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 Friday, March 2nd, at 3 p.m., the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read in favour of Ronald Andrew Balding, Bertram Eastwood Dixon, M.Sc., A.I.C., A.C.G.F.C., Arthur Glover, M.Sc., A.I.C., Ralph Gordon Harry, A.I.C., Reginald Milton, B.Sc., Roy Warren Watridge, B.Sc., F.I.C.

The following were elected Members of the Society:—Donald Burton, M.B.E., D.Sc., F.I.C., Arthur Sereld Houghton, M.Sc., F.I.C., Homi Ruttonji Nanji, B.Sc., Ph.D., D.I.C., A.I.C., Harold Overton, B.Sc., John Milner Russell, B.Sc., Walter Frederick Waters, B.Sc., A.I.C.

THE Annual General Meeting of the Society then followed, when Special Resolutions were passed for the alteration of certain Articles of Association of the Society, and the President delivered his Presidential Address.

The following were elected as Officers and Council for the year 1934:—

President.—John Evans, 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. Eynon, 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, E. M. Hawkins, L. H. Lampitt, H. Lowe, C. H. Manley, C. E. Sage, J. R. Stubbs, J. F. Tocher, E. Voelcker.

Anniversary Dinner

THE Society of Public Analysts was founded in August, 1874, and its first Annual Meeting was held in February, 1875. On Friday, March 2nd, 1934, the Society (whose scope and title were extended in 1907 to include analysts other than Public Analysts) held a dinner at the Trocadero Restaurant to commemorate the sixtieth year of its foundation.

The members and guests, who numbered 126, were received by the President, Mr. F. W. F. Arnaud, F.I.C., and Mrs. Arnaud, and he afterwards took the chair at the dinner.

The guests of the Society included the Rt. Hon. Lord Cornwallis, C.B.E., D.L., J.P.; Sir Isidore Salmon, C.B.E., D.L., J.P., M.P.; Sir Robert Robertson, K.B.E., D.Sc., F.I.C., F.R.S. (Government Chemist); Sir William J. Pope, K.B.E., D.Sc., LL.D., F.I.C., F.R.S.; Professor J. F. Thorpe, C.B.E., D.Sc., F.I.C., F.R.S. (President of the Institute of Chemistry); Professor G. T. Morgan, O.B.E., D.Sc., F.I.C., A.R.C.S., F.R.S. (President of the Chemical Society); Mr. William Macnab, C.B.E., F.I.C., M.I.Chem.E. (President of the Institution of Chemical Engineers); Sir Bernard Spilsbury, M.A., M.B., B.Ch., F.R.C.P. (President of the Medico-Legal Society); Dr. Charles Porter, M.D., M.R.C.P., M.O.H. (President of the Society of Medical Officers of Health); Dr. J. T. Dunn, D.Sc., F.I.C. (President of the Society of Chemical Industry); Mr. J. F. Blackshaw, O.B.E. (Dairy Commissioner, Ministry of Agriculture); Mr. James Stenhouse, A.C.G.I. (President of the Institute of Brewing); Dr. C. H. Hampshire, M.B., B.S., M.R.C.S., L.R.C.P., F.I.C. (Chairman of the Pharmaceutical Conference); Mr. J. Egerton Quested, J.P.; Mr. R. B. Pilcher, O.B.E. (Registrar of the Institute of Chemistry); and Mr. R. A. Beck.

After the toasts of His Majesty the King and the Members of the Royal Family had been honoured, the President proposed the health of the Houses of Parliament. Mr. Arnaud pointed out that Public Analysts owed their very existence to Parliament, for they were a direct outcome of the Food and Drugs Acts of 1860 and 1872, a large proportion of the regulations of which was incorporated in the 1928 Act. The Report of the Departmental Committee which was enquiring into the question of food standards was awaited with interest. Unquestionably, further legislation was required to bring our food laws into unison with those of the Dominions and European countries.

LORD CORNWALLIS responded for the House of Lords, and SIR ISIDORE SALMON, M.P., for the House of Commons. Sir Isidore said that it was now recognised that industries connected with the manufacture of foodstuffs were anxious to have them pure.

SIR WILLIAM J. POPE proposed the toast of "Success to the Society." He deplored the fact that students were doing less quantitative analytical work at the present day than in his young days, since such work involved training in scientific methods. He envisaged the time when the Public Analyst would be called upon to undertake the accurate chemical determination of vitamins. At present, these determinations were made by physiologists.

The PRESIDENT, replying to the toast, referred to the steady increase of the Society in numbers and in influence, and laid stress upon the fact that the Society's journal, THE ANALYST, had won for itself an international scientific reputation. Mr. Arnaud then proposed the health of Dr. and Mrs. Bernard Dyer. He said that Dr. Dyer had been associated with the Society from its inception, 60 years ago, had been its President in 1897, and had contributed largely to its growth and influence. Dr. DYER thanked the Society for the toast.

