THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, March 6th, the President, Mr. John Evans, being in the chair.

Certificates were read in favour of Frank Bell, Ph.D., D.Sc., F.I.C., James Talmadge Dobbins, A.M., Ph.D., Daniel Joseph O'Sullivan, M.Sc., F.I.C.

The following were elected members of the Society:—Albert Edward Andrews, A.I.C., William Lewis Davies, Ph.D., M.Sc., F.I.C., George William Ferguson, B.Sc., Ph.D., A.I.C., Oswald Hitchen, B.Tech.Sc., A.I.C., John Knaggs, B.Sc., Ph.D., A.R.C.S., D.I.C., F.I.C., Norman Ratcliffe, F.I.C.

Mr. Johan Ernst Nyrop was re-elected to membership of the Society.

THE Annual General Meeting of the Society then followed, when the Hon. Treasurer presented the accounts for the past year, and the Officers and Council for the year 1935 were elected.

President.—John Evans, M.Sc., F.I.C.

Past-Presidents serving on the Council.—F. W. F. Arnaud, E. Richards Bolton, J. T. Dunn, Bernard Dyer, Edward Hinks, P. A. Ellis Richards, G. Rudd Thompson, J. Augustus Voelcker.

Vice-Presidents.—L. H. Lampitt, S. E. Melling, A. More, W. H. Roberts.

Honorary Treasurer.—E. B. Hughes.

Honorary Secretary.—G. Roche Lynch.

Other Members of Council.—A. L. Bacharach, H. E. Cox, F. G. Edmed, B. S. Evans, L. Eynon, R. C. Frederick, E. M. Hawkins, G. Hogan, Miss M. Roberts, C. J. H. Stock, J. R. Stubbs, R. W. Sutton, E. Voelcker.

In place of the usual Presidential Address, Dr. Bernard Dyer, at the invitation of the President and Council, gave an address embodying his reminiscences of the Society from its inception to the present day.

Obituary

FRANK EDWARD DAY

FRANK EDWARD DAY started his career as an assistant in the assaying laboratories of the late Mr. Riley in London. From 1902 until 1910 he worked in the laboratories of Messrs. Watney, Coombe, Reid & Co., at the Stag Brewery, London, where he added to his metallurgical experience a knowledge of other analytical methods and of bacteriology, as is shown in the series of papers of which he was part author during this time. His experience was further extended when, in 1910, he went to Limerick as head of the laboratory of the Condensed Milk Co. of Ireland. During his time there he published accounts of improvements in the Gerber process of determining milk-fat. When this firm closed down he returned to England and was for a time engaged in consulting work.

In 1927 he was appointed chemist to the Institute of Brewing Research Scheme and was engaged at Rothamsted Experimental Station in the analysis of the barleys and malts produced in an extensive investigation into the effects of soil, season and manuring on barley and malt quality. While on this work he devised a method of small-scale brewing which made it possible to continue the investigation into the study of the effects of barley, malt and hop quality on that of beer. With the centralisation of the Scheme at Birmingham University, in April, 1934, Day was moved there, and plans were made for the development of his brewing tests on an extensive scale. Unfortunately he suffered from a protracted illness at this time.

Recently he had recovered, but he died suddenly on December 30th, 1934, at the age of 51. He leaves a widow. His outstanding personal characteristic was a great cheerfulness and good fellowship, even in difficulties. He was the true analyst: a method, however routine, was always capable of improvement, and he was indefatigable in his endeavours to that end.

He obtained his London B.Sc. degree and was elected successively Associate and Fellow of the Institute of Chemistry.

L. R. BISHOP

Annual Report of Council

March, 1935

THE roll of the Society stands at 733, an increase of 20 over the membership of last year.

The Council regrets to have to record the death of the following members:

Honorary member:	Viscount Devonport
Ordinary members:	Frank Edward Day
	Arthur Leonard Harry Garside
	George William Fraser Holroyd
	Daniel John O'Mahony
	George Egerton Scott-Smith
	Robert Rattray Tatlock
	William Elland Woolcott

Lord Devonport—at that time Mr. Hudson E. Kearley, M.P.—was elected an honorary member of the Society in June, 1896. The President, Dr. Stevenson, in proposing his election, dwelt upon the essential services that Mr. Kearley, as a member of the Select Committee of the House of Commons on Food Products Adulteration, had rendered to the Council of the Society in support of its views. The Report of the Select Committee later led to the amending Act of 1899. Lord Devonport, who was interested on a large scale in the wholesale grocery and provision trade, had long previously been in consultation with the Society on the question of desirable modifications of the law relating to food products; and he, together with Dr. Cameron, M.P. for Glasgow, and other Members of Parliament, took a prominent part in a special open meeting convened by the Society in March, 1893, for the purpose of discussing a tentative Bill which Dr. Cameron had recently introduced into the House of Commons, in the hope of hastening Government action in the same direction.

Day, who joined the Society in 1913, was formerly on the staff of the Institute of Brewing Research School, and last year he held an appointment at the School of Brewing in Birmingham. He had also been engaged in agricultural research on subjects related to the brewing industry at the Rothamsted Experimental Station. Garside, who was engaged in chemistry in Manchester, had been a member since 1901. Holroyd, a member for nine years, was in charge of the Chemistry Department of the Municipal Technical College, Blackburn. Although he was not often seen at our meetings, he was an active member of the North of England Section. O'Mahony, a very senior member of nearly 40 years' standing, was Public Analyst for Cork. Another old member was Scott-Smith, who joined the Society in 1899 and served on the Council some years later. He was Public Analyst for Chesterfield.

Tatlock, who at the time of his death was in his 98th year, joined the Society in 1876. He was the doyen of the analytical profession, and had served the Society in many capacities, becoming President in 1908–9. Up to the time of his death he continued to take an active interest in analytical chemistry, and until a few years back was an active partner in the well-known firm of which he was the senior. An obituary notice, written by Mr. R. T. Thomson, appears in THE ANALYST for March, 1935.

Woolcott had been a member for 13 years and was engaged in consulting practice in Liverpool.

During the year seven meetings of the Society have been held, and the following papers have been communicated:

"The Determination of Small Quantities of Fluorides in Water." By Guy Barr, B.A., D.Sc., and A. L. Thorogood, B.Sc.

"A Test for Ethylene Glycol and its Application in the Presence of Glycerol." By A. W. Middleton, B.Sc., A.I.C.

"The Detection of Diamines in Leather." By W. Mather, F.I.C., and W. J. Shanks.

"The Determination of Free Silica in Coal-Measure Rocks." By A. Shaw, B.Sc.

"A New Apparatus for Determining the Temperature of Crystallisation of Cocoa Butter." By S. A. Ashmore, B.Sc., A.I.C.

"The Determination of Small Quantities of Germanium in the Presence of Arsenic." By S. A. Coase, B.Sc.

"The Saturated Fatty Acids of Chrysalis Oil." By S. Ueno and H. Ikuta.

"The Determination of Lead in Biological Material, with Special Reference to Bone." By G. Roche Lynch, O.B.E., M.B., B.Sc., D.P.H., F.I.C., R. H. Slater, D.Sc., Ph.D., F.R.S.E., A.I.C., and T. G. Osler, M.B., Ch.B., M.R.C.S., L.R.C.P.

"The Determination of 'Ethyl' Vanillin." By H. C. Lockwood, B.Sc., A.I.C.

"The Detection and Identification of Metallic Particles in Manufactured Products." By H. C. Lockwood, B.Sc., A.I.C.

"Discussion on Quantitative Spectroscopy and its Analytical Applications."
Introduction. By J. J. Fox, O.B.E., D.Sc., F.I.C.
"Instruments used for Spectrum Analysis and Absorption Spectrophotometry." By F. Twyman, F.Inst.Phys., F.R.S.
"Quantitative Spectroscopy and its Analytical Applications." By S. Judd Lewis, D.Sc., Ph.D., F.I.C.
"The Use of the Spectrograph in Metallurgical Analysis." By D. M. Smith. A.R.C.S., B.Sc., D.I.C.

"The Identification of Common Edible Sea Fish (with Demonstration)." By C. H. Hattersley (Chief Inspector, Fishmongers Company).

"Fish Oils and their Vitamins." By Norman Evers, B.Sc., F.I.C.

"The Composition of Fish Pastes." By H. E. Cox, D.Sc., F.I.C.

"Note on Fish Pastes." By C. H. Manley, M.A., F.I.C.

"Some Observations on the Amounts of Amines and Free Ammonia in Fish Products." By D. H. F. Clayson, B.Sc., F.I.C., and L. H. Lampitt, D.Sc., F.I.C.

"Some Observations on Methods of Estimating the Degree of Preservation of White Fish." By G. A. Reay, Ph.D. (Torrey Research Station).

*"The Question of Tannin in Maté." By W. A. Woodard and A. N. Cowland.

"A Specification for Enamelled Hollow-ware." By J. H. Coste, F.I.C., and D. C. Garratt, B.Sc., Ph.D., F.I.C.

"Antimony Compounds extracted from Enamel-ware by Citric Acid Solutions." By R. H. Burns, B.Sc., A.I.C.

"Chemical Examination of the Seeds of *Santalum album* of Mysore." By Y. V. S. Iyer.

"The Chemical Examination of Furs in Relation to Dermatitis. Part V. The Action of Acid on Bandrowski's Base." By H. E. Cox, D.Sc., Ph.D., F.I.C., and J. U. Lewin, B.Sc., F.I.C.

"The Use of Infra-Red Rays for Distinguishing between Inks and Pigments." By C. Ainsworth Mitchell, M.A., D.Sc., F.I.C.

"Vitamin Potency and Associated Characteristics of Cod-liver Oil." By R. S. Morgan and H. Pritchard.

* Work done under the Society's Analytical Investigation Scheme.

The North of England Section has held five meetings, at which the following papers have been read:

"The Micro-Determination of Molecular Weights of Volatile Liquid Compounds." By A. F. Colson, B.Sc., A.I.C.

"Note on the Determination of Chromium in the Presence of Iron, Aluminium and Phosphoric Acid." By J. Haslam, M.Sc., A.I.C., and W. Murray.

"The Composition and Freezing-point of Colostrum." By G. D. Elsdon, B.Sc., F.I.C.

"The Technique of the Freezing-point Test for Milk." By G. D. Elsdon, B.Sc., F.I.C., and J. R. Stubbs, M.Sc., F.I.C.

"Old Masters and Modern Forgeries." By Professor A. P. Laurie, M.A., D.Sc., F.R.S.E.

"The Composition of the Amniotic Fluid." By Arnold R. Tankard, F.I.C., D. J. T. Bagnall, F.I.C., and F. Morris, F.I.C.

"A Note on the Dictionary of Colour Standards of the British Colour Council." By Arnold R. Tankard, F.I.C.

"Mrs. Beeton, the Housewife and the Factory." By E. Hinks, B.Sc., F.I.C.

"The Effect of Grinding in the Power Mill on the Albuminoid Content of Feeding Stuffs." By F. Robertson Dodd, F.I.C., and C. Robertson Louden, B.Sc., F.I.C.

"The Examination of Ginger." By G. D. Elsdon, B.Sc., F.I.C., and Miss C. Mayne, B.Sc., A.M.C.T.

"The Hortvet Freezing-point Process for the Examination of Milk; Correction Factors and the Influence of Stirring." By J. R. Stubbs, M.Sc., F.I.C.

"Difficulties in Determining the *p*H Values of Various Liquids." By D. Burton, D.Sc., F.I.C.

"The Determination of Water in Foodstuffs." By H. M. Mason, M.Sc., F.I.C.

"The Determination of Moisture in Cereal Products by Distillation with Tetrachloroethane." By J. M. Tucker, B.Sc., F.I.C.

The November meeting of the Society was devoted to a discussion on Quantitative Spectroscopy and its Analytical Applications. At this meeting the Society was fortunate in having Messrs. Fox, Twyman, Judd Lewis, and D. M. Smith as the principal speakers, and the usefulness of the evening was enhanced by the excellent demonstration of apparatus which was shown by Messrs. Hilger, Ltd.

Later in the same month the Society took part in a joint meeting with the Food Group of the Society of Chemical Industry, when a demonstration of the principal kinds of edible fish was given by Mr. C. H. Hattersley, Chief Inspector, Fishmongers' Company, and a number of papers dealing with fish and fish products were read.

THE ANALYST for 1934 has 856 pages, which, once more, creates a record. The Publication Committee accepted 46 papers for publication, these covering a wide range of subjects and being concerned with the analysis of food and drugs (including vitamins), and of organic and inorganic compounds, gas analysis, and toxicological or forensic subjects.

Among the papers that gave rise to special discussion mention may be made of that on Free Silica in Coal-Measure Rocks, by Mr. A. Shaw, and that on The Determination of Lead in Biological Material, with Special Reference to Bone, this paper being contributed by Drs. Roche Lynch, Slater and Osler.

THE ANALYST also contained 51 Notes on subjects of analytical interest, the usual notes from legal cases, summaries of Government Reports, and a large number of abstracts from other journals.

An important event of the year was the publication, as a brochure, of the Assistant-Editor's Bibliography of Heavy Metals occurring in Food and Biological

Material, the separate sections of which had previously appeared serially in THE ANALYST. The Council has congratulated Mr. T. H. Pope on the completion of this valuable piece of work.

The Honorary Treasurer reports that the accounts for the past year show that the Society has maintained its usual satisfactory financial position, the income fully meeting the expenditure involved during the year.

HONORARY MEMBERSHIP OF THE SOCIETY.—The Council is very pleased to record that Professor G. T. Morgan, O.B.E., D.Sc., LL.D., F.R.S. (President of the Chemical Society), and Professor J. F. Thorpe, C.B.E., D.Sc., F.R.S. (President of the Institute of Chemistry), have consented to be elected Honorary Members of the Society.

MEMBERS OF 40 YEARS' STANDING.—Rule No. 7a, which exempts members of 40 years' standing from further payment of subscription, comes into force in 1935. In response to notices informing such members of this rule, the Honorary Treasurer has received letters from many of them, expressing their pleasure and appreciation of the Society's recognition of their long and uninterrupted membership.

STANDING COMMITTEE ON UNIFORMITY OF ANALYTICAL METHODS.—The Chairman has informed the Council that, although no reports have been published during the year, the work of the Sub-Committee is steadily progressing. Two further reports—one on the Determination of Lead in Food Colours, the other on the Determination of Unsaponified Fat in Soap—are already in draft, and it is hoped that these will soon appear in THE ANALYST.

As a result of a letter from the Government Chemist, the Milk-Products Sub-Committee has carried out tests on the methods that have been proposed as international ones for the determination of fat and moisture in cheese, and the findings of the Sub-Committee were forwarded to the international body concerned. The methods of Reports 1 to 3 of this Sub-Committee have been recommended for use by the Fédération Internationale de Laiterie.

The co-operation of the Standing Committee of the Society has been sought by the British Standards Institution in establishing the specification of a standard light for Lovibond tintometer readings, and investigation of this matter is proceeding.

During the year Dr. H. E. Cox has been appointed Chairman of the Unsaponified Fat in Soap Sub-Committee (*vice* Mr. L. V. Cocks, who has retired), and Mr. B. D. W. Luff, F.I.C., has joined the Sub-Committee as a nominee of the London Chamber of Commerce and of Messrs. Unilever, Ltd. Mr. F. Thomas, of Messrs. Williams Bros., Ltd., of Hounslow, has been appointed one of the Society's representatives on the Metallic Impurities in Food Colours Sub-Committee.

NORTH OF ENGLAND SECTION.—The Honorary Secretary of the Section reports that five meetings have been held during the year.

The Hortvet freezing-point results, contributed by members of the Section and others, have been collated; the full statement, which has been submitted to the Publication Committee, includes the results for about 3500 samples of milk. It is believed that this work of the Section will prove very useful to Public Analysts and to all concerned with the cryoscopy of milk.

A very successful Summer Meeting was held at Llandudno in June. Prof. A. P. Laurie gave a lecture on "Old Masters and Modern Forgeries," which was very much appreciated. A resolution of congratulation on having attained his eightieth birthday was sent to Dr. J. A. Voelcker.

The good attendance at meetings has been maintained. Ten new members have been enrolled during the year, and there has been only one resignation, that of a member who has left the district. Seventy-six subscriptions have been received, the highest number yet recorded.

The Honorary Secretary wishes to express his thanks to the Chairman (Prof. W. H. Roberts), the Committee and members of the Section for their loyal support and regular attendance during the year.

PROPOSED NEW SECTION OF THE SOCIETY.—The Council has approved in principle the formation of a Scottish Section of the Society on the lines of the North of England Section. The Council hopes that Scottish members will lend their full support to the scheme and will communicate with Dr. Tocher of Aberdeen on the subject.

ANALYTICAL INVESTIGATION SCHEME.—Two grants have been made from the fund, and in each case the work has been completed and accepted by the Publication Committee for publication in THE ANALYST. Five problems are still under investigation.

REPORTS OF THE SUB-COMMITTEES OF THE STANDING COMMITTEE ON UNIFORMITY OF ANALYTICAL METHODS.—The Council has hitherto accepted these reports; but has not taken the responsibility of recommending the methods laid down in them as standard methods of analysis. In view of the anticipated adoption of the methods in the three reports on the analysis of condensed milk as international standard methods, the Council at its November meeting passed a resolution formally adopting all the reports hitherto issued by the above-mentioned Sub-Committees and approving the methods laid down in them as standard methods of analysis.

BRITISH STANDARDS INSTITUTION.—In the last report of the Council it was noted that it was hoped to establish co-operation with the B.S.I. in the matter of standard analytical processes when these were required to be included in specifications issued by the British Standards Institution. Friendly negotiations are still proceeding, and it is hoped that such a scheme of co-operation will be formulated in the near future. The Council realises that a scheme of this type may greatly increase the work falling upon active members of the Society, but at the same time it appreciates the fact that our Society is the only one fit to represent analytical chemistry in this country, and must, therefore, take a predominant part in any work involved in preparing standard methods of analysis.

CONGRESSES.

Technical and Chemical Congress of the Agricultural Industries in Paris.—The Society was represented by Mr. T. H. Pope.

Fourteenth Congress of Industrial Chemistry in Paris.—The Society was represented by Dr. L. H. Lampitt.

Public Health Congress in London.—The President attended the Congress on behalf of the Society and contributed a paper to the discussion on "Food Standards and the Report of the Departmental Committee on the Composition and Description of Food."

The Council desires to thank these gentlemen who have kindly acted as its delegates.

DEPARTMENTAL COMMITTEE ON THE COMPOSITION AND DESCRIPTION OF FOOD.—The Council welcomes, on the whole, the report of the Departmental Committee on the Composition and Description of Food; and, in view of the fact that that report was issued in March of last year, expresses the hope that the Government will at an early date introduce legislation to give effect to the main findings of the Committee.

OTHER ACTIVITIES.—Among other activities to which reference should be made are the following:—

Further negotiations have taken place with the Food Manufacturers' Federation concerning the sale of jams.

The discussion on standards for vinegar and malt vinegar with the Malt Vinegar Brewers' Federation has been continued, and the suggested definitions agreed upon have been published in THE ANALYST (1935, p. 2).

The Scottish Milk Marketing Board Scheme was discussed with the Public Analysts' Association for Scotland.

The observations of the Council were obtained on a further Report of the Fertilisers and Feeding Stuffs Advisory Committee.

PRESIDENTIAL ADDRESS.—The Council has, with the approval of the President, suggested that the President be relieved of delivering the first of the two addresses which by custom have been given at the Annual General Meetings during his term of office. This year the Council has invited Dr. Dyer to address the meeting, and intends to ask some distinguished chemist to give a lecture at each alternate Annual General Meeting in the future.

The Council congratulates Prof. T. P. Hilditch and Dr. L. H. Lampitt on their appointment as members of the Food Investigation Board of the Department of Scientific and Industrial Research.

The Council desires, in conclusion, to record its thanks to those members who have so generously given up their time to further the interests of the Society by serving on various committees, within and without the Society, during the year.

JOHN EVANS, *President*
G. ROCHE LYNCH, *Honorary Secretary*

Dr. Dyer's Address at the Annual General Meeting

AT the outset of his address, Dr. Dyer pointed out that the occasion was particularly appropriate, since it was the Diamond Jubilee of the Society, which held its first regular meeting in February, 1875, when Dr. Redwood was President. Dr. Dyer also drew attention to the interesting fact that he and Mr. W. Charles Young, with whom he had talked over the telephone that morning, were the only survivors of that historic occasion. He explained that most of what he had to say had already appeared in "Fifty Years of the Society of Public Analysts," by himself and Dr. Mitchell, in 1932. Notwithstanding this, however, Dr. Dyer in his inimitable kindly way gave a most interesting résumé of the men and work of the Society, in all the activities of which he had been intimately concerned, since its inception. Much of the early work of the Society was concerned with food adulteration, which at that time was gross and widespread, although gradually analytical chemistry in general was brought within its scope, and in 1906 this was recognised when the title of the Society was enlarged to include Analytical Chemists other than Public Analysts.

Portraits of all of the successive Presidents were shown on the screen, as well as those of the eminent workers in the early days of the Society, and Dr. Dyer made them live again by his comments on their work and personalities. Several of the earlier Presidents were well known as Medical Officers of Health who had also been appointed Public Analysts, such as Dr. Hill of Birmingham and

Dr. Adams of Maidstone. Later distinguished occupants of the presidential chair included A. H. Allen, Otto Hehner, Sir Thomas Stevenson, Dr. Dyer himself, Dr. J. A. Voelcker, E. W. Voelcker and Alfred Chaston Chapman.

Dr. Dyer also touched on the history of the Society in connection with the Institute of Chemistry and the Government Laboratory, and laid stress upon the fact, that, in spite of a certain coolness and misunderstandings in earlier days, the most cordial relations had for many years existed between the Society and these bodies. Evidence of this cordiality was afforded by the presence of Sir Robert Robertson and Mr. R. B. Pilcher at the meeting.

A vote of thanks to Dr. Dyer for his delightful address was proposed by Dr. J. A. Voelcker and seconded by Mr. G. Rudd Thompson, who suggested that Dr. Dyer's set of slides should be deposited in the archives of the Society.

A Specification for Enamelled Hollow-ware

By J. H. COSTE, F.Inst.P., F.I.C., and D. C. GARRATT, B.Sc., Ph.D., F.I.C.

(*Read at the Meeting, December* 5, 1934)

Enamelled ironware vessels are largely used for culinary purposes, and most users are familiar with the rapid deterioration of the glazed surface of the interior, especially when these vessels are used for acid foods, such as fruits. This is obviously due to selective solution of the material of the glaze and "opacifier." The occurrence of outbreaks of antimony poisoning, traced to the preparation of lemonade in enamelware vessels, shows that some danger may attend their use. Monier-Williams[1] has done a considerable amount of work on the antimony-content of enamels used on ironware, but there is very little other precise information available, although it is well known that highly siliceous enamels are more resistant to attack than those in which base predominates.

About a year ago it was desired to prepare a specification for the properties of the glaze on enamelware for use in public institutions. It was primarily initiated as a measure to guard against risk of poisoning by the action of liquids on these enamels, but eventually it became apparent that the test had a very definite bearing on the quality of the enamel and its durability when in use. Sample vessels (pie-dishes, jugs, mugs, etc.) from British manufacturers of repute were obtained for examination, in order that precise data might be available for this purpose.

It was found that the action of boiling solutions of citric or acetic acid of equal hydrion concentration, poured into the vessel to be examined and allowed to remain in contact with the surface for a defined time, did not differ greatly, and it was therefore decided to use citric acid as a typical fruit acid. The action was measured by evaporating to dryness a known fraction of the acid solution which had stood in the vessel, igniting in a silica dish over a Bunsen burner and relating the weight of the mineral residue to the area of the interior of the vessel exposed to the action of the solvent. This area can usually be calculated by a little simple geometry.

When an enamel surface has once been attacked by acid, subsequent applications dissolve further smaller quantities of material, and it is, therefore, difficult to show the effect of varying strengths of acid on the same surface; but the fact that stronger solutions (at the low concentrations used) exerted a greater solvent action was shown by repeated applications of hot 0·5 per cent. citric acid solution on the same surface followed by hot 2·0 per cent. citric acid. Table I shows that, under similar conditions of time and temperature, two vessels of very different acid-resistance each yielded more material to the 2 per cent. solution than to the last previous 0·5 per cent. solution.

TABLE I

	Amount dissolved per sq. cm. (*a*) Mg.	(*b*) Mg.
With boiling 0·5 per cent. citric acid, cooled 24 hours	0·38	1·02
Action repeated on the same surface ,, ,, ,,	0·24	0·51
,, ,, ,, ,, ,, ,, ,, ,, ,,	0·21	0·17
With boiling 2·0 per cent. citric acid ,, ,, ,,	0·35	0·89

The effect of the length of time of contact between the enamel surface and acid is shown in Table II. Here, again, the difficulty of showing the effect on the same surface is apparent, but, after stabilisation of the rate of solution by continued application of 2 per cent. acid, a marked increase was seen in solvent action after 72 hours' cooling, compared with the preceding 24 hours' application, showing that length of time of contact governed the solubility of the enamel.

TABLE II

	Amount dissolved per sq. cm. Mg.
With boiling 2 per cent. citric acid, cooled 24 hours	0·81
Action repeated on the same surface ,, ,, ,, ...	0·65
,, ,, ,, ,, ,, ,, ,, ,, ,, ...	0·51
,, ,, ,, ,, ,, ,, ,, ,, ,, ...	0·33
,, ,, ,, ,, ,, ,, ,, 72 ,, ...	0·75

Table III shows the total enamel coating per unit area on some typical articles examined, with the corresponding amounts of surface-enamel material removed by treatment with 0·5 per cent. citric acid.

TABLE III

	Total enamel per sq. cm. Mg.	Material removed per sq. cm. Mg.	Acid-affected area
Bowl	73·5	4·40	Glaze dulled
Pie-dish	81·3	2·09	Glaze removed. Exposed surface rubbed off in powder
Bowl	70·9	0·17	Glaze apparently unaffected
Bowl	57·1	0·13	,, ,, ,,

The total amount of material removed from the enamel by acid treatment is sometimes remarkably high. An article recently examined yielded as much as

7·5 mg. per sq. cm. of surface to 0·5 per cent. citric acid solution in 24 hours, amounting to 1·328 g. in 250 ml. of liquid, and in many cases after one treatment with acid the opacifier could be rubbed off by hand.

