but only the hydrated mineral.

The results given above show that it is not sufficient to determine the silica solely in the insoluble residue, after fusion with pyrosulphate (as is the practice of some analysts), but that that in solution must also be determined, unless, of course, it has been ascertained beforehand that the silicates present are not attacked by the pyrosulphate.

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GOVERNMENT CHEMICAL LABORATORIES
PRETORIA

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.

LOSSES OF IODIDE FROM IODISED SALT

IODISED salt is widely used in New Zealand, and the Regulations under the Sale of Food and Drugs Act require it to contain not less than one nor more than two parts of iodides (calculated as potassium iodide) in 250,000 of salt. It is sold in 1½-pound cardboard cartons (one maker encloses the carton in a tin) and in 5-pound pound cotton bags, and usually contains approximately 1 per cent. of magnesium carbonate.

It has long been recognised that losses of iodide occur on storage, but there was no reliable information available as to the extent or causes of the losses. As the matter is of importance, it was decided to make a thorough investigation to ascertain if under ordinary conditions of storage the losses are serious. The amounts of iodide in 22 samples of salt in cartons, comprising four different brands, and in 24 samples of salt in bags, also comprising four different brands, were first determined. One brand of bagged salt did not contain magnesium carbonate. It was found that with the salt in cartons the two most widely sold brands contained on the average 0·75 part of iodide in 250,000; the other two contained 1·5 parts. Of the salt in bags, the most widely sold brand contained 1·5 part of iodide and the others 0·8 part. These results were somewhat surprising, as it was expected that losses would be greater from the bags, and that therefore they would have the lower iodide-content, it being assumed that they were approximately of the same iodide-content when packed. All the samples were quite dry and free running.

A large number of cartons and bags were then filled with salt, the proportions of iodide in which had been carefully determined, and were stored for six months, this being considered the maximum period during which the salt would normally be held in warehouse and shop. The proportions of iodide (calculated as potassium

iodide), in parts per 250,000, found in six typical samples each of salt in cartons and in bags were as follows:*

	Iodide as potassium iodide, parts per 250,000			
	Salt in cartons		Salt in bags	
	Aug. 1935	Feb. 1936	Aug. 1935	Feb. 1936
A ..	0·50	0·24	0·77	0·73
B ..	0·60	0·43	0·83	0·70
C ..	0·63	0·41	1·40	1·13
D ..	0·97	0·76	1·87	1·67
E ..	0·73	0·41	2·00	1·57
F ..	1·50	1·35	2·20	1·83

The samples all remained dry and free-running.

It will be seen that the loss from the salt in cartons is proportionately greater than from that in the bags. With the exception of A and B of the samples in bags, all the salt contained magnesium carbonate, but the proportionate loss was no greater in these two samples.

The distribution of the iodide at the end of the six months was significant. The top, middle and bottom portions of all the samples were separately analysed, and the following table shows six typical results:

	Iodide as potassium iodide, parts per 250,000		
	After six months		
Original	Top	Middle	Bottom
2·0	2·0	1·9	1·1
2·0	1·8	1·8	1·1
1·6	1·4	1·3	0·7
0·9	0·9	1·0	0·6
1·6	1·3	0·9	0·8
0·8	0·8	0·8	0·6

It will be seen that in every instance the greater part of the loss is from the bottom of the bag, and this was also found to apply to several series of samples stored in cartons.

One series of samples was stored under somewhat damp conditions. Although not wet, these samples at the end of the six months were all caked, but this did not have any appreciable effect on the losses or the distribution of the iodide.

It was then decided to ascertain if there was really any loss to the atmosphere, as is sometimes assumed. A number of samples were prepared in the two following ways:

(*a*) The salt (100 g.) was spread very thinly over the bottom of a flat porcelain basin, thus giving a large exposed surface.

(*b*) The same quantity of salt was similarly spread over a filter-paper placed flat in the bottom of a dish, as described in (*a*).

Both series of samples were exposed to the atmosphere for six months.

It was found that the salt in contact with porcelain did not lose iodide, but that there was considerable loss from the salt on the filter-paper. The filter-papers, when washed with hot water, yielded sufficient iodide to account fully for the loss. The presence or absence of magnesium carbonate did not influence this result. A

* All the determinations were made by the method of Andrew and Mandeno (ANALYST, 1935, **60**, 801).

number of bags and cartons in which salt had been stored were then examined, and considerable amounts of iodide were recovered by washing with hot water.

It was therefore concluded that under ordinary conditions of storage there is a migration of the iodide to the cardboard or fabric of the container, very probably due to the moisture difference between the material of the container and the salt. This would also explain why the loss is greater at the bottom of the container, whether in carton or bag, as the salt in this position is in contact with the largest proportional area of the absorbing surface. This conclusion was further supported by the fact that samples stored for six months in sealed, and also in loosely covered wide-mouthed glass jars, showed no loss and no redistribution of the iodide.

The practical conclusions of this work are:—Provided that the salt as manufactured contains 1·5 parts of iodides per 250,000, the amount should not fall below 1·0 on storage for six months under ordinary conditions, and would thus comply with the standard when sold. The loss of iodide from iodised salt under ordinary conditions is entirely due to absorption of iodide by the cardboard or fabric of the container. The loss is proportionately greater from 1½-lb. cardboard cartons than from 5-lb. bags. Suitably lacquered tins or other impervious containers would be more suitable for iodised salt than the present cardboard cartons.

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THE FLUOROMETRIC DETERMINATION OF THE ACID AND SAPONIFICATION VALUES OF LAC

FOR a study of the constitution of lac and its components it is essential to determine the acid and saponification values. With dark coloured lacs (with colour index greater than 20), such as Burma Kusum and saponified solutions of the ether-soluble resin, the thymol blue indicators fail to give a sharp end-point, and potentiometric methods must then be used, despite the long time needed for titration and the susceptibility of the electrodes to poisoning.

In the course of experiments, one of us (Murty) found that when lac is titrated with alkali, the fluorescent colour changes from orange-red to green, rather sharply, towards the end-point. This colour change, however, when observed through a spectroscope, is not accompanied by the disappearance of the red, or the appearance of a blue band. Hence, reliance has to be placed only on judgment by the eye. With experience, however, the narrow limits within which the lac solution loses any suggestion of the orange-red fluorescence and assumes a bright parrot-green fluorescence can be easily detected, and an end-point in the titration with alkali can be fixed. This end-point is slightly further towards the acid region than that indicated by thymol blue (as external indicator).

Whilst this method works well with pale coloured lacs, it was found impossible to detect any sharp change in the fluorescence end-point with dark coloured products of the type of Burma and Siam lacs. In these lacs the dye, laccaic acid, which is present in considerably larger proportion than in Indian lacs, may be responsible for masking the end-point. A solution of this dye, while exhibiting a brick-red fluorescence in the acid range, shows no fluorescence and remains dark when rendered alkaline. The resin constituents of lac do not contribute to the fluorescence, for bleached lac does not show any fluorescence, and carbon-decolorised lac only a faint one. Hence, the other colouring matter present in lac, namely, erythrolaccin, and not laccaic acid, is responsible for the green fluorescence in the alkaline region. In fact, it is this substance that serves as a fluorescent indicator during titration in ultra-violet light.

For detecting the end-point with dark coloured, bleached and carbon-decolorised lacs, either α- or β-naphthol can be used as fluorescent indicator. The latter is more suitable, however, as the change to bright violet fluorescence is sharp and takes place at a point between the end-points indicated by thymol blue and the bright parrot-green fluorescence of lac.

When β-naphthol is added to lac solution there is a very narrow region (0·05 to 0·1 ml. of *N*/10 potassium hydroxide solution) of dull ash-grey fluorescence through which the fluorescent colour of lac changes from bright green to bright violet. This dull ash-grey point, which cannot be confused even with the slightest green fluorescence, is taken as the end-point of the titration. For lacs of very dark colour 1 ml. of a 1 per cent. alcoholic solution of β-naphthol will be found to be ample. For light coloured lacs and bleached lacs a much smaller quantity can be used. The titration is done in a dark room in a thin-walled Pyrex or quartz flask, and the reflected fluorescent radiation from the lac solution in the flask is viewed at an acute angle to the incident radiation from a mercury-arc lamp, filtering through Wood's glass. A glass float, rendered fluorescent by filling it with a solution of quinine in sulphuric acid, is used inside the burette to enable readings to be observed as the titration proceeds.

The acid and saponification values of lac, lac constituents, rosin and sandarac obtained by this method agree well with the values obtained by the potentiometric method, using the quinhydrone electrode. With exceptionally dark samples, however, the end-point can be judged only after the manifestation of distinct fluorescence due to β-naphthol. With such samples the results obtained will be 2 to 3 per cent. higher than those obtained by the potentiometric method.

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GINGER WITH LOW WATER-SOLUBLE ASH

In July, 1937, a sample of ground ginger which was submitted under the Food and Drugs (Adulteration) Act, 1928, was found to have a water-soluble ash of 0·7 per cent. Other determinations gave the following results:

	Per Cent.
Total ash	2·3
Ethereal extract, total	5·3
Ethereal extract, volatile	1·1
Aqueous extract	11·3
Alcoholic extract	4·3
Fibre	3·6

The combination of a low water-soluble ash with a reasonably high aqueous extract was so unusual that further enquiries were made. Further samples have since been examined, with the following results:

	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Total ash	2·3	3·1	2·1	2·4
Soluble ash	0·8	1·0	0·3	0·8
Aqueous extract	9·5	11·2	8·7	8·7
Alcoholic extract	5·1	4·6	4·4	4·4
Ethereal extract, total	6·4	5·7	4·7	—
Ethereal extract, volatile	2·2	1·5	1·2	—
Fibre	3·2	3·7	3·6	—

The striking peculiarity of these samples is that the soluble ash is much lower in proportion than the aqueous extract. If the low figure for soluble ash is due to excessive soaking of the whole roots during the washing process, it would appear that this process removes a greater proportion of the soluble mineral matter than of the total soluble matter. Some experiments along these lines were conducted by J. F. Liverseege (*Adulteration and Analysis of Foods and Drugs*, London, J. & A. Churchill, 1932), who found that by soaking a "washed Cochin root ginger" for four days in water the soluble ash was reduced from 2·8 per cent. to 0·9 per cent., whilst the aqueous extract was reduced from 11·2 to 6·4 per cent. In this instance the diminution in soluble ash was 68 per cent., whilst the diminution in aqueous extract was only 43 per cent. These experiments, therefore, suggest, but possibly do not prove, that the deficient character of the present samples is due to excessive washing.

Some experiments on whole Jamaica ginger along similar lines were commenced. A supply of whole Jamaica ginger obtained from a reputable supplier was divided into five portions. One portion was examined in its then condition, whilst each of the others was soaked in about four times its weight of water. The duration of soaking varied with the separate portions from one to seventeen hours.

The results are set out in the following table:

		Ginger soaked, air-dried, and then ground in the laboratory			
		Soaking in hours			
	Original	1	2	5	17
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Total ash	3·4	3·0	2·6	2·3	2·0
Soluble ash ..	2·7	2·3	1·9	1·7	1·5
Aqueous extract ..	15·9	13·3	12·1	11·9	11·4
Alcoholic extract ..	3·7	3·7	3·7	3·8	3·7

From these results it would seem not unlikely that a very low soluble ash, coupled with an average or low aqueous extract, may be due to excessive soaking of the root either by accident or design. Whether such soaking is to the prejudice of the purchaser is perhaps not quite so easy to decide.

The laboratory results for soaking are very similar to those of Liverseege. To obtain figures similar to some of those given above it seems obvious that very prolonged and quite unnecessary soaking will be required. It may be that the more striking results obtained on the samples of unknown origin are due to a low original water-soluble ash or to the use of larger volumes of wash water in the commercial treatment.

I am indebted to my former colleague, Miss C. Mayne, B.Sc., A.I.C., A.M.C.T., for the analytical figures given in this note.

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Department of Scientific and Industrial Research

ANNUAL REPORT FOR THE YEAR 1936–37*

THE Annual Report of the Department of Scientific and Industrial Research opens with an eloquent tribute to the late Lord Rutherford. His last act as Chairman was the shaping of the present Report, which is signed by Lord Riverdale,† the new Chairman of the Council.

During the year consideration has been given to two directions in which it may be possible to strengthen the contacts between industry and the National Physical Laboratory. With improved conditions of industry the basis of the charges made for special investigations and tests has been reviewed, and it is anticipated that some reduction of the charges may be possible in special circumstances. Arrangements have also been made whereby the staff of the Laboratory will be available to visit works to study practical problems of production and to plan investigations and carry them out on suitable terms under the conditions obtaining in manufacturing practice. The new development is one that should prove attractive to industry.

The Report records substantial progress in practically all directions of the Department's work, both in the researches carried out by the research establishments of the Department itself, and in the laboratories of the research associations, formed on a co-operative basis in various industries under the Department's auspices. The associations' financial resources, encouraged by the present conditions of grant, maintain an upward tendency. The aggregate income subscribed by industry has now practically reached £250,000, and the Government's grants amount to nearly half that sum.

Among the investigations to which special attention is directed, are the following:

FOOD INVESTIGATION.—A general survey of the work of the Food Investigation Board for 1936 has been published (*cf.* ANALYST, **1937, 62**, 795). In the present report the Director of the Board describes the progress of various individual investigations.

Ultra-violet Light and the Storage-life of Meat.—Experiments are in progress on the value of ultra-violet light in prolonging the storage-life of meat. The light does not penetrate far into tissues, and in meat the intensity at a depth of 0·2 mm. is only one-thousandth of the intensity at the surface. Intensities of the order of 800 microwatts per sq. cm., applied for 1 to 5 minutes, result in an appreciable reduction in the numbers of bacteria and fungi on the surface of foodstuffs. On the other hand, irradiation for 5 to 10 minutes with this intensity produces oxidative rancidity in thin films of fat. The value of the method therefore depends upon the balancing of these two effects.

Freezing of Bacterial Proteins.—Experimental work on the effects of freezing solutions of native bacterial proteins, extracted from the ground dried cells, has shown that a portion of the protein undergoes rapid denaturation in the frozen state at temperatures near −2° C., but that denaturation is inappreciable at −20°C. A correlation between this effect and the relative rates of death of bacteria at those temperatures in the frozen state has been obtained.

Bacterial Infection of Eggs.—Bacterial counts on a large number of new-laid eggs have shown that they are practically all sterile, and remain so even after storage under controlled conditions for nine months at 0° C. in air and carbon dioxide. The shell, however, carries a large and heterogeneous flora, including organisms capable of producing rotting if they are allowed to penetrate the shell.

* H. M. Stationery Office, Adastral House, Kingsway, London, W.C.2, 1938. Price 3s. net.
† Formerly Sir Arthur Balfour.

A study has been made of some of the factors favouring bacterial penetration of the shell and of the organisms responsible for the various types of rots.

Formation of Nitrosohaemoglobin and the Colour of Bacon.—The colour of bacon is due to nitrosohaemoglobin, formed by the action of nitrite on haemoglobin in the muscle. The mechanism of the reaction has been studied, with the following results. The formation of nitrosohaemoglobin as the sole product is due to the fact that the muscle maintains a reducing condition; in ordinary solution, in the absence of oxygen, equivalent amounts of nitrosohaemoglobin and methaemoglobin are formed unless a reducing agent is present. Over the range *p*H 7·6 to 5·2 the rate of reaction increases with decreasing *p*H. In the presence of oxygen nitrosohaemoglobin is slowly oxidised to methaemoglobin; if, however, a considerable excess of nitrite is present, the final product is a green pigment with a characteristic absorption band in the red.

Composition of Wood-smoke used in Curing Fish.—The chemical composition of wood-smoke used in curing fish is being investigated at the Chemical Research Laboratory. Using the partial combustion of 1-lb. charges of oak chippings in an electrically heated silica tube as a source of smoke, it was established that the whole of the volatile products, after being cooled in an ordinary condenser, could be collected by passing them through activated charcoal in a series of traps cooled in succession to −20° and −80° C. Methods of analysis applicable to the aqueous condensate and to the products recovered from the traps have been developed, and in particular the reduction of chloric acid by formaldehyde in the presence of silver salts has been shown to be a specific quantitative reaction for this aldehyde.

Size of Cells in the Flesh of Apples.—A study of the microscopic structure of apples has revealed differences in the average size of the cell in the flesh of different varieties. Fruits of varieties normally picked late in the season have the largest cells, while early varieties have the smallest. The level of respiratory activity is relatively higher in varieties with small cells than in those with large cells, an interesting example of how metabolic activity may be related to microscopic structure.

New System of Refrigeration for the Transport and Storage of Food.—A short time ago a new system of refrigeration, known as the "jacket" system, was developed at the Ditton Laboratory of the Department. The new system has been installed, with modifications, in most of the new tonnage in the Australian and New Zealand trade, and during the year arrangements were made for officers of the Department to sail in some of the ships so equipped to examine its practical working. The basis of the investigation had to be wide, since the system involved changes in the method of carriage of all the ships' refrigerated cargoes frozen, including butter, cheese, frozen meat, chilled meat in gas storage, pears and apples. In the tests some 350 electrical resistance thermometers, spaced throughout the cargo, were used. The full data obtained from the expedition are under detailed consideration, but the indications are that the new system is working very satisfactorily. In the great bulk of a stack of 50,000 cases of apples the temperature was uniform within 0·5° F. Moreover, with the new system 3000 more cases can be carried than with normal storage. The Report points out that at the present time the margin of uncertainty in specifying the best temperature for a mixed cargo of apples is about 2° F. Thus the precision of control possible in the refrigerated space aboard ship has come abreast, or even surpassed, the precision demanded by biological definition.

Gas-storage of Fruit.—The success that has attended the commercial development of gas-storage of home-grown apples—that is, storage in an atmosphere containing just the right amount of carbon dioxide—is well known. A second investigation carried out with William pears and with Conference pears has shown that the pear responds to gas-storage even better than the apple. When gas-stored, the pears ripen more slowly on removal from store, thereby allowing

the trade more time for marketing them. Since the value of pears consumed in the United Kingdom is approximately £2,000,000, and home production is responsible for only a small amount of the total, there would appear to be scope for a considerable increase in the growing of pears in this country.