It became obvious, after examination of many articles, all triple-coated, guaranteed acid-proof and free from antimony, that few enamels used commercially could be considered as substantially acid-proof, and that requirements in this direction must be based on limits of attack rather than on actual immunity.

On the basis of the results obtained, the following clause for acid-resistance was inserted in the specification:

> "Enamelware vessels will be considered to be sufficiently resistant to acid if, when filled as full as is convenient with a boiling 0·5 per cent. solution of citric acid in water and allowed to stand for 24 hours without being heated or artificially cooled, the amount of ash yielded on ignition of the residue obtained when a definite proportion of the solution is evaporated does not exceed 1·0 mg. per sq. cm. of surface exposed to the action of the acid, and if on repetition of the treatment with a fresh similar volume of the boiling acid solution not more than a further 0·5 mg. per sq. cm. is obtained."

In practice, the articles for examination are first washed out with distilled water, and the above test is then applied, loss of water by evaporation from the hot solution being prevented by covering the vessel with a glass plate. Before evaporation of the aliquot part in a silica dish the solution is well stirred, care being taken not to touch the sides of the vessel, as the surface in some cases becomes quite friable. If the residue from the first acid treatment is less than 0·5 mg., the second treatment is considered unnecessary.

Since the inclusion of the above clause in the specification 150 samples of enamelware have been examined in the Council laboratory, and the results of these are given in detail in Table IV.

Rejection of specimens not passing the acid-resistance test would appear justified from the fact that the last 50 samples showed a marked improvement in quality, a much smaller proportion of those submitted failing to pass the test, or yielding a high extract.

TABLE IV

Amount dissolved per sq. cm. Mg.	100 Specimens		50 Specimens	
	1st acid application	2nd acid application	1st acid application	2nd acid application
above 5	1	—	—	—
5 to 4	8	1	—	—
4 to 3	13	2	3	—
3 to 2	3	9	1	—
2 to 1·7	6	1	—	—
1·7 to 1·3	2	2	1	—
1·3 to 1·0	11	1	7	1
1·0 to 0·7	13	1	13	1
0·7 to 0·3	27	18	21	4
0·3 to 0·1	10	13	4	14
less than 0·1	6	2	—	—
not determined*	—	50	—	30

* These were either above the specification limit or below 0·5 mg. per sq. cm. for first application.

A clause in the specification required that all enamels were to be certified "free from antimony, lead, arsenic or other deleterious or poisonous ingredients," but many were found to contain antimony in appreciable quantity and were consequently rejected. Those which passed the "acid resistance" clause were submitted to a qualitative test for antimony. It was found by experiment that the following test was applicable:

About 2·0 g. of the glaze, containing the opacifier, were chipped off and ground to a fine powder in an agate mortar. This was extracted with 1 : 1 hydrochloric acid for half an hour on a steam-bath, the extract was diluted and filtered, excess of oxalic acid was added to retain tin in solution with hydrogen sulphide, and the liquid was saturated with this gas. In the presence of antimony the usual orange precipitate was obtained and, if appreciable, the amount was then determined quantitatively. For this, the enamel was dissolved by evaporation with sulphuric, nitric and hydrofluoric acids, to eliminate silica, and boiled with hydrochloric acid. Any insoluble matter was fused with sodium peroxide and sodium carbonate, and the mass was extracted with hydrochloric acid. The antimony in the bulked solutions was precipitated as sulphide and determined by means of bromate (W. W. Scott).[2] Of the first hundred samples submitted for analysis, 13 contained antimony in considerable quantity, ranging from 0·34 to 2·80 per cent. calculated on the total enamel, and forty-one of the accepted samples contained traces of antimony insufficient to warrant rejection. Of the next fifty articles tested, only 3 contained antimony, and then only in traces—a marked improvement in standard. It is probable that many of the manufacturers were unaware of the presence of antimony in their goods, one firm having assured us that they had not used it for over a year. A sample of acid-resisting glaze for use on enamelware, received from a manufacturer whose finished articles had been rejected, was found to be free from antimony, and probably the source of the contamination in this case was the opacifier.

The antimony compounds extracted from enamelware by citric acid solutions are dealt with by Mr. R. H. Burns in the following paper.

Since this investigation was begun, another aspect of the importance of acid-resisting properties of enamel has shown itself—namely, the solution of boron compounds in appreciable quantities by the acid.

The question whether small quantities of boron are deleterious to health has given rise to considerable discussion, but the Government Departmental Committee on Preservatives in 1925 were unanimously of opinion that compounds of boron were sufficiently harmful to justify their total prohibition as preservatives, and it is admitted that boric acid adversely affects some people. The 1934 B.P. Codex indicates that boric acid is but slowly excreted, so that its effect is cumulative.

Table V shows that between one-third and two-thirds of the matter extracted by acid from the enamels examined consists of boric acid. Assuming the enamels to be used in the form of two-pint jugs containing half-pint quantities, then 0·5 per cent. citric acid would extract 0·4 to 1·7 grains of boric acid. These results have been obtained on samples of comparatively low acid-solubility, as the enamels of high acid extract were no longer available. By comparison, these would show boric acid contents of approximately 5 grains per half pint. Although these are

not large doses compared with the Pharmacopoeia limits of 5 to 15 grains, they are sufficient to make desirable a reasonably high acid-resistance in enamelware.

TABLE V*

Specimen	Total enamel	Boric acid in enamel	1st acid extract	Boric acid in 1st extract	2nd acid extract	Boric acid in 2nd extract
Bowl	61·6	10·26	0·29	0·16		
Jug	92·6	13·66	1·20	0·36	0·98	0·33
Bowl			1·74	0·60	0·72	0·43
Jug			1·00	0·39		
Pie-dish			0·38	0·16		

* All results expressed in mg. per sq. cm.

An acid extract from an enamel examined quite recently showed a fluorine-content of 30 p.p.m. (calculated as sodium fluoride), equivalent to solution of 0·05 mg. from each sq. cm. of surface attacked. This amount in the extract is highly significant, having regard to the possibility of "fluorosis." Ainsworth[3] has recently shown that there is a connection between very small amounts (4·5 to 5·5 p.p.m.) of fluorine in water and "mottled teeth" in children, thus confirming the results of many other workers. Although the amounts of fluorine extracted from enamels are not being continuously ingested, their exclusion is desirable.

As increased amounts of both boric acid and fluorides weaken the resistance of enamels to acids, we have an added justification for the adoption of the acid-resistance test suggested in this paper.

SUMMARY.—(1) The enamel on enamelled ironware has been shown to be dissolved to a considerable extent by comparatively weak solutions of organic acids.

(2) Solubility of the enamel is dependent on the strength of acid and length of time of contact.

(3) A specification for "acid-resistance" has been formulated.

(4) In the manufacture of enamels it is not sufficient to avoid the use of known antimony compounds. The absence of antimony from the constituents should also be ensured.

(5) Acid extracts may contain appreciable quantities of boron and significant amounts of fluorine.

Our thanks are due to Mr. C. M. Willcox, M.A., B.Sc., A.I.C., for most of the "acid-resistance" figures.

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Antimony Compounds Extracted from Enamelware by Citric Acid Solutions

By R. H. BURNS, B.Sc., A.I.C.

(*Read at the Meeting, December* 5, 1934)

The following results were obtained in the course of experiments carried out, at the suggestion of Mr. J. H. Coste, in this laboratory, on samples of enamelware submitted for use in the Council's Institutions. It should be pointed out that this investigation was started before the publication of the official report by Monier-Williams on this subject.[1]

The general idea was to reproduce the conditions likely to arise in households where acid liquids, such as home-made lemonade, are prepared and stored in enamel vessels. The sample selected was a jug which passed the acid-resistance test,* and was therefore less likely to be attacked by food-acids than one of a lower silica-content.

Antimony may be present in an enamel in the ter-, quadri-, or quinquevalent condition.[2] The trioxide and pentoxide are both soluble in citric acid solution, whilst the tetroxide is insoluble. Thus in the extractions antimony in both the tervalent and the quinquevalent condition may occur. No attempt was made in these experiments to differentiate between these two forms, because it was felt that, although it is generally accepted that only soluble salts of tervalent antimony are toxic, there are insufficient data to show that salts of quinquevalent antimony are non-injurious.

So-called "lemonade crystals" vary greatly in composition, and may contain from 5 to 50 per cent. of tartaric acid, or citric acid, or both, whilst lemon juice contains approximately 8 per cent. of its weight of citric acid. Thus, the test solution used, which was 0·5 per cent. citric acid, was probably weaker and consequently less corrosive than that met with in common use.

The enamel of the vessel used in these experiments had an antimony-content of 0·98 per cent., and the surface area exposed to attack was 246 sq. cm.

In the first series of experiments, the results of which are shown in Table I, 400 ml. of boiling 0·5 per cent. citric acid solution were poured into the jug, and allowed to stand in the cold, for the number of hours stated. The solution was then poured off, and the antimony-content of 100 ml. was determined. This process was repeated five times. As will be seen, extract (2) was higher in antimony-content than extract (1), this presumably being due to the time taken for the initial glaze on the surface to be destroyed. After this, smaller amounts of antimony compounds were continuously extracted. During this treatment the enamel was visibly attacked to a slight extent, with consequent flaking. The antimony in extracts (3) and (4) was therefore re-determined after removal of suspended matter by centrifuging, the results being:—(3) 2·2 mg. per l., and (4) 2·0 mg. per l. As these figures are essentially the same as those obtained directly, they eliminate

* See preceding paper in this issue by J. H. Coste and D. C. Garratt.

the chance of any antimony tetroxide present in the flakes being subsequently dissolved in the hydrochloric acid used in the determination, and thus causing the value for the total antimony extracted by the citric acid to be too high.

TABLE I

Extract	Antimony extracted: Mg. per litre	Antimony extracted: Grains per pint	Antimony extracted: Mg. per sq. cm.	Number of hours
1	3·3	0·029	0·0054	18
2	5·6	0·049	0·0091	18
3	2·1	0·018	0·0034	18
4	2·1	0·018	0·0034	18
5	3·2	0·028	0·0052	48

Next, the jug was washed out and scoured, and the above process was repeated, the antimony figures then obtained being given in Table II. It is obvious from the higher results obtained that cleaning exposes a new surface to the action of the acid, and thereby constitutes an added danger in the use of antimony enamelware in households.

TABLE II

Extract	Antimony extracted: Mg. per litre	Antimony extracted: Grains per pint	Antimony extracted: Mg. per sq. cm.	Number of hours
1	7·2	0·063	0·0117	18
2	7·2	0·063	0·0117	18
3	3·5	0·031	0·0057	18
4	5·0	0·044	0·0081	18

Lastly, 400 ml. of boiling 0·5 per cent. citric acid solution were again poured into the jug, and successive amounts of 50 ml. were withdrawn and analysed after the time stated. The results are shown in Table III. They illustrate the great danger of storage in enamelware of this nature. The increase in the amount of antimony in the extracts may be considered remarkable when the hardness of the original enamel and the comparatively small total antimony-content of the glaze are taken into consideration.

TABLE III

Extract	Antimony extracted: Mg. per litre	Antimony extracted: Grains per pint	Number of hours
1	3·6	0·032	18
2	8·6	0·075	90
3	10·0	0·088	162
4	14·6	0·128	360
5	20·0	0·175	498

By chipping off and weighing the enamel from a measured surface area, it was estimated that approximately 227 mg. of antimony were present in that portion of the glaze liable to attack by the citric acid solution. Of this amount,

6·5 mg. (2·9 per cent.) were extracted in the first series of experiments, 9·2 mg. (4·1 per cent.) in the second, and 5·8 mg. (2·6 per cent.) in the third, leaving 205·5 mg. (90·4 per cent.) of the total antimony undissolved. In comparing the results obtained in the third series of experiments, it must be remembered that the surface area subjected to attack was decreasing throughout the experiment by reason of the removal of liquid.

The method employed for the determination of the antimony in the extracts was a modification of the method given by Clarke,[3] in conjunction with the Reinsch test, and was as follows:

To an aliquot portion of the liquid an equal volume of concentrated hydrochloric acid was added, together with approximately 2 g. of oxalic acid, the solution was heated to boiling, 1 g. of sodium hypophosphite was added, and the solution boiled for ten minutes. The antimony present was then deposited on copper foil, dissolved off the latter with sodium peroxide, and finally estimated colorimetrically by the method given in that paper.

In examining the figures given under grains per pint in the tables, it is interesting to bear in mind that the emetic dose for soluble tervalent antimony compounds is given as equivalent to 0·18 to 0·36 grain of antimony, whilst the usually accepted maximum figure for arsenic in foods and drinks is 1/100th grain per pound or gallon, respectively.

In conclusion, whilst it is realised that the amount of antimony in the extracts obtained in this particular instance may not be definitely harmful, it is felt that the data given in this paper constitute a useful support to the case for the total prohibition of antimony in enamelware.

SUMMARY.—(1) Antimony compounds are extracted from "hard" enamels by the action of dilute citric acid solutions.

(2) Cleaning and scouring of enamel vessels expose a new surface to the action of the citric acid, with consequent increase in the amount of antimony extracted.

(3) Storage of citric acid solutions in enamelware is shown to be dangerous, owing to the rapid increase of the antimony-content of the stored solution.

(4) A slightly modified method is given for determining the antimony-content of such solutions.

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The Hortvet Freezing-point Process for the Examination of Milk: Correction Factors and the Influence of Stirring: II & III

By J. R. STUBBS, M.Sc., F.I.C.

(*Continued from p.* 154)

PART II

Investigation of Correction Factors

Criticism has been levelled against the Hortvet method for the determination of freezing-points on the ground that it does not indicate "true" freezing-points. This criticism is loosely expressed, and applies to every method of cryoscopy based on the principle adopted by Rüdorff and developed by Raoult and others, *viz.* supercooling the liquid under examination, and then inducing crystallisation by the addition of a small particle of the solid solvent. The "true" freezing-point of a solution, that is to say, the temperature at which that solution is in exact equilibrium with the solid solvent when the two are in contact with each other, so that the quantities of each remain constant in amount, is not directly indicated by any of the methods of the kind referred to above; what is obtained is a figure from which, by the application of certain factors, the "true" freezing-point may be calculated.

A more serious criticism is that passed by Monier-Williams[8] to the effect that the design of the Hortvet apparatus does not permit, at least readily, of the determination of the correction factors which are necessary for arriving at "true" freezing-points. This statement, and closely related ones, made to me by several observers, are well summed up by Monier-Williams (*loc. cit.*) in the words, "It is, in my experience, very difficult to get a satisfactory measurement of the supercooling correction, K, in Hortvet's apparatus." Consequently, attention is directed in this part of the paper to the study of correction factors in connection with the use of the Hortvet apparatus and technique.

When a dilute aqueous solution is cooled below its freezing-point and a particle of ice is introduced, freezing takes place, and the latent heat of formation of the ice warms up the solution to the observed freezing-point. The ice remains in the liquid and, therefore, if only pure ice separates, the original solution becomes concentrated to an extent which depends on the amount of ice formed. The observed freezing-point is, therefore, the freezing-point of a stronger solution than the one placed in the freezing-tube and, in consequence, the observed freezing-point is lower than the "true" freezing-point, that is, the freezing-point of the original solution. The supercooling correction, when applied to the observed freezing-point, corrects for the influence or "error" due to supercooling.

In the standard cryoscope of Hortvet the jacket surrounding the freezing-tube contains methylated spirit which facilitates the abstraction of heat by the cooling-bath, and this alcohol remains in place throughout the experiment. The cooling-

bath is, therefore, removing heat from the freezing-tube and contents during the time that the temperature is rising after freezing commences, until the observed freezing-point is reached. The nett loss of heat thus caused has to be counterbalanced by the formation of more ice; the solution is, therefore, still further concentrated, and an additional correction, the "heat-transference" factor, must be determined before the "true" freezing-point can be obtained from the observed freezing-point.

In the Hortvet apparatus there is no means provided whereby these two effects, supercooling and heat-transference, can be separately studied. If the alcohol could be removed from the space surrounding the freezing-tube when it has served the purpose of accelerating the cooling of the liquid under examination, the abstraction of heat therefrom while the temperature is rising after freezing has commenced would be eliminated, assuming that the thermal insulation is perfect, enabling the effect of supercooling alone to be studied; and, by operating on the same liquid with and without alcohol in the jacket around the freezing-tube, the freezing-points obtained would provide data from which the heat-transference factor can be calculated; if the same amount of supercooling is used in each case the difference between the two freezing-points will be proportional to the heat-transference.

Monier-Williams, in the apparatus recently devised by him (1933), has included such an arrangement; the inner tube of the cooling-bath is provided with a tube and tap by which the alcohol can be removed with a suction pump. It is possible to modify the standard Hortvet apparatus in a similar way; a description and illustration of such an arrangement have been published. (Elsdon and Stubbs.[9])

The object of the withdrawal of alcohol being to isolate the freezing liquid from the influence of the cooling-bath, the freezing-tube should be kept central in the slightly larger tube of the cooling-bath in which it is placed. This was achieved, in the following experiments, by passing a thin rubber band round the lower part of the freezing-tube. This simple device, though admittedly not as satisfactory or convenient as the steel springs used by Raoult for the same purpose, or as the brass points employed by Monier-Williams, was yet quite effective; this was proved by placing the freezing-tube with the band in position on a hard, flat surface, when, in spite of the exertion of considerable downward pressure on the tube, the rubber band prevented contact between the tube and the surface.

(1) *The Supercooling Correction*

In order to ascertain the supercooling correction, separate portions of the same sample of milk were taken and supercooled to varying extents; the alcohol was then drawn off, the reading of the thermometer taken, and crystallisation induced, as usual, by introducing a particle of ice. The freezing-points corresponding to different amounts of supercooling were thus observed. From these data the "true" freezing-point, that is, the freezing-point for supercooling "nil" was ascertained in each case by means of a graph. The freezing-point depressions were plotted as ordinates and the corresponding degrees of supercooling as abscissae. The straight line passing through these points, produced, gives at the intersection with the axis of ordinates, the freezing-point for supercooling "nil."

It was originally intended to employ four different amounts of supercooling for each sample of milk, *viz.* about 1·5, 1·0, 0·8, and 0·5° C. It was found, however, that the differences in the readings of the thermometer corresponding to these different amounts of supercooling were in the neighbourhood of 0·002°—an amount so small that the unavoidable errors of observation might possibly approach the same order. It was, therefore, decided to employ only two different amounts of supercooling, as widely apart as practicable, say about 1·5° and 0·8°, and to increase the number of samples examined.

It was stated by Hortvet that, unless a much greater amount of supercooling than 0·5° is employed in the use of his cryoscope and technique, the rise of the mercury column is not sufficiently pronounced, and that there is more or less wavering, so that difficulty arises in deciding on the exact point at which the top of the column becomes stationary. Elsdon and Stubbs (*loc. cit.*)[9] found the same result when using a supercooling of less than about 0·8°; the mercury rose very slowly, and did not maintain a steady position for any appreciable time, and the proper freezing-point might not, under these circumstances, be attained.

In the first experiments, made with the object of ascertaining the supercooling correction, it was observed that where the amount of supercooling was small, that is, less than say 0·75°, even in the absence of alcohol in the jacket surrounding the freezing-tube, the rise of temperature, when freezing occurred, was very slow—so slow, indeed, as to suggest doubts whether the thermometer would indicate the freezing-point of the milk, influenced only by supercooling, owing to the reading being affected by the length of time which elapses and the possibility of imperfect thermal insulation, causing a nett loss of heat from the freezing tube and contents. To give an instance; in an experiment when the supercooling was 0·71° the time required for the mercury column to rise until, on observation through the telescope with the aid of the horizontal cross-wire, the ascent became imperceptible, was $9\frac{3}{4}$ minutes, as compared with about $3\frac{1}{4}$ minutes when the same milk was supercooled 1·49°. It will be seen later that, in the absence of alcohol in the space surrounding the freezing-tube, the heat insulation of the milk is not perfect; a nett loss of heat occurs, for it is possible to carry through a freezing-point determination under such conditions. The difference between the two methods of working—with and without alcohol—results in a longer time being required for the cooling of the milk when the space around the freezing-tube is occupied by air.

There were also the difficulties of judging when the rising column of mercury had reached the highest point, due to the very slow movement which occurred in that region, and of getting satisfactory readings, owing to the short time that elapsed before a fall took place.

The idea of following strictly the Hortvet technique, as regards stirring, for these particular experiments was therefore abandoned. In the first series of experiments, the results of which are recorded in Table III, four or five stirrings of three strokes each were employed, and in the second series the mechanical stirrer, working at the rate of 40 strokes per minute, was in operation all the time, the thermometer rising until tapping became necessary. It does not appear that these variations in stirring caused any significant differences in the results obtained, but the times of rising of the mercury, after two different extents, large and small,

of supercooling, were diminished and rendered less unequal, and the observation of the highest point reached by the thermometer, in the case of the lesser extent of supercooling, was made more satisfactory.

One is prepared to admit that, other things being equal, it would have been preferable to carry out these experiments by following the Hortvet technique as regards stirring, but, unfortunately, it was found impossible to obtain, with small amounts of supercooling, readings considered to be satisfactory.

One observation may be recorded here, although, at present, it is not claimed that any particular significance is attached to it. When the lesser amount of supercooling was employed it was invariably found that the rise of the mercury column, after tapping the thermometer, was greater than in the case of the larger extent of supercooling. As the result of several experiments it was found that this increment was about 0·030° in the former instance, and about 0·003° in the latter.

In order to eliminate the effect of variations in the dimensions or thickness of the freezing-tubes the same tube was used for the two experiments on the same milk.

TABLE III

The Effect of Supercooling in the Hortvet Apparatus

	Degrees of supercooling	Δ	K
(*1st series*) *read by hand-lens*			
66070 M.D.	1·46	0·553	0·013
	0·74	0·548	
42127 Bn.D.	1·47	0·540	0·008
	0·78	0·537	
36219 L.D.	1·59	0·543	0·009
	0·74	0·539	
7011 D.	1·45	0·536	0·012
	0·80	0·532	
60031 A.D.	1·47	0·545	0·013
	0·88	0·541	
33566 Rs.D.	1·43	0·543	0·011
	0·76	0·539	
(*2nd series*) *read by levelled telescope*			
7039 D.	1·49	0·541	0·009
	0·62	0·537	
25441 H.B.D.	1·49	0·538	0·011
	0·78	0·534	
25446 H.B.D.	1·48	0·535	0·011
	0·81	0·531	
83704 Ws.D.	1·45	0·526	0·008
	0·75	0·523	
42267 Bn.D.	1·47	0·541	0·011
	0·78	0·537	
42268 Bn.D.	1·47	0·543	0·011
	0·80	0·539	
		Average	0·011

An equation to express the relation between the true and observed freezing-point depressions and the supercooling is given by Raoult[10] as:

$$C' = C + CSK \quad .. \quad .. \quad .. \quad .. \quad (I)$$

where C′ represents the observed freezing-point depression; C, the freezing-point depression after correction for supercooling or the "true" freezing-point depression; S, the supercooling in degrees centigrade; and K a constant.

The values for K obtained by substitution in the above equation of the ascertained values for C, C′ and S are recorded in Table III. It will be seen that the individual values vary from 0·008 to 0·013, with an average of 0·011. The greatest difference between the two extreme values for K corresponds with a difference in reading of the thermometer of rather less than 0·002°.

From the average value of K obtained above, it appears that the true freezing-point depression of a milk is increased by the fraction 0·011 of the true freezing-point depression for one degree of supercooling.

When the value of K has been determined for one particular apparatus, volume and nature of solution, and method of working, the true freezing-point may be calculated from the equation $C = \frac{C'}{1 + KS}$ by substituting the observed values for C′ and S, and 0·011 for K.

A rough approximation to the value of K may be calculated by a different method. It is not contended that the value so obtained is anything but approximate, but it should at least show the order of magnitude. A method similar, however, to that described below was employed by Raoult, based on the consideration of the water-values of the materials involved, and apparently regarded by him as worthy of consideration.

The formula I given by Raoult is an abbreviated form, the full expression being:

$$C = C' - \frac{CS}{L}\left(1 + \frac{r}{R}\right) \quad .. \quad .. \quad .. \quad .. \quad (II)$$

where C, C′ and S have the same significance as in the previous formula, L represents the latent heat of formation of solid solvent (for water = 80); r, the water-value of the wetted parts of the freezing-tube, stirrer and thermometer (with mercury); and R, the water-value of the solution under examination.

It would appear that formula II applies only when the specific heat of the liquid in the freezing-tube is unity, and therefore R represents both the weight and the water-value of the solution. It could be made of more general application by taking into account the specific heat of the freezing liquid in cases where it differs from unity. If W is the weight in grams of a solution whose water-value is R and specific heat H, we have R = WH, and the above formula could be modified thus:

$$C = C' - \frac{CS}{L}\left(H + \frac{r}{W}\right) \quad .. \quad .. \quad .. \quad (III).$$

In the apparatus I used, where 35 ml. of milk were taken of average sp.gr. 1·03 and specific heat 0·93, the water-value of the milk = 35 × 1·03 × 0·93 = 33·5 g. The portion of the glass freezing-tube wetted by 35 ml. of milk weighed 23·5 g., and, taking the specific heat of glass as 0·197, the water-value will be 23·5 × 0·197 = 4·63 g.

The brass ring and wetted part of the stem of the stirrer weighed 4·65 g., and, the specific heat of brass being taken as 0·094, the water-value is $4{\cdot}65 \times 0{\cdot}094 = 0{\cdot}44$ g. Considering the mercury in the bulb of the thermometer as 53·4 g., estimated from the size of the bulb and neglecting the glass envelope, the water-value will be $53{\cdot}4 \times 0{\cdot}033 = 1{\cdot}76$ g. The total number of calories, therefore, required to heat up the system after one degree of supercooling will be $33{\cdot}50 + 4{\cdot}63 + 0{\cdot}44 + 1{\cdot}76 = 40{\cdot}3$. This heat is supplied by the latent heat of formation of ice at the rate of 80 calories per g. of ice. The ice formed will therefore be $40{\cdot}3 \div 80 = 0{\cdot}5$ g. in $35 \times 1{\cdot}03 = 36{\cdot}0$ g. of milk. The fraction by which the original milk is concentrated will be $0{\cdot}5/36 = \mathrm{K} = 0{\cdot}014$.

If, owing to the small amount of stirring, the freezing-tube does not partake in the rise of temperature, the number of calories required to warm the remainder of the system to the freezing-point after one degree of supercooling will be $33{\cdot}5 + 0{\cdot}44 + 1{\cdot}76 = 35{\cdot}7$ calories. The production of this heat requires the formation of $35{\cdot}7/80 = 0{\cdot}44$ g. of ice; the resulting fractional concentration would then be $0{\cdot}44/36 = \mathrm{K} = 0{\cdot}012$.

The expression $\frac{\mathrm{CS}}{80}\left(\mathrm{H} + \frac{r}{\mathrm{W}}\right)$, contained in the formula III above when $\mathrm{L} = 80$, represents the error in the reading of the freezing-point depression due to the concentration of the original solution resulting from supercooling. The values for H, r, L and W depending, as they do, on the instrument and on the amount and kind of liquid used—are constant for one particular apparatus and equal quantities of the same kind of solution operated on. We may therefore write K for the expression

$$\frac{1}{80}\left(\mathrm{H} + \frac{r}{\mathrm{W}}\right),$$

where K is a constant, and thus obtain formula I. K is the fraction of the true freezing-point depression by which, at ordinary atmospheric pressure, the true freezing-point depression is increased, if pure ice separates, for one degree of supercooling when the solution suffers neither nett loss nor gain of heat from the surroundings during freezing; it also denotes the amount of ice formed in one gram of the original solution or, if pure ice separates, the fraction by which the original liquid is concentrated, owing in each case to a supercooling of 1° C.

In the above two methods of calculating the value of K it is assumed that only pure ice separates on freezing. If there separated, in addition, one or more of the ingredients which affect the freezing-point, the reasoning would no longer be valid; the solution remaining would then be concentrated, not by an amount equal to that of the ice separated, but by a less amount depending on the quantity and nature of the ingredients, other than ice, which separated. Few observers appear to have directed their attention to the investigation of this point. Monier-Williams[11] draws the conclusion from his own work that pure ice separates from the freezing milk where only small quantities of ice, compared with the quantity of milk used, are in question.

It would appear to be a fact that very little indeed has been recorded in the literature with regard to the investigation of the freezing-point of a liquid containing several substances in solution. Raoult, H. C. Jones, Loomis and others, apparently

worked generally, perhaps it could be said exclusively, with a single substance dissolved in a pure solvent.

In the equation of Raoult, quoted above, it is further assumed that the stirring is thorough, causing the ice and solution to be brought into immediate and thorough contact with each other, conditions which, if ever quite fulfilled in working with any apparatus, are certainly not fulfilled in the case of the Hortvet cryoscope and technique, or even when the Hortvet stirrer is manipulated continuously during the rise of temperature which follows the inception of freezing, as was done in the experiments recorded in Table III, second series.

It will be observed that the above average value of K is somewhat less than the approximate value calculated from the weights and specific heats of the materials constituting those portions of the apparatus which participate in the rise of temperature that takes place on freezing, and is even slightly less than the value for milk alone, *viz.* 0·93/80 = 0·0116, assuming the specific heat of milk to be 0·93. The number of investigators, however, who have determined the specific heat of milk appears to be extremely limited. Two points should be mentioned in this connection, both of which might conceivably tend to cause the value of K to be a little low. First, if the comparatively slight agitation which occurs even when the Hortvet stirrer is manipulated continuously throughout the experiment, is not sufficient to cause thorough mixing, and there is failure to warm up to the observed freezing-point the whole of the materials whose surfaces are wetted by the milk, less heat would be required, and therefore less ice would be formed, thus diminishing the value of K, as compared with the case when the whole of the system wetted by the milk is raised to the observed freezing-point. If the metal starter, by means of which a particle of ice is introduced into the liquid, is inserted when the thermometer is in position in the freezing-tube, it will be seen that the point at which crystallisation begins must always be quite near to the bulb of the thermometer, so that, whether there is stirring or not, the latent heat of formation of ice is first liberated near to the bulb of the thermometer.

Again, it has been pointed out that a longer time is required with the Hortvet technique for the mercury to assume the stationary position after only a small, as compared with a larger, amount of supercooling has been employed, and this is the case, but to a less extent, when stirring is used. Since the cooling-bath is maintained at a temperature below that of the freezing liquid, and the insulation caused by the air-jacket around the freezing-tube is not perfect, more heat will be abstracted in the case of the lesser amount of supercooling during the rise of temperature which accompanies freezing of the supercooled liquid, because the temperature then remains for a longer period in that region where the abstraction of heat is greatest in a unit of time; this will cause a slight further depression of the freezing-point in excess of that due to supercooling alone, thus bringing the reading for the lesser nearer to that for the greater supercooling, and consequently diminishing the value of K calculated from these observations.

(2) *The Heat Transference Correction*

A brief reference has already been made in this paper to the effect on the freezing-point when abstraction of heat by the cooling-bath, from the liquid in the

freezing-tube, takes place while the temperature is rising from the point at which freezing is induced until the stationary position of the mercury column is reached. In the form of apparatus devised by Raoult and used in his latest work (1898), the freezing-tube containing the liquid to be examined was first cooled to about zero in a separate cooling mixture, and then placed in a slightly larger tube fitted to the cooling-bath; the freezing-tube was thus surrounded by an air-space which greatly diminished gain or loss of heat. Moreover, the cooling-bath, just before the inoculation of the liquid in the freezing-tube with ice, was adjusted to such a temperature that, at the observed freezing-point, only as much heat was extracted from the freezing-tube and contents as gained admittance from the surroundings in spite of insulation, together with that generated by stirring. This temperature of thermal equilibrium of the freezing-tube and contents with the surrounding media, called the "convergence temperature," was maintained to the end of the experiment. By so arranging the conditions of working that the convergence temperature coincided with the observed freezing-point the "error" due to heat transference was rendered negligible.

The arrangement adopted by Monier-Williams (1914) was similar in principle, but, in order to avoid the use of a separate cooling-bath, he introduced ether into the jacket surrounding the freezing-tube during the cooling process to reduce the time needed for refrigeration; this ether he removed before inducing crystallisation. In his later design of cryoscope (1933) the jacket contains 15 per cent. alcohol, which is removed, just prior to the commencement of freezing, but without any adjustment of the cooling-bath to cause the convergence temperature to coincide with the observed freezing-point.

From this, it will be seen that the Hortvet apparatus is distinguished from the other cryoscopes mentioned in that, when the technique recommended is observed, the action of the cooling-bath continues unchecked during the time the temperature is rising after freezing has begun, until the observed freezing-point is reached; if the true freezing-point is desired, a correction for the heat transference which takes place during this period must therefore be applied to the observed freezing-point, to compensate for the "error" so introduced.

The following experiments were carried out to ascertain the heat-transference factor for the Hortvet apparatus and method of working. A portion of milk was examined, the whole operation of determining its freezing-point being completed with methylated spirit in the space surrounding the freezing-tube; another observation was then made on the same portion of milk, but the alcohol was removed immediately before freezing was induced. With the second milk examined the experiment where alcohol was withdrawn was made before that in which the alcohol remained; this sequence was varied alternately in consecutive experiments.

The amount of supercooling in the experiments was, as nearly as possible, the same in every case—about 1·20°—and on only one occasion differed by as much as 0·03° C. in the two observations on the same milk. In these circumstances the supercooling correction is constant in amount for the same sample of milk, and the difference in the observed freezing-points, with and without the presence of alcohol, will be due to heat transference. The results are given in Table IV. The Hortvet technique was followed as regards stirring in all these experiments.

TABLE IV

The Effect of Heat Transference in the Hortvet Process

	With alcohol Δ	Without alcohol Δ	Difference K'C	K'
Read by hand-lens				
53425 R.D.	0·534	0·532	0·002	0·004
53426 R.D.	0·550	0·547	0·003	0·005
48051 By.D.	0·548	0·546	0·002	0·004
48052 By.D.	0·538	0·534	0·004	0·008
53428 R.D.	0·549	0·545	0·004	0·008
53430 R.D.	0·544	0·542	0·002	0·004
Read by levelled telescope				
46 Middleton	0·557	0·554	0·003	0·006
48 ,,	0·552	0·549	0·003	0·006
49 ,,	0·552	0·549	0·003	0·006
51 ,,	0·554	0·550	0·004	0·008
25447 H.B.D.	0·550	0·547	0·003	0·006
25449 H.B.D.	0·543	0·539	0·004	0·008
			Average	0·006

No difference could be observed in the freezing-point of water in experiments with or without alcohol in the outer jacket.

The correction to be applied to the observed freezing-point depression for the "error" due to heat transference has been given by Raoult as:

$$\frac{C}{L}\left(1+\frac{r}{R}\right)\frac{z}{Z},$$

where C, L, r, and R, have the same significance as in the formula II, already given, to obtain the correction due to supercooling, and z is the time which elapses from the commencement of freezing until the temperature has become nearly stationary. Z is the time necessary for the freezing-tube and contents to cool or warm one degree by heat transference at the temperature of freezing, but without the formation of ice. This correction is positive if heat is abstracted, and negative if heat is added.

The form

$$\frac{C}{L}\left(H+\frac{r}{W}\right)\frac{z}{Z},$$

where H represents the specific heat, and W the weight of the liquid under examination, will render the formula of more general application.

Now, as, in the case of the formula given for the supercooling correction, for the same apparatus and conditions of working, and equal amounts of the same kind of solution, L, r, H and W are constant, Z is also constant under these conditions. Unless the time, z, is the same in all cases we cannot, strictly speaking replace the part of the above expression $\frac{1}{L}\left(H+\frac{r}{W}\right)\frac{z}{Z}$ by a constant. But if the time taken for the mercury to rise, when freezing takes place, is assumed to be always the same, we can *then* write

$$\frac{C}{L}\left(H+\frac{r}{W}\right)\frac{z}{Z}=CK',$$

where K′ is the fraction of the true freezing-point depression by which the true freezing-point depression is increased if pure ice separates, owing to heat transference, during the rise of temperature from the lowest to the highest point which results on freezing; it is also the amount of ice formed in one gram of the original solution during that interval, and, if pure ice separates, it represents also the fraction by which the original solution is concentrated under the same circumstances.

To obtain K′, we must first of all obtain the true freezing-point depression, C (it being assumed that no heat transference takes place) by using the formula

$$C = \frac{C''}{1 + KS} \qquad .. \quad .. \quad .. \qquad (IV)$$

where C″ represents the observed freezing-point depression obtained when alcohol is absent, S the degrees of supercooling, and K = 0·011. This value for C may then be substituted in formula VI, where C′ is the observed freezing-point depression with alcohol present. The values for K′ given in Table IV have been thus obtained.

These values are less than that obtained by Monier-Williams[8] for his own new apparatus, *viz.* 0·0096, which appears to indicate that there is less heat transference in Hortvet's cryoscope than in that of Monier-Williams. The difference may be due to there being less heat abstraction through the thick walls of the glass freezing-tube than through the thin sheet brass of which the tubes are composed in the E.M.B. Model of Monier-Williams' apparatus, glass being a very bad conductor of heat compared with brass, and the walls very much thicker in the former case. The stirring, too, as has been previously stated, is very much more vigorous in Monier-Williams' method of working, which will tend to promote cooling.

Attention should be directed to another point in this connection. Since the removal of alcohol, previous to the inoculation of the supercooled milk with ice, does not entirely abolish nett loss of heat from the freezing-tube and contents to the cooling-bath, the value obtained for K′ would seem to be a measure of the difference between heat transference with and without alcohol; what might be called the "residual" heat transference, that is, nett loss of heat remaining when no alcohol is used, is left undetermined and by so much the value of K′, derived from the substitution of the appropriate values in equations IV and VI, will be low.

(3) *The Total Correction in the Hortvet Process*

The total correction which should be applied to the observed freezing-point depression to obtain the true freezing-point depression, depends upon the sum of the factors due to supercooling and heat transference.

The full equation given by Raoult[10] where there is a nett loss of heat, and modified to apply to dilute solutions in general, is:

$$C' = C + \frac{CS}{L}\left(H + \frac{r}{W}\right) + \frac{C}{L}\left(H + \frac{r}{W}\right)\frac{z}{Z} \qquad .. \quad .. \qquad (V)$$

which, under certain fixed conditions previously stated in this paper, may be abbreviated to:

$$C' = C + KCS + K'C \qquad .. \quad .. \quad .. \quad .. \qquad (VI);$$

for 1 degree of supercooling this becomes:

$$C' = C + C(K + K')$$

or

$$C' - C = (K + K')C,$$

that is, the difference between the observed and true freezing-point depressions $= (K + K')C$. We have seen that $K = 0{\cdot}011$ and $K' = 0{\cdot}006$, whence

$$C' - C = 0{\cdot}017 \times C.,$$

i.e. the indicated effect of supercooling and heat transference is that the true freezing-point depression is increased by 0·017 of its value, if pure ice separates, for each degree of supercooling, and the amount of ice formed in 1 g. of the original milk is 0·017 g. when there is one degree of supercooling; also, if pure ice separates, the concentration of the original milk is increased in the same circumstances by 0·017 of its value, or approximately 1/60. The supercooling recommended by the A.O.A.C. regulations is from 1·0° to 1·2°. Taking the latter figure, the observed freezing-point depression in the Hortvet cryoscope will be $0{\cdot}011 \times 1{\cdot}2 + 0{\cdot}006 = 0{\cdot}019$ of the true freezing-point depression greater than the true freezing-point depression. If the observed freezing-point depression be taken as 0·540, then a total correction of about 0·010 is indicated as the deduction to be applied to obtain the true freezing-point depression. But it has already been pointed out that the values obtained for K and K′ are probably slightly low, owing to reasons connected with the lack of thermal equilibrium of the freezing-tube and contents with their surroundings while the formation of ice is in progress and the jacket round the freezing-tube contains air only.

It should be noted that the value $KS + K'$ is not the amount which should be deducted from the observed freezing-point depression to give the true freezing-point, but the *fraction* of the true freezing-point depression, which should be so used.

PART III

Some Miscellaneous Observations made during the Course and Arising out of the Preceding Work

During the progress of the work that has been described in Parts I and II of this paper, many considerations arose relating more or less closely to the subjects under investigation. Some of these are mentioned in this part of the paper.

(1) *The influence of the omission of alcohol from the space surrounding the freezing-tube*

The heat transference factor in the Hortvet apparatus, although not large, might be reduced to very small dimensions if no alcohol at all were employed in the jacket surrounding the freezing-tube, and there would be also a reduction in the amount of manipulation required, as compared with that when alcohol is used, for facilitating the cooling of the milk and its removal before freezing is induced. An increase in the time required to carry out an experiment would, however, be expected.

The following observations were made:—The time which was required for 35 ml. of milk to cool from zero to −1·0°, and from −1·0° to −1·7° (*i.e.* a supercooling of approximately 0·5° and 1·2°, respectively), (*a*) with the use of methylated

spirit, (*b*) without methylated spirit, the cooling-bath being maintained at −3·0° in each case, and (*c*) without spirit, with the cooling-bath kept at −7·0°. The results are given in Table V.

TABLE V

	Temperature of cooling-bath °C.	Time required to cool from 0·0° to −1·0°	Time required to cool from −1·0° to −1·7°	Time required to cool from 0·0° to −1·7°
With alcohol	−3·0	2 min. 0 sec.	2 min. 0 sec.	4 min. 0 sec.
Without alcohol	−3·0	8 ,, 45 ,,	15 ,, 19 ,,	24 ,, 4 ,,
Without alcohol	−7·0	2 ,, 45 ,,	2 ,, 26 ,,	5 ,, 11 ,,

From the above table it appears that, if the use of alcohol were dispensed with, during the process of cooling, the duration of an experiment would be greatly increased, unless the cooling-bath were reduced considerably below the temperature (−3·0°) specified in the A.O.A.C. regulations. On the other hand, if the temperature of the cooling-bath be maintained at −7·0° throughout the experiment, the heat transference factor is bound to be greatly increased.

(2) *The jacket surrounding the freezing-tube*

Since there was no intention in the designing of the Hortvet apparatus to isolate the freezing-tube and contents from the action of the cooling-bath during the latter part of the experiment, no arrangement was made to have substantial clearance between them. In Raoult's later apparatus there was a clearance of about 2·5 mm., and in Monier-Williams' new design one of 2·5 to 3·0 mm. is laid down, with a lower limit of 2·5 mm. In the A.O.A.C. regulations no specification is given for the internal diameter of the metal tube of the cooling-bath—the external diameter is to be 33 mm.; the instructions also prescribe that the freezing-tube "shall fit closely" into it. The average diameter of the freezing-tubes I used was 29·8 mm., and the internal diameter of the tube containing it 32·0 mm., leaving a clearance of approximately 1 mm. only. That the heat transference was not greater than was found, was probably due to the bad thermal conductivity of glass and the nearly complete absence of stirring.

This small amount of clearance is not very easy to work with conveniently when no alcohol is used. It was therefore decided to modify the apparatus by using a wider metal tube in the cooling-bath with the ordinary type of freezing-tube, so as to give a clearance of 3 mm., and the ordinary metal tube with a narrower freezing-tube to give the same amount of clearance. It is intended to proceed with experiments along these lines.

Another difficulty in the withdrawal of alcohol from the modified standard Hortvet apparatus, is that the rubber collar at the flange of the freezing-tube is apt to make an airtight joint and so prevent the withdrawal of alcohol. This difficulty was overcome by inserting short lengths of wire between the rubber and the glass. Some more convenient arrangement is desirable should the apparatus be modified, for routine use, so as to include the withdrawal of alcohol.

Further, in connection with the thermal insulation of the freezing-tube, the following facts were observed. There is described in the preceding section an experiment in which no heat-conducting liquid was used in the jacket around the

freezing-tube, and it was found that the time taken for the temperature of the milk in the freezing-tube to cool from 0 to −1·7° was about 24 minutes; in another experiment the corresponding time was 33 minutes. The experiments were carried out under exactly the same conditions except that different milks and freezing-tubes were used. It seems probable that the longer time required in the second instance was due to one or both of the following reasons:—To the external diameter of the freezing-tube being less—it could only have been slightly so—and thereby slightly increasing the insulating space, and to the thicker walls of the tube. If the effect of a slight variation in the dimensions of the freezing-tube leads to a difference of 9 minutes in the time required for cooling from 0° to −1·7°, it seems an additional argument for increasing the insulating jacket to, say, about 3·0 mm., if heat transference is to be reduced to a minimum.

(3) *The measurement of the rate at which the temperature rises in the supercooled liquid after freezing commences*

In the experiments recorded in Part I of this paper, the time of rising of the mercury was taken as the period from the commencement of the rise until there was a definite retardation. The adoption of this point of pronounced retardation, to fix the end of the period of ascent, was more or less satisfactory if about equal degrees of supercooling were used in the neighbourhood of 1·2° or more; but when the supercooling was less than 0·8 or 0·9°, the case was quite different. There does not then occur the same rapid rise followed by a definite falling off in speed near the highest point; the rate of rising of the column diminishes gradually as it passes from a definite rise to the position when it appears to be practically stationary, and the point at which retardation begins is further from the position of rest.

Another method of procedure tried consisted in fixing the horizontal cross-wire of the levelled telescope on the top of the mercury column when retardation first occurred and repeating the operation as the mercury rose, noting the time when no further rise was perceptible.

With varying amounts of supercooling, owing to the different manner in which the rise of the mercury took place, it was considered impossible to obtain results by either method which could be claimed to be entirely satisfactory even when operating on the same sample of milk. There was, of course, a longer time registered, for the same milk, by the latter method of measurement, than when the first rapid and more obvious rise, only, was observed.

(4) *The use of a heat-conducting liquid between the freezing-tube and the cooling-bath*

It has been explained that, with the object of hastening the extraction of heat from the liquid under examination, observers have used a conducting medium surrounding the freezing-tube. Dekhuizen[12] used mercury for this purpose, whilst Monier-Williams in his earlier form of cryoscope used ether, and in the later (1933) form, 15 per cent. alcohol. Hortvet used methylated spirit, whilst Raoult left the space empty.

When a liquid is used, the surfaces of the tubes forming the jacket are certain to remain wet after the bulk of the liquid has been withdrawn, and it would appear

possible that evaporation to a greater or less extent must take place, resulting in the absorption of a certain amount of heat.

Raoult states that his formula applies only when there is no condensation of moisture on the outside of the freezing-tube, and the same might be said, on theoretical grounds, concerning evaporation from the same surface.

Another point is that the conducting liquid at a temperature between, say, $-1{\cdot}7°$ and $-3{\cdot}0°$ is suddenly replaced by air at the temperature of the room; moreover, some air may be drawn through with the last portions of alcohol.

Summary and Conclusions

1. The effects of three different methods of stirring in the Hortvet apparatus have been investigated. No significant differences in the observed freezing-point of the same milk were found when following the Hortvet technique or operating the Hortvet stirrer continuously, or when using a flat and more efficient stirrer during the rise of the mercury from the lowest to the highest point as the milk froze.

2. The values obtained with the Hortvet cryoscope for the supercooling and heat transference factors cannot be considered to be entirely satisfactory; reasons are given which may account for this. It seems certain that similar criticism applies, more or less, to other cryoscopes in which the conditions of experiment are not arranged so that the convergence temperature is the same as the observed freezing-point. It would, indeed, apply in some measure to Raoult's elaborate instrument and technique, if the precaution were neglected to arrange that the convergence temperature coincides with the observed freezing-point, for, in his experiments the solution was cooled from 0° until a supercooling of $0{\cdot}5°$ was obtained, with the temperature of the cooling-bath maintained at $-5{\cdot}0°$ to $-6{\cdot}0°$, and an air-jacket round the freezing-tube. The Hortvet apparatus was not intended to serve for the determination of correction factors.

3. Three courses for the cryoscopic examination of milk appear to be open:
   (*a*) To use an apparatus of precision, in which the freezing liquid at the observed freezing-point is in thermal equilibrium with its surroundings.
   (*b*) To discard altogether any attempt to obtain the correction factors of supercooling and heat transference, and to use a standard apparatus and method of procedure in all experiments. The results will be comparable, notwithstanding the fact that the figures obtained differ a little from true freezing-points.
   (*c*) To standardise the apparatus used, by comparison with a method of precision, such as that of Raoult or Monier-Williams, using the same milk in each case.

My thanks are due to Mr. W. J. Shutt of the Department of Physical Chemistry, Liverpool University, for great assistance from discussions of the principles underlying cryoscopy, and for the benefit of constructive criticism to him and to Dr. Monier-Williams and Mr. A. N. Leather. I am indebted to my colleague, Mr. R. J. Taylor, for efficient and willing help in devising necessary modifications of apparatus.

I wish to thank Mr. G. D. Elsdon for interest and facilities to carry out the investigation.

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ERRATA IN PART I (ANALYST, March, 1935).—P. 148, 8 lines from bottom of page. *Omit* the words "from the thermometer."

P. 150, 2 lines from bottom of page. *For* "29·5 mm." *read* 26·0 mm.

A Modification of Thorpe and Holmes's Method for the Determination of the Total Proportions of Methyl, Ethyl, *Iso*-propyl and Propyl Alcohols

BY S. S. AIYAR, M.SC., PH.D., F.I.C., AND P. S. KRISHNAN, M.A., A.I.C.

INTRODUCTION AND SCOPE.—This investigation is the outcome of the definition of the term "spirit" under the Indian Customs Tariff, whereby methyl, ethyl, *n*-propyl and *iso*-propyl alcohols are assessable to spirit duty.

The Indian Customs Tariff defines spirit as follows:

> The words "spirit" and "spirits," where used in items 30, 31 and 32 of the Statutory Import Tariff, Part II, Schedule II, to the Indian Tariff Act, 1894 (VIII of 1894), are not confined to ethyl alcohol, but also cover all other alcohols the proof strength of which can be readily ascertained. This description does not apply to alcohols other than those that (*a*) are miscible with water in all proportions at ordinary temperatures, and (*b*) at a temperature of 51 degrees Fahrenheit have, in the pure state, a specific gravity relative to water of not more than 0·923 (twelve-thirteenths). These conditions are satisfied by ethyl, methyl, normal-propyl and *iso*-propyl alcohols.

It was found that the determination of alcohol in preparations containing *iso*-propyl alcohol by the Thorpe and Holmes method did not give the true spirit-strengths, as it does with preparations containing ethyl or methyl alcohol. Thus it became necessary to study the behaviour of these alcohols, which would be classed as "spirit" under the above definition, and to work out a modified procedure for the determination of the propyl alcohols.

Initial qualitative examination showed (i) that both *n*-propyl and *iso*-propyl alcohols are miscible with petroleum spirit; (ii) that both are partly "salted out" from aqueous solutions by sodium chloride; (iii) that they have only limited solubilities in saturated sodium chloride solution (at about 85° F.); and (iv) that both alcohols can be removed from petroleum spirit solution by water to a much larger extent than by saturated brine.

The last observation suggested that in these cases a modification of Thorpe and Holmes's method, consisting in washing the petroleum spirit extract a few times with small quantities of water following the first brine wash, might give more correct values. This has been experimentally confirmed.

EXPERIMENTAL.—The following four alcohols were examined:—Normal propyl alcohol (Kahlbaum), *iso*-propyl alcohol (pure, Merck), ethyl alcohol and methyl alcohol (absolute alcohols dehydrated and distilled in the laboratory).

The routine method, which is based on Thorpe and Holmes's procedure for the determination of ethyl alcohol in essences and medicinal preparations (*J. Chem. Soc.*, 1903, **83**, 314), consisted in diluting a suitable volume of the sample to about 100 ml., saturating it with common salt, extracting twice with successive portions of 25 ml. of petroleum spirit, combining the petroleum spirit extracts, washing them twice (25 ml. each time) with saturated brine, and distilling the combined brine layers to obtain 100 ml. of distillate (Column A in Table I gives the results obtained by this method).