ROAD TAR RESEARCH.—Investigations on road tar at the Chemical Research Laboratory have been largely devoted to the changes that occur when tar is exposed under various conditions. The greatest cause of change is undoubtedly loss of oil, and it has been shown that the loss (L) for tars exposed in thermostatic conditions can be expressed in the form $L = IT^m$, where I is the loss during the first 24 hours, T is the duration of exposure, and m is a constant. The value of I for tars prepared by oiling back the same pitch is largely determined by the viscosity of the tar, and considerable variations in the oil constituent may be made without greatly affecting the relationship. The value of m measures the decline in the rate of loss during exposure. Measurements of loss of oil, however, are important only in so far as they can be related with changes in viscosity produced by this loss, and it is satisfactory to record that a close approximation has been obtained between viscosity changes produced by exposure at 25° C. and by distillation *in vacuo* (16 mm.) to the same loss. These methods open up a possibility of predicting the condition of tar after prolonged exposure from observations made during 48 hours' exposure.

Viscosity changes of tars exposed out of doors are greater than might be expected from the observed loss of weight but, on the other hand, the skin formed on tar in the open is such that loss of oil and change of viscosity are quickly inhibited. The enhanced viscosity is probably due to the action of light and oxygen on the skin, which then acts as a protective layer upon the underlying tar.

FOREST PRODUCTS RESEARCH.—*Seasoning of Timber.*—In connection with research work centring round the seasoning of timber, an investigation of the influence of the rate of drying of timber and other factors on the resultant shrinkage has been started, and it has been shown that, in compressed wood, shrinkage or expansion caused by variation in moisture-content is greater than in untreated wood of the same species. The stresses set up in timber during seasoning, as a result of the outer layer becoming drier than the inner portion, and a technique for the study of the internal strains produced thereby, have also been the subject of investigation.

Effects of Rots on the Strength of Timber.—The comparative effects of brown and white rots on the strength of timber are being examined, and it has been demonstrated by tests that beech attacked by brown rot fungus (*Coniophora cerebella* Pers.) shows a greater loss in toughness and resistance to compression for a given loss in weight than it does when attacked by a white rot (*Polystictus versicolor* Linn. Fr.). This indicates that where the loss in weight is due to depletion of the cellulose only, the resultant loss in strength is greater than when the same loss in weight is caused by depletion of both cellulose and lignin.

THE NATIONAL PHYSICAL LABORATORY.—The present report deals briefly with some of the items of special interest described more fully in the Report of the Laboratory (ANALYST, 1937, **62**, 460).

WATER POLLUTION RESEARCH.—A survey is given of the work of the Board (*cf.* ANALYST, 1937, **62**, 301), with particulars of later progress in some of the investigations.

Water-softening Material from Fuller's Earth.—In the method of treatment finally adopted the fuller's earth is first mixed with dilute hydrochloric acid, then dried and baked at 550°–600° C., and treated with solutions of sodium silicate and sodium aluminate. The product has a base-exchange value equal to that of the imported treated clays and has the advantage that it is less liable to disintegration. During the year further samples of British clays have been tested, but none has shown a base-exchange value equal to that of the fuller's earth product.

Exchange Properties of Synthetic Resins.—Recent experiments have shown that the exchange values of the synthetic resins not only vary with the phenol, tannin or aromatic base from which they are derived, but are dependent also on the detailed conditions of preparation. For example, the base-exchange value of resin made from sulphited quebracho tannin is largely dependent on the proportion of sodium bisulphite allowed to react with the tannin before it is converted into a resin by addition of formaldehyde. Within limits, the larger the proportion of sulphite the greater the base-exchange value of the final resin. It has been found, however, that the quebracho tannin resins with the highest base-exchange value are to a small extent soluble in water. Quebracho tannin resins with lower base-exchange values appear to be insoluble in water and in dilute solutions of acids and alkalis. In view of the possible use of the resins for the treatment of water for drinking, experiments are in progress with the object of determining the possibilities of the water being contaminated by substances derived from the resins. These experiments involve the determination of minute quantities of organic matter.

The possibility of utilising the resins for the removal of boron and fluorine from natural waters is also under investigation. Boron to the extent of a few parts per million in water used for irrigation is detrimental to the growth of certain crops, and recent surveys in different parts of the world have indicated that fluorine in drinking water to the extent of one part per million causes the dental defect known as mottled enamel.

CHEMICAL RESEARCH.—*Chemotherapy.*—In further extension of the group of compounds of type $AsO_3H_2.C_6H_4.NH_4.NH.CO[CH_2]_n.CO.NR_1R_2$, an oxalyl type of compounds ($n = 0$) has now been prepared. These compounds are trypanocidally active, but in general they are much more toxic than their homologues in the malonyl ($n = 1$) and succinyl ($n = 2$) series.

Microbiology.—The significance of the sulphate-reducing bacteria for the anaerobic corrosion of metals, notably of steel and cast iron, is being studied both in the field and in the laboratory. Work is in progress also on the control of the growth of the sulphate-reducing bacteria under natural conditions.

Experiments with *B. suboxydans* have confirmed the belief held that aeration of its cultures increases the rate both of its growth and of its conversion of sorbitol into sorbose, or of glucose into gluconic acid. The effect of acids on the enzymic activity of *B. suboxydans* has been shown to inhibit in the first instance the break-down of glucose to carbon dioxide. Subsequently the ability of the organism to transform glucose into gluconic acid is gradually destroyed. These observations are interpreted as indicating that the enzymic system of *B. suboxydans* has at least two independent functions.

Exploratory work has been carried out on the micro-flora of oil storage tanks.

The relationship of the *Myxococcus* which decomposes polysaccharides to other micro-organisms is in process of being worked out. For this purpose it has been necessary to devise a method for the staining of the nuclear substance of various micro-organisms.

Determination of Germanium.—A study has now been completed of all the known procedures for determining germanium, and some modifications have been suggested. In the determination of the metal as pyridine germanomolybdate attempts have been made to replace the pyridine by other organic amines, since the above-mentioned compound is appreciably soluble in water. Quinoline and cinchonine are the most suitable, but they show a tendency to produce slight precipitates with the excess of ammonium molybdate used.

COCOA, CHOCOLATE, SUGAR CONFECTIONERY AND JAM RESEARCH.—*"Cocoa red."*—Evidence has been obtained that during the fermentation of cocoa beans "cocoa red" condenses to form brown compounds. The ratio of "cocoa red" to condensed tannins is therefore an index of the degree of fermentation of the raw cocoa beans, and a method of determining this ratio has been devised. A similar

chemical change occurs during roasting, but other changes take place, in addition, during fermentation.

Gelatin in Pastilles.—Pastilles or "gums" are frequently made with a basis of gelatin. In one instance these pastilles were found to become tough and almost completely insoluble in water. An extensive examination of these goods revealed the fact that the effect was due to an action between the gelatin and certain of the flavouring essences used. The result has been that the manufacturers of these goods have since been able to avoid the occurrence of this defect.

FOOD MANUFACTURERS' ASSOCIATION.—The study of the bacteriology of pickles has been continued, and the causes of the discoloration of bacon have been investigated.

Subjects connected with the canning of meat and fish products that are being dealt with include (1) the penetration of heat into packages of various kinds and sizes, filled with different types of products; and (2) the pressure developed in these packages during sterilisation.

Tyrosine in Fish Products.—In products made from fish which have been preserved raw by packing in salt a white deposit or film sometimes occurs. This deposit has been identified as tyrosine, a product resulting from autolytic changes in the protein of the fish. It is, of course, not injurious in the slightest degree, as when protein is digested in the body this product is being formed along with others of a similar nature. The white films, however, when seen on these products, *e.g.* anchovy paste, herring fillets in oil, and such like, render them unsaleable, as purchasers think they must be unsound. A study is, therefore, being made of the development of tyrosine in the fish, with a view to finding some means of overcoming the defect.

COLLIERY OWNERS' RESEARCH ASSOCIATION.—The research work of the Association is now carried out at the Royal School of Mines. The investigations connected with silicosis have included continuation of the study of the incidence of silicosis, pneumonoconiosis and chronic bronchitis in relation to conditions of work underground. The physiological effect of inhalation of the small quantities of nitrous fumes likely to be encountered in certain underground operations (often about 0·002 per cent.) has still to be ascertained. Further tests with regard to the concentration of NO_2 in headings or after blasting have therefore been postponed for the time being until the experiments now being carried out at St. Bartholomew's Hospital have indicated the minimum quantity which will cause harmful effects to the lung.

Composition of Fine Dust.—Tests on the quantity and composition of very fine dust (*i.e.* less than 5μ) produced when drilling in various rocks have shown that the harder the rock the greater the amount of fine dust formed; a quartzite, for example, gave a dust production twice that from a Cannock Chase silkstone. Since the harder the rock the greater the number of shot holes and the longer the time spent in drilling, the greater, in consequence, will be the amount of dust breathed by the workman during his shift, other factors being equal. If no precautions are taken to remove this, the danger from lung trouble is increased, particularly since it has been found that the fine dust from the harder rock usually contains a higher percentage of free silica and one more nearly equal to that of the original rock, than does dust from softer material. For comparison with coal-mining conditions tests have also been carried out in quarries and other places where highly siliceous materials are being handled. The dust concentrations in such places have, in general, been found to be very low compared with those formed during most underground operations. Investigation of the composition and fineness of materials used for stone-dusting has been continued. In view of the great differences found between dusts in regard to the quantity of material below 5μ in particle size, it has been deemed desirable to ascertain by means of the Buxton Laboratory apparatus the influence of this size upon the explosibility of mixtures formed with a standard coal dust. The results so far obtained are very instructive, but require confirmation.

Ministry of Health

ANNUAL REPORT OF THE CHIEF MEDICAL OFFICER FOR 1936*

THE Report opens with an Introduction on the State of Public Health, summarising the progress in national health and in medicine during the past one hundred years, and this is followed by eleven chapters dealing with the principal aspects of the work undertaken by the seven sections into which the Medical Department of the Ministry of Health is subdivided.

VITAL STATISTICS.—The population of Great Britain, as enumerated at the census in April, 1931, was 44,795,357. Of this total, 39,952,377 represents the population of England and Wales. The estimated mid-year population in 1936 of England and Wales was 40,839,000, of which 19,591,000 were males and 21,248,000 females. The change in age constitution—towards a rise in the average age of the population—has continued. The natural increase in the population was 109,528, as compared with 121,355 in 1935, a decrease of 11,827. This Chapter gives the more important statistics for births and deaths in England and Wales and discusses the certification of causes of death.

Chapter III (General Epidemiology) includes an account of three extensive outbreaks of infectious disease conveyed by raw milk (enteric fever, enteritis and scarlet fever, respectively). No human cases of psittacosis were reported during the year, but the disease was demonstrated on several occasions in birds (parakeets) from Australia, Holland and Belgium.

Chapter IV deals with maternal and child welfare, Chapter V with tuberculosis, Chapter VI with the insurance medical service, Chapter VII with venereal diseases, and Chapter VIII with cancer.

In Chapter IX (Relation of Food to Health and Disease) a survey is given of a number of noteworthy publications dealing with various aspects of human nutrition, the most authoritative, so far as this country is concerned, being those of the Advisory Committee on Nutrition (ANALYST, 1937, **62**, 387), and of the Health Section of the League of Nations.

Milk (Special Designations) Orders, 1923, 1934 and 1936.—The recent developments of work under the 1936 Order, particularly the large increase in the number of licences for the production of accredited milk, make it desirable that as great a degree of uniformity as is possible should be attained in regard to requirements of equipment and methods. Details, however, do not always lend themselves to precise quantitative measurement, and may have to be considered in the light of associated circumstances which may offset them advantageously or otherwise. In many of the more important details of equipment and methods a fair measure of uniformity may be attained, and the Ministry's milk inspectors are visiting licensing authorities, especially those responsible for granting producers' licences, with the object of assisting them in this respect.

Tuberculin Tests.—Under the 1936 Order "Accredited" herd owners may now retain any reactors discovered in the herd, but no reactors from any other herd may be added. This enables herd owners gradually to eliminate reactors and thus qualify for "Tuberculin Tested Milk" licences without serious disorganisation of their regular milk supply.

Efficient Pasteurisation.—Attention is now more generally devoted to checking the efficiency of pasteurisation of milk, for it has been found that stricter control is very necessary. Tubercle bacilli have in some instances been found in milk sold as pasteurised. The obligation to detect in what way the pasteurisation plant or technique is at fault rests with the licensee, and if he cannot deliver milk which satisfies the requirements of the phosphatase test, he should not continue to hold a licence.

* H.M. Stationery Office, Adastral House, Kingsway. 1937. Pp. 253. Price 4s. net.

The Methylene Blue Reduction Test.—The necessity for scrupulous adherence to the details of the method prescribed in the Milk (Special Designations) Order, 1936, is of importance not only in the interests of the producer and consumer, but also because if a licensing authority should revoke a producer's licence on the ground of non-compliance with the requirement of the Order in respect of this test, the licensee has the right of appeal to the Minister, and in such an event the Minister would have to be satisfied that the test was carried out in the manner directed in Memorandum 139/Foods.

Nutritive Value of Pasteurised Milk.—The practical work (in elementary schools) of the investigation organised by the Milk Nutrition Committee was concluded in July, 1936, and the data are now being analysed. The results so far obtained seem to show that the supplements of two-thirds pint of milk have had a definite, and that of one-third pint a less definite effect on the rates of growth. Evidence that there is no significant difference in nutritive value between raw and pasteurised milk continues to accumulate. (*Cf.* Report of Milk Nutrition Committee, ANALYST, 1937, **62**, 463; Wilson, Minett and Carling, *J. Hyg.*, 1937, **37**, 243); "The Relative Values of Raw and Pasteurised Milk in the Feeding of Calves," Hannah Dairy Research Inst., *J. Dairy Res.*, 1937, **8**, No. 3.)

ICE CREAM.—The "cold mix" method, now becoming popular with small vendors, has the advantage of simplicity and cheapness, but unless pasteurised milk is used and care is taken to prevent contamination, the final products may show high bacterial counts. In Lichfield Borough 123 persons were affected with gastro-enteritis; all the infected persons had eaten ice cream manufactured by one firm.

LEAD IN SARDINES.—At a conference of Port Medical Officers of Health, in 1933, it was agreed that sardines should, at most, contain only negligible traces of lead. Representations were made by the trade that some little time would be necessary for the canners to make the required alterations in their methods to attain the desired degree of freedom from lead, and accordingly it was decided to defer taking action for a reasonable period when the amount of lead was not considerable. In practice this resolved itself into action being taken only when the lead exceeded 20 parts per million. During the last three years there has been a marked improvement in the lead-content of samples submitted, but there is a risk that traders may now regard the provisional limit of 20 p.p.m. of lead as an amount which sardines may contain without objection. Accordingly, it was decided at a conference of Port Medical Officers that this provisional limit should be revised and a stricter criterion of judgment enforced. It was agreed that after July 1st, 1937, action would be taken if consignments of sardines contained more than 5 p.p.m. of lead, and that this amount would be tolerated for a limited period only, the ultimate requirement being that sardines should be free from lead or contain only negligible traces of lead.

TIN IN SUGAR.—Analyses of sugars on the market have revealed the presence of 3 grains or more of tin per lb. In certain canned foods it is impracticable to avoid a small contamination with tin, and it has been suggested that in such foods the amount should not exceed 2 grains per lb. This suggested provisional limit is for contamination that cannot at present always be avoided and is not to be regarded as implying that tin in these amounts is free from objection. It is not an argument that can be used to justify the deliberate addition of tin to food. Local authorities may reasonably consider that the deliberate addition of tin to sugar is an unjustifiable process and that the interests of the consumer are not truly served by such an addition.

HONEY AND HONEY SUBSTITUTES.—There are now on the market a number of preparations containing honey diluted with invert sugar of glucose syrup. These preparations are commonly sold under some such designation as "Prepared Honey" with the intimation that the product is a mixture of honey and invert

sugar or glucose. Traders interested in the sale of honey assert that the term "Prepared Honey" is not a sufficient distinction and that the word "honey" should not be used in connection with such a product. Sometimes the word "prepared" is not clearly distinguishable, and the declaration of the presence of added invert sugar or glucose is not always very conspicuous. There is, of course, no objection on health grounds to the sale of a mixture of honey and invert sugar, and it is possible that some people may prefer the milder flavour of this mixture to the stronger flavour of pure honey. But it is important in the interests of the purchaser that he should know exactly what he is getting, and that "Prepared Honey" should be so described as to leave no doubt on this matter.

ACETIC ACID POISONING.—In March, 1936, a man entered an eating-house and ordered a meal. Seeing a bottle labelled "—'s Very Highly Concentrated Table Vinegar," he remarked that he liked strong vinegar and took a considerable quantity of it. He died shortly afterwards in hospital. The bottle contained about 60 per cent. acetic acid. The directions on the bottle, which was about the size of an ordinary wine bottle, stated that the contents should be added to four gallons of water, a dilution of approximately 1 in 13, to prepare them for use.

More recently a death from acetic acid poisoning took place in another town. It appeared that the vendor sold both acetic acid and mineral water, and by a deplorable error delivered to a restaurant a jar of acetic acid in mistake for one of mineral water.

Chapter X of the Report contains surveys of the health services, and Chapter XI deals with medical research and international health. The subjects discussed include chemotherapy in streptococcal and other infections, and some dangers of cosmetics (with a full list of references).

THERAPEUTIC SUBSTANCES ACT.—A factor that increases the work of the Licensing Authority is the frequent modification of substances of well-established therapeutic value, such as the combinations of protamine and zinc with insulin, or the perfection of new preparations closely allied to those long in use, for instance, staphylococcus toxoid.