In the proposed procedure the modification consists in washing the combined petroleum spirit extracts twice with 25 ml. of water instead of brine. The results for this method are recorded under Column B in Table I.

The "plain distillation" consisted in diluting 25 ml. to 125 ml., distilling, and collecting 100 ml. of distillate. The results are given under Column C.

Thus, three distillations, A, B and C, were carried out for each kind of alcohol, or each strength thereof, with the results tabulated below.

TABLE I

Name of alcohol and strength	1 Proof strength of distillate; from spirit tables*			2 Calculated proof strength of original liquid by multiplication of data in column 1 by 4			3 Calculated vol. per cent. of alcohol; from appropriate alcohol tables (original liquid)		
	A	B	C	A	B	C	A	B	C
Methyl alcohol, absolute (Note 2)	48·8	48·5	48·0	195·2	194·0	192·0	Temperature correction not available		
Ethyl alcohol, absolute	43·8	44·1	44·1	175·2	176·4	176·4	99·52	100·68	100·68
n-Propyl alcohol, absolute	9·75	26·2	46·2	39·0	104·8	188·8	Table not available		
Iso-propyl alcohol, absolute	14·5	39·1	45·0	58·0	156·4	180·0	28·72	88·68	100·08
Iso-propyl alcohol, 20 per cent.	10·4	10·7	11·55	41·6	42·8	46·2	20·0	20·6	22·4
Ditto, 30 per cent.	12·7	15·0	15·7	50·8	60·0	62·8	24·5	30·2	30·6
Ditto, 40 per cent.	14·3	18·1	19·4	57·2	72·4	77·6	28·9	37·68	40·96
n-Propyl alcohol, 20 per cent.	8·9	10·4	10·7	35·6	41·6	42·8	Table not available		

Note (1). The specific gravities could not be determined at 60° F., owing to local conditions. They were determined at laboratory temperatures and appropriate corrections were applied.

Note (2). These apparently absurd figures are due to the fact that the relationship between specific gravity, volume strength and proof spirit is not identical for methyl alcohol and for ethyl alcohol, the divergence being the greatest in the region of 25 per cent. v/v, the strength that had been chosen for the experiments. The percentage by volume of methyl alcohol present could not be calculated, as temperature-correction tables for specific gravity were not available.

From the results it is clear that by using the routine procedure based on Thorpe and Holmes's principle, propyl alcohols are only partly recovered when their strength exceeds 20 per cent. v/v. The loss increases with increase in the strength of the original sample. It was also found that, by washing the petroleum spirit layer with distilled water, more of these alcohols could be recovered (see

* "Spirit Tables," published by H.M. Stationery Office, under the authority of the Commissioners of His Majesty's Customs and Excise.

Column 3B of Table I). As the recovery was still not quite satisfactory, further experiments, in which the number of washings with water was increased, were made, with a view to ascertaining the minimum number of washings required to remove most, if not all, of the alcohols. These experiments were restricted to *iso*-propyl alcohol, as, in our experience, next to ethyl alcohol, *iso*-propyl alcohol is the solvent in most common use. In order to get some idea how the method would work in the presence of other interfering substances, a series of determinations on an artificial essence was made. The "essence" was prepared by dissolving 10 ml. each of alcohol-free orange and lavender oils in 350 ml. of *iso*-propyl alcohol, and making the solution up to 500 ml. with water. A blank solution was also prepared by diluting 350 ml. of the *iso*-propyl alcohol to 500 ml. with water. The actual "proof spirit" content of the essence was found by distillation of the blank solution.

In this and the following series of experiments with the "essence" a further slight modification was introduced, the spirituous liquids being shaken with petroleum spirit only once. The quantity, however, was increased to 50 ml. Again, in the preliminary experiments, petroleum spirit had been washed with 25 ml. of water each time, but in these later experiments only 10 ml. of water were used for each washing. Before the petroleum spirit extract was shaken with water, it was in every instance washed once with 10 ml. of saturated brine. One series of these experiments showed that, with five aqueous washings of 10 ml. each time, the alcohol could be recovered within 3 per cent. of theory.

To confirm this and to ascertain whether further washings effected any improvement, a similar "essence" was distilled under the conditions tabulated in Table II.

TABLE II

Experimental detail		Proof spirit obtained from the combined brine layer, brine wash, and aqueous washings Per Cent.	Proof spirit recovered from petroleum extract after the aqueous washing specified in column 1 by further washing twice with 50 ml. of water each time Per Cent.	Total of figures in columns 2 and 3 Per Cent.
10 ml. brine wash only		40·9	77·0	117·9
1. 1 × 10 ml. H_2O wash	In addition to first wash with 10 ml. of brine	69·3	47·2	116·5
2. 2 × 10 ml. H_2O wash		93·7	23·1	116·8
3. 3 × 10 ml. H_2O wash		107·1	9·9	117·0
4. 4 × 10 ml. H_2O wash		112·2	3·4	115·6
5. 5 × 10 ml. H_2O wash		115·9	2·3	118·2
6. 6 × 6 ml. H_2O wash		116·3	1·8	118·1

DISCUSSION OF RESULTS.—The experiments were conducted under routine laboratory conditions. From the results in column 2 it is clear that more than 5 washings serve no useful purpose. The spirit not recovered after 5 washes is only 2 parts in 118, which may be regarded as within the limits of experimental error and negligible.

It is also obvious that, for rapid routine work, the number of the washings should be reduced to the minimum consistent with efficiency.

It has been observed that the quality of the petroleum spirit affects the

quantity of spirit recovered; this was especially noticeable in the experiments in which the petroleum spirit extracts were washed only once or twice with water.

METHOD RECOMMENDED.—We recommend the following modified procedure for the determination of total spirit-content when the presence of *iso*-propyl alcohol is suspected:—One hundred ml. of the alcoholic liquid (original sample or distillate) containing approximately 30 per cent. of proof spirit is saturated with common salt and shaken with 50 ml. of petroleum spirit (b.p. 40° to 60° C.), and allowed to separate. The brine layer is drawn off and the petroleum spirit extract is washed with 10 ml. of saturated brine, followed by five successive washings with 10 ml. of water. The brine layers and aqueous washes are combined and distilled, and 100 ml. of distillate are collected. The distillate is cooled to laboratory temperature, and its spirit-content is determined by the specific gravity method.

This work was carried out in the Laboratory of the New Custom House, Bombay, and is published with the permission of the Government of India.

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.

COLOUR REACTIONS FOR THE IDENTIFICATION OF HYDROGENATED FISH OILS

IN Tortelli and Jaffé's test (*Annali Chim. Appl.*, 1914, **2**, 80; Abst. ANALYST, 1915, **40**, 14) a transient pink colour, changing to bright green, is obtained with hydrogenated fish and marine animal oils. Davidsohn (*Z. angew. Chem.*, 1915, **29**, 560) found that hydrogenated vegetable oil also gives a green colour, and this is in accordance with our experience. As the transient rose colour described by Tortelli and Jaffé may sometimes escape notice, we have modified their test so as to obtain a persistent pink colour.

Three g. of the melted hydrogenated oil are dissolved in a test-tube in 6 ml. of a mixture of chloroform and glacial acetic acid (1 : 1). Bromine is added, drop by drop, from a burette until a very faint pink colour appears (best seen against white paper); as a rule, two or three drops are sufficient. The test-tube is then set aside, and within 10 minutes a very characteristic reddish-violet colour appears. With other oils and tallows the pink colour does not appear, but, after the addition of a few more drops of bromine, the colour gradually changes from green to brown.

The following is an alternative method of applying the test:—The melted fat (2·5 ml.) is dissolved in the mixture of chloroform and glacial acetic acid, the solution is treated with 1 ml. of a 10 per cent. solution (by weight) of bromine in chloroform, and the cylinder is allowed to stand. With a hydrogenated marine animal or fish oil the rose colour gradually changes, after a few minutes, to a deep purple, which remains unaltered for a long time. Pure hydrogenated vegetable oils give, under these conditions, either no colour or a green or greenish-yellow colour. With mixtures of hardened vegetable and marine animal or fish oils the characteristic purple colour is perceptible in the presence of as little as 5 per cent. of the latter.

The following results were obtained with samples of imported hydrogenated oils and some non-hydrogenated oils:

TABLE I

Hydrogenated Fish Oils

	Name of oils		Colour reaction	Conclusion
(1)	Edible hardened fish oil	Japan) ..	Purple	Hydrogenated fish oil
(2)	,, fish oil products	(do.) ..	do.	do.
(3)	Hydrogenated fish oil ,,	(do.) ..	do.	do.
(4)	Edible hardened oil	(do.) ..	do.	do.
(5)	,, oil product	(do.) ..	do.	do.
(6)	Technical hardened fish oil	(do.) ..	do.	do.
(7)	Edible hardened whale oil	(Denmark) ..	do.	do.

TABLE II

Hydrogenated Vegetable Oils

	Name of oils	Colour reaction	Conclusion
(1)	Medakol (United Kingdom)	Brown	Not a hydrogenated fish oil
(2)	Eraco (do.)	do.	do.
(3)	Hydrogenated vegetable oil, "Lotus" brand	No colour	do.
(4)	do. "Lily" brand	do.	do.
(5)	do. "Scale" brand	do.	do.
(6)	do. "Cross Swords" brand ..	do.	do.
(7)	do. "Wheel" brand	do.	do.

TABLE III

Non-hydrogenated Oils

	Name of oils	Colour reaction
(1)	Poppy-seed oil	Yellow
(2)	Sesame oil	do.
(3)	Olive oil	do.
(4)	Coconut oil	Brown
(5)	Castor oil	Yellow
(6)	Tallow	Brown
(7)	Ghee	do.

Mixtures of hydrogenated fish-oil products included in Table I, in the proportion of 5 and 10 per cent., with hydrogenated vegetable products in Table II, were also tested. A distinct purple shade was obtained with the 10 per cent. mixtures in half-an-hour, whilst with the 5 mixtures a faint purple colour appeared after an hour.

Dr. H. B. Dunnicliff, Special Chemical Adviser to the Central Board of Revenue, India, has applied this test in his laboratory at Lahore to a large number of samples of hydrogenated and non-hydrogenated oils, and has obtained results analogous to those given in the foregoing tables.

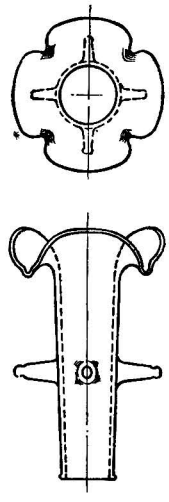
This investigation was carried out in the Chemical Laboratory, Calcutta Custom House, and the paper is published by permission of the Collector of Customs, Calcutta.

We wish to thank the Special Chemical Adviser and his assistant, Monohar Lal, for their interest in the work.

M. N. GHOSE
H. K. PAL

CHEMICAL LABORATORY
CALCUTTA CUSTOM HOUSE

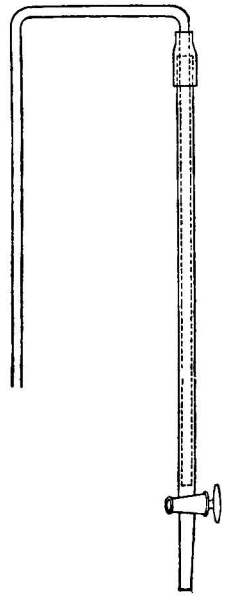
ADAPTER COLLARS FOR USE IN FILTRATION



FILTRATIONS through pulp, with funnels in the necks of flasks, are apt to suffer from two evils. If the funnel fits the neck of the flask too well, it often seals it up altogether; consequently the pressure of the air inside the flask stops filtration. On the other hand, if either the funnel or the neck of the flask departs too much from the circular, the funnel is liable to be balanced precariously on two points of the neck, and a slight jar may cause the upsetting of a considerable amount of liquid from a full funnel. The collars shown in the figure were devised to remedy these two defects. Each collar consists of a piece of wide glass tubing turned over at the edge at one end to form a flange, this flange being pressed into "lips" at four points; close to the other end of the tube four small glass arms are sealed on to the wall, from which they project at right angles like the spokes of a wheel. When the tube is slipped into the neck of the flask, the glass arms should be of such a length as not to allow too much play inside the neck; the flange should be wide enough to rest on the top of the neck, the "lips" allowing free passage of air between the funnel and the neck. The funnel-stem is passed through the collar in the ordinary way; the indentations of the flange serve to hold it steady, and there is no possibility of air lock. Being made entirely of glass, the collar can easily be rinsed free of splashes.

B. S. EVANS

RESEARCH DEPARTMENT
WOOLWICH ARSENAL, S.E.



A SIMPLE SYPHONING DEVICE

THE apparatus consists of two parts: an ordinary syphon tube and a slightly wider straight tube with a tap. The width of the straight tube should be such that it will slide easily over the syphon tube; the length, from one end to the tap, a little shorter than the longer arm of the syphon. The straight tube is attached to the longer arm of the syphon by a rubber connection, fitting not too tightly, so that it can readily be slid along the arm. To use the apparatus, it is disconnected, the tap is closed, and the straight tube filled with water (or other liquid); it is then slid on to the syphon tube and pushed to the top; if the shorter arm is then immersed in the liquid to be syphoned, the straight tube drawn down to the end of the longer arm, and the tap opened, the syphon will start to flow.

B. S. EVANS

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A DEVICE FOR PREVENTING THE LOSS OF STOPPERS, TAPS, ETC.

IF stoppers or taps are attached to their special vessels by means of string the latter soon rots, and is liable to break at any moment. Thin stainless iron wire is an admirable substitute for string in this respect, and will stand many months of ordinary laboratory usage before needing replacement.

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Notes from the Reports of Public Analysts

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

CITY OF BIRMINGHAM

Report of the City Analyst for the Fourth Quarter, 1934

Of the 1290 samples of food and drugs submitted during the quarter, 100 were bought formally and 1190 informally.

Talc in Sweets.—A sample of cough drops contained 0·75 per cent. of talc. This was used as a dusting powder to prevent the sweets from sticking together, and it is possible that it had accumulated at the bottom of the jar in which the sweets were kept. The firm was cautioned.

"Non-brewed Table Vinegar."—This consisted of artificial vinegar. Table vinegar should be made from malt, and, as the bottle was labelled both as table vinegar and as non-brewed vinegar, there was a contradiction in terms. The firm was cautioned.

Malt Vinegar with Abnormally Low Constituents.—A sample, sold as malt vinegar, contained abnormally small percentages of solids, ash, phosphates and nitrogen, giving rise to the suspicion that vinegar other than that derived from malt was present. At an interview with one of the directors of the firm manufacturing the vinegar it was definitely stated that only malt and grain were used, and an invitation to visit the brewery and see the process was accepted. Samples of the materials used and of the product at various stages of manufacture were taken, and these are being analysed in order to try to discover the reason for the abnormally low figures.

H. H. Bagnall

COUNTY OF KENT

Report of the County Analyst for the Fourth Quarter, 1934

Gregory Powder.—One sample had been compounded in accordance with the 1914 Pharmacopoeia, whereas it should have been prepared according to the 1932 edition. The 1914 powder contained light magnesia, which in the more recent Pharmacopoeia is replaced by heavy and light magnesium carbonate.

Iodine Ointment.—Two samples of non-staining iodine ointment showed considerable deficiencies in iodine; they contained 0·78 and 2·0 per cent., respectively. A purchaser has every right to expect this ointment to be made according to the formulary of the British Pharmaceutical Codex, and, under those conditions, the ointment would contain approximately 5 per cent. of iodine.

Poultry Manure.—There has been some question as to the residual manurial value of poultry manure, the composition of which shows considerable variations. The manure may have been sold wet (green), or partly dried by the addition of earthy material or by exposure to the air. In the latter case there is usually a considerable loss of ammonia during exposure, but some poultry manure is now dried artificially by means of heat. The composition also depends to some extent upon the food of the poultry. Hence, a general price is assigned to this manure which has no real relation to the constituents of manurial value. In these circumstances compensation values for poultry manure applied might well be based on Voelcker and Hall's *Tables for Feeding Stuffs*. If the composition of the poultry manure concerned is known, there is no reason why it should be treated

differently from fertilisers and the usual scale of compensation not be adopted. In the latter case the compensation award might well be one-third of the price paid, after taking one crop, and one-sixth after two crops. Though poultry manure usually acts quickly, Dr. Voelcker has shown that there is a distinct manurial value remaining after one crop.

AGRICULTURAL LIME.—Limes offered for sale vary greatly in composition, and this applies not only to those produced in the district, but also to different proprietary and well-known brands. From the analysis which makers are forced to give when selling lime it is often difficult for the farmer to assess the real value of the article offered. Burnt lime is sometimes offered in the slacked or partly slacked state, and then, in addition to the impurities originally present in the limestone, the lime will contain water, probably amounting to about 25 per cent. A carbonate of lime analysed during the quarter contained, besides other impurities, no less than 22 per cent. of sandy matter. It is, therefore, essential that a purchaser should pay great attention to the quality of lime or ground limestone which he intends to purchase, and ascertain which of the products is the cheapest.

WASTE APPLE FROM CIDER PRESSES.—This has only low manurial value, largely owing to the amount of water left in the pressings. A sample recently examined contained only 0·31 per cent. of nitrogen, 0·16 per cent. of phosphoric acid, and 0·42 per cent. of potash.

CASTOR BEAN IN GROUND-NUT CAKE.—A sample of decorticated ground-nut cake was found to contain castor bean. Although the quantity estimated in this case amounted to only 0·08 per cent., I have no doubt that it was the cause of damage to stock. The occasional occurrence of castor in feeding stuffs during the part year has caused uneasiness in the minds of many agriculturalists. In the view of some people, sufficient care is not taken by importers to ascertain that cakes are free from castor, but difficulties in this connection are due to the fact that frequently the castor bean is unevenly distributed in a feeding stuff. About a year ago I found a considerable amount of castor bean in a sample of screw-pressed linseed cake submitted to me. Although the rest of this consignment was carefully searched, there was no further evidence of castor, and the cake was fed to stock without any apparent injury. Stress has been laid upon the point that the amount of castor found in a sample of a feeding stuff is no criterion of the quantity present in the bulk, but the fact is that, when any quantity of castor is found in a part of a consignment, a far larger proportion may occur in any other part. Any prosecution for the sale of a feeding stuff containing this poisonous ingredient is rendered almost impossible on account of the difficulty of sampling on the premises on which the feeding stuff is sold or exposed or offered for sale. Although strict precautions have been taken with some foreign-pressed cake to exclude castor by the hand-picking of seed and other supervision, castor seeds still occasionally find their way into the finished cake. The appropriate Advisory Committee appointed by the Minister of Agriculture is to give consideration to the amendments of the Fertilisers and Feeding Stuffs Act, so that the declaration of the presence of poisonous materials in feeding stuffs may be made more effective.

F. W. F. ARNAUD

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

"IODINE OINTMENT": A QUESTION OF WARRANTY

On December 10th, 1934, two summonses, issued at the instance of the Hammersmith Borough Council under the Food and Drugs (Adulteration) Act in respect of the sale of iodine ointment were heard at the West London Police Court. Evidence was given that in each case a pot labelled "iodine ointment" was purchased from a stall in Shepherd's Bush Market, and that 2d. was paid for each pot. In one case the pot was marked 1s. 3d.

The Public Analyst (Mr. F. W. Edwards, F.I.C.) reported that one of the samples contained no free iodine and no potassium iodide, and that the other contained no free iodine and only 0·4 per cent. of combined iodine. Both samples consisted mainly of coloured petroleum jelly.

The formulae of the British Pharmacopoeia, 1914, and of the British Pharmaceutical Codex, 1934, require iodine ointment to contain 4 per cent. of iodine and 4 per cent. of potassium iodide.

Both defendants pleaded guilty, and a penalty of 20s. with 21s. costs was imposed in each case.

On January 1st, 1935, a similar summons, issued by the Hammersmith Borough Council, was heard at the Kensington Petty Sessional Court.

In this case, evidence was given as to the purchase from one of the defendant's branch stores of one pot of iodine ointment. The purchase price was 3d.

The certificate of the Public Analyst showed the sample to consist of iodine 0·06 per cent.; potassium iodide, nil; combined iodine (other than potassium iodide), 0·4; and a base (mainly petroleum jelly), 99·54 per cent. The sample was therefore deficient in potassium iodide to the extent of 100 per cent. and in free iodine to the extent of 98·5 per cent.

Dr. J. B. Howell, the Medical Officer of Health for the Borough of Hammersmith, gave evidence as to the uses of iodine ointment. He said that, in his opinion, the amount of free iodine in the sample would be useless as an antiseptic, and that the use of such an ointment would confer a sense of false security upon a person using it.

For the defence it was contended that (*a*) since the current edition (1932) of the British Pharmacopoeia no longer included iodine ointment, there was now no fixed standard for the ointment; (*b*) since the Customs and Excise Authorities had agreed that the pot of ointment, with the wording as sold by the defendants, was not liable to Medicine Stamp Duty, it was not a medicine and was, therefore, outside the scope of the Food and Drugs Act; and (*c*) for commercial purposes there was a standard different from that of the British Pharmacopoeia and the British Pharmaceutical Codex. The defence further pleaded a warranty. After a lengthy hearing a fine of £15 was imposed with 5 guineas costs. It was intimated that an appeal would be lodged.

The appeal to the London Sessions was heard on March 8th. Mr. Glyn-Jones, opening the case for the respondent, described the composition of the "iodine ointment" bought from the appellants, and said that the British Pharmacopoeia 1914 and the B.P. Codex required iodine ointment to contain 4 per cent. of iodine and 4 per cent. of potassium iodide, and that the base described in the 1914 B.P. was glycerin, and prepared lard, which should be 92 per cent. No importance was attached to the difference of the base of the ointment.

The applicants had raised a defence under Section 29 of the Food and Drugs (Adulteration) Act, 1928, and relied upon a warranty from their suppliers, the manufacturers of the ointment, but the warranty was, in fact, a document which had been sent by the applicants to the manufacturers, stipulating certain conditions; and he (counsel) submitted that a warranty could not come into existence to satisfy the Act, by the act of a purchaser making a stipulation which the vendor accepted, not in writing, but by his conduct.

The Bench having discussed the case in private, Sir Percival Clarke, the Chairman, announced their decision as follows:—"The matter has been argued before us and greatly simplified by learned counsel, and it resolves itself now into practically one point, and one only, and that is whether or not the applicants have brought themselves within Sec. 29, Sub-sec. 1*b* of the Food and Drugs Adulteration Act, 1928. In that sub-section the defendant or applicant is to be discharged from the prosecution if he proves to the satisfaction of the Court, first that he purchased the article in question as the same in nature, substance and quality as that demanded of him by the person to whom he sold the article, and with a written warranty to that effect, and that he had no reason to believe, at the time he sold it that it was otherwise, and that he sold the article in the same state as when he purchased it. The main point, and practically the only point which has been argued before us, was that this was supplied with a written warranty to the effect that it was the same in nature, substance and quality as that which was supplied or demanded of him by the person to whom he sold the article. We have looked with care at the alleged warranty, and we do not think that that warranty is sufficient in itself to be described as a warranty, within the meaning of the section. As that is one of the necessary details that the applicants would have to prove, and as they have failed in satisfying us of that, the result must be that the appeal will be dismissed."

The Court allowed fifty guineas costs.

Mr. Beyfus pointed out that the applicants had bought very large quantities of goods in the belief that they had a warranty, and asked the Court to state a case upon this point of law, which might affect hundreds of other cases if they should arise.

Sir Percival Clarke agreed to do so.

"DEVONSHIRE" AND "CORNISH" CREAM IN SCONES AND CAKES

On January 18th two catering firms were summoned at the Wood Green Police Court by the Middlesex County Council for selling, respectively, cream scones and cream cakes containing fat which was not milk-fat.

Mr. R. A. Robinson, for the County Council, said that as the firms had pleaded guilty there would be no need for evidence. The facts were that at the local shops of these firms there had been sold to the public scones described by one of the defendants as "Devonshire Cream Scones," and cakes described by the other defendants as "Cornish Cream Cakes." Samples of the two articles were analysed by the Public Analyst, who reported that the cream-like substance in each case was not dairy cream, the former containing 95 per cent., and the latter 83 per cent. of fat foreign to milk-fat.

"If these articles were sold simply as cream scones and cream cakes," said Mr. Robinson, "there might be room for argument as to the propriety of their sale, but, the application of the adjective 'Devonshire' carries a certain definite and unmistakable meaning to the public mind."

The description that was given would undoubtedly be associated in the public mind with dairy cream, and it was somewhat surprising that firms of this magnitude should allow such labels to be used.

Mr. Glyn Jones, addressing the Bench on behalf of the defendants, said that it was common knowledge that the filling in cream buns bought from a baker was

not, as a general rule, dairy cream at all. That fact was so well known that one could find in the dictionary the definition of the word "cream" given as follows: "Used in relation to confectionery, a cream-like substance used in the filling of cakes." The word "cream" could not be held by itself to denote "dairy cream," or otherwise the terms "boot cream" and "salad cream" would not be correct descriptions.

Since the Government made the Order forbidding the use of preservatives in cream it had been impossible to use dairy cream for confectionery purposes, unless the cakes were intended for almost immediate consumption. Bakers had, therefore, been driven to the use of substitutes. In these cases a vegetable oil of much greater purity, bacteriologically, than the ordinary standard for dairy cream had been used.

The description "Cornish" cream, counsel agreed, might lead the public to think of clotted cream, and the firm was henceforward going to omit that description.

With regard to the description "Devonshire," the word had been used by the defendant company to describe several different kinds of confectionery. The description had been applied since 1911, and he believed that the "fillings" were really Devonshire cream up to four or five years ago, when the Order as to preservatives was introduced.

In announcing the judgment of the Bench, the Chairman said that in these cases the confectionery might have looked like "Devonshire" or "Cornish," but they were described as really being such, and that was where the difference lay. Having regard to the high reputations of these firms, it had been decided to dismiss the cases under the First Offenders' Act, but to award two guineas costs in each case. It was, of course, understood that the names of these delicacies were to be revised.