Zinc Protamine Insulin.—Protamine insulin, though a distinct advance upon ordinary insulin, did not altogether satisfy those workers whose aim was to devise a modification of insulin which would adequately control the blood sugar level of a severe diabetic by a single injection in the 24 hours. The attainment of this ideal was brought a step nearer by the discoveries of D. A. Scott, of Toronto, in 1935. Scott and Fisher had already shown that crystalline insulin was a true chemical compound of insulin and zinc, and they now demonstrated that the delayed action of protamine insulin depended upon the presence of zinc and allied metals in this preparation. Moreover, the addition of traces of zinc and the adjustment of the *p*H to 7·2 resulted in the formation of a zinc-protamine-insulin compound which was more stable than Hagedorn's protamine insulin and had a more prolonged effect on the blood sugar. The exact nature of this new preparation is still not completely known, but the stability of the suspension is well established and gives it an obvious advantage over ordinary protamine insulin, which has to be issued in two bottles containing the protamine insulin itself and the buffer solution, respectively.

Metropolitan Water Board

THIRTY-FIRST ANNUAL REPORT ON THE RESULTS OF CHEMICAL AND BACTERIOLOGICAL EXAMINATION OF THE LONDON WATERS FOR THE TWELVE MONTHS ENDED 31ST DECEMBER, 1936*

THIS Report consists of an introduction and twenty sections under the following headings:—(1) Bacteriological Section; (2) Biological Section; (3) Chemical Section; (4) Chlorination; (5) Wells; (6) Prefiltration Waters; (7) Resistance to Filtration and Microscopical Appearances of the Prefiltration Waters; (8) Walton Works; (9) Kempton Park Works; (10) Stoke Newington Works; (11) Filtration Statistics (1936); (12) Works Efficiency; (13) Epping Sewage and Cobbins Brook; (14) Waltham Abbey Well; (15) Complaints; (16) Visits; (17) The Thames as a source of Potable Water; (18) Meteorological Notes; (19) General, Bacteriological and Chemical Tables; (20) A Study of Factors influencing the Viability of Coliform Organisms; A Summary and Conclusions and Index. Though mainly concerned with the London waters, the Report contains much that is of general interest in water examinations, and particularly in the bacteriology of water, and it is the object of this summary to give a very brief account of these points of interest.

In the introduction a general survey is made of all the Board's activities throughout the year and of the chemical and bacteriological investigations undertaken. One notes with much interest that the Board has decided to provide new laboratories, the building of which, at an estimated cost of £75,116, is now under construction at New River Head. The relative significance of typical and atypical lactose fermenters is discussed at some length, and several observations are recorded which indicate that the appearance of the latter is the first danger signal of potentially harmful pollution. Interesting reference is made to what is described as the bio-electro-chemical process by which cast-iron pipes trenched in clay are corroded, the iron of the pipe going into solution by electrolytic action in the salts of the soil, the graphite acting as cathode, and the process becoming progressive by the action of hydrogen sulphide liberated by anaerobes of the *Vibrio desulphuricans* type, whereby the iron is removed from the sphere of reaction.

BACTERIOLOGICAL TESTS.—In (1)—the Bacteriological Section—an account is given of a critical investigation of the Eijkman *B. coli* test; this has been applied to samples in parallel simultaneously with the routine test, and the results are compared. By the former test (incubating at 45° C.) 506 typical lactose fermenters were isolated, as compared with 738 by the latter (incubating at 42° C.), whilst of atypicals only 28 were isolated by the former as against 264 by the latter test. Thus, whilst the Eijkman test shows a greater proportion of typical *B. coli* (95 per cent.) than the routine test (74 per cent.), the total number of typical *B. coli* isolated is considerably less.

Further investigation has been made of the Rapid Indole or Indole Presumptive test, in which 10 ml. of the water are added to an equal volume of double-strength peptone water and tested for indole after 20 to 24 hours' incubation. A positive reaction, together with production of acid and gas in MacConkey's broth, is reported as unsatisfactory, and this rapid test has been found of great value in waterworks control. One notes that of 4000 samples tested in this way and also by the routine *B. coli* test, the number showing combined indole production and typical *B. coli* (isolated from 42° C. incubation) was 426, and the number showing indole production and acid and gas in MacConkey broth (at 42° C.) was 636, the balance being made up by the number of atypicals. The discrepancy between the two was greater in the summer months than in the period January to March, the numbers being 74 and 66, respectively.

* By Lt.-Col. C. H. H. Harold, O.B.E., M.D., Ch.B., D.P.H. Price 10s. 6d.

The study of the *Coli aerogenes* group has been continued. In 1936 the River Thames yielded 59·1 per cent. of *B. coli*, 24·1 per cent. of intermediates, and 6·4 per cent. of *aerogenes-cloacae* types. The author regards the presence of the atypicals, not as a sign of remote pollution but as an early indication of imminent dangerous pollution, and perhaps particularly so in the water of deep wells. O'Meara's and Barritt's modifications of the Voges–Proskauer reaction are described, and the great advantage, particularly of the latter, is illustrated; the addition of 6 per cent. of an alcoholic solution of α-naphthol increases the speed of the reaction and makes it more defined. The use of tellurite agar and broth for the isolation of *Streptococcus faecalis* is described; this method has proved far superior to the drying and heating techniques. The subcultures are made from the primary MacConkey tubes either upon the tellurite agar direct or preferably into tellurite broth and subsequently upon tellurite agar. (Agar, 2; lactose, 0·5; peptone 1, dipotassium hydrogen phosphate (anhydrous), 0·2; sodium chloride, 0·5; potassium tellurite added as a sterile solution, 0·0067 per cent. (or 1 in 15,000).)

Szper's medium for the isolation of typhoid and paratyphoid bacilli from water.—A description is given of this test, and the results obtained with this medium are compared with those given by the method of Wilson and Blair. The great advantage of Szper's medium is that it is added to the water in the ratio 1:5, so that large volumes of water can be tested. It is, in fact, a concentrated ox-gall-brilliant green tetrathionate broth of the following composition:

A	Broth (1 kg. of minced beef to 400 ml. water)	100 ml.
	Sodium chloride	2 g.
	Bacto peptone	5 g.
	Bacto ox-gall	2·5 g.
	Adjusted to *p*H 7·8 and autoclaved for 20 minutes at 15 lb.	
B	Calcium carbonate, analytical reagent quality (22·5 g.), autoclaved for 20 minutes at 15 lb. pressure in a 250-ml. flask.	22·5 g.
C	Sodium thiosulphate, analytical reagent quality, 50 per cent. solution, sterilised by steaming for 20 minutes	40 ml.
D	Iodine 20 g. Potassium iodide 25 g. Distilled water 100 ml.	8 ml.
E	Brilliant green (Gurr) 1 per cent. aqueous solution	4 ml.
	A, C, D, and E are added to B.	

For use 1 part is added to 5 parts of the water and subcultured on lactose—bile-salt—agar after 24 hours' incubation.

Results obtained with this medium compare very favourably with those obtained with Wilson's medium, and it is very much easier to use.

An experiment is recorded in which paratyphoid bacilli were isolated from ordinary Thames water to which was added 0·3 per cent. of sewage effluent, probably containing only 1 paratyphoid bacillus per litre. The strength of the medium must be modified to suit the particular investigation; double-strength medium without brilliant green was found to be best for the isolation of cultivated *B. typhosum*.

Susceptibility of Paratyphoid and B. coli Organisms to Chlorination.—Experiments are described which were devised to throw further light on the relative susceptibility of *B. paratyphosum* B. and *B. coli* to chlorination. These were carried out both with artificially cultured organisms and with freshly excreted bacteria, advantage being taken of the presence of the latter in the Epping sewage effluent since the outbreak of paratyphoid fever in 1931 and the fact that the

numbers present and the numbers of *B. coli* are regularly determined and known fairly accurately.

The effect of chlorination was tested in three classes of water—(1) the very pure Deptford well water, (2) filtered Thames water, (3) the Epping sewage effluent. It was found to vary somewhat in different experiments, but it is interesting to note that: the paratyphoid bacilli were killed in (1) within 5 minutes by as small a dose as 0·05 p.p.m.; in (2) within 10 minutes by 0·3 p.p.m.; in (3) within 30 minutes by 0·75 p.p.m. of chlorine; also *B. paratyphosum* B was found more susceptible than *B. coli* to chlorination.

Viability of Coliform Organisms.—In the Study of Factors influencing the Viability of Coliform Organisms (Section 20) an investigation of their extraordinary multiplication in boiled "hard" water, as free from organic matter as that from the Deptford well, is recorded. (Similar behaviour in boiled "hard" water was recorded by another observer at a meeting of the Institute of Water Engineers in June, 1919.)

PHOTO-ELECTRIC TURBIDIMETER.—In the Chemical Section (3) an account is given of the photo-electric turbidimeter that has been invented and developed during the year and used mainly in the examination of raw and stored waters.

OTHER CHEMICAL INVESTIGATIONS.—These include an investigation of the taste-imparting properties of Bituminous Coatings of Water Mains, of the purity of the peptone used in the bacteriological department, of a colorimetric method for the estimation of phosphates in natural waters, and of the action of metals on tap water before and after softening by the base-exchange method.

The General Bacteriological and Chemical Tables (Section 19) show that 95·7 per cent. of the Thames-derived waters examined (3055 samples) contained no typical *B. coli* in 100 ml. This was true also of 96·5 per cent. of all London waters as supplied to consumers (6098 samples), 96·6 per cent. of all samples from the Kent wells, and 92·7 per cent. of all samples from the Lee Valley wells; this is a very high standard of purity.

Oils from Irish-grown Plants*

THIS preliminary report deals with the possibility of producing in Ireland fatty oil-bearing seeds, essential oils and other economically important oils. No absolute conclusions can at present be reached, but a *prima-facie* case is definitely made out for further agricultural and technological research. The plan of the report is to present for each oil a summary of data, collected from a large number of sources and embodying much up-to-date information, dealing with cultivation and harvesting in various countries, diseases and pests affecting the crop, recorded analyses of seeds, silage, cakes, oil, and so on. An account then follows of the work carried out at the College grounds at Cork, at the University Farm and at the Mallow Nurseries, with analyses of the oils actually produced. A few essential oils are dealt with, and in an Appendix the methods used in analysis are given. A report follows on the cultivation of oil-yielding plants and herbs at MacLysaght's Nurseries, Mallow.

The fatty oils dealt with are linseed, rape, mustard and poppy (all of which are considered feasible to grow in Ireland and are found to yield normal products), hemp, sunflower and *Mercurialis* oils. It is pointed out that at present no conclusions can be drawn as to yields, owing to the smallness of the areas cultivated,

* Preliminary Report by J. Reilly, D.Sc., F.I.C., and D. F. Kelly, M.Sc., *Agric. Bull.*, No. 4, 92 pp. Cork University Press, 1937. Price 2s. 6d.

e.g. a quarter of an acre only is devoted to linseed. The analyses of the Irish-produced oils were as follows:

	Sp.gr. at 15·5°	n_D^{40}	Saponification value	Iodine value
Linseed	0·9330	1·4748	194·5	177·2
Rape	0·9130	1·4659	177·5	97·5
Sunflower (1) ..	0·9220	1·4681	196·5	133·3
,, (2) ..	0·9230	1·4684	194·9	136·0
Hemp-seed oil ..	0·9300	1·4720	191·9	155·1
Mustard	0·9200	1·4650	171·6	92
Poppy	0·9110	1·4675	191·5	138·4

The usual characteristics of the oil from *Mercurialis annua* are as follows:—Sp.gr. at 15° C., 0·935–0·937; n_D^{15}, 1·4848–1·4861; iodine value, 205·9–215·5; insoluble bromides, 65–80 per cent. On exposure to the sun the oil dries in about 3 hours.

The cultivation of sunflower is not viewed very optimistically, in spite of various favourable opinions as to its suitability in England, but further work, especially of the nature of variety trials, would have to be carried out before deciding the point. So far, poppy cultivation has proved more promising, and it is suggested that this oil may serve to displace to a considerable extent imported cotton-seed and allied oils, use being possibly made of partial hydrogenation. Hydrogenation of hemp or mustard-seed oils might also produce a product to replace the whale oil at present in use. The work on hemp is regarded as inconclusive, particularly as hemp did not prove a very hardy subject. The great number of male plants produced by *Mercurialis annua* is a handicap in growing this crop, as the sex cannot be discerned easily until the plants are very forward.

Of the essential oils, lavender, peppermint and dill were considered, but so far their cultivation is practically undeveloped in Ireland. Some experimental work previously carried on at Cork (*Economic Proceedings of the Royal Dublin Society*, 1926, 1927, 1929) showed that Irish-grown plants could produce oils of lavender, peppermint, chamomile and rosemary of a character equal to the best Mitcham oils. D. G. H.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

The *p*H Value as an Index of the Quality of Alimentary Pastes. P. Duquénois. (*Ann. Falsificat.*, 1937, **30**, 412–415.)—The following procedure serves as a rapid test for the quality of alimentary pastes, such as macaroni, vermicelli, etc. The paste (10 g.) is broken up into pieces, mixed with 100 ml. of water and brought rapidly to boiling point. The time of boiling is counted from the time boiling begins. By the use of a stirring rod, frothing and adherence of the paste to the bottom of the vessel are prevented. The degree of milkiness of the liquid is noted, and boiling is continued until the pieces of paste can be broken easily when pressed with the rod against the sides of the vessel. The liquid, while still boiling, is decanted on to a pleated filter-paper, 16 to 18 cm. in diameter, and the filtrate is collected in a graduated vessel. After ten minutes the volume of the

filtrate is read, and its turbidity is observed against a dark background. The *p*H of the filtrate (2 or 3 ml.) is determined by adding one drop per ml. of a suitable indicator, no correction being made for errors due to salt or protein. Pastes made from the flour of strong wheat give a clear filtrate of 40 to 50 ml. The products of weak or damaged wheat give turbid filtrates of only a few ml. With pastes of medium quality the filtrate measures 20 to 30 ml. The residue left after decantation of the liquid should be firm, elastic, translucent and of a slightly yellow colour, and should retain its original shape. The products of weak, inferior flour are soft, shapeless and colourless. The *p*H of the filtrate corresponds with the acidity found by extraction of the paste with neutral 90 per cent. alcohol for 12 hours, and titration in the presence of phenolphthalein. Experiments show that pastes having a *p*H less than 5·4 give a titratable acidity greater than that generally permissible. Those having a *p*H greater than 5·9 have a lower acidity, and are of good quality. Methyl red is therefore the appropriate indicator, being yellow at *p*H 6·0 and red at *p*H 4·4. Bromocresol green (blue at *p*H 5·2 and green at *p*H 3·6) serves for values below 5·2, and bromothymol blue (yellow at *p*H 6·0 and yellowish-green at *p*H 7·6) for values above 5·9. A. O. J.

Examination of the Fat of Goats' Milk. A. Chollet and A. Camus. (*Ann. Falsificat.*, 1937, **30**, 405–410.)—Cream from goats' milk was churned into butter, and the clear fat was separated by melting and decantation. Fat was obtained from goats' cheese by extraction with ether in a Soxhlet apparatus. The samples of fat (seven in number) were then examined and compared with the fat from cows' milk. The results obtained were as follows:—The Crismer value (40·4 to 42·4) is lower than that of cows' butter-fat; the Planchon value (12·6 to 18·3) is considerably lower, but appears subject to great variation; the saponification value (233·0 to 245·1) is generally higher, but sometimes falls below the maximum value for cows' butter-fat; the iodine value (16·6 to 26·9) is generally lower, but the ranges again tend to overlap. The refractive index does not differ greatly from that of cows' butter-fat. The figures for soluble volatile acids (Leffmann–Beam procedure) are slightly lower, and those for insoluble volatile acids are much higher than for cows' butter-fat, thereby confirming previous statements that goats' milk-fat is the richer in caprylic and capric acids. The ratio

$$R = \frac{\text{insoluble volatile acids} \times 100}{\text{soluble volatile acids}}$$

varies from 8 to 15 for cows' milk-fat and from 36·5 to 43·1 for the samples of goats' milk-fat investigated, and appears to be a useful criterion for distinguishing the two fats. Experiments showed that fat may be extracted from cheese by either of two methods, the chemical properties of the fat being unaffected by differences in the procedure. By the first method the cheese, shredded if hard or mixed with sand if soft, is extracted with ether in a Soxhlet apparatus; by the second and more rapid method the cheese is just covered with hydrochloric acid (sp.gr. 1·125) and heated until the casein dissolves, and the fat is extracted by shaking the mixture with ether. After evaporation of the ether the fat is washed with boiling water on a filter until free from acid. Three samples of cheese were prepared—one from goats' milk, one from a 3: 1 mixture of goats' milk and cows' milk, and the third

from a 1:1 mixture of goats' milk and cows' milk. After being allowed to ripen for about six weeks the cheeses resembled the local commercial product in flavour, appearance and occurrence of mould (*Penicillium glaucum*). The fats separated from these samples were examined, and the figures obtained were compared with those obtained by calculation from the known constants of the fats of the constituent milks. It was found that the constants were practically unaffected by the ripening process, except that the amount of insoluble volatile acids was slightly diminished, the ratio R being correspondingly affected. The results obtained were as follows:

	Goats' milk		25 per cent. cows' milk		50 per cent. cows' milk	
	Found	Calc.	Found	Calc.	Found	Calc.
Volatile acids—						
Soluble ..	19·8	19·7	21·3	21·2	22·7	22·7
Insoluble ..	7·3	7·5	5·8	6·4	4·9	5·2
Ratio, R	36·6	38·1	27·2	30·2	21·6	22·9
Saponification value (Koettstorfer)..	236·5	237·0	237·0	237·9	234·6	236·1
Planchon value ..	18·9	18·1	20·1	20·1	31·0	33·8

The methods described will probably be found applicable to the examination of cheese made from mixtures of unskimmed milk of cows and goats. It would be possible to prevent the use of skimmed cows' milk by fixing a sufficiently high standard for the fat-content of the cheese expressed on the dry substance. The work is being continued to determine the limits of variation of the constants of the fat of goats' milk. A. O. J.

Diacetyl in Normandy Butter. C. Brioux and E. Jouis. (*Compt. rend.*, 1937, **205**, 526–528.)—In connection with the French Law of 2nd July, 1935, prohibiting the use of diacetyl as an "improver" in butter, information was needed on the diacetyl-content of normal butter, and at the request of the French Minister of Agriculture, the diacetyl-content of butter from certain districts in northern France was studied. Samples, about 130 in number, from markets and industrial and co-operative dairies were analysed, generally within 48 hours of being taken. The sensitive colorimetric method of Pien, Baisse and Martin (*Le Lait*, 1937, p. 673) was used on a sample weight of 400 to 500 g. Of the samples, 76·3 per cent. contained very small quantities of diacetyl, varying from mere traces to 0·5 mg. per kg. The samples with larger amounts, varying from 1 mg. to 1·5 mg. per kg., and one exceptional sample containing 2·5 mg. per kg., were all obtained from co-operative and industrial dairies. Acetylmethylcarbinol was also determined in some samples by determination of the diacetyl formed after oxidation with ferric chloride. Of the butters examined, 73 per cent. contained 1·3 to 25 mg. per kg. of acetylmethylcarbinol, and the highest amount found was 69·1 mg. per kg. In general but not invariably, the lower the proportion of diacetyl found, the lower was the proportion of acetylmethylcarbinol. Cream is richer in diacetyl, and particularly in acetylmethylcarbinol, than the butter churned from it, the two compounds passing preferentially into the buttermilk. The following results were

obtained on products analysed on the same day as the butter was made, or at the latest the next morning (Royville Dairy, Seine-Inferieure):

		Diacetyl (mg.)*	Acetylmethylcarbinol (mg.)*
16th June	Cream	2·25	176·7
	Butter	1·13	23·4
	Buttermilk ..	4·32	198·1
23rd June	Cream	1·92	95·2
	Butter	1·50	42·4
	Buttermilk ..	3·10	195·3

Diacetyl naturally occurring in butter seems to disappear fairly quickly, whether by volatilisation, by reduction to acetylmethylcarbinol, or by other means was not established. The following results were obtained on butter kept in a cool cellar:

	Diacetyl (mg.)*	Acetylmethylcarbinol (mg.)*
Day following churning ..	1·50	42·4
After 5 days	0·60	—
After 18 days	0·13	—
After 27 days	0·05	20·4

The authors suggest that it would be useful to have corresponding results for products from dairies in other parts of the country. S. G. C.

Mineral Constituents of Coffee Infusions. Thiellement and D. Florentin. (*Ann. Falsificat.*, 1937, **30**, 415–416.)—In an investigation to determine if samples of coffee infusion had been adulterated, particularly with phosphates, analyses were made of the mineral constituents of normal coffee infusions made with 10 g. of roasted coffee and 100 ml. of boiling water. The infusion was filtered rapidly and evaporated to dryness, and the residue was ignited at dull red heat. The results obtained are expressed in grams per litre of infusion, corresponding with 100 g. of coffee. The first figure in each instance refers to San Paulo (Brazil) coffee and the second to Robusta (Madagascar) coffee. Total mineral matter, 3·38, 3·60; phosphoric anhydride, 0·237, 0·293; sulphur trioxide, 0·109, 0·078; calcium oxide, 0·176, 0·066; magnesium oxide, 0·205, 0·228; potassium oxide, 2·00, 2·20; sodium oxide, 0·276, 0·291. Adulteration with phosphate is therefore not indicated unless the P_2O_5 figure exceeds 0·300 g. per 100 g. of coffee. The very high potassium-content and the relatively high magnesium-content of the infusion, are noteworthy. A. O. J.

Effect of Decortication on the Constituents of Philippine Ginger. J. Marañon and L. Ll. Cosme. (*Philippine J. Sci.*, 1937, **63**, 405–406.)—According to the U.S. Food and Drugs Act, dried ginger imported into the United States should conform to the following requirements: starch, 42 per cent. or more; crude fibre, 8 per cent. or less; calcium oxide, 1 per cent. or less; cold water extract, 12 per cent. or more; total ash, 7 per cent. or less; ash insoluble in hydrochloric acid, 2 per cent. or less; ash soluble in cold water, 2 per cent. or more. It was found

* Presumably per kg.

(Marañon and Caguicla, *Philippine J. Sci.*, 1935, **58**, 171) that many samples of undecorticated Philippine ginger do not conform to these requirements, some being deficient in starch and others containing more than the permissible amount of ash. To determine the effect of decortication, complete rhizomes were washed to remove soil and split longitudinally, one half being decorticated and re-washed before both halves were dried in the sun. During decortication care was taken not to damage the oil-bearing sub-epidermal cells. Analyses of both halves were made in accordance with the official methods for spices and condiments (Methods of Analysis of the A.O.A.C., 4th Ed., 1935, p. 445). It was found that by decortication the composition of the rhizome was changed in the following respects:—(1) the starch-content was increased on the average by 14·9 per cent., (2) the ash was reduced by 11·2 per cent. and the crude fibre by 22·8 per cent., (3) the ash soluble in water was slightly reduced, and (4) changes in the other constituents were not consistent. Compared with ginger from other countries, Philippine ginger is characteristically high in crude fibre, ash and extractive matter soluble in ether and alcohol, but low in starch. Decortication caused the composition to approach more nearly to the requirements but, when the starch-content was too low or the ash rather high, decortication did not produce sufficient change in these constituents to make the ginger conform to the required standards. Careful selection of the root-stock and repeated cultivation and selection based upon analysis should eventually produce a Philippine ginger suitable for export. A. O. J.

Pharmacognosy of "Bulgarian" Belladonna Root. A. E. Bailey. (*Pharm. J.*, 1938, **140**, 77.)—It has been suggested that the "Bulgarian" belladonna root which is used in the "Bulgarian treatment" of post-encephalitic parkinsonism differs from the belladonna root of commerce. A supply of 2 kg. of guaranteed "Bulgarian" root was therefore examined. Its morphological and histological characters, which are fully described, differed only slightly, if at all, from those of the ordinary root of commerce. In two samples of this batch, which were analysed by the B.P. (1932) method, the percentages of alkaloid were 0·238 and 0·247, respectively; these are much lower than for the B.P. belladonna root. The following qualitative tests were made on the final titrated solution of the alkaloids (corresponding to a 0·065 per cent. solution of the total alkaloids calculated as hyoscyamine):—(*a*) Mayer's reagent: immediate white precipitate; (*b*) Froehde's reagent: faint turbidity; (*c*) Dragendorff's reagent: immediate brownish-red precipitate; (*d*) Bromine water and (*e*) Gold chloride: no precipitates (owing probably to the weakness of the solution); (*f*) Vitalli's reaction: 2 or 3 drops of the solution, evaporated with fuming nitric acid in a porcelain dish, gave a faint residue, which became violet on moistening with alcoholic potassium hydroxide solution. Most solanaceous alkaloids give reaction (*f*). These results, and those of physiological tests on the eye of a rabbit, indicate that the chemical constituents of the alkaloids of the Bulgarian and the B.P. roots are similar. Any pharmacological properties peculiar to the Bulgarian root are considered to be due either to some degradation product formed by hydrolysis during the preparation of the decoction used, or by enzyme action, or, alternatively, to some non-alkaloidal constituent. Further investigation is being made.

A Bulgarian belladonna root which was analysed by Kuiper and van der Wielen, using the Swiss Pharmacopoeia method, contained 0·58 per cent. of total alkaloids. It is thought probable that samples of the Bulgarian root will vary greatly in appearance and quality. E. B. D.

Biochemical

Relation between Taste and Constitution of Derivatives of Malondihydrazide. J. J. Blanksma and H. de Graaf. (*Rec. Trav. chim. Pays-Bas*, 1938, **57**, 3–12,)—Malon-dihydrazide has a very sweet taste. In the series $CHR(CONHNH_2)_2$, where $R = C_nH_{2n+1}$, sweetness diminishes as n increases from 0 to 3. Butylmalondihydrazide and the higher homologues, and also benzylmalondihydrazide, have a bitter taste. Sweetness appears to depend on the presence of the group $CONHNH_2$. When the above-mentioned series is acetylated, the acetyl derivatives have little or no sweetness. Thus, malondi-(acetylhydrazide) is only faintly sweet, methylmalondi-(acetylhydrazide) is faintly sweet with a bitter after-taste, the *n*-propyl derivative is tasteless with a faint bitter after-taste, and higher homologues are bitter. Condensation products of the alkylmalondihydrazides with aldehydes and ketones are bitter when soluble in water and tasteless when insoluble. Thus, the condensation products with acetone are all soluble in water and extremely bitter; the di-(benzalhydrazide) and the anisal and piperonal derivatives are insoluble and tasteless, but sometimes have a bitter after-taste. Other derivatives examined were diethyl hydrazinomalonate, $CHNHNH_2(COOC_2H_5)_2$, and hydrazinomalon-dihydrazide, $CHNHNH_2(CONHNH_2)_2$; both are insoluble in water and tasteless. Details of the preparation, physical properties, and solubility in various organic solvents are given for many of these derivatives. E. B. D.

Estimation of Sulphydryl Groups in Proteins. R. Kuhn and P. Desnuelle. (*Z. physiol. Chem.*, 1938, **251**, 14–18.)—2, 6-Dichlorophenolindophenol has been used for the estimation of cysteine, but the reaction requires to be carried out at 100° C., and so cannot be used for native proteins. Porphyrindin, a blue dye, and porphyrexide, a red dye, having higher redox potentials than 2, 6-dichlorophenolindophenol, are preferable, for they react quantitatively at low temperatures. Porphyrindin has been used because of its more intense colour. One volume of the protein solution to be tested is mixed with three volumes of $M/10$-phosphate buffer of pH = 7·2 ($M/2$-phosphate if the solution is acid) in a Thunberg tube, so that the mixed solution contains at most 12 to 15 mg. of protein per ml. Three ml. of this solution are heated in an atmosphere of pure nitrogen for 10 minutes in the steam-bath, if it is required to denature the protein. The tube is shaken to obtain a finely-divided precipitate of protein and cooled. The dye is added from a pipette and the tube is again filled with nitrogen. When 2, 6-dichlorophenolindophenol is used (for denatured proteins) the tube is heated for a further 10 minutes in the boiling water-bath, but with porphyrindin it is cooled to 0° C., and the colour is observed after 5 to 7 minutes' shaking. A series of experiments on these lines with widely different amounts of dye will give an

approximate idea of the amount required, the exact quantity being found by further tests, with closely-graded amounts of dye. The porphyrindin solution is not stable, and a fresh solution should be prepared daily (7 mg. of dye in 10 ml. of water). It is standardised against pure cysteine; 1 mg. of cysteine is equivalent to 1·16 mg. of porphyrindin or to 2·97 mg. of 2, 6-dichlorophenolindophenol.

F. A. R.

Standardisation of 2, 6-Dichlorophenolindophenol. M. H. Menaker and N. B. Guerrant. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 25–26.)—An improved method of standardising solutions of 2, 6-dichlorophenolindophenol, to be used for the determination of ascorbic acid, is based on the quantitative conversion of iodide into iodine by the dye. Fifteen ml. of the dye solution are pipetted into a 50-ml. flask, 0·5 to 1·0 g. of potassium iodide and 0·5 to 1·0 ml. of 25 per cent. sulphuric acid are added, the solution is shaken, and the liberated iodine is titrated with 0·01 *N* sodium thiosulphate solution; 1 ml. of 0·01 *N* sodium thiosulphate solution is equivalent to 0·88 mg. of ascorbic acid. The advantages of the new method are that the use of one of the standard solutions (iodine) required by the older methods is eliminated, and that the end-point is sharper than in previous methods.

F. A. R.

New Method for the Standardisation of the Dye used for the Determination of Cevitamic Acid (Vitamin C). R. E. Buck and W. S. Ritchie. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 26.)—*Cf.* previous abstract.

[*Abstractor's Note.*—In an editorial note which accompanies this and the preceding paper it is explained that by an unusual coincidence two papers describing an improved method for the standardisation of 2, 6-dichlorophenolindophenol were submitted for publication within a few days of one another. The methods described are apparently identical. The paper by Menaker and Guerrant, which reached the journal first, is given in full, the other paper in the form of an abstract only.]

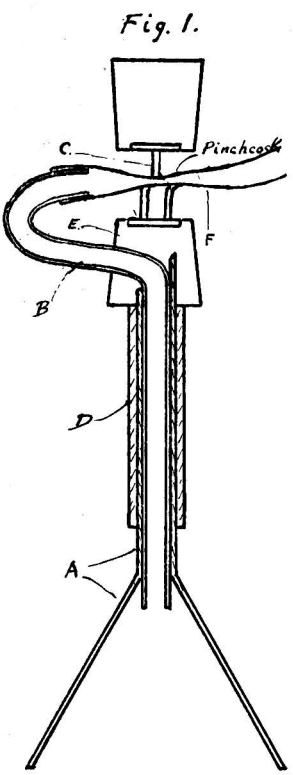
F. A. R.

Effect of Sterilisation and Storage on the Antiscorbutic Power of Lemon Juice. G. Mouriquand, H. Tête, G. Wenger, and P. Viennois. (*Compt. rend.*, 1937, **204**, 1904–1907.)—Sterilisation of fresh lemon juice for 1½ hours at 120° C. caused no appreciable loss of antiscorbutic power; 5 ml. of either fresh or sterilised juice per day protected 250- to 300-g. guinea-pigs on a vitamin-deficient diet over a test-period of 100 days; 3 ml. per day appeared to give satisfactory results up to a 30-day test-period, but subsequently slight scorbutic symptoms were observed, although the weight increase was normal or nearly normal. Lemon juice, whether freshly pressed or sterilised, rapidly lost its antiscorbutic properties when kept in a vessel open to the air. Values obtained for the "iodine index" of lemon juice were as follows: freshly-pressed juice, 75 mg. per 100 ml.; sterilised, 70 mg. per 100 ml.; kept in contact with the air, 55·5 mg. per 100 ml. (after 8 days), 25·3 mg. per 100 ml. (after 15 days), 10·4 mg. per 100 ml. (after 20 days); kept under nitrogen, 70·4 mg. per 100 ml. (after 70 days).

S. G. C.

Bacteriological

Filling Device for Bacteriological Media. W. Hickson. (*J. Inst. Brewing*, 1938, **44**, 50–52.)—An apparatus is described suitable for transferring media in bulk from, *e.g.*, a large flask, into small bottles or tubes under aseptic conditions. The apparatus comprises an inverted glass funnel A, and a piece of glass tubing, B, which passes downwards through the stem of A and projects about half-an-inch into the body of the funnel. The upper part of B is bent sharply at right angles at the extremity of the funnel-stem, and then with a U-bend backwards and slightly upwards, so that it terminates opposite the jaws of the pinch-cock C. Before these parts are fixed together a sleeve D must be provided. This may consist of a short length of metal tubing, or of heavy-walled glass tubing, through which the stem of the funnel will easily pass. A funnel should be selected with a stem having walls as parallel as possible, as this will provide the best sliding fit. These parts are held together by means of the cork E, which also operates against one finger-plate of the pinchcock. A hole is made of such diameter that it will fit snugly on the extremity of the funnel-stem. Another hole of the diameter of the tube B is bored at right angles to the first hole, which it meets in the centre of the cork. A piece is excised from the side of the cork of the same width as, and extending downwards from, the small side-hole; the parallel-sided cuts penetrate into the large centre hole. The cork may now be fitted over the end of the funnel-stem, and the bent tube B becomes seated in the side-opening. Before the arrangement is permanently fixed a little cementing material, such as plastic wood, may be introduced into the hole in the cork. The excised piece of cork is then replaced and bound tightly in position with twine. The sliding sleeve D is held firmly in a clamp, thus enabling the funnel to slide freely up and down within suitable limits. A second clamp, carrying a further cork, is so arranged that this cork is directly above the cork E and at such a distance that the finger-plates of the pinchcock may be gripped in between. A slight depression, made by means of a cork-borer, in the opposing surfaces of the corks, will prevent the pinchcock from slipping out of position. Should the spring of the pinchcock be unnecessarily strong, it may be weakened by means of a file. The rubber siphon tubing F is attached to the end of the glass side-tube B and passes between the jaws of the pinchcock, and the other extremity is attached to the outlet-tube of the reservoir. When the siphon has been started, upward pressure of the inverted funnel will release the flow of the liquid, which stops instantly and sharply when the pressure is withdrawn.



D. R. W.

Results obtained in a Co-operative Investigation of Bacteriological Media for Milk Counts. J. Howard Brown, C. W. Bonynge and Harris Moak. (*Amer. J. Hyg.*, 1938, **27**, 12–18.)—Comparison is made of milk counts in A.A.M.M.C. agar with counts in the standard nutrient agar (S.N.A.) of the American Public Health Association, the data being collected from 25 laboratories in different localities. The composition of the A.A.M.M.C. agar was as follows:—Agar, 1·5; beef extract, 0·3; peptone, 1·0; sodium chloride, 0·5; dextrose, 0·1 per cent. in distilled water and adjusted to *p*H 6·8 to 7·2, the peptone being a mixture of beef and casein digest. The A.A.M.M.C. agar is shown to give considerably higher counts than the S.N.A. agar, the difference being greater the poorer the quality of the milk. The average counts were higher than those obtained with the S.N.A. agar by 10 per cent. with Certified milks — pasteurised by 31 per cent. with Certified milks — raw, by 55 per cent. with other pasteurised milks, and by 62 per cent. with other raw milks. The highest average plate count for Certified milk—raw was 9773 per ml.; the lowest 800 per ml. The City reporting the highest average for ordinary pasteurised milk (40,041 per ml.) reported an average of 240 per ml. for Certified milk — pasteurised. The lowest average reported for ordinary pasteurised milk was 2175 per ml. *Coli* group organisms were found in 36 per cent. of the samples of ordinary pasteurised milk, indicating either inefficient pasteurisation or contamination after pasteurisation in about one-third of the samples. About 80 per cent. of the samples of certified milk—pasteurised had counts below 500, and it is significant that all but one of the samples having counts above 500 were from localities where all the milk is required to be pasteurised—a fact suggesting relaxation of care in this respect. D. R. W.