Medical Research Council

REPORT FOR THE YEAR 1933–1934*

THE Report of the Committee of the Privy Council for Medical Research gives an outline of the provision made for the work of the Medical Research Council, and an account of changes in the membership of the Council and of the relations with other Government Departments.

The Report of the Medical Research Council (pp. 9–166) is divided into eight sections: I, Introduction. II, The National Institute for Medical Research. III, The Determination of Biological Standards and the Methods of Biological Assay and Measurement. IV, The Department of Clinical Research. V, External Research Schemes. VI, Industrial Health. VII, Travelling Fellowships. VIII, Conclusion.

Among the sections on subjects of chemical, as well as medical, interest are those on chemical work relating to bacteriology, and the control of the nervous system, and on the measurement of vitamins.

CHEMICAL PROBLEMS OF BACTERIOLOGY.—The researches include studies of the photodynamic inactivation of viruses, and of the conditions which allow some inactivated viruses to retain their capacity of increasing resistance to infection; the preparation of alcohol-soluble antigens from bacilli of the Salmonella group, and from the cholera vibrio. It is clear that the subject of bacteriology is being rapidly changed by the great advances in knowledge on the chemical side which are constantly being made.

* H. M. Stationery Office. Cmd. 4796. 1935. Price 3s. net.

"*Sporogenes Accessory Factor.*"—This is a substance found by Fildes and Knight in various animal and vegetable extracts, and is favourable to the growth of many kinds of bacteria. Human urine is a good source of the principle, which has not yet been separated in a pure state, although it has been shown that it is a relatively simple, ether-soluble acid, which can be distilled in the form of an inactive methyl ester and recovered in full activity by hydrolysis.

PHARMACOLOGICAL CHEMISTRY: *Ergot.*—The search by Dr. Dudley for the water-soluble active principle of ergot has been continued, and the active substance has been separated in a sufficient degree of purity to establish its existence as a separate entity.

CARBOHYDRATE METABOLISM.—It has been found that the antiglyoxalase effect of pancreatic extract is due partly to the mono-amino acids in auto-digests of the pancreas. Further work has been done on the chemical effects of toxaemia on the activity of insulin, and on the mechanism of glycogen deposition in the liver in response to insulin on the one hand or adrenaline on the other.

STEROLS AND RELATED SUBSTANCES: VITAMIN *D*.—The new structural formula for ergosterol and the nature of the internal changes that convert it by stages into calciferol, based on the work of Adam and Askew, may be regarded as established. A critical review of recent developments in the chemistry of the sterols has been contributed by Dr. Rosenheim and Dr. King to the *Annual Review of Biochemistry*.

It has been proved that the curious absence of vitamin *D* from the brain cannot be attributed to a destructive action.

PROLONGED INHALATION OF TAR DUST, ETC.—Experiments have been continued on the continuous exposure of mice to dust from tar-treated road-surfaces, and, in addition to the high incidence of skin warts, many of which become malignant, a large increase in the occurrence and size of primary growths of the lung has been observed. No definite conclusion, however, is yet justified as to the possible relation between these results in mice and the increase in recent years of the incidence of malignant lung tumours in man.

ACCLIMATISATION OF MAMMALS TO REDUCED PROPORTIONS OF OXYGEN.—Experiments on the acclimatisation of mammals to reduced tensions of oxygen have also been continued. Reduction of the proportion of oxygen in the air to 10 per cent. cannot be tolerated indefinitely, but acclimatisation to the presence of 0·3 per cent. of carbon monoxide is more readily obtained. The effect on such acclimatisation of preliminary treatment with small doses of manganese and cobalt is under investigation.

THE MEASUREMENT OF VITAMINS.—The second International Conference on Vitamin Standardisation was held in London in June, 1934, and the standards provisionally adopted at the earlier conference, in 1931, were reviewed (*cf.* ANALYST, 1932, **57**, 521).

The standards for vitamin B_1 and vitamin D were adopted on a more permanent basis, and without immediate change. In the case of the standard for vitamin *D*, the Conference considered reports presented on behalf of Professor Windaus of Göttingen and Mr. Webster of the National Institute for Medical Research, which showed that the pure crystalline vitamin *D* (vitamin D_2, calciferol) possesses a practically unlimited stability under conditions of preservation which are easily realised. The Conference, in re-adopting the present standard, consisting of a solution in oil of a particular preparation of the mixed products obtained by irradiation of ergosterol, further decided that, if the supply should prove insufficient or the standard show signs of becoming in any respect unsatisfactory, it should be replaced by a solution in oil of the pure calciferol (vitamin D_2), the unit value of that substance being then accepted at 40,000 per milligram.

The Conference adopted pure β-carotene as the basic standard for vitamin *A* activity, in place of the provisional standard of impure, mixed carotene; the unit of measurement is the activity of a certain weight of that material. It was further decided that a subsidiary standard of cod-liver oil, the unit value of which had been accurately determined in terms of the pure carotene standard, should be prepared and held available for certain purposes.

For vitamin B_1 the standard adopted in 1931 is retained; it is a preparation made from rice polishings by the method of Jansen and Donath.

As the result of the recent work of Szent-Györgyi and others, the standard for vitamin *C* is now to be expressed in terms of *l*-ascorbic acid.

It is of interest to note that the International Conference has approved a purely physical method for the estimation of vitamin *A* in liver extracts and other rich sources; this involves the determination of the coefficient of absorption by means of a spectrophotometer, and serves as an alternative to a biological test.

INTERNATIONAL INSULIN STANDARD.—The preparation of the new international standard insulin is now approaching completion. A large quantity of the purest insulin obtainable by careful recrystallisation has been prepared by Dr. Scott on behalf of the Toronto Insulin Committee. The material is now being distributed into, and sealed in, small containers, in a perfectly dry form, and as soon as its unit value has been determined by international agreement it will be distributed in place of the relatively impure standard which has served as the world basis for insulin activity since 1925.

NATIONAL COLLECTION OF TYPE CULTURES.—The number of cultures of bacteria and micro-fungi distributed to workers at home and abroad again exceeded 5000 in the year under review, and over 200 new cultures were added to the collection at the Lister Institute. Among the new types are a *Staphylococcus aureus* strain used in the standardisation of disinfectants (Insecticide strain of Reddish), and Hungarian wine yeasts from Budapest.

Arrangements have been made with the Forest Products Research Laboratory, Princes Risborough, by which its extensive collection of wood-destroying fungi, and fungi causing discoloration in timber, will in future be listed in the publications of the National Collection. The types conserved include some 180 separate species of fungi.

Department of Scientific and Industrial Research

FOOD INVESTIGATION BOARD

REVIEW OF DEVELOPMENT DURING 1932–1933*

THE current issue of the *Index to the Literature of Food Investigation* opens with a review of 15 pages on developments during 1932 to 1933, written by Miss A. E. Glennie. The subjects are surveyed under the following headings: Gas Storage of Animal Products. Rancidity. Marine-animal Oils. Milk and Milk Products. Eggs. Freezing of Animal and Vegetable Tissues. Fruit Juices. Storage and Transport of Fruit.

The literature surveyed deals with the biochemistry, bacteriology, and chemical and physical changes of the various products, and with the problems associated with freezing, canning, and sterilisation. A reference to the abstract of the paper in this or previous volumes of the *Index* is attached to the name of each author cited.

* *Index to the Literature of Food Investigation*, Vol. 6, No. 1 (1934). H.M. Stationery Office, 1935. Price 5s. net.

International Tin Research and Development Council

FIRST GENERAL REPORT, 1934*

THE International Tin Research and Development Council, composed of delegates appointed by the Governments of the principal tin-producing countries, has been established for the purpose of acquiring and disseminating scientific and technical knowledge relating to tin, its alloys and chemical compounds, the processes involved in the production of these materials, and their applications. The objects of the researches and other activities of the Council are to discover and develop new industrial applications of tin, to improve the existing products and processes, and to assist tin consumers in overcoming technical difficulties and problems relating to tin.

The need for an organisation for carrying out systematic research and development on behalf of the tin industry was realised by a group of tin-producing companies in 1929, and funds were provided to establish the Tin Research and Industrial Applications Committee. Several important investigations were begun and continued until the inauguration of the Council.

The present statement constitutes the first general report on the activities of the Council since its inauguration. A progress report was circulated in April, 1933, and a more comprehensive survey was submitted in October, 1933, but it was realised at the time that no adequate report could be made until a complete survey of the position with respect to tin had been undertaken in the chief industrial countries, particularly in the U.S.A.

The researches already in progress have been planned to investigate basic problems in all the major applications of tin, and the present report gives an account of the progress made in each of the chief lines of investigation.

TINPLATE.—The inspection of the tin coating on manufactured sheets of tinplate is almost entirely visual, although certain ductility tests are applied to the steel, and classification as to quality is therefore based upon obvious visible defects. Notwithstanding the knowledge gained as to the origin of these defects and methods for overcoming them, the proportion of prime plates seldom exceeds 75 per cent., and is often much less. There are also invisible defects which at present are not subjected to regular scrutiny. These consist chiefly of minute discontinuities in the coating, leaving steel uncovered by tin, with the results that rapid rusting occurs when the tinplate is exposed to moist atmospheric conditions, and that hydrogen sulphide is produced on contact with acid products, *e.g.* in the canning industry. Although methods of alleviating the trouble in some degree have been found, a real solution of the problem has not yet been discovered.

The Council's researches on tinplate, which have been carried out after discussions with tinplate manufacturers, can makers and canning research establishments, fall into the following groups:

(i) *Researches on Tinplate as Manufactured.*—Special attention has been given to the examination of tinplate manufactured under different conditions, and, in particular, with hot-rolled steel which has been normalised, to secure a fine-grained structure prior to tinning; and with the recently developed cold-rolled steel.

A new method for detecting the presence of invisible defects was developed during the research at Woolwich, and an improved process for the preliminary

* Published by the International Tin Research and Development Council. 1934. Mansfield House, 378, Strand, London, W.C.2.

cleaning of the sheets prior to the test has recently been evolved. A technique for direct metallographic examination has been devised, whereby defects can be observed under the microscope at high magnification (Hoare, *J. Iron and Steel Inst.*, **1934, 129**, [i], 253). A rapid and reliable method for determining the variation in thickness of tin coatings over the surface of the sheet has also been evolved; this is important, because the number of defects is related in some measure to the thickness of the coating.

Much valuable information is being obtained from a study of sheets tinned under controlled conditions in an experimental tinning machine at Woolwich. This machine produces coatings on steel sheet ranging from 1 to 4 lbs. of tin per basis box, thus covering the range of commercial coatings.

It has been found possible, by a combination of hot-tinning with electro-deposition, to produce tin coatings practically free from pores.

(ii) *Defects caused by Deformation.*—The various methods of testing developed are proving of great value in investigating the causes of breaks which may appear in the coating as the result of deformation, *e.g.* in the manufacture of containers. A study has also been made of the brittle tin-iron compound which forms between the tin and the steel, and a new technique has been developed for revealing its presence and distribution (cf. *Technical Publication*, No. 2, Iron and Steel Institute).

In the course of the investigations certain distinct advantages have been established for the use of the cold-rolled tinned steel.

(iii) *Corrosion of Tinplate.*—Investigation in this field of research is being co-ordinated in Great Britain, France, Germany, Norway, and the U.S.A. In view of the differences of opinion regarding the mechanisms of corrosion, it was arranged that an analysis should be made of all the conclusions based on fact and of the hypotheses advanced to explain the facts. The survey emphasises the importance of the variation in the electric potential difference occurring between tin and steel in contact with the fluids in foodstuffs. At discontinuities in the tin coating there are set up electric currents passing between the tin and the areas of exposed steel, and corrosion of one or both metals may occur, depending on a number of conditions, such as the acidity of the foodstuff, the presence of air, etc. (cf. *Technical Publication*, No. 5, "The Electrochemical Behaviour of the Tin-Iron Couple in Dilute Acid Media," Faraday Society).

Various attempts have been made to diminish the attack on the tinplate by adding a suitable corrosion inhibitor, but, so far, the results have been uncertain and inadequate.

The work so far done on the merits of different kinds of steel tends to prove that the purer form of steel that can be used in the new cold-rolling process results not only in fewer breaks in the tin coating on deformation, but also in a lower rate of attack on the exposed steel. The cold-rolling method permits of the use of steel of higher purity, especially as regards phosphorus-content; the thickness of the steel is controlled more uniformly, and the structure is finer and more uniform than in that normally produced by hot-rolling.

SOLDERS.—Numerous technical inquiries as to the resistance of solders to corrosion have been received, and in several cases, particularly in connection with food products, it has been possible to show that the use of high-tin solders offers definite advantages. For rapid soldering operations, *e.g.* in can-making, the solder has to penetrate small crevices, and fluidity is likely to be the decisive factor in the soundness of the joint. Certain impurities, particularly liable to be introduced when secondary tin is used in the manufacture of the solder, may have a direct bearing on certain anomalies in behaviour that have been observed. Researches on this question are in progress.

WATER PIPES.—The lead alloy containing 1·5 per cent. of tin and 0·25 per cent. of cadmium has found increasing application in certain districts for water pipes,

owing to the advantages of light weight and improved resistance to attack by soft water. A recent competitor is lead containing a small amount—about 0·05–0·06 per cent.—of tellurium (*cf.* ANALYST, 1933, **58**, 366).

An important direction in which tin may find an increased use in water pipes arises from the fact that certain waters have a solvent action on lead and on all the lead alloys proposed for pipes. There are grounds, therefore, for anticipating that a tin-lined pipe, whether of lead or one of the above-mentioned alloys, would be so superior as to justify the increase in cost that would be involved.

Although tin-lined lead pipes are at present being manufactured, it is considered that in their present form they are unsuitable to meet adequately the competition of pipes of other materials and that a lighter pipe is required, such as may be obtained by the use of a relatively strong lead alloy lined with tin or a tin alloy. Researches are necessary to evolve a pipe having the requisite properties, *e.g.* to withstand high water pressures, and to ensure that they will also be suitable for hot water. Data are being obtained for the Council as to the minimum thickness of tin that will ensure adequate protection of the underlying lead alloy, and also as to suitable methods of jointing, whereby no lead is exposed when two lengths of pipe are united.

ACTION OF ABRASIVES AND CLEANERS ON TIN COATING.—When the conditions for the production of satisfactory tin coatings have been clearly defined, there is still the problem of obtaining harder coatings capable of resisting the wear and cleaning operations to which they are exposed in service.

The alkaline cleaners commonly used in the dairy and other industries have a marked corrosive action on tin coatings. A study, therefore, of additions which inhibit this corrosive action without detracting from the detergent power of the cleaner, has been made. Cleaners of this type have already been introduced, but leave room for improvement. An inhibitor of considerable promise has been discovered, and, when the work has reached a suitable stage, the information will be disseminated in order to encourage the use of non-corrosive cleaners. The ease with which tin is abraded is leading to a decrease in the use of triple and quadruple tin coatings. It is anticipated that when the work on harder tin coatings is further advanced, it will be possible to recommend the use of such coatings to eliminate the troubles encountered.

Corrosive attack on tin coating is experienced in certain important applications in the brewing industry. Even small amounts of tin dissolved in this way cause the beer to become turbid. Investigations are being carried out on (1) the influence of additions of other metals to tin, and (ii) suitable treatment of the tinned surface with the object of forming a resistant film. Encouraging results have already been obtained in both these directions, and in some of the coatings now under examination the attack has been reduced to a negligible quantity. Other cases of the corrosion of tin will be investigated in the light of this investigation.

OTHER INVESTIGATIONS.—Other subjects under investigation include problems connected with bearing metals, with the preparation of alloys from powdered metals, with other lead-tin alloys, bronzes, the addition of other elements to tin, electrodeposition of tin and tin alloys, anodic oxidation and dyeing of tin, spraying of tin, collapsible tubes, tin foil, block tin pipe, tin in steel and nickel alloys, and tin compounds. A new use for tin has been found as an electrode in an accumulator; the essential features of the cell are electrodes of tin and lead peroxide, respectively, in an electrolyte of dilute sulphuric acid. The whole cell is filled with porous acid-resisting ceramic material in which the acid is absorbed, so that it is in effect a dry cell. Since no gas is evolved during use, the cell may be sealed after charging, thus preventing leakage of acid.

An investigation of the anti-knock qualities of a range of organic compounds of tin is in progress in collaboration with the research organisation of a group in

the oil industry. The effects of tin compounds in diminishing the rate of oxidation of lubricating oils is also being considered.

The Report, which occupies 37 pages, concludes with an account of the Council's Bureau of Technical Information, its Statistical Office, and its facilities for technical inquiries. Arrangements have been made for technical publications of the Council to appear in three series: A, reprints of original research papers relating to the work of the Council's investigators; B, monographs setting forth existing knowledge on the various aspects of tin and its applications; C, brochures dealing with new applications of tin. A list of the publications issued up to the present is appended.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Detection of Altered Eggs. J. Grossfeld and J. Peter. (*Z. Unters. Lebensm.*, 1935, **69**, 16–29.)—The form of decomposition here considered is that beginning in the yolk of the egg and caused by bacteria, among which probably *Mesentericus* species predominate. As lower fatty acids (butyric, etc.) are formed, the name "cheesy" putrefaction is suggested for this change, although the expression "faecal" putrefaction is sometimes used. The extent of the alteration may be indicated by the "decomposition quotient," which represents one hundred times the ratio of the P_2O_5 soluble in isopropyl alcohol to that soluble in aqueous (95 per cent.) ethyl alcohol (*cf.* Grossfeld and Walter, *ibid.*, 1934, **68**, 270). This quotient is influenced mainly by the glycerophosphoric acid liberated by decomposition of the lecithin; in undecomposed eggs its value is theoretically 0, and when there has been complete decomposition of the lecithin it is 100. With fresh, and with old but unaltered hens' and ducks' eggs, with hard-boiled eggs, and with one water-glass egg, values of the quotient below 6 were found, both on the yolk alone and on the whole egg-content; the age of the egg does not affect the value. When cheesy putrefaction sets in, the quotient rapidly reaches high values, and the change occurring in one day at summer temperature may be considerable. Following the formation of glycerophosphoric acid, this undergoes slow breakdown, with production of phosphoric acid.

When tested similarly, fresh milk gives quotients of 71 to 80, wheaten flour 34·7 to 40, rye meal 37·4, oat flakes 29·5, and soya-bean meal 9. Egg food-pastes show values varying widely according as fresh or spoiled eggs are used in their preparation. With flours and egg food-pastes, extraction with absolute alcohol and benzene together gives practically the same results as boiling with isopropyl alcohol under a reflux condenser, and extraction with 90 per cent. alcohol the same as boiling with aqueous alcohol in a reflux apparatus. T. H. P.

New Form of Adulteration of Eggs? V. Froboese. (*Z. Unters. Lebensm.*, 1935, **69**, 14–15.)—Reference is made to a communication from a State school of poultry-breeding entitled "The Egg-yolk Colour Problem Solved," and recently published in a German poultry journal. The "solution" consists in

mixing with the hens' food a cod-liver oil emulsion coloured blood-red by means of a dyestuff. This dyestuff is transported rapidly, as such, to the yolk of the eggs produced. It is claimed that this procedure does not constitute adulteration, as artificial coloration of other foodstuffs such as butter, jam, etc., is permissible.

T. H. P.

Supposed Diminution of Lecithin in Egg-Paste Products. W. Diemair, F. Mayr and K. Täufel (*Z. Unters. Lebensm.*, 1935, **69**, 1–9.)—The so-called retrogression of lecithin occurring during storage of egg food-paste products is attributable mainly to chemico-colloidal alterations in the mixture of flour and lecithin. All the observations seem to be explicable by the formation of absorption compounds of the ingredients, this resulting in depression of the solubility of the lecithin in its ordinary solvents. Any biological decomposition of the lecithin is of minor importance. Experimental results described indicate that both carbohydrates and proteins participate in the changes concerned, and that fat plays no part. In investigations on this phenomenon, treatment of the material with water prior to extraction with alcohol is inadvisable, since the amount of alcohol-soluble phosphorus is a function of the amount of water added.

T. H. P.

Distinction between Egg-yolk and Vegetable Lecithin in Food-pastes. H. Kluge. (*Z. Unters. Lebensm.*, 1935, **69**, 9–13.)—The fact that the ratio of lecithin phosphoric acid to sterols is very much greater in egg-yolk than in vegetable lecithin preparations may be utilised, in conjunction with other tests, for the detection of vegetable lecithin in food-pastes. If the egg-content of the material, as calculated from the lecithin phosphoric acid, is greater than that calculated from the sterols present, the presence of a vegetable lecithin preparation is indicated. Weyl's lutein test is also useful in this connection: the dry residue from the acetone extract is dissolved in ether and treated with solid sodium nitrite and dilute sulphuric acid. With the oil from egg food-pastes the deep yellow ethereal solution then undergoes almost complete decolorisation, whilst with that from vegetable lecithin the yellow colour persists virtually unchanged. The iodine (Hübl) value of the oil likewise furnishes useful indications; the oil from a sample of egg food-paste gave the value 70·7, whilst the oils from two products prepared with a vegetable lecithin preparation had the iodine values 117·8 and 108, respectively. An iodimetric method of determining sterols, based on Szent-Györgyi's and Tillmans' work, is described in detail. T. H. P.

Determination of Copper in Milk. L. W. Conn, A. H. Johnson, H. A. Trebler and V. Karpenko. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 15–23.)—A large number of methods have been tried. A method involving separation of the copper as sulphide or by micro-electrolysis followed by colorimetric determination with ethyl dithiocarbamate was found satisfactory. *Ashing.*—A 25- to 200-ml. sample of the milk (according to the copper-content) is evaporated to dryness in a platinum vessel, or in a quartz vessel which has previously been extracted with sodium acetate solution (according to Elvehjem, Hart and Steenbock, *J. Biol. Chem.*, 1929, **83**, 27); the copper contamination from porcelain crucibles may be considerable. The addition of 5 drops of glacial acetic acid prevents foaming.

The residue is finally ashed in a muffle-furnace at a dull red heat (not over 565° C.). *Hydrogen sulphide precipitation.*—The ash is dissolved, as far as possible, in 2 ml. or more of 20 per cent. hydrochloric acid by warming; the solution is transferred to a 15-ml. centrifuge tube and centrifuged to remove any residue. Ammonia is added until a slight permanent precipitate of calcium phosphate is formed, and the solution is acidified to give an excess of 1 per cent. of hydrochloric acid. The solution is adjusted to a volume of 10 ml., and saturated with hydrogen sulphide, the containing tube being first heated in boiling water (10 minutes), and then placed in cold water (5 minutes) during the passing of the gas; the tube is stoppered and kept overnight. The liquid is centrifuged, and the precipitate is washed by centrifuging and decantation with 2 ml. of hydrogen sulphide water containing 1 per cent. of hydrochloric acid. The copper sulphide is dissolved in 4 drops of fuming nitric acid in the tube, which is then heated in boiling water for 10 minutes. After cooling, 5 ml. of water and a slight excess of ammonia are added, and the liquid is diluted to 10 ml. *Micro-electrolysis method.*—The milk-ash is dissolved, as far as possible, in the minimum amount of nitric acid (1 : 1); the solution is centrifuged to remove any residue, and is finally diluted to 6 to 10 ml. The copper is deposited electrolytically by a method similar to that of Pregl ("*Quantitative Organic Microanalysis,*" 1930). The deposited copper is dissolved off the platinum cathode in 1 ml. of nitric acid (1 : 1), and the solution is rendered slightly ammoniacal and diluted to 10 ml. *Colorimetric determination.*—To an aliquot part of the clear copper solution obtained as described above, containing 0·001 to 0·005 mg. of copper, are added 2 ml. of ammonia (strength not stated), and the volume is brought to 10 ml.; 1 ml. of aqueous sodium diethyl dithiocarbamate solution (0·1 per cent.) is added. The yellow colour is immediately compared colorimetrically with a set of 9 standards covering the range from 0·001 to 0·005 with intervals of 0·0005 mg. of copper, prepared in a similar manner from copper sulphate solution. Stress is laid upon the point that throughout the course of the method, vessels, reagents and distilled water free from contamination with copper should be used. Tests on milks containing added copper gave good results. *Results.*—The copper-content of uncontaminated raw milk was found to range from 0·051 to 0·132 p.p.m., with an average of 0·077 p.p.m. for 18 samples. The copper in 7 samples of pasteurised milk varied from 0·088 to 0·741 p.p.m., and in 5 samples of dried milk from 1·37 to 17·15 p.p.m. During the manufacture of milk powder, milk exposed to copper equipment takes up considerable amounts of the metal. S. G. C.

Pink Stains in Cheeses. J. Keilling. (*Ann. Falsif.*, 1935, **27**, 600–602.)—From time to time there appear on certain cheeses, first on the surface and subsequently in the superficial layers, irregularly distributed pink stains (*le rouge des tablards*), accompanied by a bitter taste, with formation of gaseous bubbles. The stains were found to be due to a surface-infection of nitrate, which penetrated the cheese and was denitrified by the superficial bacteria, the resulting nitrite giving rise to a pink colour in contact with the cheese mass. If sterile nitrate is brought into contact with sterile cheese, no stain results, but a fragment of cheese to which a few ml. of a dilute solution of sodium nitrate were added developed within 36 to

48 hours a pink colour which progressively penetrated the cheese and was accompanied by the formation of gas. In the course of a few days a positive reaction for nitrite was obtained. D. G. H.

Test for Distinguishing between Meat Extract and Yeast Extract. R. O. Blench. (*Chem. and Ind.*, 1935, **54**, 148.)—About 10 g. of the sample are digested in a mortar with 20 ml. of a 70 per cent. aqueous solution of acetone, the yellow supernatant liquid is decanted on to a filter, and the clear filtrate is tested as follows: To 3 ml. of the filtrate are added a few drops of strong bromine water, which causes the colour to darken. (If an excess of bromine is added, the dark colour disappears, and is not restored by reducing agents.) With yeast extract a dark red colour develops after 5 minutes, 2 ml. of chloroform are then added, and the mixture is shaken. The chloroform layer which separates on standing has a deep reddish-violet colour. This test was applied to commercial yeast extracts and to an experimental extract prepared in the laboratory from air-dried brewer's yeast; in every instance the same result was obtained. Several of the well-known meat extracts were then submitted to the test, but none gave the reaction, which may possibly be due to tryptophan. Good results were obtained with mixtures of yeast extract and meat extract; 15 per cent. of yeast extract could be easily detected, and a faint reaction was observed with a mixture containing 10 per cent. In testing mixtures containing only a small proportion of yeast extract very little bromine must be added. Similar acetone extracts of egg-yolk and of the fat-free portion of cheese gave a pink colour with bromine.

Diastase in Mixtures of Artificial and Natural Honeys. E. Waltzinger. (*Z. Unters. Lebensm.*, 1935, **69**, 77–79.)—The lack of diastase in these mixtures is attributed to the fact that the acid used in the manufacture of the artificial honey is not neutralised, honey diastase being particularly sensitive to acid. In a factory visited, the artificial honey was produced by heating sucrose to 90° C. with tartaric acid in a concentration of 0·22 per cent. This amount of acid, which was left wholly un-neutralised, was patently sufficient to attack the tinning of the inversion vessel and, although not great enough to bring the acidity of the product above the permissible maximum, proved adequate to destroy the diastase of the natural honey subsequently admixed. T. H. P.

Content of Chlorides, Calcium and Magnesium in the Cocoa Nib. J. Grossfeld and E. Lindemann. (*Z. Unters. Lebensm.*, 1935, **69**, 45–50.)—The percentage chloride, calcium, magnesium, and phosphoric acid contents of cocoa beans and nibs and bulk cocoa have been determined, with the following results: Cl (11 samples), 0·030 ± 0·007 or NaCl, 0·050 ± 0·009; Ca (15 samples), 0·075 ± 0·018 or CaO, 0·11 ± 0·03; Mg (3 samples of nibs), 0·29 ± 0·01 or MgO, 0·48 ± 0·02; P_2O_5 (3 samples of nibs), 1·05 ± 0·05 or PO_4, 1·41 ± 0·08. The chloride was determined by extracting the ash with 0·05 *N* sulphuric acid, clearing the solution with potassium ferrocyanide and zinc acetate, and titrating with 0·01 *N* mercuric nitrate solution in presence of sodium nitroprusside. The titration was carried out in a darkened room, and the liquid was illuminated from the side with a microscope lamp or the like, so that the initial appearance of the Tyndall effect produced by a slight excess of the mercury solution could be observed. T. H. P.

Differentiation of Expressed Cocoa Butter from that Extracted with Solvents. A. Castiglioni. (*Ann. Falsif.*, 1935, **28**, 24–27.)—Since the physical constants of these two types of butter may be very similar, and since Aufrecht's test (ANALYST, 1929, **54**, 346) may sometimes give misleading results according to the nature of the manufacturing process and to the amount of shell present in the raw material, additional tests are desirable. Schmandt's method (*Z. angew. Chem.*, 1929, **42**, 1039) has therefore been adapted to these products, 0·5 to 1 g. of the fat being melted in a test-tube and shaken with 3 ml. of glacial acetic acid. When the acid layer has separated it is observed in filtered ultra-violet light, a bright green-yellow fluorescence being obtained with solvent-extracted products, and no colour with expressed cocoa butters. Molin's antipyrine test (*Pharm. Zeit.*, 1904, **49**, 925) has also been adapted for the purpose, a mixture of 0·5 g. of cocoa butter, 2 ml. of 95 per cent. alcohol, 3 ml. of hydrochloric acid (*d.* 1·19) and a few crystals of antipyrine being boiled and allowed to cool. The liquid layer develops a red colour which is apparent in the presence of 0·2 g. of solvent-extracted fat. (In the analogous reaction, which may be used as a test either for antipyrine or for vanillin, the above procedure is followed, the cocoa butter being replaced by the vanillin and the alcohol being finally removed on the water-bath; an orange-yellow colour shows a positive reaction.) These reactions are not given by the usual adulterants of cocoa butter (*e.g.* coconut oil and palm oil). Morawsky's test for solvent-extracted and expressed olive oils (*cf.* Fachini, *Giorn. Chim. Indust. Applic.*, 1926, **8**, 174, 428) may also be applied to cocoa butter, 0·5 g. being warmed with 3 ml. of acetic anhydride. A drop of sulphuric acid (*d* 1·53) is then added to the filtrate from the cooled liquid, when solvent-extracted products give a fugitive violet colour changing to pale green, whilst expressed butters do not give the intermediate violet shade, but turn green immediately. J. G.

Seed Oil of the Bael Fruit Tree (*Aegle Marmelos*, Corr.). R. Child. (*J. Amer. Chem. Soc.*, 1935, **57**, 356–357.)—The fruit of the Bael or Beli tree, *Aegle Marmelos*, Corr. (Nat. Ord. *Rutaceae*), is used in India for the treatment of dysentery. Nine fruits yielded 200 seeds of average weight 0·118 g. and containing 23·5 per cent. of shell and 76·5 per cent. of kernel. The kernels contained 8·35 per cent. of moisture and 45·0 per cent. of oil. The colourless clear oil, which had a faint odour of linseed, gave the following values:—Sp.gr. 30/4° C., 0·918; n_D^{40}, 1·4647; dispersive power ω, 0·0202; saponification value, (i) 193·6, (ii) 196·7; iodine value (Wijs), (i) 108·0, (ii) 107·1; free fatty acids (as oleic acid), (i) 0·42, (ii) 1·26 per cent.; unsaponifiable matter, 1·58 per cent.; thiocyanogen value, 24 hours, 70·4; Hehner value, 93·7; saturated acids (corr.), 23·9 per cent. The approximate composition of the first sample was: Palmitic, 15·6; stearic, 8·3; oleic, 28·7; linoleic, 33·8; and linolenic acid, 7·6; glyceryl (C_3H_2), 4·4; and unsaponifiable matter, 1·6 per cent. These constants are very similar to those of other oils of the *Rutaceae* family (*Calodendron capense*, *Limonia Warneckii*, *Citrus limonum* and *C. aurantium*). The non-fatty residue of the kernels is very rich in nitrogen, containing about 70 per cent. of protein.

D. G. H.

Quantitative Determination of Powdered Linseed. H. Saber. (*Quart. J. Pharm.*, 1934, **7**, 645–653.)—Linseed possesses a well marked sclerenchymatous layer, one cell thick, which may be readily identified in the powder, and the method for determining the quantity of linseed present in a powder is based on the area per g. of the sclerenchymatous tissue present. To determine this area about 10 g. of the seeds are first defatted, and the amount of oil present in the dried sample is determined. Four g. of the defatted residue are reduced to No. 85 powder, and 0·1 g. is thoroughly mixed with 0·05 g. of lycopodium spores, and rubbed to a smooth paste with 1 ml. of 0·1 per cent. phloroglucinol solution in alcohol. The solution is left to evaporate almost to dryness, and 1 ml. of concentrated hydrochloric acid is added, a few drops at a time, to the residue, with rubbing after each addition, after which a few drops of glycerin and 1 ml. of chloral hydrate solution (5 : 2) are incorporated, and the preparation is made up to about 10 ml. with a suspending liquid consisting of 2 vols. of glycerin, 1 vol. of tragacanth mucilage, and 2 vols. of water. One drop of the mixture is removed to a microscope slide by means of a tube of 2 to 3 mm. bore, and the area of the particles from the sclerenchymatous layer is determined in comparison with the number of lycopodium spores, as for the epidermis of a leaf (Wallis and Saber, *Quart. J. Pharm.*, 1933, **6**, 655). The mean result for a sample of linseed 40 years old was 34·38 sq.cm. per g. of the sample dried at 100° C., and 49·7 for the fat-free dry sample, and for a sample of fresh linseed, 30 and 50·9 sq.cm., respectively. Variations of the area of the sclerenchymatous layer for individual seeds per g. were from 26·7 to 58·7 sq.cm., the mean value being taken as 37·7. The examination of 10 samples from plants cultivated in different districts and obtained from different sources showed a considerable range in size of seed, but samples grown under similar environmental conditions possessed almost the same quantitative characteristics (size, and area of sclerenchymatous layer). Differences in the conditions of environment affect the area of the sclerenchymatous layer per g. to the extent of 15 per cent. of the mean value, and the degree of variation is not altered by drying or by defatting the seeds. This degree of variation is identical with that due to similar causes observed in the epidermal area results for a number of leaf samples of the same species. The application of the method of procedure to the determination of the proportion of linseed in mixed cakes is given in detail; a mixed cake of linseed, soya-bean, and pea flour, containing 12 per cent. of linseed, gave an experimental figure of 11·7 per cent. D. G. H.

Volatile Oil of Yarrow (*Achillea Millefolium*, Linne.) R. L. McMurray. (*Amer. J. Pharm.*, 1935, **107**, 33–34.)—Steam-distillation of a quantity of yarrow yielded 235 ml. of an oil of intense blue colour, having sp.gr. at 25° C., 0·9066; n_D^{25}, 1·4703; and $[\alpha]_D$, −14·11°. The $[\alpha]_D$ was determined in 95 per cent. alcoholic solution in a 50-mm. tube, and the results agreed with the value obtained by Aubert (*J. Amer. Chem. Soc.*, 1902, **24**, 778), but not with that of Haensel (*Haensels Bericht*, 1901, **4**, 25). The earliest record of the production of a blue volatile oil from yarrow is that of F. Hoffman in 1719 (*De Millefolio*, German Ed., Schaaf-Garben). D. G. H.

Identification of Gum Arabic. I. C. Ritsema. (*Pharm. Weekblad*, 1935, **72**, 105–106.)—The following tests (of which the first three were adapted from those of the Dutch Pharmacopoeia and are sensitive to 1 part in 5) were applied to solutions of a number of specimens of gum arabic of satisfactory external appearance, although it is not certain that they were all derived from *Acacia Senegal*:—Ferric chloride solution gave a brown gel which dispersed when shaken. A saturated solution of borax or borax powder gave a white gel which dispersed on shaking. Alcohol gave no gel, but a white precipitate which disappeared on shaking. Basic lead acetate solution gave a white precipitate; the reaction is sensitive to 1 part in 10,000, although it is desirable to make a comparison with a blank test, as the precipitate takes a little time to appear. If to 5 ml. of a 5 per cent. solution of the sample are added a little benzidine and 1 drop of a 3 per cent. solution of hydrogen peroxide, "benzidine blue" is obtained after 1 minute. The preparation of the solution and the reaction should be carried out in the cold, as the peroxidase responsible for the reaction is destroyed at a temperature of 50 to 60° C. Although it is stated that the peroxidase content of gum arabic decreases on ageing, samples which had been in the possession of the author for several years gave stronger reactions than purchased commercial samples. J. G.

Titration of Barbital with Silver Nitrate by the Method of H. Budde. J. M. A. Hegland. (*Pharm. Weekblad*, 1935, **72**, 128–129.)—The author prefers this method (cf. *id.*, 1934, **71**, 1019) to the alkalimetric (Dutch Pharmacopoeia) method, as it avoids errors inherent in the observation of a change in colour, especially when the sample is originally coloured. The sample (200 to 230 mg.) is dissolved in a solution of 1 g. of anhydrous sodium carbonate in 30 g. of water, and titrated with 0·1 *N* silver nitrate solution, a drop at a time and with continuous shaking, until a permanent faint opalescence results. The end-point is best observed against a dark ground, and is confirmed by the production of a heavy precipitate by the first drop of reagent in excess. The method was compared with the Pharmacopoeia method, 0·1 *N* sulphuric acid being used instead of hydrochloric acid for the titration of salts of barbital. Mean results in ml. of 0·1 *N* alkali and silver nitrate, respectively, are:—Luminal verum, 9·7, 9·65; Dial verum, 9·6, 10·0; Luminal loco, 9·7, 9·93; Dial loco, 9·90, 10·00; Medinal loco, 9·4 (ml. of 0·1 *N* sulphuric acid), 10·7. J. G.

Auto-oxidation of Ether. M. Landon. (*Bull. Soc. Chim.*, 1935, **2**, 53–57.)—Although ether tends to undergo auto-oxidation, with the formation of peroxides, even in the dark, this reaction is very much more rapid in the presence of light. The formation of peroxides is accelerated by the presence of aldehydes, but is retarded by water and especially by acids; alkalis hinder the appearance of oxidation products. The action of ultra-violet light was not studied, as the rise in temperature due to the incidence of the rays becomes more important than any oxidation which might take place. The nature of the container is important. For storage purposes, ether should be kept in the dark and be free from aldehydes, but it is difficult to keep pure ether except in the presence of sodium, which reduces any oxidation product as soon as it is formed. For the removal of peroxides from ether, treatment with sodium hydroxide, followed by distillation, is recommended. S. G. S.

Determination of Peroxides in Ether. M. Landon. (*Bull. Soc. Chim.*, 1935, **2**, 34–53.)—Two methods of determination of peroxides in ether are suggested, one being titration with $N/10$ potassium permanganate solution, and the other titration of the iodine liberated from potassium iodide solution. The titration with potassium permanganate in the presence of sulphuric acid is quantitative, but gives the total peroxide and does not distinguish between free peroxide (hydrogen peroxide) and combined peroxide (ethyl peroxide). Since the amount of iodine liberated from potassium iodide is a function of the time allowed for the reaction, it does not give a quantitative result, but it does allow the difference between the free and combined peroxide to be determined. The ether (20 ml.) is mixed with 2 ml. of 10 per cent. potassium iodide solution, shaken continuously for 5 minutes, and then titrated with $N/100$ sodium thiosulphate solution. The determination is then repeated, shaking for 20 minutes. If the first result exceeds the second, the ether contains a large amount of free peroxide; but, if the reverse is the case, most of the peroxide is in the combined form. If the ether is acid in reaction, this method is useless, and, in any case, an isolated result is of no absolute value, but is only comparative. Ether which has been exposed to light for any length of time will contain most of the peroxide as hydrogen peroxide, and a permanganate titration is indicated. The presence of nitrites and their effect on the result of these titrations must not be overlooked, and Ilosvay's reaction should always be tried. S. G. S.

Occurrence of Resins in Tobacco Smoke. A. Wenusch. (*Z. Unters. Lebensm.*, 1935, **69**, 81–85.)—A large proportion of the solid components of tobacco smoke consists of a mixture of a neutral resin, an essential oil, and various resin acids. Whether the resin and resin acids of the smoke are chemically identical with the resinous compounds of the original tobacco has not yet been decided. The smoke from 350 cigarettes, corresponding with about 300 g. of tobacco actually smoked, yielded: 0·4 g. of resin acid soluble in ether and precipitable by lead acetate in alcoholic solution; 1·4 g. of resin acid soluble in ether, but not precipitable by lead acetate in alcoholic solution; 2·2 g. of resin acid insoluble in ether; 2·7 g. of unsaponifiable resin soluble in ether, and 0·5 g. of oil volatile in a current of steam. T. H. P.

Constituents of Derris Resin. R. S. Cahn and J. J. Boam. (*J. Soc. Chem. Ind.*, 1935, **54**, 42–45T.)—Although those derris resins which contain only small amounts of rotenone (designated "Sumatra type") yield, on treatment with alkali, 50 to 60 per cent. of crude toxicarol, it is shown that the toxicarol is not present as such in the resin. A new dimorphic substance of insecticidal properties, undoubtedly occurring free, has been isolated from Sumatra type of root by simple crystallisation. The carbon tetrachloride solution of the resin, when kept for long periods, deposited a gradually increasing yield of crystals (5 per cent. in 2 weeks), and these, on fractional extraction with alcohol, yielded 1·8 per cent. of pure rotenone and 0·55 per cent. of a new individual substance (m.p. 189° C.). If crystallised from acetone, however, the substance melted at 192° to 194° C., reverting to the first form when kept in a vacuum desiccator or dissolved in other

solvents. The probable formula is $C_{23}H_{22}O_7$, and the substance differs from isomeric tephrosin in being phenolic and not readily losing the elements of water, and from the isomeric toxicarol in being colourless. It appears that *dl*-toxicarol, and at least part of the *dl*-deguelin, do not occur as such in the resins, nor does more than a small amount of tephrosin (either optically active or inactive), whilst deguelin occurs, at least partly, as the *l*-form or as a single derivative or precursor thereof. The remaining deguelin and tephrosin occur in some form of combination or as simply related precursors, and nothing is known as to the mode of combination of the toxicarol, but it is unlikely that large amounts of simple esters of the *dl*-form are present. The preparation of toxicarol, acetyl rotenone, dehydrodeguelin and certain esters is described. The esters of toxicarol are readily hydrolysed by acid, and since derris resins which yield at least 40 per cent. of toxicarol with alkali do not yield it with acid, it is concluded that esters of *dl*-toxicarol are absent from such resins. The conclusion that the value of a derris root or resin can be assessed only by the rotenone-content is quite unjustified, and, since deguelin, tephrosin and toxicarol do not occur as such in the root (or occur only in very small quantities), data as to their relative toxicities are inapplicable to assessment of the root. D. G. H.

Determination of Rotenone in Derris Root and Resin. R. S. Cahn and J. J. Boam. (*J. Soc. Chem. Ind.*, 1935, **54**, 37–42T.)—The toxicity of derris root is due to a mixture of compounds obtained as a resin by extraction with various organic solvents; from the solution of this resin in carbon tetrachloride a crystalline "complex" rotenone separates. Certain modifications in the carbon tetrachloride method of determining rotenone are suggested, but, even in the modified form, low results are obtained if the resin contains less than about 17 per cent. of rotenone, and with very small amounts the method fails, owing to the phenomenon of "hidden" rotenone, *i.e.* rotenone that can be determined only when special methods are adopted, possibly owing to the presence of an inhibitor of crystallisation. For the determination, the derris root should pass entirely through a 50-mesh sieve before sampling, and should be dried in a vacuum desiccator until not more than 5 per cent. of moisture remains. Enough of the powdered root is taken to yield 5 to 10 g. of extract to trichloroethylene in 8 hours, the solvent being changed after 4 hours, and if the second solution acquires more than a very pale yellow colour a further extraction is carried out with another quantity of solvent. The combined solutions of extract are evaporated until thickening occurs and bubbling begins, when a gentle current of air is blown into the flask, which is rotated over a naked flame until the odour of hot derris resin is apparent. The flask is weighed and the resin rapidly dissolved in 2 parts of warm carbon tetrachloride saturated with rotenone (x g. of resin, $2x$ ml. of CCl_4), cooled, seeded if necessary, and kept overnight. The crystals are collected, with the aid of the water-pump, on a disc of Whatman No. 1 (not hardened) filter-paper, washed with the saturated carbon tetrachloride until the filtrate is nearly colourless, and dried to constant weight in air below 50° C. The weight of the complex, multiplied by 0·72, gives the weight of rotenone. Total extract is determined by evaporating the trichloroethylene solution to dryness, and heating the residue

until constant in weight in an oven at 100° C. To detect "hidden" rotenone, 1 g. of rotenone and 4 g. of the resin are dissolved in 10 ml. of carbon tetrachloride saturated with rotenone, and the solution is kept overnight and then treated as described above. The rotenone carbon tetrachloride crystals, which separate in the determination, are at best only 90 to 95 per cent. pure, and probably not more than 80 to 90 per cent.; their purity may be determined by stirring the complex in 5 parts of alcohol and leaving the solution overnight, when solvent-free rotenone crystallises out. The percentage yield which is termed the percentage alcohol recovery, is regarded as the best indication of purity. D. G. H.

Biochemical

New Method for the Determination of the Acid-Base Balance in Food Materials. J. Davidson and J. A. Le Clerc. (*J. Biol. Chem.*, 1935, **108**, 337–347.)—The acid-base balance in a food material is generally determined by computations based on its content of the acid-forming elements, phosphorus, sulphur, and chlorine, and the base-forming elements, potassium, sodium, calcium, and magnesium. The quantities of these elements in the food are converted into ml. of normality values, and the difference between the sum of the acid values and the sum of the base values is the base balance or the acid balance, as the case may be. When the mineral analysis of the food is not an object in itself, this procedure is lengthy, and, in addition, is liable to certain errors. The question whether phosphorus should be considered bivalent or tervalent is a vexed one, and losses of chlorine, sulphur, etc., during ashing may give false results. The suggested procedure is based on the direct titration of the ash, with corrections for sulphur and chlorine lost during the combustion. The requisite amount of material is ashed in a platinum dish at 550° C. The ash is dissolved in an excess of 0·5 *N* acid, and is titrated back with 0·1 *N* alkali. Sulphur and chlorine are also determined on the original material, with and without means of preventing losses—magnesium nitrate being used to prevent the loss of sulphur, and sodium carbonate the loss of chlorine. The differences between the results of the two respective determinations of sulphur and chlorine are the quantities of these elements lost during combustion. These losses are converted into "normal" acid values, and subtracted from, or added to, the titration values, according to whether it is a base or an acid balance. The use of phenol red or any indicator that registers the exact neutral point (pH 7·0) is proposed in place of the commonly used methyl red or phenolphthalein. S. G. S.

Nutritive Value of the Fatty Acids of Lard and some of their Esters. S. Lepkovsky, R. A. Ouer and H. M. Evans. (*J. Biol. Chem.*, 1935, **108**, 431–438.)—The fatty acids were isolated from lard by the usual saponification procedure. They were then distilled and esterified with glycerin to form a "synthetic" lard. For the normal growth of rats the synthetic product is just as satisfactory as the natural one, when fed in the proportion of 25 or 60 per cent. of the diet. The free fatty acids, both alone and with the addition of glycerin, were good sources of energy when fed as 25 per cent. of the diet, but were inferior

to the glyceride at the 60 per cent. level. The methyl and ethyl esters were also good on the 25 per cent. basis, but on the 60 per cent. basis the methyl esters gave poor growth, whilst with the ethyl esters an initial mortality was followed by a fair growth of the survivors. Propylene glycol was the best of the dihydric alcohols, ethylene and diethylene glycols, both being poor and causing serious lesions in the kidneys of the experimental animals. S. G. S.

Determination of Iodine in Blood and Thyroid. I. Bellucci and R. Vigni (*Gazz. Chim. Ital.*, 1934, **64**, 634–643.)—With careful working, the organic matter of blood or thyroid may be completely destroyed by treatment with potassium hydroxide, without loss of iodine. From 10 to 15 grms. of blood, treated with a very small amount of potassium oxalate as an anti-coagulant, are weighed in a nickel dish (8 to 10 cm. wide and 4 to 5 cm. high) and mixed, by means of a thin nickel rod, with 0·25 g. of potassium hydroxide in concentrated, boiling solution. The dish is then gently heated on an asbestos gauze over a ring burner 3 cm. across, the mass being kept stirred until a black, spongy residue is obtained. Heating and stirring are then continued over the naked flame as long as vapours are emitted. When the dish has cooled, the mass is moistened and mixed with 5 ml. of 6 per cent. hydrogen peroxide solution rendered faintly alkaline with potassium hydroxide. After 10 or 15 minutes, the dish is carefully heated, first on the asbestos gauze and later over a naked flame, the mass being stirred until a uniform, gray ash remains. This is treated with 10 ml. of the hydrogen peroxide solution and the heating is repeated. The ash is next moistened with water, scraped to the bottom of the dish, dried by heating on the gauze and finally heated for 15 to 20 minutes over a naked flame. The whitish residue is extracted three times with 8 to 10 ml. quantities of boiling water, the extracts being filtered through an 8 cm. filter (Schleicher and Schüll N. 589/2), on which the whole ash is ultimately washed. The filter and residue are returned to the dish, moistened with a few drops of concentrated potassium hydroxide solution, and incinerated as before. The combined filtrates and washings are next transferred to the dish and the whole is evaporated to dryness on the gauze and afterwards heated for about 5 minutes over the bare flame.

After being moistened with water, the ash is ground by means of a small agate or glass pestle with three small quantities (3 to 4 ml.) of 95 per cent. alcohol, the alcoholic extracts being decanted into a small porcelain dish and evaporated to dryness on a water-bath. The residue is taken up in water and transferred to a small beaker so as to give 10 or 15 ml. of solution containing the iodine as potassium iodide. This is oxidised to iodate by heating the liquid to incipient boiling for 3 to 4 minutes with a few drops of dilute potassium hydroxide and a few crystals of potassium permanganate, excess of which is then destroyed by adding a few drops of strong alcohol to the hot solution. Any separated manganese dioxide is removed by filtration, the filtrate and washings being evaporated to 6 or 7 ml. Traces of nitrite present are destroyed by boiling the liquid gently for 3 or 4 minutes with 0·5 to 1 ml. of glacial acetic acid and 0·1 g. of urea. The cooled solution is shaken with a few cg. of potassium iodide and a few drops each of dilute (1:4) sulphuric acid and carbon disulphide. The iodine is then

determined by titration with 0·002 *N* sodium thiosulphate solution (run in from a micro-burette) until the amethyst colour of the carbon disulphide solution of the iodine just disappears.

Fresh thyroid is freed from fat and surrounding connective tissue and is cut into thin slices which are spread on a clock-glass and dried to constant weight in a vacuum over sulphuric acid. The dry material is powdered in a mortar and 0·5 to 1 g. is treated with 0·5 g. of potassium hydroxide. The subsequent procedure is as described above, except that the final volume of the solution may be increased to 10 to 15 ml., which is titrated with 0·004 *N* thiosulphate.

Test experiments with sucrose to which about 10γ of iodine were added gave satisfactory results. Two samples of blood taken a few days apart from a normal individual showed, respectively, 9·86 and 10·7γ per 100 g. Other results were: Patient, just convalescing after pulmonitis, 183γ; patient suffering from genital adipose dystrophia, 135γ. A human thyroid, having the abnormal weight 60 g. (fresh), contained 72·8 mg. of iodine per 100 g. of dry matter (*cf.* Abst., p. 275).

T. H. P.

Effective Method of Extracting Vitamin B_1. S. Itter, E. R. Orent and E. V. McCollum. (*J. Biol. Chem.*, 1935, **108**, 571–577.)—Extraction of vitamin B_1 from yeast by means of gaseous hydrogen chloride in the presence of methyl alcohol has been found to be more effective than extraction with aqueous hydrochloric acid. The dried yeast (100 g.) is suspended in 50 ml. of absolute methyl alcohol, and into this mixture is passed a stream of dry gaseous hydrogen chloride until a concentration of approximately 4 *N* is attained. The acidified mixture is allowed to stand overnight and then filtered through a Buchner funnel. The residue is washed with 200 ml. of absolute methyl alcohol, and the washings and filtrate are evaporated *in vacuo* to a thick syrup. Biological tests indicated that the residues contain no vitamins B_1 or B_2, but that the extract is as active, in proportion, as the original yeast. The extract is also unusually low in alkaline elements and provides a good source of vitamin B_1 for inorganic deficiency studies.