Agricultural

Determination of Pyrethrin I in Commercial Insecticides containing Pyrethrum or Pyrethrum Extract. D. A. Holaday. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 5–6.)—The Seil method for the determination of pyrethrin I in commercial mineral oil—pyrethrum insecticides containing essential oils or perfumes (Seil, *Soap*, 1934, May, p. 89) is not satisfactory. Wilcoxon's method (*Contrib. Boyce Thompson Inst.*, 1936, **8**, 175–181) is satisfactory for pyrethrum powder only. The author has modified this method by removing unsaturated organic compounds before determining the reduced mercury, and has found this modified method to be valid for the analysis of plant sprays containing essential oils, derris resins, soaps and other spreaders, tobacco extract, alcohol or acetone. The suggested procedure is as follows. A sample containing 20 to 75 mg. of pyrethrin I is heated under reflux in a 300-ml. Erlenmeyer flask for 1 to 1½ hours with 15 ml. of 0·5 *N* alcoholic sodium hydroxide solution (more sodium hydroxide solution may be necessary for samples containing large quantities of perfumes or essential oils). The material is transferred to a 600-ml. beaker and sufficient water is added to bring the aqueous layer up to 200 ml. A few glass beads are added, or, preferably, a boiling tube is used, and the aqueous layer is boiled down to 150 ml., after which it is transferred to a 250-ml. volumetric flask, treated with 1 g. of kieselguhr (Filter-Cel) and 10 ml. of 10 per cent. barium

chloride solution, made up to volume, and allowed to settle (more barium chloride solution may be needed to obtain a clear solution). A volume of 200 ml. is filtered off, treated with 5 ml. of sulphuric acid (1 + 4), filtered into a 500-ml. separating funnel, and extracted with two 50-ml. portions of petroleum spirit. The extracts are washed with several 10-ml. portions of water and filtered through a cotton plug into a 250-ml. separating funnel, and the cotton is washed with 5 ml. of petroleum spirit. The petroleum spirit is extracted by vigorous shaking with 5 ml. of 0·1 *N* sodium hydroxide solution. The aqueous layer is drawn off into a 100-ml. beaker, and the petroleum spirit is washed with 5 ml. of water which is added to the contents of the beaker. Ten ml. of Denigès' reagent (U.S.P. XI) is added to the liquid, which is left for 1 hour, after which it is treated with 20 ml. of acetone, and the reduced mercury is precipitated with 3 ml. of saturated salt solution. The liquid is warmed to about 60° C., filtered through a small filter paper (7 to 9 cm.), and washed with 10 ml. of hot acetone, all the precipitate being transferred to the paper. The precipitate is washed with two 10-ml. portions of hot chloroform, and the paper and contents are placed in a 250-ml. glass-stoppered conical flask, treated with 30 ml. of conc. hydrochloric acid and 20 ml. of water, cooled, and then treated with 6 ml. of chloroform or carbon tetrachloride and 1 ml. of iodine monochloride solution (prepared by dissolving 10 g. of potassium iodide and 6·44 g. of potassium iodate in 75 ml. of water, adding 75 ml. of hydrochloric acid and 5 ml. of chloroform in a glass-stoppered bottle, and adjusting to a faint iodine colour (chloroform) by adding dilute potassium iodide or potassium iodate solution). The liquid is then titrated with 0·01 *M* iodate solution (2·14 g. of potassium iodate per litre). Potassium iodate reacts with mercurous salts to form mercuric salts and iodine. Further addition of iodate in the presence of hydrochloric acid oxidises the iodine to iodine monochloride.

1. $5HgCl + 6HCl + KIO_3 = I + 5HgCl_2 + KCl + 3H_2O$.
2. $2I_2 + KIO_3 + 6HCl = 5ICl + KCl + 3H_2O$.
3. $4HgCl + KIO_3 + 6HCl = 4HgCl_2 + ICl + KCl + 3H_2O$.

Addition of iodine monochloride does not alter the volume relations between reduced mercury and iodate solution and aids in the titration of small quantities of mercury. The end-point is taken when the colour disappears from the chloroform layer. As the end-point is not permanent, the titration should be completed rapidly with vigorous shaking after each addition of iodate. One ml. of the iodate solution is equivalent to 4·4 mg. of pyrethrin I. E. M. P.

Determination of Rotenone in Derris and Cube. II. Extraction from the Root. H. A. Jones and J. J. T. Graham. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 19–23.)—Five extraction methods were compared: (1) Soxhlet extraction, (2) boiling—multiple-extraction, (3) boiling—aliquot part method, (4) room temperature—multiple-extraction, and (5) room temperature—aliquot part method (Beach, *Soap*, 1936, **12**, 109, 111). In method (2) the sample was heated with the solvent under a reflux condenser on the steam-bath for 1 to 2 hours and filtered by suction. The residue was washed on the filter with hot solvent and then again heated under reflux with fresh solvent, followed again by filtration and washing.

This was followed by a third "refluxing," filtration and washing. In method (3) the sample was heated under reflux with a weighed quantity of solvent on the steam-bath for 2 to 3 hours. After the contents of the flask had cooled to room temperature, solvent was added to replace that lost, and the extraction mixture was chilled in the refrigerator and filtered through pleated filter-paper, precautions being taken to prevent evaporation of solvent. An aliquot part by volume of the filtrate was taken. Method (4) was similar to method (2), but was carried out at room temperature. Method (5) was substantially that described by Beach. The sample was shaken for 4 to 18 hours with an accurately measured volume of solvent, the remaining procedure being as in method (3). For convenience, the weights of samples were 10 to 30 g., depending on the quantity of rotenone known to be present. The volume of solvent in ml. used in the aliquot-part methods was about 10 times the weight of the sample in grams; in the multiple-extraction methods this volume of solvent was used for each successive extraction. In the aliquot-part methods the volume of the aliquot part taken was two-thirds of that of the original solvent. When carbon tetrachloride was not used as solvent, most of the solvent was recovered by distillation, the extract was evaporated to dryness, taken up in carbon tetrachloride, and again evaporated to dryness, this process being repeated two or three times. Occasionally, chloroform at room temperature extracted a small quantity of material that was insoluble in hot carbon tetrachloride; the carbon tetrachloride solution of the extract was then filtered hot and the residue was washed with hot carbon tetrachloride. Rotenone was crystallised from the extract as the carbon tetrachloride solvate by the procedure already published (Jones, *Ind. Eng. Chem., Anal. Ed.*, **1937**, **9**, 206–210). The residues from the multiple extractions were tested for rotenone by boiling for at least 1 hour with acetone, filtering, evaporating the filtrate to dryness, dissolving the extract in a quantity of acetone such that 1 ml. was equivalent to 2·5 g. of the original root sample, and testing portions of the solution by the modified Durham colour test (Jones and Smith, *Ind. Eng. Chem., Anal. Ed.*, **1933**, **5**, 75–76). The table gives results for a sample of powdered derris root extracted by these methods with various solvents.

Method	Solvent	Rotenone per cent.	Modified Durham colour test on the residue
Soxhlet			
Continuous for 24 hours	Carbon tetrachloride	6·2	Strongly positive
Flasks changed after 3 hours	Carbon tetrachloride	7·0	Strongly positive
Boiling—multiple extraction	Benzene	7·1	Medium positive
	Carbon tetrachloride	6·4	Strongly positive
	Chloroform	6·8	Faintly positive
	Ethylene dichloride	6·9	Faintly positive
	Trichloroethylene	6·7	Medium positive
	Ethyl acetate	6·7	Medium positive
	Benzene-alcohol azeotropic mixture	6·9*	Negative
Boiling—aliquot part	Benzene	6·9	—
Room temperature—multiple extraction	Chloroform	7·4	Medium positive
Room temperature—aliquot part	Chloroform	7·4	—
	Benzene	7·0	—
	Ethyl acetate	7·5	—

* Solvate very impure compared with that from other methods.

The room temperature—aliquot method with chloroform is recommended as being the most convenient. Extraction by this method is complete, as is shown by the facts that the results agreed with those by the benzene-boiling—multiple extraction method, the residues from which showed practically complete extraction, and that the residues from the chloroform—room temperature—multiple extraction method showed practically complete extraction. Beach's method, involving shaking for 2 to 3 hours followed by standing overnight and then another hour's shaking, gives almost complete extraction, but shaking overnight (about 18 hours) is recommended as being more convenient and assuring complete extraction. To obtain satisfactory results the samples must be ground sufficiently fine for at least 95 per cent. to pass a 60-mesh sieve. Samples containing a high ratio of rotenone to total extractives are more difficult to extract than those with lower percentages of rotenone. When the ratio of rotenone to total extract is about 40 per cent. or over, extraction at room temperature with successive portions of chloroform is necessary to obtain satisfactory extraction. This method should also be used as a check if there is any doubt as to the completeness of extraction by the aliquot part method. It is probably preferable not to dry the samples before extraction, though drying at room temperature, as in a vacuum desiccator, may be permissible. The moisture-content of samples received in the U.S.A. is, however, not sufficiently great to interfere with their analysis. E. M. P.

Spectroscopic Determination of Traces of Copper and of other Elements in Wire Grasses. L. L. Rusoff, L. H. Rogers and L. W. Gaddum. (*J. Agric. Res.*, 1937, **55**, 731–738.)—The spectroscopic determination of copper was carried out on the ash after mixing it with a known proportion of a cadmium salt to provide an internal standard. Grasses collected from areas on which cattle showed severe symptoms of "salt sickness" (a nutritional anaemia) and also from areas on which the animals were always healthy, showed no appreciable difference in copper-content, which ranged from 6·2 to 8 p.p.m. The following elements, which also showed no significant differences in amount as between the two areas, were found spectroscopically in traces in the samples of grass: aluminium, barium, boron, lead manganese, strontium, titanium and zinc. S. G. C.

Organic

Determination of Halogens in Organic Substances. J. A. Sanchez. (*J. Pharm. Chim.*, 1938, **27**, 5–18.)—The method involves dry oxidation with potassium permanganate in a sealed ampoule, followed by volumetric determination of the halogen in the aqueous extract. The combustion ampoules are about 10 cm. in length, made of resistant glass tubing 1·5 cm. in diameter and of 1 mm. wall thickness, closed at one end and drawn down to a narrow neck at the other. A 0·02-g. sample of the substance is intimately mixed in a small glass mortar with 0·8 g. of potassium permanganate and 0·25 to 0·3 g. of pumice powder. The mixture is transferred completely to a small piece of metal foil, and divided into approximately equal portions, which are transferred without loss into two similar ampoules. The ampoules are closed by sealing in a flame, and the contents are distributed evenly

along the length of each ampoule. For the combustion process, the ampoule is placed inside a copper tube, closed at one end, 25 to 30 cm. in length and 2 cm. in diameter. This tube is held horizontally by tongs and slowly moved through the flame of a Bunsen burner, the time of heating being 2½ minutes; it is desirable to rotate the tube axially during the heating to prevent the ampoule fusing and sticking to the copper tube. The two ampoules, after having been heated in turn and allowed to cool on a metal plate, are rinsed in distilled water and placed in a small bottle of fairly thick glass (200 to 300 ml. capacity) together with about 20 ml. of water; the bottle is closed with a rubber stopper and shaken to break the ampoules. The liquid is transferred to a beaker by rinsing out the bottle with water. The liquid is heated, and sufficient hydrogen peroxide is added to destroy the permanganate colour, leaving a precipitate of brown manganese oxides, which are then filtered off, washed with water, and rejected. The filtrate, which is alkaline, contains the whole of the halogen: chlorine as chloride, bromine as bromide and iodine as iodate. For the determination of chloride the solution is acidified with nitric acid, neutralised with a slight excess of calcium carbonate, and then titrated by the Mohr titration with the use of potassium chromate as indicator. For bromide, it is recommended to distil the liquid after the addition of manganese dioxide and 20 per cent. of sulphuric acid, the bromine being received in potassium iodide solution and the liberated iodine titrated with standard sodium thiosulphate solution. For iodate, the solution is first boiled to destroy any hydrogen peroxide present, and the iodate is then determined in the usual way by the addition of acid and potassium iodide and titration with standard thiosulphate solution. Good results were obtained in tests with a number of organic halogen compounds, including compounds such as hexachlorobenzene, which give rise to difficulties in the Carius method. S. G. C.

Detection and Determination of Traces of Formaldehyde. J. M. Hambersin. (*Bull. Soc. Chim. Belge*, 1937, **46**, 519–524.)—Several workers in the past have recorded the colour-reaction of formaldehyde with α- or β-naphthol, but the formation of precipitates by these reagents observed by the present author has not hitherto been described. Qualitative tests were therefore carried out by adding 5 ml. of sulphuric acid (sp.gr. 1·84) to a mixture of 0·1 to 0·5 ml. of the sample to be tested and 5 ml. of a solution (saturated at 20° C.) of α- or β-naphthol in such a way as to form a separate layer with a sharp zone of separation. With acetaldehyde a yellow and a brown-yellow colour, respectively, was obtained at the zone of separation, the sensitiveness of the reaction being 0·075 mg. The respective colours with formaldehyde were pale blue and green, the acid layer being coloured rose with β-naphthol. This rose colour was apparent with 0·0025 mg. of formaldehyde and, unlike the green colour of the separation zone, its intensity was proportional to the amount of formaldehyde present, although when this was increased to 0·0375 mg. a precipitate resulted. For the quantitative test a range of colour standards corresponding with 0·0025 to 0·0300 mg. of formaldehyde was freshly prepared in test-tubes as described above, and the colour match was made after gently shaking the tubes so as to distribute the colour uniformly throughout the bottom layer without, however, allowing the two layers to mix. The degree

of accuracy obtainable was 5 to 15 per cent. For gravimetric work the solution of β-naphthol should first be cooled to a few degrees below the temperature at which filtration is to take place and then filtered clear. The sulphuric acid (25 to 30 ml.) is added slowly to a mixture containing the formaldehyde (*e.g.* 5 mg.) and 100 ml. of reagent, and after it has been shaken vigorously, the mixture is boiled for a few minutes, so that the precipitate flocculates, leaving the liquid clear. On the next day the mixture is filtered off on a tared Gooch crucible, and the precipitate is washed with cold water, and, finally, 3 times with hot water in order to remove any β-naphthol which may have crystallised out. As the result of 10 experiments in which 0·00224 to 0·01518* of formaldehyde were used, it was found that the ratio of the weight of precipitate to that of the formaldehyde taken is 10:1, and on this basis the amount of the aldehyde could be determined with an error of − 7·7 to + 2·6 per cent. The precipitate (m.p. 171° C.) appears to be a formic acetal of β-naphthol; it is very soluble in ether or alkali solutions, slightly soluble in alcohol or benzene, and insoluble in water or moderately strong sulphuric acid; it is decolorised by ammonia but not by sodium or potassium hydroxide, and it is soluble in acetic acid, producing a yellow colour. The results were checked by the iodine method, and also by converting the formaldehyde into aldoxime by means of hydroxylamine hydrochloride and titrating the hydrochloric acid liberated. Under the conditions of the method acetaldehyde does not give a precipitate, although when the solution is cooled a light yellow precipitate, soluble in warm water, separates. Formaldehyde may therefore be determined in the presence of acetaldehyde if the precipitate is washed well with hot water, the maximum recorded error, using 0·00892 and 0·0080* respectively, being +8·83 per cent. J. G.

Determination of Ethyl Phthalate in the Presence of Essential Oils, and Natural and Synthetic Perfumes. Y. R. Naves and S. Sabetay. (*Bull. Soc. Chim.*, 1937, **5**, 102–105.)—The following two methods are recommended for the determination of ethyl phthalate in perfumes and balsams. *As dipotassium phthalate.*—One to 2 g. of the sample are boiled under reflux for one hour with an excess (*e.g.* 25 ml.) of *N*/2 potassium hydroxide solution in commercial absolute alcohol (99·7 to 99·9 per cent.) in a conical flask immersed in a water-bath and provided with a cooling tube. After an hour's boiling the cooling tube is rinsed with 5 to 10 ml. of absolute alcohol, which is added to the saponification liquor. The flask is cooled on ice and the precipitate is centrifuged and filtered on to a small Buchner funnel or a G3 or G4 glass crucible. It is then washed with 30 to 50 ml. of ice-cold absolute alcohol and heated in an oven at 140° C.; or it may be moistened with water and then heated to constant weight at 105°–110° C. If treated in this way the precipitate contains no alcohol. The weight of precipitate obtained, multiplied by 0·917, gives the weight of ethyl phthalate in the sample. If other acids, the potassium salts of which are insoluble in alcohol, are present, it is necessary to ascertain (*e.g.* by the formation of phenolphthalein, resorcinol or eosin) if the precipitate contains any potassium phthalate. Pure Peru balsam yields a precipitate consisting of a mixture of benzoate and cinnamate. *As lead*

* For the gravimetric method the weights given are presumably in grams.—J. G.

phthalate.—This method is valid only in the absence of oxalates, citrates, phosphates and esters which form lead salts insoluble in water. The precipitated potassium salt is dissolved in 30 to 50 ml. of water and treated with 2 ml. of acetic acid. Any precipitate which forms is removed by filtration or centrifuging and the liquid is preferably extracted with benzene. The aqueous extract is treated almost at the boiling point with 30 ml. of 10 per cent. lead acetate solution, cooled, decanted several times and filtered. The precipitate is washed with cold water containing a few drops of acetic acid until the washings give no precipitate of lead iodide with potassium iodide (the minimum quantity of water should be used), and dried to constant weight at 105° C.—110° C., or, preferably, at 140° C. The weight of the precipitate, multiplied by 0·7335, gives the quantity of ethyl phthalate, with an error of +10 to 20 per cent. The identity of the lead salt is ascertained by the formation of phthaleins.

For the analysis of Peru balsam the lead phthalate method is recommended, as the balsam contains benzoates and cinnamates which yield potassium salts insoluble in alcohol. With one sample, 1·9235 g. of the balsam gave 0·4655 g. of salts insoluble in alcohol and no trace of lead phthalate, whereas 2·0275 g. of a commercial "colourless" balsam yielded 1·3369 g. of alcohol-insoluble potassium salts and 2·3020 g. of insoluble lead salts, corresponding with 1·2125 g. of ethyl phthalate (59·8 per cent.). The presence of lead phthalate was confirmed by the formation of fluorescin. E. M. P.

Separation of the Highly Unsaturated Acids of Fish Oils by Molecular Distillation. E. H. Farmer and F. A. Van den Heuvel. (*J. Soc. Chem. Ind.*, 1938, **57**, 24–31.)—The separation of the highly unsaturated acids of fish oils has been partly solved by molecular distillation in a Waterman-type still. The thoroughly de-gassed methyl esters of the mixed unsaturated acids from cod-liver oil are allowed to flow downwards in a thin film over the surface of a heated vertical glass cylinder. The inner side of a glass cylinder, co-axial with the first, and arranged at a suitable distance, acts as a cooling surface, and the intermediate space is evacuated to about 10^{-4} mm. of mercury. As the film flows downwards it emits molecules which condense on the cooling surface and run down into a receiver, whilst the undistilled residue of oil falls from the bottom of the heated surface into a second receiver. Separation factors for a continuous still, which are given in detail, include ratio of condensation for two substances and factors governing it, vapour pressures of fatty acids, separation ratio of long chain fatty acids or esters, and other factors affecting the degree of separation. In the experiments on cod-liver oil the mixed unsaturated acids were obtained by the lithium soap—acetone treatment of the total fatty acids and weighed 950 g. A preliminary distillation without fractionation gave 900 g. of distillate, which was fractionated with the distilling surface successively at 56°, 66°, 82°, and 95° C., the residue on each occasion except the last being subjected to distillation at the next highest temperature. A second fractionation was carried out with the surface successively at 45°, 56°, 66°, 77°, 82°, 95°, and 100° C. Four fractions in all were obtained, with about 350 g. of material as connective fractions and distillable residue. The first fraction (225 g.) represented the ester of practically

pure C_{22} acid; this was confirmed by the hydrogen value, analytical data and X-ray examination. The third (110 g.) and fourth (83 g.) fractions gave immediately, on hydrogenation, esters of C_{18} and C_{16} acids, respectively, of a very satisfactory degree of purity; the second fraction (131 g.) has not yet been completely examined. Isomerisation or polymerisation cannot be appreciable in this method, since the highest temperature employed has been 110° C., and the average time of contact with the heated surface only about 15 seconds per distillation. A satisfactory separation of the mixed acids into fractions which are homogeneous as regards chain-length of the component acids is accomplished in two fractionations. It is shown that the principal acid of cod-liver oil, and with little doubt of Japanese sardine oil, is the C_{22} hexaene, acid, and not the pentaene (clupanodonic) acid. Clupanodonic acid appears to be absent from both cod-liver and Japanese sardine oils, at least in significant amounts, and is regarded as a heat alteration product. The relation of the hydrogen value (or iodine value) of the fish oil acids to the refractive index affords a means of distinguishing original acids and their heat-altered derivatives, for on plotting one against the other, a straight line is produced unbroken until a point corresponding with the C_{22} hexaene acid is reached, after which it continues in a new direction. The implications of this break have been worked out, and it is assumed to express a definite natural relationship between structural and physical properties of the component acids, so that by referring to the curve it can be determined with some confidence if a given product was an original component of the mixed fish oil acids or only one altered by heat. Clupanodonic acid is seen to lie remote from the curve.

D. G. H.

Course of Hydrogenation in Mixtures of Mixed Glycerides. W. J. Bushell and T. P. Hilditch. (*J. Chem. Soc.*, 1937, 1767–1774.)—When mixtures of palmito-di-unsaturated glycerides and tri-unsaturated glycerides, such as form the bulk of such natural fats as cottonseed oil and pig depot fat, are hydrogenated, the first group is largely converted into palmitostearins before any tristearin is formed, and the present work seeks the explanation. A number of mono-oleo-disaturated glycerides were prepared synthetically and from natural products, binary mixtures were made up containing equal amounts of, *e.g.* an oleodistearin and an oleodipalmitin, the mixtures were hydrogenated halfway to complete saturation, and the composition (the tristearin-content) was determined. The results showed that the suggestion tentatively advanced before that the position of the oleic group in the glyceride molecule affects the ease with which it undergoes hydrogenation, is incorrect. Mixtures consisting of equal parts of mono- and di-oleo, mono- and tri-oleo or di- and tri-oleo glycerides, were then hydrogenated to the point where the mixture should contain approximately 50 per cent. of fully saturated and 50 per cent. of mono-oleo disaturated glycerides. Results showed that, in the main, the more unsaturated component of the mixture is attacked first and is hydrogenated until both components reach the same degree of unsaturation, after which hydrogenation proceeds simultaneously and indiscriminately. However, hydrogenation of a less unsaturated component proceeds to some extent while the more unsaturated components are still being reduced to that stage.

This is shown by experiments in which (*a*) α-oleodipalmitin and triolein and (*b*) α-palmitodiolein and triolein were hydrogenated to iodine values of 25 and 29, respectively (*i.e.* degree of unsaturation corresponding approximately with that of mono-oleo-disaturated glycerides alone). No tristearin was present in either mixture, and the fully saturated glyceride content was 17 and 14 per cent., that is to say, by the time the average unsaturation was reduced to that of mono-oleo-disaturated glycerides, 25 to 30 per cent. of the less saturated components (but none of the triolein) had been transformed into completely saturated glycerides. All unsaturated components in a mixture of glycerides are thus attacked concurrently during hydrogenation, but reduction of the more unsaturated compounds is more rapid until uniformity is reached. The extreme degree of apparent selectivity shown in the production of palmito-glycerides during hydrogenation of such fats as cottonseed oil and pig depot fat is shown to be due to the higher proportion of palmito-oleo-glycerides present (75 and 80 per cent., respectively, instead of 50 per cent.), superimposed on other influences. For, on altering the proportion of the components in mixtures of α-oleodipalmitin or α-palmitodiolein with triolein, results were obtained resembling exactly those observed in the hydrogenation of the above-mentioned fats. For example, 50 per cent. of α-oleodipalmitin and 50 per cent. of triolein hydrogenated to an iodine value of 15·8 gave 52 per cent. of fully saturated glycerides containing 39 per cent. of tristearin, whilst 75 per cent. of tri-oleo product and 25 per cent. of triolein hydrogenated to an iodine value of 16·5 gave 44 per cent. of fully saturated glyceride with only a trace of tristearin. D. G. H.

Properties of Linolic Acids prepared by Debromination and by Low-Temperature Crystallisation, with a Proposed Method of Quantitative Estimation. J. B. Brown and J. Frankel. (*J. Amer. Chem. Soc.*, 1938, **60**, 54–56.)—α-*Linolic acid* was prepared by fractional crystallisation of the fatty acids of maize (corn) oil. The unsaturated fatty acids of the oil were brominated in cold ether, and excess of bromine was removed by washing with sodium thiosulphate solution. After the solution had been dried and most of the ether had been distilled off, the tetrabromides were precipitated with petroleum spirit and purified by four re-crystallisations from petroleum spirit at −20° C. They contained 52·9 per cent. of bromine (cal. 53·3) and had m.p. 114·5° C. One hundred and eighty-five g. of these bromides were added gradually to 1500 ml. of hot 95 per cent. alcohol, and 200 g. of zinc powder in a 3-litre flask, a few drops of conc. hydrochloric acid being added from time to time as catalyst. The alcohol was kept boiling by the heat of the reaction. After addition of all the bromides the mixture was heated under reflux for 30 minutes, and the alcoholic solution was then filtered and acidified with hydrochloric acid. Three-quarters of the alcohol were removed under reduced pressure, water and ether were added, the ethereal layer was separated, and the ether distilled. The resulting mixture of linolic acid and ethyl ester was distilled under reduced pressure, the product was saponified with alcoholic potassium hydroxide, and the pure linolic acid was recovered and distilled. *Linolic acid* may be prepared by low-temperature crystallisation from maize (corn) oil (*J. Amer. Chem. Soc.*, 1937, **59**, 3) by dissolving 2 kg. of the un-

saturated acids of the oil, prepared by acetone procedure at −20° C. (about 67 per cent. of linolic) in acetone (75 g. per litre) and crystallising in 2-litre batches at −50° C. in a bath of dry ice and alcohol. The crystals were filtered off rapidly, and the filtrate was cooled to −70° C. The resultant crystals were warmed under reduced pressure to remove the acetone and distilled at 2–3 mm., about 70 to 80 g. of undistilled acids being left in the flask. The yield was 380 g., with a purity of about 93·5 per cent. The analytical data for (*a*) α-linolic acid prepared as described, and (*b*) crystallisation linolic acid were as follows:—m.p. (*a*) −6·8° C., (*b*) −7° C.; n_D^{20}, (*a*) 1·4691, (*b*) 1·4682; iodine value, Wijs, (*a*) 180·9, (*b*) 175·0; purity from iodine value, (*a*) 100, (*b*) 93·5; mean molecular equiv., (*a*) 282·9, (*b*) 281·5; tetrabromide value, (*a*) 90·6, (*b*) 86·8; purity from tetrabromide value, (*a*) 100, (*b*) 95·8. A method for the quantitative determination of linolic acid in a mixture of fatty acids, based on the tetrabromide value, is to weigh 1·5 to 2·0 g. of the fatty acids into a tared 50-ml. centrifuge tube and to add at once 30 to 35 ml. of low b.p. petroleum spirit. The tube is placed in an ice-salt bath and an excess of bromine is added, drop by drop, with constant stirring. After standing at 0° C. for at least 4 hours the mixture is centrifuged, 30 ml. of cold petroleum spirit are added, and the bromides disintegrated and stirred for 5 to 10 minutes in an ice-water bath. The washing is repeated 3 times, and the resultant tetrabromides are dried to constant weight. D. G. H.

Composition of the Seed Fat of *Trichosanthes cucumeroides*. H. P. Kaufmann, J. Baltes and H. Büter. (*Ber.*, 1937, **70**, 2535–2537.)—The seed-fat of *Trichosanthes cucumeroides*, a Japanese plant known as "Karasu uri," belonging to the *Cucurbitaceae*, has been examined. The presence of trichosanic acid was established by the isolation of its maleic anhydride compound. Oleic acid and linolic acid were also shown to be present. The oil and fatty acids had the following characteristics, respectively: diene value, 24·8, 26·7; thiocyanogen value, 77·8, 82·9; "partial iodine value," 139·8, 147·8. The fat contained 1·4 per cent. of unsaponifiable matter, and from the values of the constants the composition of the fatty acids was computed to be: trichosanic acid, 29·3; linolic acid, 42·1; oleic acid, 20·0; saturated acids, 8·6 per cent. F. A. R.

Determination of the "Hydrogenation-iodine Value" and its Application in the Analysis of Essang Oil. H. P. Kaufmann and J. Baltes. (*Ber.*, 1937, **70**, 2537–2544.)—The usual method of determining iodine values fails to give correct results when licanic acid is present, as this enolises. Then, too, some highly unsaturated acids are not fully iodinated, and with other acids some substitution occurs. The authors therefore recommend the measurement of the degree of unsaturation of oils or fatty acids by quantitative hydrogenation, using a platinum catalyst. A convenient apparatus for this purpose is described and illustrated. The amount of hydrogen absorbed per 100 parts of the fat is calculated in terms of the equivalent amount of iodine, and this value is termed the "hydrogenation iodine value." The results obtained are in close agreement with the theoretical values.

An examination of the seed fat of *Ricinodendron africanum*, a tree native to West Africa and belonging to the *Euphorbiaceae*, has been made. The seeds,

with the husk, contained 15 to 19 per cent. of fat, or, without the husk, 40 to 50 per cent. The presence of α-elaeostearic acid, linolenic acid, linolic acid and oleic acid was established. The mixed acids had the following characteristics: saponification value, 193·1; hydrogenation iodine value, 176·2; partial iodine value, 137·1; thiocyanogen value, 80·1; diene value, 41·2. From these the composition of the mixed fatty acids was computed to be: elaeostearic acid, 45·1; linolic acid, 17·4; oleic acid, 25·7; saturated acids, 6·4 per cent. The unsaponifiable matter amounted to 0·9 per cent. F. A. R.

Calculation of the Composition of Fats from their Constants. H. P. Kaufmann and J. Baltes. (*Ber.*, 1937, **70**, 2545–2549.)—The authors have devised a method of computing the composition of a mixture of fatty acids based on the determination of certain constants. The iodine value, or where this gives incorrect results, the "hydrogenation iodine value," is assumed to measure the total degree of unsaturation. The "partial iodine value," obtained by the use of bromine in carbon tetrachloride, is a measure of the total unsaturation, except with elaeostearic acid, which behaves towards the reagent as though it possessed only two double bonds instead of three. The thiocyanogen value corresponds with one double bond in oleic acid, linolic acid, licanic acid and elaeostearic acid, and with two double bonds in linolenic acid. The diene value corresponds with one double bond in licanic acid and elaeostearic acid, and is zero with acids containing no conjugated double bond system. If the qualitative composition of a fatty acid mixture is known, it is possible (according to the authors) to calculate the proportion of any of the above-mentioned unsaturated acids and (by difference) the total saturated acids from the above constants. Formulae are given for calculating the composition of various mixtures of acids.

[*Abstractor's Note.*—There is no indication in the paper that the method has been tested by applying it to mixtures of acids of known composition.]

F. A. R.

Relations between the Constants of Wood Oil. E. D. G. Frahm and D. R. Koolhaas. (*Rec. Trav. chim. Pays-Bas*, 1938, **15**, 79–89.)—Compounds with conjugated double bonds may be estimated in wood oil by the diene method of Diels and Alder (*Annalen*, 1928, **460**, 98), as improved by Ellis and Jones (ANALYST, 1936, **61**, 812–816). Iodine is used as a catalyst and heating is continued for 1 hour. In a large number of oils from *Aleurites montana* seed, the linear relation:—diene value $= 1400(n_D^{25} - 1{\cdot}4681)$ was found to exist for fresh oils. All the differences observed between the experimental and calculated diene values were within the error of observation. In oils with a high acid value the refractive index was lowered and the calculated diene number was too low, but the lowering was only 0·0002 for an acid value of 7·1; this is not sufficient to upset the correlation between diene value and refractive index. Other relations which were determined were:—bromometric iodine value $= 925(n_D^{25} - 1{\cdot}3414)$; Wijs iodine value $= 1300(n_D^{25} - 1{\cdot}3883)$; the dispersion measured with an Abbé refractometer, $n_F - n_C = 0{\cdot}25(n_D - 1{\cdot}4367) \pm 0{\cdot}0003$; time of gelation at 282° C. $= 71{\cdot}4 - 0{\cdot}857$ (diene value) $+ 0{\cdot}3$ (acid value). For the time of gelation the discrepancy between the observed and calculated values was usually not more than half-a-minute. In 70

fresh oils examined the difference was more than 1 minute in only 5 cases (maximum 2·3 minutes for an oil extracted with petroleum spirit). These formulae apply only to fresh oils, for polymerisation occurs as the oils become old. E. B. D.

Separation of Carbonyl Compounds from Waxes. H. A. el Mangouri. (*Biochem. J.*, 1937, **31**, 1978–1980.)—The method of Anchel and Schoenheimer (*J. Biol. Chem.*, 1936, **114**, 539) for separating ketones from unsaponifiable matter of animal origin by means of *p*-carboxyphenylhydrazine has been modified in order to make it applicable to the separation of ketonic substances from the unsaponifiable matter of waxes. A quantity of the material estimated to contain 0·2 to 0·5 g. of the ketone is added to 50 ml. of 95 per cent. ethyl alcohol containing 0·2 to 0·5 g. of purified *p*-carboxyphenylhydrazine, 0·3 ml. of acetic acid and 0·3 ml. of pyridine, and the whole is heated under reflux for 4 hours. After cooling, the mixture is run into 100 ml. of dilute hydrochloric acid to remove the pyridine, and the precipitated hydrazone is filtered off, washed with water, and dissolved in 80 ml. of boiling methyl alcohol. Two ml. of a saturated solution of calcium chloride in methyl alcohol and 10 ml. of a saturated solution of baryta in methyl alcohol are then added and boiling is continued for another ten minutes. The presence of the calcium chloride makes the precipitation of the barium salt of the hydrazone more complete. The mixture is filtered on a hot water funnel, and the residue is washed three times with boiling methyl alcohol. The barium salt is then decomposed with warm dilute hydrochloric acid, and the free hydrazone is extracted with ether. The ethereal extract is washed and distilled, and the residue dissolved in 15 ml. of warm 95 per cent. alcohol. The solution is heated for 5 hours beneath a reflux condenser with 0·25 ml. of 40 per cent. formaldehyde solution in order to split the ketone. The alcohol is distilled off, and the residue is partitioned between potassium carbonate solution and ether. The free ketone is obtained by distilling the ethereal layer. Any paraffin hydrocarbons or alcohols present are contained in the methyl alcoholic filtrates. Ketonic primary and secondary alcohols can be separated as easily as simple ketones, but the hydrazone is then not readily split by formaldehyde, and it is necessary to use alcoholic pyruvic acid. The method has been successfully applied, with yields of 75–80 per cent., to the isolation of *n*-nonacosan-15-one from cabbage-leaf wax. The following waxes were shown to contain no ketone: apple cuticle wax, tea-leaf wax, coffee-bean wax and sugar-cane wax. F. A. R.