S. G. S.

Quantitative Determination of Ascorbic Acid. (Vitamin *C*). H. Tauber and I. S. Kleiner. (*J. Biol. Chem.*, 1935, **108**, 563–570.)—The reducing action of ascorbic acid on acid ferricyanide solution has been made the basis of a colorimetric method of determining vitamin *C*. To remove interfering substances, about 20 g. of the material are ground up with acid-washed sand in the presence of hot 8 per cent. acetic acid, a total volume of 100 ml. being used. The combined extracts are centrifuged and filtered if necessary. To 50 ml. of the extract 15 ml. of a 20 per cent. solution of mercuric acetate are added, and the reaction to Congo-red is adjusted, if required, with calcium carbonate until it is only slightly acid. The solution is again centrifuged and filtered if necessary. If, on testing with mercuric acetate, a precipitate still forms, this treatment must be repeated, but, if no precipitate is produced, the mercury is removed from the filtrate by passing hydrogen sulphide through the solution. When the mercuric sulphide has been filtered off the hydrogen sulphide must be removed, after the vessel has stood

overnight, by bubbling nitrogen through the liquid. If it is desired to omit this preliminary treatment, the material under investigation is ground up with sand and 10 per cent. trichloroacetic acid for animal tissue, or hot 8 per cent. acetic acid for plant tissue. At least three extractions should be made, a total of 20 ml. of acid being used for each 10 g. of material, and the liquid decanted each time. The combined extracts are then centrifuged at high speed, and the clear liquid is diluted to a definite volume with the respective acid and filtered, if necessary. To 5 ml. of the clear fluid 2 ml. of the ferricyanide solution are added, and to 1 ml. of the standard ascorbic acid solution are added 4 ml. of the requisite acid and 2 ml. of the ferricyanide solution. Rubber stoppers are inserted in the tubes, the contents are well mixed, and the tubes are placed in a water-bath at 40° C. for 3 minutes. The contents of the tubes are then cooled, and 5 ml. of the ferric gum solution are added. The blue colour develops quickly, and the colorimetric determination may be made immediately with a yellow light filter (*cf.* Folin and Malmros, *J. Biol. Chem.*, 1929, **83**, 115). The potassium ferricyanide solution is an aqueous one of 0·4 per cent. strength. The ferric gum solution is prepared by suspending, on a copper wire screen, 20 g. of soluble gum ghatti in 1 l. of water for 18 to 36 hours. The screen is then removed and sedimentation is allowed to take place. After decantation or filtration, 5 g. of anhydrous ferric sulphate dissolved in 75 ml. of 85 per cent. phosphoric acid plus 100 ml. of water, are added to the gum solution. To the mixture are then added, in small portions, about 15 ml. of 1 per cent. potassium permanganate solution, to oxidise reducing substances in the gum and possible traces of ferrous iron in the ferric sulphate. After 24 hours at room temperature the solution is clear and ready for use. The standard solution of ascorbic acid is prepared by dissolving 25 mg. of pure ascorbic acid and 50 mg. of pure cystine in 90 ml. of boiling 0·01 *N* hydrochloric acid solution. After cooling, this solution is diluted to 100 ml. with water. Cystine is used to inhibit the auto-oxidation of the ascorbic acid, which would occur rapidly in its absence, but the solution prepared as described will last for one day.

S. G. S.

Determination of the Common Carotenoids and Analyses of Carotene and Leaf Xanthophyll in Thirteen Plant Tissues. E. S. Miller. (*J. Amer. Chem. Soc.*, 1935, **57**, 347–349.)—The Willstätter and Stoll methanol-ligroin (89 and 92 per cent.) partition method (*Untersuchungen über Chlorophyll*, Berlin, 1913) was found to be quantitative only when corrected. A new method for the extraction of the carotenoids was devised, from 1 to 10 g. of green (or 0·05 to 0·5 g. of dry) samples of various grasses and sugar-cane hybrids being used. The samples are macerated with 25 ml. of acetone and 25 g. of quartz sand, and to the extract are added 20 ml. of 95 per cent. ethanol saturated with potassium hydroxide. Alternate maceration and extraction are repeated three times with 25-ml. portions of acetone, and then twice with 35 ml. of ether, and the extraction of the pulp and sand with ether is completed in a Soxhlet extractor on the water-bath. The combined extracts are shaken gently with 1·5 l. of water, and the water is separated. If saponification is not complete, a further 10 ml. of ethanol (saturated with potassium hydroxide) are added, extraction is carried out with

100 ml. of ether, and the washings are added to the former washings. The ethereal extracts are washed 4 times with 500-ml. portions of water, the funnel being left for 3 to 4 minutes (5 to 8 minutes for the final washing) before the aqueous washings are drawn off. The ethereal solution (150–200 ml.) is evaporated *in vacuo* to 50 to 60 ml., measured and made up to 100 ml., and analysed the same day. Analysis by the Willstätter and Stoll partition method showed that the 13 plant samples contained either no α-carotene or less than 0·7 per cent. The following results are the averages (in parts per million) of determinations on duplicate samples:

	Total carotenoids	β-carotene	Leaf xanthophyll	Ratio of β-carotene to leaf xanthophy
Hordum sativum	115·4	31·7	84·0	1:2·65
Bromus inermis	285·0	51·3	238·5	1:5·55
Zea mays, L. (Country gentleman)	263·0	46·2	216·3	1:4·68
Zea mays, L. (Golden bantam)	288·5	37·3	221·7	1:3·29
Setaria italica	302·5	83·0	220·5	1:2·65
Sudan grass	445·0	91·1	354·0	1:3·88
Sugar-cane hybrid	478·0	140·0	338·7	1:2·42

D. G. H.

Toxicological

Toxicological Detection of Ergot. H. Kluge. (*Z. Unters. Lebensm.*, 1934, **68**, 645–650.)—For this purpose use is made of: the colouring matter, sklererythrin; the alkaloids, ergotinin, ergotoxin, and ergotamine; and the red colouring matter not precipitated by lead acetate or by subsequent removal of the lead by means of hydrogen sulphide. The material, rendered distinctly acid with 10 per cent. tartaric acid solution, is digested on a water-bath at about 75° C. with about the threefold quantity of 90 per cent. alcohol. The cooled liquid is filtered, and the residue again digested with alcohol, and filtered, the combined filtrates being evaporated in a vacuum. The syrupy residue is mixed with alcohol until precipitation begins and is then poured in a thin stream, with constant swirling, into the five-fold volume of alcohol. After 12 hours the liquid deposits a brown precipitate, which is filtered off. The filtrate is again evaporated in a vacuum to a syrup, which is dissolved in hot water, the solution being then cooled and filtered to remove fat. The aqueous filtrate, acidified with 2 drops of hydrochloric acid, is shaken with three quantities of ether, and the united ethereal extracts are washed with a little water and passed through a small, dry filter (A), giving ethereal extract I. The acid aqueous solution is made alkaline with sodium carbonate solution and again extracted thrice with ether, the ethereal extract (II) being purified as before.

In presence of sklererythrin, filter A shows a delicate cherry-red colour, which changes to violet-red when the filter is moistened with alcohol and exposed to

ammonia vapour. The ethereal extract I is transferred to a separating funnel, and 5 ml. of saturated sodium bicarbonate solution are run in to form a lower layer. On gentle swirling, a violet-red ring forms, the colour permeating the whole liquid on shaking. When the alkaline layer is separated, acidified with hydrochloric acid, and shaken with 5 ml. of ether, the ethereal layer shows absorption bands at 527 to 543$m\mu$ and 485 to 507$m\mu$. If the ethereal layer is shaken with 2 ml. of the sodium bicarbonate solution, it shows three absorption bands at 550 to 575, 515 to 530, and 485 to 495$m\mu$, respectively. When material isolated from the stomach or intestines is used, the results of the spectroscopic examination are, however, unsatisfactory. Capillary analysis gives better results: The sodium bicarbonate solution is acidified and shaken with 2 ml. of ether, the ethereal extract being placed in a test-tube containing a narrow strip of filter-paper, which protrudes from the tube. As the ether evaporates, the lower portion of the paper assumes a delicate red colour, which deepens to a stable (for weeks) violet-red under the action of ammonia vapour.

To test for the ergot alkaloids, the ethereal extract II is purified by shaking it with 10 ml. of very dilute hydrochloric acid, making the acid liquid alkaline with sodium bicarbonate, and shaking with ether. The ethereal solution is concentrated at room temperature to about 3 ml., 1 ml. of this being mixed with 1 ml. of glacial acetic acid, and 1 ml. of concentrated sulphuric acid containing a trace (about 0·1 per cent.) of ferric chloride run into the tube to form a layer at the bottom. In presence of ergot alkaloids, a blue inter-layer ring gradually forms and later spreads through the ether layer. The remainder of the ether concentrate is evaporated to dryness, and the residue is dissolved in 1 ml. of concentrated hydrochloric acid and tested by means of the ordinary alkaloid reagents.

Ergot separated from organs requires purification before testing. The hydrochloric acid solution is treated in a centrifuge tube with a few drops of potassium-mercuric iodide solution and centrifuged. The separated precipitate is freed from traces of liquid by means of filter-paper, then digested with excess of anhydrous acetone, and again centrifuged. The clear acetone solution, containing the alkaloids, is treated with very dilute sodium hydroxide solution and shaken three times with ether. The united ethereal extracts are evaporated to dryness, and the residue, taken up in a few ml. of chloroform, is mixed with 2 drops of sodium sulphide solution, 2 drops of sodium carbonate solution, and 1 to 2 ml. of water. The mixture is shaken with two portions of chloroform, evaporation of the filtered chloroform extracts yielding the alkaloids in highly pure state. The reactions of the alkaloids separated from organs are shown only faintly, and hence are only given if relatively large amounts of ergot have been taken. Such separated alkaloids do not respond to pharmacological tests. T. H. P.

Bacteriological

Polystictus Versicolor. **[Wood-rotting fungus]. B. A. Jay.** (*Kew Bull.*, 1934, No. 10, 1–15.)—*Polystictus versicolor* (L.) Fr., has been the cause of most of the rotting, under damp conditions, of felled hardwoods in Britain; it is the most serious of all wood-rotting fungi which attack the dead wood of broad-leaf trees, and it is the

most cosmopolitan species to be found on the sap wood of such trees. It is absent from living trees. The individual sporophores are about 7 cm. wide and 4 cm. deep, and they may be bracket-shaped or resupinate and usually overlap one another on the wood, forming dense masses. The fungus grows vigorously on a medium consisting of 2 per cent. of malt extract and 2 per cent. of agar-agar in water, growth being thicker but slower in the presence of 1 per cent. of malic acid. Slope and plate cultures show a smooth, pale yellow or white, closely-woven mat of felty mycelia, with a tendency to zonation, the disappearance of the brown colour of the medium as growth proceeds being a useful means of identification, although it may be produced by other species. Fruit bodies are absent. The mature hyphae are 3 to 4μ wide, and are hyaline and have a few septa, usually with clamp connections, the tips being swollen and frequently bifurcated. Rhomboidal crystals occur in most cultures. Cultures from different hosts were identical, and the spores retained their vitality in the dry state for at least 3 months. Optimum growth at 23° C. is between pH 4·6 and 5·6, there being no growth below 3·0 or above 7·3 (pH adjusted with malic acid or potassium hydroxide). The lowest lethal temperature is 60° C. for 15 minutes (*cf.* Cartwright and Findlay, *Ann. Bot.*, 1934, **48**, 481), and the lowest concentration of agar-agar required to produce the maximum rate of growth is 4 per cent.; light has a slight inhibiting effect. Wood blocks are best inoculated by inserting them in Roux tubes containing slope cultures of fungus in which the agar reaches just above the constriction; this enables the wood to be attacked by the fungus, but prevents staining or undue wetting by the medium. The maximum loss in weight recorded was 80 per cent. (for an ash-block) in 4 months. The reaction of the fungus to wood preservatives was tested by shaking various amounts of a sterile solution of the preservative with the medium before plating out. The plates were examined after a week at 23° C. in order to ascertain the approximate lethal concentrations, and the experiments were then repeated, with a more restricted range of concentrations. The minimum concentration to inhibit growth was 0·2 per cent. for sodium fluoride, and 0·05 to 0·1 per cent. for coal-tar creosote B.S.S. Type A used in the form of an emulsion in 20 per cent. gum arabic solution; the lethal concentrations were 0·2 to 0·5 per cent. in both cases, and less than 0·5 per cent. for zinc chloride. Exposure of a plate-culture to the vapour evolved from a pad of filter-paper soaked in formalin and placed in a beaker for 30 minutes, 1 hour and 2 hours, stimulated, inhibited and prevented subsequent growth on 2 per cent. malt slopes, respectively. In order to determine the minimum amount of preservative to prevent growth on a particular wood, blocks of the wood were soaked in various strengths of preservative for 4 hours in a vacuum, and then dried and placed on slope-cultures, and the losses in dry weight were compared with those of controls. Values for sodium fluoride were 0·5 per cent. on beech, 2·0 on ash, over 2·0 on elm, and over 2 per cent. for creosote on beech; the heartwood of oak (*Quercus pedunculata*) was even more resistant. The best methods of prevention of decay are to creosote permanent erections, and to dry felled wood as soon as possible before rot begins; a 4 per cent. solution of sodium fluoride is recommended where creosote cannot be used, but contact with water not only washes this out, but also produces conditions favourable for growth. J. G.

Organic

Acids of Chinese and Esparto Grass Waxes and the Hydrocarbons of Esparto and Candelilla Waxes. F. J. E. Collins. (*J. Soc. Chem. Ind.*, 1935, **54**, 33–35T.)—*Acids of Chinese Wax.*—In continuation of the work of Francis, Piper and Malkin (*Proc. Roy. Soc.*, 1930, A, **128**, 247), an attempt was made to separate the acid $C_{26}H_{52}O_2$ from the mixture of acids present in the wax, including $C_{28}H_{56}O_2$ and some $C_{24}H_{48}O_2$ and $C_{30}H_{60}O_2$. A prolonged systematic fractional distillation (in a vacuum of 0·5 mm.) of the ethyl esters of the mixed acids resulted in only a partial separation. Tests on the fractions showed that the coincidence of the m.p. of an ester or acid with that of a known synthetic ester or acid may be, and often is, fortuitous, and is therefore, no criterion of purity; the only method of establishing the identity of a pure *n*-fatty acid of high carbon-content is by comparisons of the m.p. and of the *B* and *C* *X*-ray crystal spacings of the acid and ester with the corresponding data for the synthetic compounds (cf. *loc. cit.*). A better separation was obtained by repeated molecular distillation of the ester fractions obtained in the first operation at 10^{-6}mm. in a constant-temperature still (*cf.* Bruin, *Bur. Stand. J. Res.*, 1929, **2**, 470), the contents of which were stirred by an iron ball kept in motion by an external electro-magnet. Eventually a fraction was obtained which yielded an acid (m.p. 86·5° C.), which crystallised in separate sharp-edged crystals, and control tests on the lines suggested above indicated that it consisted mainly of the acid $C_{26}H_{52}O_2$ with traces of the acids $C_{24}H_{48}O_2$ and $C_{28}H_{56}O_2$. A further extension of this method could be used to obtain the pure acid, but larger quantities of material would be required.

Esparto Grass Wax.—This is a dark brown, hard, brittle material, with m.p. 70° to 74° C.; acid value, 30; saponification value, 75. A mixture of ether and acetone (1 : 2) extracted a brown resinous material which was rejected, the residue being saponified. The solution was evaporated, the hydrocarbons and alcohols present were extracted with hot petroleum spirit, the acids in the residue were liberated from the potassium salts and converted into barium salts, which were washed exhaustively in succession with boiling alcohol, acetone and benzene, and the acids were again liberated and converted into the ethyl esters. These were fractionated in the molecular still, the procedure being similar to that already described. The general conclusion is that the free or combined acids in Chinese wax have, on an average, a lower carbon-content than those in esparto wax, the lowest acid containing 24 and 26 C atoms, respectively; the presence of $C_{32}H_{64}O_2$ and of $C_{34}H_{68}O_2$ in esparto wax was also indicated. *Hydrocarbons from Esparto and Candelilla Waxes.*—Both waxes contain approximately 70 per cent. of a hydrocarbon which has similar properties in the two cases (*cf.* Meyer and Soyka, *Monatsh.*, 1913, **34**, 1159). The mixture of alcohols and hydrocarbons extracted after saponification (cf. *supra*) was, therefore, acetylated (to prevent dehydration of the alcohols) and distilled in a vacuum of 10^{-3} mm., the distillate being saponified and the resulting product recrystallised repeatedly from a mixture of benzene and alcohol, in which the alcohols are more soluble; further purification was obtained by oxidation on the water-bath with potassium dichromate and glacial acetic acid, followed by treatment with warm concentrated sulphuric acid and crystallisation from benzene. The

hydrocarbons from the two sources then appeared identical in all respects, and were composed chiefly of the *n*-paraffin $C_{31}H_{64}$, about 4 per cent. of another hydrocarbon being present in the product derived from esparto. The synthetic hydrocarbon $C_{31}H_{64}$ (*cf.* Chibnall, *Biochem. J.*, 1931, **25**, 2072) has a well-marked transition-point at 62° to 63° C.; a second at 67·4° C.; m.p. 67·5° C.; and resolidifies at 67·2° C. Corresponding figures for the hydrocarbons of esparto wax and candelilla wax, respectively, were:—61° to 61·5° C., 62° to 63° C. (both indefinite); 66·7°, 67·5° C. (both well-defined); 67·7°, 67·8° C.; and 67·4°, 67·4° C. The transition-points were obtained only after treatment with sulphuric acid. So far as is known at present, the acids of waxes of this type are all members of the *n*-aliphatic series, and have an even number of carbon atoms, whilst the hydrocarbons have an odd number of carbon atoms. J. G.

Determination of Selenium in Organic Materials. H. C. Dudley and H. G. Byers. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 3–4.)—Selenium has been found in the tissues, blood, faeces and urine, and also in the milk, of animals which have ingested seleniferous food. The following methods are proposed for the pre-treatment of the materials prior to determination of selenium. Fifty to 100 g. of the material (blood, flesh, eggs, etc.) are covered with 150 to 200 ml. of concentrated nitric acid, and the whole is kept at room temperature for 2 to 3 hours, with occasional stirring; 50 ml. of hydrogen peroxide (30 per cent.) are added, with vigorous stirring if frothing occurs, and the vessel is allowed to stand overnight. The mixture is warmed slowly on a steam-bath until frothing subsides, 50 ml. of hydrogen peroxide and 20 ml. of concentrated sulphuric acid are added; the liquid is evaporated to a paste on a steam-bath, and, after cooling, 100 ml. of hydrobromic acid (45 per cent., containing sufficient bromine to colour it a deep yellow) are added. The mixture is distilled to give 50 to 75 ml. of distillate, in which the selenium may be determined, *e.g.* by the method of Robinson (*id.*, 1934, **6**, 274). For milk samples, 500 to 1000 ml. should be taken; for this, and for other fatty materials, *e.g.* egg yolk, it is desirable to carry out the final evaporation on a hot plate. For urine, the sample may be as large as desired; the residual pasty material, if highly coloured, may be decolorised by a third treatment with hydrogen peroxide. *Clinical test for selenium in urine.*—A 100- to 500-ml. sample is mixed with 25 ml. of concentrated nitric acid and 30 ml. of hydrogen peroxide (30 per cent.), slowly warmed, with stirring, until frothing ceases, and evaporated to dryness; a re-evaporation with 10 ml. of hydrogen peroxide is necessary if the residue is coloured dark yellow; 10 ml. of hydrobromic acid (20 to 25 per cent., coloured yellow with a small drop of bromine) are added. The liquid is filtered into a test-tube, and 0·25 to 0·5 g. of sodium bisulphite, hydroxylamine hydrochloride or hydrazine sulphate is added; it is gently warmed for 15 minutes, and kept for 1 to 3 days. Selenium, if present, precipitates out as a pink powder. As little as 0·05 mg. of selenium, added as sodium selenate, was thus detected in 50 ml. of horse urine. S. G. C.

Indicator Properties of Dinitroaniline Azo Dyestuffs. H. Wenker. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 40–41.)—A range of azo dyestuffs has been prepared, 2, 4- and 2, 6-dinitroaniline and their sulphonic acids being used as

diazotisable amines, with 1- and 2-naphthol and their sulphonic acids as azo components, and the couplings being made in dilute sulphuric acid solution. The colour-change points of these dyes in solution were investigated. It was found that (i) only azo components with *para* couplings, *viz.* 1-naphthol, 1, 6-, 1, 7- and 1, 8-naphthol-sulphonic acids, gave indicators of strong colour contrast and relatively narrow *p*H range; (ii) dyes with the nitro groups in the 2, 4- position of the diazo components are preferable to those with the nitro groups in the 2, 6-position, as the former give in alkaline solution bluer and brighter shades, and the latter, redder and duller shades with less colour-contrast; (iii) a few of the new dyes compare well with nitrazine yellow (*Ind. Eng. Chem.*, **1934**, **26**, 350) in colour, intensity and contrast, but are inferior in solubility and narrowness of the *p*H range.

S. G. C.

Determination of Sulphur and Sulphate in Wool. R. T. Mease. (*U.S. Dept. Commerce Research Paper, R.P.* 731.)—Wool protein contains 3 to 4 per cent. of sulphur, probably entirely as cystine. During dyeing and finishing some of this may be converted into sulphates, and these may be increased by absorption of sulphurous or sulphuric acid from the air. The wool is prepared for analysis by washing in a 1 per cent. solution of a neutral soap at 70° C. for 30 minutes, rinsing with distilled water at the same temperature, and then extracting in a Soxhlet extractor for 16 hours with alcohol, followed by 6 hours with ether. The residue is air-dried, rinsed with distilled water at 70° C., and again dried and conditioned at 70° F. and 65 per cent. humidity. The fibres are cut into short lengths and mixed thoroughly. Although the Carius method was used for the determination of total sulphur, the author found that the following method involving the use of an oxygen bomb gave greater accuracy:—About 0·5 g. of the prepared wool is wrapped in filter-paper and bound with pure silk. This is laid on a rectangular piece of filter-paper of such a size that, when laid on top of a platinum crucible, the four corners rest on the rim and support the rest of the paper free from contact with metal. The crucible is placed on the ignition platform of a bomb calorimeter, and about 50 ml. of a 2 per cent. aqueous solution of ammonium carbonate are placed in the bomb with sufficient oxygen to give a pressure of 150 to 180 lbs. per sq. in. The specimen is ignited, and, after standing for 10 minutes, the ammonium carbonate solution is removed and filtered. After acidification the sulphur is precipitated as barium sulphate in the usual way. For the determination of sulphate sulphur the methods studied were (*a*) digestion with potassium hydroxide solution, and (*b*) digestion with concentrated hydrochloric acid, the latter being preferred. About 1 g. of the wool is placed in a Pyrex test-tube, 19 cm. long and of 75 ml. capacity. To this are added 20 ml. of 30 per cent. (by weight of HCl) solution of hydrochloric acid, and the whole is heated in a water-bath until the wool dissolves. The solution is cooled, diluted with an equal volume of water, and filtered. The sulphate in the filtrate is determined in the usual manner.

S. G. S.

Inorganic

Quantitative Determination of Thorium by Means of Picrolonic Acid. F. Hecht and W. Ehrmann. (*Z. anal. Chem.*, 1935, **100**, 87–98.)—Picrolonic acid produces in thorium solutions a crystalline precipitate which, after attaining constant weight, has the composition $Th(C_{10}H_7N_4O_5)_4.H_2O$, with a thorium factor 0·1782. The precipitant contains 2·64 g. of reagent per l. (ANALYST, 1931, **56**, 833, determination of calcium). The neutral thorium solution should be free from alkali and ammonium salts. If nitric acid is present, the solution is evaporated to dryness, and the residue is taken up with the smallest possible quantity of water (for 0·01 g. thorium), and sufficient acetic acid to provide 2·5 to 3 volumes per cent. of free acid after completion of the precipitation. The liquid is heated, and the precipitant is added, drop by drop, during gentle boiling. When precipitation appears to be complete, the rest of the reagent (0·01 g. of thorium requires 50 ml.) may be added all at once. The solution is cooled for at least an hour in an ice-box, and then filtered through a sintered glass crucible; the precipitate is washed 3 to 4 times with ice-cold water (*i.e.* until the washings are colourless), and dried to constant weight in a current of dust-free air (suction). The time required for drying is from 1 to 3 hours; it is not advisable to determine more than 0·1 g. of metal. Very accurate results are claimed. The procedure is especially suitable for micro-work; it does not provide a means for the separation of thoria from the rare earths. W. R. S.

Determination of Thorium with *o*-Hydroxyquinoline. F. Hecht and W. Ehrmann. (*Z. anal. Chem.*, 1935, **100**, 98–103.)—Thorium is precipitated as the compound $Th(C_9H_6ON)_4.C_9H_7ON$, containing 24·347 per cent. of metal. The solution, free from other precipitable metals, is made faintly ammoniacal, and the precipitate is re-dissolved by dropwise addition of 10 per cent. nitric acid. Sufficient acetic acid is added to provide for 2·5 per cent. acidity in the final bulk. The liquid is heated to gentle boiling and treated, drop by drop, with the reagent (4 g. of the base in 8 g. of glacial acetic acid, diluted to 160 ml.), 6 ml. being required for 0·01 g. of metal. If, after addition of half the quantity of reagent, no precipitate has appeared, strong ammonium acetate solution should be slowly added until the precipitate formed no longer re-dissolves. The remainder of the precipitant is added with gentle boiling throughout the manipulation. The precipitate forms pale red heavy crystals. When precipitation is complete, 5 to 10 ml. of strong ammonium acetate solution are added. The final volume is 30 to 200 ml. for a few mg. to 100 mg. of thorium. When cold, the solution is passed through an air-dry sintered glass crucible, the precipitate is washed with cold or tepid water until the washings are no longer yellow, and the crucible is dried to constant weight by suction in air. Very concordant results are claimed both in macro- and micro-work.