Inorganic

Quantitative Separations by Means of Pyridine. E. A. Ostroumow. (*Ann. Chim. anal.*, 1938, **20**, 9–12.)—The author summarises his investigations on the separation of iron, aluminium, chromium, uranium, titanium and zirconium from manganese, cobalt, nickel, alkaline earths and alkalis (ANALYST, 1936, **61**, 723, 795; 1937, **62**, 495). Zinc cannot be separated by the agency of pyridine, the hydroxide precipitate being strongly contaminated with that metal. The operation is carried out in chloride solution substantially free from sulphate. The neutral solution, containing 5 to 10 g. of ammonium chloride per 100 ml., is stirred

and treated with dilute ammonia, added drop by drop until the liquid is slightly and permanently turbid; the cloudiness is removed with a few drops of dilute hydrochloric acid. After addition of methyl red, the liquid is heated almost to boiling, stirred vigorously, and treated dropwise with 20 per cent. pyridine solution until it turns yellow. If the precipitate prevents observation of the colour change, pyridine is added until its odour becomes pronounced. An excess of 15 to 20 ml. of precipitant is then added, and the beaker is left on the water-bath until flocculation is complete. If necessary, more pyridine is to be added at this stage. The precipitate is collected and washed with 3 per cent. ammonium nitrate solution containing a few drops of pyridine. The weight of the precipitable oxides should preferably not exceed 0·1 g.; the separation is claimed to be complete in one precipitation. W. R. S.

Analysis of Jewellers' Platinum Alloys. H. Holzer and E. Zaussinger. (*Z. anal. Chem.*, 1938, **111**, 321–337.)—The alloy is rolled out to a very thin sheet, which is carefully scoured, boiled with dilute hydrochloric acid, washed with alcohol, and dried by heating. A weighed quantity (0·2 to 0·4 g.) is dissolved in boiling *aqua regia*, fresh portions being used, if necessary, after decantation of the spent acid. The resultant solution is evaporated to dryness on the water-bath, and the residue is evaporated repeatedly with hydrochloric acid until free from nitric acid, a little sodium chloride being added. The final chloride solution is filtered, and the washed residue is ignited in a tared platinum crucible. After evaporation with hydrofluoric acid, the weight of metallic residue (if any) is added to the iridium result.

Base Metals and Gold.—The feebly acid filtrate is treated, drop by drop, at 60° C. with saturated sodium nitrite solution until evolution of gas ceases and the liquid has assumed a pale greenish-yellow tint. The solution is then boiled for 15 to 30 minutes, cooled to 60° C., and neutralised with sodium carbonate solution added, drop by drop, in presence of phenolphthalein until there is a permanent red tint. The precipitate is allowed to flocculate on the water-bath at about 60° C., collected, well washed with warm water, and extracted with dilute nitric acid; the base metals pass into the filtrate, whilst gold remains insoluble.

Palladium.—The alkaline nitrite filtrate is cautiously acidified with dilute hydrochloric acid, boiled until nitric oxides are expelled, and treated while boiling with hydrogen peroxide to ensure oxidation of any platinous salt. The liquid is treated at 60° C. with a freshly-prepared, hot-saturated aqueous solution of dimethylglyoxime. When precipitation is complete, the beaker is cooled in running water and allowed to stand for 30 minutes. The precipitate is collected and treated in the usual manner for the determination of palladium.

Rhodium and Iridium.—The filtrate from the palladium precipitate is boiled with hydrogen peroxide for the destruction of the precipitant, and divided into two. The first half is neutralised with sodium carbonate, diluted to 200 to 400 ml., treated with 20 ml. of 10 per cent. sodium bromate solution, and digested for some time at 70° C. A 10 per cent. sodium bromide solution is then added, drop by drop, and the liquid is heated to boiling, more bromate and bromide being added. The precipitate is left to settle on the water-bath. Iridium comes down readily as

a black precipitate, whilst rhodium requires one to two hours' boiling and gives an olive-green precipitate. In association, iridium induces more rapid precipitation of the rhodium. The precipitate is collected, washed with hot ammonium nitrate solution, and dried at 110° C. in a porcelain crucible. The crucible is covered with a perforated mica plate and heated to 180° C. in a stream of hydrogen. After reduction of the metal compounds the paper can be ashed as usual without risk of loss. The ignited metals are heated in hydrogen, cooled in carbon dioxide, and weighed. They should be tested for adsorbed alkali by lixiviation with water.

Rhodium.—The second half of the filtrate is treated in the same way as the first, but the washed hydrolysis precipitate is transferred (with the filter) to a 500-ml. conical flask, together with 15 ml. of strong sulphuric acid. The paper is destroyed by heating and adding a little nitric acid. After cooling, the acid is diluted and again evaporated until white fumes appear. The cold acid is diluted with 200 to 300 ml. of water and heated to boiling, and the rhodium is precipitated with titanous chloride solution acidified with hydrochloric acid, the presence of excess of reducing agent being ascertained by the bleaching of methylene blue added to the solution. The precipitate coagulates after more or less prolonged boiling. It is filtered off and dissolved (with the paper) in strong sulphuric acid, and the precipitation is repeated. The precipitate is dried, ignited in air and then in hydrogen, and cooled in an atmosphere of carbon dioxide. Iridium is found by difference.

Platinum.—The bromate-bromide filtrate is boiled and gradually treated with hydrochloric acid for the destruction of the bromate. It is neutralised with sodium carbonate and boiled, and the platinum is precipitated with hydrazine hydrochloride. The precipitate is ignited and weighed; it should be tested for adsorbed alkali by leaching with hot acidulated water. W. R. S.

Determination of Silicon in Steel. G. Charpy. (*Compt. rend.*, **1937**, **205**, 506–508).—The determination of silicon in steel, carried out for specification purposes, is discussed. Consideration of the results of numerous determinations made by experienced chemists by weighing the silica obtained after rendering it insoluble by the usual process of evaporating with acids showed that figures obtained could not be relied on to agree to within less than 0·02 per cent. Somewhat lower figures were obtained by the use of the hydrofluoric acid volatilisation process, in particular when aluminium had been used to deoxidise the steel, owing to the presence of alumina in the silica residue. The author considers that the only certain method for determining silicon in steel is to employ attack of the metal by chlorine gas, by which only silicon present as such in the steel is volatilised, whilst silicon present as silica dispersed in the metal is not included. No details of this method are given. The following example is quoted of silicon determinations in two steels deoxidised with aluminium, which were required by specification to contain less than 0·03 per cent. of silicon.

	Silicon, per cent.		
	(*a*) From weight of "silica residue"	(*b*) From HF volatilisation	(*c*) Chlorine volatilisation method
(1)	0·024	<0·01	<0·01
(2)	0·055	0·041	0·028

It is pointed out that steel (2) would be liable to rejection unless method (*c*) were used. The author concludes that complete details of any method of chemical analysis should accompany a specification. S. G. C.

Two Modifications of Cobalt Quinaldinate. N. K. Dutt. (*J. Indian Chem. Soc.*, 1937, **14**, 572–573.)—Anhydrous cobalt quinaldinate is red, whilst the dihydrate is cream-coloured. The addition of a neutral solution of a cobalt salt to a neutral solution of sodium quinaldinate in the cold yields a precipitate of the cream-coloured cobalt quinaldinate; on boiling the mixture the precipitate becomes granular, but does not change colour. When the solutions are acidified with acetic acid the yellow variety is precipitated in the cold, as before, but on heating the mixture on a steam-bath, the colour of the precipitate changes to red. Precipitation from hot acidified solution yields the red variety at once. In the absence of liquid the cream-coloured variety was stable on heating up to a temperature of 160° C., above which it lost water of hydration and changed into the red modification. It is suggested that the two molecules of water of hydration are directly attached to the central cobalt atom which has a co-ordination number of six; in the red anhydrous variety the co-ordination number of the cobalt is four. S. G. C.

Microchemical

Qualitative and Semi-quantitative Spot-tests using a Jena Glass Spot-plate. H. Schäfer. (*Mikrochimica Acta*, 1937, **1**, 144–153.)—Owing to its transparency a spot-test plate made of Jena glass ("Jenaer Glastüpfelplatte") is suitable for all reactions, no matter what the colour of the reaction products. The best background is either white or black. An advantage of these plates is that they may be used for fluorescence tests and microscopical examinations. They are very convenient for semi-quantitative work, such as, for example, the determination of iron as ferrocyanide or as thiocyanate in quantities of material containing from 1 to 5γ of iron, the determination of silver as chloride (7 to 24γ), silver with dithizone (0·13—1·7γ), barium as sulphate (2–10γ), and the determination of hydrogen ion concentration. For each determination about six comparison drops containing a known amount of the ion in question, throughout the expected range, are treated with the reagent under the same conditions as the unknown sample, which can then be compared with the standard solutions. J. W. M.

A New Melting-point and Sublimation Apparatus with Built-in Thermometer. L. Fuchs. (*Mikrochimica Acta*, 1937, **2**, 317–328.)—Heating blocks with thermo-electric measurement have several disadvantages, such as the high cost, the fact that the instrument must be very carefully calibrated, and the necessity for an ice-water mixture for the cold joint, or knowledge of the temperature of the cold joint. A good thermometer is as accurate and much simpler and cheaper. A model is constructed with a circular thermometer inserted in a groove in the hot plate, which is electrically heated. The sides and base of the hot plate are insulated, and during use the top surface is protected from the surrounding

air by a glass plate laid loosely over the top. The crystals are viewed in incidental light, so that a dark background is essential; this is supplied by a highly polished blackened metal plate, 2·5 by 2·5 cm. The crystals for melting-point determination are placed on this plate, between two thin cover-slips, and viewed under the microscope. For evaporation and subsequent sublimation the preparation is also placed between cover-slips in either of the two cylindrical pits (with black bases) in the hot plate. When the daylight is good no lamp is necessary. The base of the hot plate is made to rotate. The results of melting-point determinations show a maximum deviation of ±1° C. up to 200° C., and of ±2° C. from 200° C. upwards. (Apparatus made by Reichert, Vienna.) J. W. M.

Micro-determination of Water in Inorganic Substances. I. F. Hecht. (*Mikrochimica Acta*, 1937, **1**, 194–204.)—The apparatus is similar to the Pregl micro combustion apparatus, but is simpler in form, as oxygen is not necessary for the heating, and the absorption of carbon dioxide is eliminated; as in the Pregl method, a supply of pure air is necessary. There is a single-pressure regulator, containing distilled water, a bubble-counter and U-tube attached. The bubble-counter contains conc. sulphuric acid, and the U-tube is filled with magnesium perchlorate (anhydrone) which is used throughout for the absorption of water. The combustion tube is the newer model with side-arm attachment and is made of quartz (25 cm. long and 8 mm. in diameter). The only filling in the tube is a mixture of equal parts of lead oxide and lead peroxide to absorb any oxides of sulphur or hydrogen chloride or fluorine which might be liberated. This filling is kept in place by two small pads of glass-wool. No breaking device of compressed asbestos is required, as is necessary in the combustion of organic matter. The absorption tubes are U-tubes of the Friedrich type, with taps which may be turned off while the tubes are waiting to be weighed. Two similar absorption tubes are used in series, each filled with anhydrone. The second tube is used as a tare; in this way any errors due to temperature and pressure variation are eliminated, as more care is necessary in weighing than in the determination of hydrogen. The Pregl-Mariotte flask and protecting tube, filled with anhydrone in this instance, are retained. The combustion tube is heated by an electric furnace which gives a temperature up to 900°–950° C. For special purposes this is replaced by a furnace with platinum windings, instead of nichrome; this attains temperatures of 1200°–1400° C. The portion of the tube containing the lead oxides is heated with the usual constant-temperature bath to 180°–190° C. Samples of about 10 mg. are used, unless an exceptionally high water-content is expected. The samples are weighed in a platinum boat which is inserted in the middle of the combustion tube, where the temperature is the highest; after the boat a small diffusion body of quartz, which has just been glowed out in a Bunsen flame, is placed in the combustion tube. This serves to prevent any back diffusion of water. The heating is carried out with a gas flow of 4 ml. per minute. This may be increased to 5 ml. per minute when the water is seen to be coming over. The metal hook for heating the constriction at the entrance of the absorption tube, as in the Pregl method, is essential. The electric furnace heating is discontinued after 25 minutes, and air is passed through for a further 10 to 15 minutes. The absorption tube and tare are

wiped in the usual way after they are disconnected, but the dry chamois leathers must not be over-dry. After the tubes have stood for 15 minutes near the balance the taps are opened for 10 to 15 seconds, and the tubes then left for a further 10 to 15 minutes hung on the balance and then weighed. Three analyses of water-content of a mineral gave values 1·61, 1·59, 1·67 per cent. as compared with the macro value (H. F. Harwood) 1·48 per cent. Other determinations on Merck's potassium hydrogen carbonate gave 8·96 per cent.; theoretical, 8·99 per cent. J. W. M.

Volumetric Determination of Poly-hydroxy Alcohols. R. Rappaport, I. Reifer and H. Weinmann. (*Mikrochimica Acta*, 1937, **1**, 290–299.)—Both periodate and iodate may be determined in the same sample. The iodine set free in the presence of potassium iodide at a *p*H range 4·4 to 7 corresponds with the periodate present. After acidification the iodine corresponding with the iodate (both that originally present and that formed) is set free on the addition of potassium iodide and titrated with thiosulphate. Glucose may be determined both in acid and alkaline solution by the periodate method. The glucose is oxidised with periodate on the water-bath, whereby periodate is reduced to iodate. The excess of periodate is then determined iodimetrically after cooling. The reagents required are: (1) A solution of crystalline potassium iodate containing about 1 g. per 1 litre. (2) Dilute (5 per cent.) sulphuric acid. (3) *N* potassium carbonate solution. (4) A 12 per cent. solution of secondary potassium phosphate. (5) Buffer mixture for the determination in alkaline solution: 3 g. of secondary potassium phosphate and 2 g. of primary potassium phosphate are dissolved in water and made up to 100 ml. (6) Pure potassium iodide. (7) A 0·25 per cent. starch solution. (8) A 0·005 *N* thiosulphate solution. *Method.*—The acid sugar solution (about 150 mg. per litre) is measured into Hagedorn–Jensen sugar-tubes, and 10 ml. of a mixture of 8 ml. of reagent (1) and 2 ml. of reagent (2) are added to each sugar-tube and to 3 blank tubes. All the tubes are heated for 20 minutes on the water-bath, and, after cooling, 4 ml. of reagent (4) are added, followed by a crystal of potassium iodide; the liquids are then thoroughly mixed and the titration is carried out. Sorbitol and mannitol can also be determined by this method. Sorbitol may be determined in the presence of dextrose by determination of the dextrose by the usual Sujita–Iwataka method (see Rappaport, *Mikrochemie des Blutes*, Vienna, 1935, p. 135), followed by the determination of the sum of sorbitol and dextrose by the periodate method. Galactose may be determined similarly, but the oxidation can be effected only in acid solution. The determination of galactose in the presence of sorbitol (or mannitol) is carried out in the same way as the determination of dextrose in the presence of sorbitol (or mannitol). Good results are obtained. J. W. M.

Microchemical Examination of Explosives and Ammunition. A. A. Azzam. (*Mikrochimica Acta*, 1937, **2**, 283–286.)—Spot tests are successfully applied to detecting nitrate, ammonium salts, chlorate, aromatic nitro-compounds, nitric acid esters and the combustion products of black gunpowder, either in gunpowder and explosives, or in the residual traces left on textiles or other objects. Some brands of shot contain traces of silver, detectable by the rhodanine spot-test;

this sometimes enables the different origins of different shot to be established. There are also variations in the amounts of bismuth, arsenic and antimony in shot. Comparative tests for these elements enable different types of shot to be distinguished. J. W. M.

Physical Methods, Apparatus, etc.

Benzene-d_6 as a Solvent for Optically-active Substances. H. Erlenmeyer and H. Schenkel. (*Helv. Chim. Acta*, 1938, **21**, 114.)—The authors have previously shown (*id.*, 1936, **19**, 1199; *Nature*, 1936, **138**, 547) that the number of deuterium atoms which replace atoms of ordinary hydrogen in the racemisation of mandelic acid when heated at 140° C. in deuterium oxide is in accordance with Hund's modification of Werner's classical theory of the transformation. It was also found in the course of these experiments that the compound containing the deuterium had a lower [α] than the corresponding ordinary hydrogen compound, and this conclusion was confirmed by L. Young and C. W. Porter (*J. Amer. Chem. Soc.*, 1937, **59**, 328) for *d*-hexyl methyl carbinol-d_1, and for α-methyl benzylamine-d_2. The present authors have also shown (*Helv. Chim. Acta*, 1936, **19**, 1381) that a solution of methyl isopropyl phenyl benzyl ammonium nitrate in deuterium oxide has an $[\alpha]_D$ 0·86 ± 0·25° less than that obtained in ordinary water. In the present instance the experiment has been extended to comparisons of solutions of mandelic acid methyl ester in ordinary benzene and in benzene-d_6 (cf. *id.*, 1935, **18**, 1464), both solvents being dried over fused calcium chloride and distilled before use. The respective values obtained were $[\alpha]_D^{20}$, 174·78 ± 0·13° and 173·44 ± 0·26°; $[\alpha]_{5105\cdot6}^{20}$, 252·88 ± 0·13° and 251·32 ± 0·26°. The ratio $[\alpha]_D$ $C_6H_6/[\alpha]C_6D_6$ is therefore 1·008 for the D-line and 1·006 for the line 5105·6. J. G.

Estimation of Medullation in Wool Samples. P. R. McMahon. (*J. Text. Inst.*, 1937, **28**, 349–360T.)—Elphick's method (ANALYST, 1933, **58**, 109), in which medullation is rendered visible by cleaning a small staple of wool in petroleum spirit, teasing it out into a thin film of fibres, and immersing it in benzene over a black background, does not lend itself to quantitative work because of the large personal factor involved, particularly in calculating the percentage of medullated fibre in the staple, and in weighting the result arbitrarily according to the type or grossness of the medullae. The method has been improved by the present author, who estimated the total length of medullated fibre in the sample, instead of the percentage of medulla by volume. A photographic standard was prepared, having narrow zones and showing the appearance in benzene of various percentages of medullated fibre at a standard degree of teasing of 300 fibres to the inch. The results agreed well with those obtained by direct counts, but although simple, was too slow for routine use. The fact that when immersed in benzene, hair reflects considerably more light than wool was next used, a linear relationship being established between the light reflected and the percentage volume of medulla calculated from measurements of sp.gr. (see below). The apparatus finally adopted consisted of a tray containing the benzene, in which the sample was immersed, made from a slab of opal glass with a flashed black surface; by drilling through the black flashing until a small dot of white opal was visible, a known area,

for scanning purposes, could be made. Uniform illumination was provided by four 200-watt Phillips' "Argenta" bulbs, supplemented by suitable matt reflectors, a resistance and voltmeter being used to maintain constant conditions; these illuminated an area far larger than necessary, but produced the desired degree of uniformity. The light reflected vertically from the sample was received in a velvet-lined box supported over the specimen, and it passed via a projection condenser (Bausch and Lomb, PM 25, diameter 5·25 inches, focal length 4 inches) to a Weston "Photronic" photo-electric cell in circuit with a Cambridge galvanometer. The n_D^{20} of the benzene used should be between 1·490 and 1·495. In making a test the illuminating system is adjusted so that the deflection of the galvanometer is independent of the object in the tray, and the galvanometer is then set to zero with the tray in position, and the deflection is noted when a standard reflecting surface, such as a grey enamel plaque, is immersed in the benzene. The sample to be tested is rinsed in petroleum spirit to remove grease and dirt, teased out to a constant thickness (see below), and allowed to dry in air. It is then submerged in the benzene, air-bubbles being avoided, and the deflection of the galvanometer is read; another reading is then taken, using the standard plaque. It is desirable that the samples should be conditioned in air of controlled humidity before the test, but so long as the variations in the humidity of the air are not abnormal, the error they produce does not exceed 5 per cent., and then only with strongly-medullated samples for which the accuracy is not of such great importance. Tables show the effects on medullation of storage over calcium chloride for 5 months, and of variations in the thickness with which the sample is spread out in the tray. For rapid work grey enamel plaques, calibrated against wools having known degrees of medullation (as determined by the sp.gr. method, see below), may be used as standards; 400 samples per day, equivalent to about 60 sheep, may be evaluated. Tables give typical results, and photographs show the corresponding degrees of medullation measured; the reproducibility after an interval of 3 weeks is satisfactory. If the photo-electric index of medullation is expressed in cm. per g., the approximate range of values encountered in practice falls between 2·0 for samples of pure wool and 50 cm. for very hairy material. Since this method is empirical, and should therefore be standardised, the possibility of determining the sp.gr. of the wool in a liquid which the fibre does not absorb was also investigated. The samples were cleaned for 15 minutes each time in 3 portions each of benzene at 45° C. and water at 55° C. (*cf.* Roberts, *J. Text, Inst.*, 1930, **21**, 127T), and dried in sp.gr. bottles in a current of air at 105° C. until a 2-g. sample was constant in weight to within 0·1 mg. "Pure crystallisable" benzene was dried over calcium chloride and added to the wool in the bottle, care being taken to avoid the presence of water vapour, and by loose packing of the wool, any air; any very small bubbles were removed by means of a long hypodermic syringe. A spring balance was used to insert the stopper of the bottle with a constant force, and a ground-glass cap was then placed over the neck of the bottle to minimise evaporation. After 60 minutes at 25° C. the bottle was weighed with the usual precautions, the estimated error of the determination being 0·05 per cent. The percentage air-space was calculated from the formula $100\ (D—D')/D$, where D and D' are the sp.gr. of pure keratin (*i.e.* 1·3008 g./ml., 25°/4° C.) and of the medullated sample,

respectively. It is assumed that the density of wool free from medulla is constant, regardless of origin (*cf.* King, *id.*, 1926, **17**, 53T). Tabulated results show that a sp.gr. of 1·3008 for pure wool (percentage air-space, 0) corresponds with a photo-electric index of 2·1, whilst the corresponding figures for a strongly-medullated fibre are 1·2230 (percentage air-space, 5·99) and 40·6 cm. per g., respectively, the relationship between the index and the air-space being found to be approximately linear. The photo-electric method is therefore preferable to determinations of the surface-area of the medullae. Departures from linearity are not due to fundamental shortcomings of the optical method so much as to variations in *D* arising from penetration of the benzene into the medullae. The method was designed originally for fleece wool, but it has been found equally suitable for use without modification, for the examination of tops. J. G.

Reviews

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY. Vol. XVI. By J. W. MELLOR, D.Sc., F.R.S., Pp. x + 811. London: Longmans, Green & Co. 1937. Price 3 guineas.

This is the completing volume of "Mellor's Comprehensive Treatise." Half of the volume deals with the intricate chemistry of platinum, whilst the General Index of the whole treatise occupies upwards of 400 pages. Noteworthy features of the chapter on platinum are: extraction, the qualitative and quantitative analysis of platinum ores and alloys, and the physical properties of the metal. A perusal of the discussion of the few simple platinum salts soon reveals how much confusion still exists regarding their nature and constitution. By far the greater amount of the text deals with the multitude of the perplexing complex compounds of platinum, a large number involving organic bases. Here the author has departed from his nomenclature, and has named and classified these compounds along the lines of the Werner Co-ordination Theory.

The General Index has been prepared by Miss E. M. Rigby. So far as can be ascertained, she has carried out her work very efficiently, for the index is certainly exhaustive. She has, however, been handicapped by the ugly and cumbersome nomenclature which Dr. Mellor has thought fit to use throughout his sixteen volumes, and in consequence the index has assumed a terrifying appearance, and is of much less value to the ordinary chemist than it might have been. Such entries, for example, as "ammonium dihypovanadatodivanadatoctocosimolybdate" appear unintelligible. Surely the index would have been of greater assistance if chemical formulae had been substituted for the names and the various compounds classified accordingly.

Despite the nomenclature, "Mellor's Comprehensive Treatise" is a remarkable and most valuable work. Here and there the text tends to be nothing but a register of chemists' names with but little indication of their respective contributions to the subject; lack of adequate space may have made this inevitable. These lists, irritating as they may be to the general reader, are of fundamental value to the research chemist.

Dr. Mellor must feel great relief now that his great treatise is nominally finished; yet in the preface to the present volume he states that three supplementary volumes are being prepared.

The heartiest congratulations and thanks of all chemists are due to Dr. Mellor on bringing so ably the "ordered treatment" of inorganic chemistry to "its appointed goal." H. T. S. BRITTON

CATALYTIC PROCESSES IN APPLIED CHEMISTRY. By T. P. HILDITCH, D.Sc., F.I.C., and C. C. HALL, M.Sc., Ph.D., A.I.C. General Editor: E. H. TRIPP, Ph.D. Second and Revised Edition. Pp. 478. London: Chapman & Hall. Price 25s.

No better exemplification of the continuous extension of catalytic processes in chemical industry can be obtained than from a comparison of the first edition, published in 1929, with the present volume. During the last ten years we have witnessed the establishment of new industries founded on new products based on polymerisation processes in which catalytic actions are all-important although not understood. As a result both of world, and especially of national economic considerations, large quantities of new fuels and lubricating oils are manufactured both from coal, olefines and the hitherto wasted "methane" fractions of the oil industries. These all owe their successful operation to the suitable choice of catalysts. It is interesting, likewise, to observe how, with the growing complexity of civilisation, industrial catalytic processes, once confined to the two large branches of chemical manufacture, namely, the heavy chemical and the biochemical divisions, are being utilised in increasing extent in the production of new organic chemicals which may be regarded as literally designed and constructed to fulfil certain specific purposes. One need only mention the newer detergents, disinfectants, and chemicals for various operations in the paint and textile industries to see how specific head groups in organic molecules are employed to attain definite chemical or physico-chemical ends.

After a general introduction the book includes a very readable survey of the manufacture and utilisation of hydrogen and hydrocarbons in the diverse reactions that have achieved technical application and of fermentation processes, and gives examples of homogeneous catalysis in liquid systems.

Perhaps the weakest section in an otherwise excellent book is the section devoted to the general principles of catalytic action. It is admittedly a difficult problem to write on general principles in chemical reactions at the present time, for we must note the great extension of possible methods of attack, both by the quantum theory, especially in orbital form, and by the transitional state concept applied to statistical mechanics, in supplementing or indeed replacing the two older methods based respectively upon the concepts of free energy and on the principles of molecular kinetics. It is true that in any method of attack where velocities are concerned it is necessary to know the detailed reaction mechanism so as to be able to calculate the collision frequency or the configuration of the transition complex, but it is just at this point, namely, the detailed reaction mechanism, that our knowledge of heterogeneous catalytic reactions is weakest.

Even in a simple catalytic reaction, such as the hydrogenation of ethylene or of oxygen at a metal surface, there is still a wide divergence of opinion as to the exact mechanism. Admittedly, more is known about the possible states of "adsorbed" gases, but the problem of interaction of two gases in the "adsorbed" phase or phases still presents many problems in which imagination may have full play.

In view of the attempts to obtain international uniformity in symbolism, it is a pity, in the reviewer's opinion, that the authors have adopted A as the symbol for "heat of activation," which is identified with, but may in reality be only equivalent to, the energy of activation. The book is very readable and well printed, and contains a surprising amount of information of value and interest to those occupied with catalytic problems. ERIC K. RIDEAL

CHEMISCHE ANALYSEN MIT DEM POLAROGRAPHEN. By Dr. HANS HOHN. Pp. 102. Leipzig: Julius Springer. 1937. Price RM.7.50 (unbound).

When the dropping mercury cathode was first used by Heyrovsky in 1923, to study the deposition of metals, the device was regarded as of academic interest only, but in the course of time it became evident that it was capable of providing a means for the detection and quantitative determination of certain ions in concentrations as low as 10^{-6} molar. The principle of the method is that a gradually increasing *E.M.F.* is applied to a cell with a dropping mercury cathode and a stationary anode, containing the solution under investigation, and the variation in current strength is observed. The discharge or reduction of each ionic species is accompanied by a rapid increase of current, the magnitude of which is related to the concentration of the ion in the solution. In the apparatus known as the polarograph, the gradual alteration of *E.M.F.* and the photographic registration of the current strength are carried out automatically, and the record obtained shows a series of waves; the height of each wave is proportional to the concentration of a particular ion. Reducible substances, other than ions, such as aldehydes, ketones and nitro-compounds, behave like ions and give definite waves. The polarograph presents, at least in theory, a simple method for micro-analysis or for the detection of traces, which is rapid and permits of several substances being determined simultaneously. It must be admitted, however, that the technique is by no means as simple as it sounds and, as workers with the apparatus will know, the polarograph sometimes behaves in a manner unaccountable to the beginner.

The book under review is, therefore, to be welcomed because it describes fully the details of manipulation of the dropping mercury cathode and explains what precautions must be taken in order to obtain reliable results. The author is associated with the famous smelting works at Duisburg, and his outlook is essentially that of the practical man. The book opens with a description of the principles and construction of the polarograph, and this is followed by twenty-eight experiments showing its possibilities and enabling the technique to be acquired. The author then gives examples of the application of the polarograph in the analysis of rocks, wines, mixed acids, boiler water, aluminium, brass,

German silver, and paper dyes. Very full references are given throughout the book to original papers. Every analyst who is contemplating the use of the polarographic method should certainly have a copy of this book; it will save him both time and anxiety. S. GLASSTONE

REPORT ON THE BRITISH HEALTH SERVICES. By the Health Group of P.E.P. (Political and Economic Planning). Pp. 430. Bound in paper boards, 7s. 6d.; in cloth, 10s. 6d.

This Report is published by an independent group of over one hundred working members of differing vocations, and aims at assembling, as completely as possible, the essential facts about the health services and their contemporary problems, with a view to breaking down sectionalism, and so enabling broader views of these services to be obtained.

In a report of this character, which extends over a very wide field of enquiry, it is pleasing to note that the first section (27 pp.) consists of a "Summary and Conclusions." This is a practice which might more often be followed, in similar documents, with great advantage to the busy reader.

Important chapters are:—Chapter III, Industrial Health; VIII, The Hospital System; X, Research and Genetics; XI, Nutrition; XV, Extent and Cost of Ill-health; and in Chapter XVI there is a Review of the Health Problem. There are two Appendixes, and many graphs and tables in the text.

The Report is a useful work of reference, and contains important and interesting information, especially valuable at the present time when physical education and the national fitness campaign are to the fore in this country. The work of the chemist does not loom large here, but in the section on Protective Services there are references to the work of Food and Drug Authorities and of Port Health Authorities, to Public Analysts, and to the efforts of our Society in relation to standards for foods. Mention is made of the inadequacy of the food laws of the country to protect the purity of the food-supply, and to the lack of control in relation to the advertising of foodstuffs. The recommendations of the Departmental Committee on the "Composition and Description of Food" are also shortly reviewed.

In the concluding section on "Commercialism and the Consumer" a timely protest is made against the extravagant statements in some of the commercial advertising and publicity of to-day. "The whole tone of commercial advertising and publicity," says the Report, "is pitched so extravagantly that even a business concern with tested products of the highest value and with a more than average regard for accuracy of statement has been known to experience great difficulty in framing advertisements, defensible from a scientific point of view, which can hope to win attention among the strident overtones of less scrupulous campaigns." It is perhaps permissible to hope for an early alteration in the law in this respect.

Under the same auspices, other volumes dealing with industrial questions, Social Services, Housing, Electricity, and Coal have been issued, and they form a series of monographs of real value to members of local authorities and their officers.

ARNOLD R. TANKARD

TRATTATO DI CHIMICA ANALITICA APPLICATA. Third Edition. Volumes I and II. By G. VITTORIO VILLAVECCHIA and COLLABORATORS. Pp. xxiii + 916, xvi + 1130, with 28 plates. Milan: Ulrico Hoepli. 1936, 1937. Price Vol. I, 85 lire; Vol. II, 115 lire.

Professor Villavecchia's Treatise, previous editions of which appeared in 1916 and 1920, is well known to all whose work involves the analysis of industrial materials. The present edition follows the form of the previous editions, but has been considerably enlarged. The material is dealt with under the main headings of (Vol. I) waters; chemical products; fertilisers; fungicides, bactericides and insecticides; cement materials; mineral colours; metals and alloys; fuels; coal-tar and its products; mineral oils and products derived from them; explosives; and (Vol. II) flours, starches and derived products; sugars and products containing them; beer; wine; spirits and liqueurs; nerve foods and condiments; meat and meat preparations; milk and its derivatives; fatty materials; industrial products from the treatment of fatty substances; essential oils; turpentine and its products; varnishes; rubber and gutta-percha; tanning materials; inks; leather; organic colours; textile fibres, yarns and fabrics. The methods given are those which are recommended in official standards and other recognised authorities for determining the quality of industrial materials. Each section begins with general remarks on the substances under consideration, followed by detailed chemical analytical methods, and for some materials, physical, microscopical and optical (refractometric and polarimetric) methods; sampling procedure and the preparation of the sample for analysis are included. For some materials, tables reproduce results of typical analyses; tables of constants are given in some sections. A subject and author index and a list of errata add to the usefulness of the book.

In the sections on food analysis, which occupy the first 560 pages of the second volume, frequent reference is made to Italian laws governing the composition of foods, a summary being given of the important points from the laws relating to the following substances: Starches, bread, food pastes, jams, beer, wine, vinegar, brandy, liqueurs, coffee, cocoa (both as berry and as powder), chocolate, meat extracts, butter, and cheese. Many of the analytical methods quoted are taken from official Italian sources. Thus, "I Metodi Ufficiali di Analisi per le Materie che interessano l'Agricoltura," 1934 and 1935, is the authority for many of the methods given for the analysis of flours, beer, wine, and vinegar, some of these official methods for wine being compared with those recommended by the International Convention for the Unification of Methods of Analysis of Wines in International Commerce, 1935, while some of the methods quoted for the analysis of spirits and liqueurs, fruit brandies, butter, and cheese are from "I Metodi Ufficiali dei Lab. del Ministereo di Agricoltura Industria e Commercia, 1905."

As the typical compositions which are given for many of the foods and other materials discussed refer to Italian products, the book can be recommended to those who want information on the subject of chemical industries in Italy.

E. M. POPE

HACKH'S CHEMICAL DICTIONARY. By I. W. D. HACKH, A.M., with the Collaboration of JULIUS GRANT, M.Sc., Ph.D., F.I.C. Second Edition. Pp. ix + 1020. London: J. & A. Churchill, Ltd. 1938. Price 48s.

Hackh's Dictionary has made for itself a place that is unique; it is essentially a dictionary to the larger chemical dictionaries such as those of Watts, Thorpe or Gmelin. Its value for this purpose was so rapidly recognised when it was first published in 1930 that it is not surprising that there has been a demand for a new edition. The volume has now been enlarged by 230 pages, and there are numerous new entries filling up gaps in the first edition or dealing with such recent work as, for example, the properties and compounds of deuterium or the composition of sex hormones.

Dr. Julius Grant, who was Professor Hackh's original collaborator, has again assisted him in the production of the new edition, with the result that, although transatlantic spelling is largely retained, the point of view is bi-national; for instance, both the American and English systems of classifying proteins are given.

The scope of the dictionary is so wide that it includes the chemical and allied terms used in medicine, pharmacology and bacteriology, and it not only defines physical processes, but also gives a description (with diagrams) of the construction of physical apparatus in common use, such as the galvanometer, interferometer and so on.

The historical part of the dictionary, largely consisting of concise entries relating to the work of pioneers in chemistry (with numerous portraits), has also been extended, and includes a large number of living chemists.

Attention was directed in the review of the first edition (ANALYST, **1930, 55**, 231) to the value to the analyst of having in a form convenient for reference the proportions of the constituents of many of the recognised reagents, such as Mayer's reagent, Nessler's reagent, Pavy's solution, and so forth; this is also a feature of the new edition.

In his preface Professor Hackh quotes the opinion of a reviewer of the first edition: "the more it is used, the more it is valued," and expresses the hope that it may still be said of the book. A careful study of the new edition suggests that that hope will be realised. EDITOR

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