W. R. S.

Volumetric Determination of Arsenic Acid. M. F. Taboury and H. Audidier. (*Bull. Soc. Chim.*, 1934, **1**, 1570–1578.)—The correct conditions for the iodimetric determination in sulphuric acid solution were ascertained. The arsenate solution (10 ml., 0·0165 to 0·000989 molar with respect to As_2O_5) is treated with 2 ml. of strong sulphuric acid and 0·8 g. of potassium iodide, and

heated on the water-bath for 10 minutes. The solution is allowed to cool, and the remaining iodine is exactly eliminated with thiosulphate. The liquid is then treated with an excess of bicarbonate, and the arsenite is titrated in the usual manner with iodine solution. W. R. S.

Determination of Zirconium in Ores by the Selenite-Phosphate Method. S. G. Simpson and W. C. Schumb. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 36.)—Preliminary separation of zirconium by precipitation as selenite followed by precipitation of the element as phosphate from the solution of the selenite precipitate in acid has been previously found satisfactory for the determination of zirconium in steel (*id.*, 1933, **5**, 211). A procedure on these lines has now been applied to ores, and has advantages when thorium is present. The ore is decomposed, and the zirconium is precipitated as selenite (*J. Amer. Chem. Soc.*, 1931, **53**, 921). If thorium is present, the precipitate is extracted with a mixture of 40 ml. of 10 per cent. oxalic acid solution and 12 ml. of 6 *N* hydrochloric acid; the thorium, remaining as oxalate, is filtered off. The filtrate is evaporated with 50 ml. of 18 *N* sulphuric acid to destroy the excess of oxalic acid. If thorium is absent, the zirconium selenite precipitate is dissolved direct in 50 ml. of 18 *N* sulphuric acid. The sulphuric acid solution is diluted to 200 ml., and any precipitated selenium is filtered off. The solution is heated to 50° C., and 20 ml. of 3 per cent. hydrogen peroxide and 50 ml. of a 20 per cent. solution of diammonium phosphate are added. After standing for 2 hours, the precipitate of zirconium phosphate is filtered off, washed with 5 per cent. ammonium nitrate solution, and finally ignited and weighed as ZrP_2O_7. Good results were obtained in tests with synthetic mixtures of zirconium dioxide with varying amounts of felspar, apatite, thoria, ceric oxide and ammonium vanadate. S. G. C.

Determination of Fluorine in Sulphuric Acid and Oleum. H. Spielhaczek. (*Z. anal. Chem.*, 1935, **100**, 184–187.)—The acid to be tested (5 to 10 ml.) is pipetted into a 30- to 50-ml. platinum crucible, which is then covered with a glass test-plate. The acid concentration is increased to 85 or 90 per cent. by addition of pure oleum. The crucible is carefully heated, for 25 minutes with a small, and 5 minutes with the full, flame, fluorine, if present, etching the glass. Very dilute acids must not be treated at once with oleum, but with sulphuric acid first, until strong enough to be miscible with oleum without undue rise in temperature. The glass plates used should be of uniform quality (cut from one window pane), and the softer side should be at once marked for use. They are rubbed with sand and dilute hydrochloric acid, the sand sliding less easily off the softer side. The plates are polished with alcohol before use. The standard scale is prepared from solutions of pure sodium fluoride (10, 1, and 0·1 g. per l.), the standards containing 0·01, 0·005, 0·001, 0·0005, and 0·0001 g. of fluorine. The limit of sensitiveness is 0·01 mg. The acidity of all the solutions is adjusted to 85 or 90 per cent. sulphuric acid. Oleum is tested by diluting with pure 50 per cent. acid to the required acidity, adding a little pure powdered sulphur, and heating to 200° C. for 10 minutes. The sulphur decomposes any fluorosulphonic acid, the slight incrustation of sublimed sulphur not interfering. Before comparison, the glass plates are rinsed, and polished until dry. W. R. S.

Detection of Nitrite with Magdala Red. H. Eichler. (*Z. anal. Chem.*, 1935, **100**, 183–184.)—A solution of 0·05 to 0·1 g. of Magdala red in 100 ml. of glacial acetic or strong formic acid is used. The reagent loses its red fluorescence and strikes a blue colour when treated with nitrite in the solid form or in solution at the ordinary temperature. Large amounts of nitrite may destroy the colour. Nitrate does not react. The test may also be carried out with filter-paper treated on one side with an aqueous suspension of Magdala red. If the prepared paper, which appears grey, is moistened with the solution to be tested, dried, and then moistened with strong acetic or formic acid, it becomes blue by the action of nitrite, otherwise red. W. R. S.

Determination of Ozone in Air. E. Briner and H. Paillard. (*Helv. Chim. Acta*, 1935, **18**, 234–237.)—The efficacy of potassium iodide solution and of mixed arsenite and potassium iodide solution as absorbing agents for ozone in small concentration (0·001 to 3·6 per cent.) has been tested. The absorbing solution was agitated in contact with the gas for periods up to 2 hours. Practically theoretical values were obtained for recovery of ozone when 20 per cent. potassium iodide solution alone was employed, with a 1-hour period of contact. On the other hand, with 0·1 *N* arsenite solution, together with potassium iodide, appreciably low results were obtained. S. G. C.

Microchemical

Microchemical References. 1932. (Part I, Supplement to *Mikrochem.*, 1933, **13**; *ibid.*, 1932. Part II, Supplement to *Mikrochem.*, 1934, **14**; *ibid.*, 1933. Part I, Supplement to *Mikrochem.*, 1934, **15**.)—References collected mainly from abstracts in the *Chem. Zentralblatt*, arranged in the alphabetical order of the authors' names under the following general divisions:—*Pure Microchemistry.*—(i) General and apparatus, (ii) Inorganic analysis, (iii) Organic analysis, (iv) Preparative chemistry, (v) Physical chemistry. *Applied Microchemistry.*—(i) Biology, (ii) Medical and pharmaceutical chemistry, (iii) Mineralogical chemistry, (iv) Technical microchemistry. J. W. M.

Collected References. Spectral Analysis. F. Pavelka and H. Molterer. (*Mikrochem.*, 1935, **17**, 47–102.)—An account of the qualitative and quantitative methods and the apparatus used, followed by 125 references with brief abstracts of each, and 5 tables consisting of photographs of spectra. J. W. M.

Collected References. Carbohydrates, II. A. Wasitzky. (*Mikrochem.*, 1934–35, **16**, 87–114.)—The references collected include qualitative micro-reactions of carbohydrates and their analytical application, especially in the food industries; the use of quantitative micro-methods in biology and in the food industries and food inspection, and the progress of microchemical carbohydrate analysis in general, 1931–34. A number of tests and methods are described with working details, and, in all, 114 references are given. J. W. M.

Spot Tests for Organic Compounds. V. F. Feigl, V. Anger and R. Zappert. (*Mikrochem.*, 1934, **15**, 190–195.)—(i) *Test for hydrazine derivatives.*—Many azo-dyestuffs formed by the coupling of diazotised *p*-amino-benzaldehyde with naphthol- and amino-naphthol-sulphonic acids form with organic hydrazine derivatives hydrazones which may possess an appreciably deeper colour than the original dyestuff. Of a large number of dyestuffs tried, the following were found to be most useful as reagents for hydrazine derivatives. (i) The azo dye formed from diazotised *p*-amino-benzyaldehyde and crocein acid (2-naphthol-8-sulphonic acid) (yellow). (ii) The azo dye formed from diazotised *p*-amino-benzaldehyde and Schäffer's acid (2-naphthol-6-sulphonic acid) (orange-yellow). (iii) The azo dye from diazotised *p*-amino-benzaldehyde and R-acid (2-naphthol-3,6-disulphonic acid) (orange). (iv) The azo dye from diazotised *p*-amino-benzaldehyde and nigrotinic acid (2,8-dihydroxynaphthalene-6-sulpho-4-carboxylic acid) (bright cherry-red). The colours refer to those of the very dilute weak acetic acid solutions. These dyestuffs have not yet been isolated as the pure solids. *Method.*—A drop of the dilute acetic acid solution of the dyestuff is mixed with a drop of a 10 per cent. solution of sodium acetate in a micro-crucible, and a drop of the aqueous or alcoholic solution of the test solution is added. The time for the colour-change depends on the concentration of the test solution, and may be as long as 15 minutes, in which case a blank test is recommended. *Preparation of the reagent.*—*p*-Amino-benzaldehyde hydrochloride is suspended in dilute hydrochloric acid, and diazotised with the calculated amount of sodium nitrite. The diazonium salt solution is poured into the solution (containing excess of soda) of the equivalent amount of the naphtholsulphonic acid, and finally acidified with acetic acid; the solution of the dyes will keep. A table is given showing the reactions of 13 different hydrazines with the 4 different reagents, together with the colour-change and the identification-limit in each case; the identification-limit varies from 50γ to 1γ.

2. *Test for aromatic and α-β-unsaturated aldehydes.*—Sodium pentacyano-amino-ferroate has been found (*Mikrochem.*, 1934, **15**, 183, Abst., ANALYST, 1935, 123) to give an intense blue colour with certain thio-ketones and with aromatic and α-β-unsaturated aldehydes, in the presence of hydrogen sulphide:

$$R.CHO + H_2S = R.CHS + H_2O$$
$$Na_3[Fe(CN)_5NH_3] + R.CHS = Na_3[Fe(CN)_5(R.CHS)] + NH_3.$$

This reaction has been adopted as a micro-test. *Method.*—A drop of the 1 per cent. solution of the reagent is mixed with a drop of a 2 per cent. solution of ammonium sulphide, free from polysulphides, in a micro-crucible and a drop of the aqueous or alcoholic test solution, together with *N*/2 acetic acid solution, is added. An intense blue colour (green in a few cases) results. A blank test should be carried out, and the acetic acid solution should not be too strong. A table is given of the sensitivity of the test and the colours formed with 15 aldehydes. The identification-limit varies from 1γ to 4γ. J. W. M.

Micro-determination of Bromides and Iodides in Presence of Chlorides. I. Bellucci. (*Gazz. Chim. Ital.*, 1934, **64**, 688–695.)—The ash obtained from blood in the way described (*cf.* Abst., p. 264) contains the whole of the chlorine, bromine and iodine of the original blood in the form of sodium halide salts. When

the ash is extracted with 95 per cent. alcohol, a little of the sodium chloride and the whole of the sodium bromide and iodide are dissolved. Evaporation of the alcoholic extract to dryness and solution of the residue in water yields a solution (10 to 15 ml.) in which the bromine and iodine ions may be determined as follows:— The solution is acidified with sulphuric acid and then treated with a slight excess of sodium nitrite, the nitrous acid thus formed liberating the iodine from the iodide, with formation of nitric oxide, whilst the hydrochloric and hydrobromic acids remain unchanged. The free iodine is removed from the aqueous solution by means of carbon tetrachloride, which is then separated, treated, drop by drop, with sodium hydroxide solution (1 : 10) until decolorised, and evaporated to dryness. The residue is dissolved in water and the sodium iodide present in the solution is oxidised to iodate by permanganate and alkali hydroxide. Excess of permanganate is destroyed and, after removal of manganese dioxide, any nitrite present is decomposed by urea after addition of acetic acid. The iodine is then determined as already described (*loc. cit.*). The aqueous solution, containing all the bromide and part of the chloride, is made faintly alkaline with sodium hydroxide and evaporated to dryness on a water-bath. The residue is extracted at the ordinary temperature with acetone, which dissolves the sodium bromide, but not the sodium chloride. The acetone extract is filtered and titrated directly with 0·01 *N* silver nitrate solution in presence of ferric alum. Determinations of bromine and iodine ions in this way in test solutions containing small proportions of sodium chloride, bromide and iodide show the method to be accurate.

T. H. P.

Physical Methods, Apparatus, etc.

Determination of Free Silica. H. L. Ross and F. W. Sehl. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 30–32.)—A petrographic immersion method is described for the determination of free silica in mineral and dust samples. It depends on counting under the microscope the number of transparent particles visible when a definite amount of the material is suspended (*a*) in fennel-seed oil, which has a slightly lower n than quartz, (*b*) in nitrobenzene, which has a slightly higher n than quartz. The numerical difference between the counts gives a measure of the proportion of particles of quartz or free silica present. To obtain the proportion by weight of quartz particles, account has to be taken of the relative sizes of the particles, which may be measured microscopically. For details of the method, with a description of the optical equipment necessary, the original paper should be consulted.

S. G. C.

Measurement of the Colour of Liquids. Application to Wines. A. Faure and R. Pallu. (*Ann. Falsif.*, 1935, **28**, 5–9.)—If a monochromatic ray of light of intensity I_0 falls on a cell with parallel faces containing the wine, then the optical density (D) = $\log I_0/I_1$, where I_1 is the intensity of the transmitted ray. D is a function of the "sale value of the colour" of the wine, the unit of colour-intensity of a wine being known as the "ROB" where 1 ROB = constant $\times D$; a photocolorimeter may then be calibrated in terms of the ROB, on the

assumptions that the walls of the cell and the water used for dilution have an optical density of zero, and that the process of dilution involves no physical or chemical change in the colouring matter. It is shown theoretically that these assumptions are justified. White light is unsuitable, because the transmission spectrum contains a pronounced red ray (at 600 to 700$m\mu$), which is independent of the colour of the wine, but blue light (460$m\mu$) gives a ray which corresponds with variations in the colour of the wine as observed by the human eye. A Toussaint photo-electric colorimeter was used, the light being passed through a blue glass filter and a cell 5 mm. thick containing the wine before falling on the potassium photo-electric cell. The resulting current is amplified and measured on a milliammeter, the cell being first calibrated by observing the currents produced after dilution of a strongly coloured wine to various extents; the undiluted wine was given a value of 100 ROB units. It is also desirable occasionally to test the apparatus with various thicknesses of a standard solution of gentian violet (which is stored in the dark), so as to ensure that the cell and its amplifier are giving regular responses. The method gives reliable results, and is more sensitive than the human eye. Table wines have values of 50 to 115, red wines about 15, and coloured wines 600 to 700 ROBS; it is possible to predetermine the final colour of a wine from the value at the time of clearing, so long as no precipitation of colouring matter occurs.

J. G.

Reviews

ELEMENTARY ANALYTICAL CHEMISTRY: QUALITATIVE AND QUANTITATIVE (CLOWES AND COLEMAN). Twelfth Edition. Revised by C. G. LYONS, M.A., Ph.D., and F. N. APPLEYARD, B.Sc., F.I.C., Ph.C. Pp. xiii+242. London: J. & A. Churchill, Ltd. 1934. Price 6s.

For the twelfth edition, this well-known text-book has been revised and partly re-written in order to bring into it such modern developments of analytical chemistry as can be advantageously introduced into elementary work. The text is arranged in five main divisions, *viz.* qualitative inorganic analysis, volumetric analysis, gravimetric analysis, inorganic preparations and organic compounds.

The qualitative section, which is on orthodox lines, is exceptionally full and clear. The introduction of the use of α-nitroso-β-naphthol and dimethyl glyoxime as confirmatory tests for cobalt and nickel, respectively, strikes a more modern note. In the 134 pages devoted to this section only one trifling misstatement has been found—the existence of a precipitant for nitrates is denied, nitron being overlooked.

The section on volumetric analysis has been entirely re-written, and is now very comprehensive. It is a pity, however, that, although a method resembling that of the N.P.L. for standardising a burette is given, no mention is made of the procedure for a pipette, and the student is still left to struggle with the problem of the "last drop." The subsections on indicators and hydrogen ion concentration are brief but adequate, although perhaps the distinction between ionised and

ionisable hydrogen might have been more strongly emphasised. Many modifications are introduced, such as, for example, the use of diphenylamine as an internal indicator in dichromate titrations. In the organic section are given the reactions of a large number of compounds, including oxalic acid, chloroform, glycine, sucrose, strychnine, and others mainly of pharmaceutical interest.

The new edition is an admirable little volume which provides the student with a firm groundwork of practical chemistry, and neither the authors nor the publishers need fear for the future of "Clowes and Coleman."

HAROLD TOMS

METHODS OF AIR ANALYSIS. By J. S. HALDANE, C.H., M.D., Sc.D., F.R.S., and J. IVON GRAHAM, M.A., M.Sc., F.I.C., F.R.C.Sc.I. Fourth Edition, revised throughout and enlarged. Pp. vii+176, 34 illustrations. London: Charles Griffin & Co., Ltd. Price 7s. 6d.

For many years Dr. Haldane's *Methods of Air Analysis* has been recognised as a work of very great value as a detailed manual of methods which had been abundantly tested by one of the world's leading authorities. The book has now been re-issued, this time with the collaboration of Mr. Ivon Graham, who has added sections which have increased the length by some fifty pages. As was pointed out in previous editions, the book in no way aims at being a treatise on gas analysis, but seeks merely to describe some methods which have been proved reliable. This treatment allows space for very full details of such selected methods.

Apart from the fact that the chapters are now numbered, there is very little alteration in the general appearance of the book. Chapter I contains a new illustrative diagram of the Haldane laboratory gas analysis apparatus; Chapter II is little altered, but has an additional section of 6 pages on an interesting apparatus for the analysis of air samples containing small proportions of higher hydrocarbons, as well as hydrogen, carbon monoxide and methane. Carbon monoxide is determined by oxidation with iodine pentoxide and measurement of the resulting carbon dioxide. In connection with the same apparatus, the authors find that palladium-asbestos at 100° C. satisfactorily effects the selective combustion of hydrogen, saturated hydrocarbons and even carbon monoxide being unaffected. The analyst will be well advised to follow scrupulously the conditions described, since it is known that workers using palladium as an agent for fractional combustion under slightly differing conditions have obtained discordant results.

Chapter III (Calculation and Statement of Results of Analysis) and Chapter IV (Portable Apparatus for Determining small Percentages of Carbon Dioxide) are practically unchanged. The old chapter on portable apparatus for the determination of carbon dioxide, methane and carbon monoxide in mines worked with naked lights is omitted. The chapter on portable apparatus for firedamp determinations is completely rewritten, the McLuckie Gas Detector being described in place of the former apparatus, which was merely a modification of the ordinary Haldane apparatus. Chapter VI, on the approximate determination of oxygen by the flame-test, contains an additional page on the Briggs Safety Lamp. Chapter IX (Determination of Moisture by Dry and Wet-bulb Thermometers) is extended from 3 to 7 pages, and two illustrations are now given. The Storrow

and the Hancock types of hygrometer are described, and also the Kata Thermometer. This last instrument is designed to measure the "cooling power" of the atmosphere, which is affected by humidity and the rate of air-circulation, and gives a much better indication of the effect of cold or hot atmospheres on the human body than temperature alone.

Chapter X, which deals mainly with the blood-test for carbon monoxide, contains additional paragraphs on the reaction between haemoglobin and nitric oxide, and on the Hartridge Reversion Spectroscope. One feels that a few more details of this very important instrument might have been given, or, at least, references to books or papers* in which its analytical uses have been described.

Chapter XI, on the accurate determination of very small quantities of carbon monoxide, is entirely new, and was certainly required. The iodine pentoxide method, to which Mr. Graham has made important contributions, is employed; the measure of the carbon monoxide is the iodine liberated, which is determined by titration. Portable and laboratory instruments for this purpose are described and illustrated. The imperative necessity for satisfactory iodine pentoxide is rightly stressed, and details of its preparation given. Chapter XII is a new chapter of 8½ pages on the application of gas analysis to the detection of spontaneous combustion in coal mines. This phenomenon, which has generally been first detected by the smell, can be detected more sensitively (and therefore earlier) by gas analysis. Apparatus for this purpose is described, the gases determined being carbon dioxide and monoxide, the former by absorption and volume-measurement (stated to be accurate to 0·003 per cent.) and the latter by iodine pentoxide and titration of the iodine.

Chapter XIII describes methods for the detection and recording of carbon monoxide. "Hoolamite," which is mentioned but not strongly recommended, is described as iodine pentoxide soaked in sulphuric acid; the mixture devised by Hoover and Lamb and called by this portmanteau name, consists, however, of pumice, iodine pentoxide and *fuming* sulphuric acid. Five very interesting pages are given to the Katz Recorder, in which the carbon monoxide is oxidised by "Hopcalite" catalyst and the heat so produced is recorded by thermo-couples.

Chapter XIV, on the recognition of other poisonous gases, has most usefully been extended from 1½ to 12 pages. A brief synopsis of the toxic properties of a number of gases is given, including, in most cases, an outlined description of a method of detection or determination. In the procedure given for the detection of hydrogen cyanide and cyanogen by the Prussian-blue method, the tyro may be misled by "sulphate" being misprinted as "sulphide." It might have been mentioned that the sensitiveness of the test is greatly increased by filtering after the treatment with ferrous hydroxide, the masking effect of the excess of iron salts being thus greatly reduced. For the same reason the quantity of ferric chloride added after acidification should be very small; "ferric chloride is then added in excess" is, although correct, rather misleading, since, for the quantities of cyanide which are likely to be present, a very small amount of ferric chloride furnishes this necessary excess. On p. 146 occurs the phrase "nitric oxide or nitrogen dioxide, NO (or N_2O_2)." The latter formula—N_2O_2 is, of course, unknown

* *e.g.* R. C. Frederick, ANALYST, 1931, **56**, 561.

—is made conspicuous by the footnote: "The compounds NO_2 and N_2O_4 have for many years been incorrectly called nitrogen dioxide." Is there, however, any more suitable name available for NO_2 than "nitrogen dioxide," and can it be strictly correct, by whatever authorities it is sanctioned, to apply this name to a molecule (NO) containing only one oxygen atom? The chapter concludes with $4\frac{1}{2}$ valuable pages of tables on the physiological effects of lack of oxygen and of the presence of various proportions of other gases.

Chapter XV, on the determination of dust in air, has been extended from 4 to 15 pages by the addition of a full description of a method of collecting dust for analysis, and an account of those interesting instruments, the Konimeter and the Owens Dust Collector. The book closes with 5 pages of tables of oxygen concentrations corresponding to various proportions of nitrogen, in the ratio existing in fresh air.

It is a tribute to the high excellence of Dr. Haldane's established methods that their description has needed so little alteration. The additions are in all respects cogent, and no greater recommendation could be given than to say that this classic monograph has been worthily brought up to date. H. R. AMBLER

PRACTICAL BACTERIOLOGY FOR STUDENTS OF AGRICULTURE. Second Edition. By ANDREW CUNNINGHAM, D.Sc. Pp. 203. London: Oliver & Boyd. 1934. Price 7s. 6d.

The introductory chapter of this work contains information on general bacteriological technique and deals with a variety of subjects, from the cleaning of glass apparatus to the preparation of culture media.

The author has felt that very elementary advice is worthy of inclusion in a book, and he therefore states, for instance, that a brush should be used in the washing of dirty test tubes, and he includes similar instructions elsewhere. However, every chapter tends to incorporate elementary instruction with advanced practical exercises. Further chapters deal with details of cultural methods and with the diagnosis and characteristics of many organisms, the latter including those found in the soil and in agricultural products, as well as those pathogenic to fowls and other animals.

As the information is almost exclusively of a practical nature, the student should use the book only in conjunction with a treatise on agricultural bacteriology. Then, for example, the association of the subject with the surmises of Pasteur and their exemplification by Warrington, Winogradsky, and others will be appreciated and interest added to the study.

Merely to scan the pages would serve as a reminder of the great extension of the science of bacteriology to many branches of agriculture and its associated industries.

The present volume is the second edition, and any faults that may have been contained in the former now appear to have been corrected. The book is one which can be confidently recommended to practical students, for, in addition to a description of the preparation of culture media and of processes employed in agricultural bacteriology, soil organisms and many others are described.

F. W. F. ARNAUD

A HISTORY OF FOOD ADULTERATION AND ANALYSIS. F. A. FILBY, M.Sc., Ph.D. Pp. 269. London: Allen & Unwin. 1934. Price 10s.

This volume is one of much interest to public analysts and all others interested in the chemistry of food. It is a thesis approved for the degree of Doctor of Philosophy in the University of London, and is graced most appropriately by a foreword by Dr. Bernard Dyer.

It is evidently the result of much patient research, often in recondite directions, and supplies information not readily available in any other treatise—not even in the admirable summary by Wynter Blyth with which all of us are familiar. Dr. Filby takes up the narrative with the beginnings of the ancient city companies which are traced from the Pepperers of Ethelred's days who first formed the Grocers' Company, and he follows the course of food analysis up to the early days of our own Society and THE ANALYST. The activities, legal and illegal, of the grocers, bakers, brewers, vintners, and distillers are discussed in order, and the nature and extent of adulteration which they practised receive critical survey. In general, it seems probable that the majority were more honest than some authors have suggested, if only for the reason that some of the alleged adulterations would not pay.

The Adam and Eve of public analysts appear to be represented by the Polliciers and Garbelers, whose duties so far back as 1300 included the removal of impurities from spices. But the first person who might really be regarded as the forerunner of the public analyst is Henry Jackson, who, in 1758, personally analysed over 100 different bakers' breads in order to ascertain the true facts in relation to their alleged adulteration. It is interesting to note how stoutly the author defends the bakers against the extravagant charges which, ever since the days of Pharaoh, have been so often made against them. He shows very reasonably how absurd are many of the statements originating in the alarmist anonymous treatise of 1757 and repeated in many subsequent works for a century. The humorous story of the baker's reply is well told.

It is not possible in this brief review to refer to the many interesting matters mentioned, though it may be noted, in passing, how history repeats itself—there is nothing new under the sun. Boerhaave, in 1735, gave a reliable test for copper in pickles and the like, and in 1755 there was published a tract, "Serious Reflections on the Dangers attending the use of Copper Vessels." Have we not, in 1935, had examples of this danger in tomato purée and other products?

We are glad to note that Dr. Filby pays tribute to the influence of food adulteration and the early analysts upon the development of the science of chemistry. The volume is a scholarly little treatise, well documented, free from sensationalism or exaggeration; one which we cordially welcome.

H. E. Cox

Publications Received

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