Dr. G. W. MONIER-WILLIAMS, in proposing the health of Kindred Societies, indicated how closely many of them were linked with the Society of Public Analysts.

Dr. CHARLES PORTER, in his reply to the toast, observed that the members of his Society (the Society of Medical Officers of Health) and of the Society of Public Analysts had together done more to benefit public health in this country than any other group of persons.

Dr. L. H. LAMPITT proposed the health of the Guests. In the course of his speech he referred to the recent appointment of Miss Muriel Roberts—the first woman to become a Public Analyst in England.

SIR ROBERT ROBERTSON, the Government Chemist, replying for the Guests, referred to the cordial relations existing between the Society and his Department, and to the fact that his staff made frequent use of THE ANALYST for the publication of analytical communications.

Mr. J. F. BLACKSHAW, Dairy Commissioner, Ministry of Agriculture, who also replied for the Guests, spoke appreciatively of the friendly relations existing between his Department and the Society.

Annual Report of Council

March, 1934

THE Roll of the Society stands at 702, a slight increase over the membership of last year.

The Society has sustained during the current year very serious losses of old and valued members, many of whom have been untiring in their energies to promote the prosperity of the Society. These include:

Edward Theodore Brewis
John Joseph Bryant
Ernest Griffiths-Jones
John Haworth
Thomas James Hutchinson
Alfred Edward Johnson
William Marshall
William Partridge
John David Roberts
George Tate
John Millar Thomson
Walter Peter Whitley
James Wood

J. Millar Thomson, at one time Professor of Chemistry at King's College, was an honorary member of the Society. He will be remembered by many who, as students at King's College, studied chemistry under him.

Brewis, 19 years a member, was mainly known for his activities on the Standing Committee, and in that capacity rendered valuable services to the Society. He had been a Member of Council and was a familiar figure at meetings.

Johnson and Wood, members for 10 and 15 years respectively, had both served on the Council, and the Council is grateful for their services.

Tate and Whitley had been members for 19 and 8 years respectively. Although not often seen at meetings they were both distinguished in their particular spheres of activity.

Partridge, during his 30 years of membership, had been a Vice-President and Member of Council. Although by nature somewhat shy and retiring, he was a regular attendant and was indefatigable in his endeavour to promote the welfare

of the Society, particularly on the Publication Committee and as a member of the Standing Committee.

Hutchinson and Marshall were both very old members of some 40 years' standing, and the Council regrets their passing.

Bryant and Griffiths-Jones joined the Society in 1924, and Roberts, although a comparatively recent recruit, took a keen interest in the Society's affairs, and was our representative on the Empire Marketing Board's Dairy Research Sub-Committee.

Haworth, a member since 1919, was well known as an authority on the examination of water and sewage.

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

"Notes on the Iron and Copper in Liver and Liver Extracts." By H. G. Rees, B.Sc., A.R.C.S., A.I.C.

"The Determination of the Freezing-point of Milk." By G. W. Monier-Williams, O.B.E., M.C., M.A., Ph.D., F.I.C.

"An Investigation of Solanine Poisoning." By S. G. Willimott, Ph.D., B.Sc.

"The Examination of Leather for the Presence of Extractable Chromium Compounds." By F. E. Humphreys, Ph.D., A.R.C.S., A.I.C., and H. Phillips, D.Sc., F.I.C.

"Use of the Phytosteryl Acetate Test in the Routine Examination of Butter Fats." By H. Hawley, M.Sc., F.I.C.

"Barium as a Normal Constituent of Brazil Nuts." By W. M. Seaber, B.Sc., F.I.C.

"The Occurrence and Origin of Lead in Canned Sardines." By L. H. Lampitt, D.Sc., F.I.C., and H. S. Rooke, M.Sc., F.I.C.

"The Chemical Examination of Furs in Relation to Dermatitis." Parts II, III and IV. By H. E. Cox, M.Sc., Ph.D., F.I.C.

"The Investigation of Japanese Beeswax." III. By H. Ikuta.

"A Specific Gravity Apparatus." By C. H. Cribb, B.Sc., F.I.C. Demonstrated by T. McLachlan, F.I.C.

"The Use of the Air-Damped Balance for the Determination of Total Solids in Milk." By Capt. John Golding, D.S.O., F.I.C.

"A Rapid Method of Determining Minute Quantities of Nitrites." By G. G. Rao and K. M. Pandalai.

*"The Analysis of Fruit and Fruit Products." By E. B. Hughes, M.Sc., F.I.C., and A. E. Maunsell, B.Sc.

*"The Examination of Fruits and Jams by Lead Precipitation." By C. L. Hinton, F.I.C.

*"Equalisation of Temperature in Electric Ovens." By F. G. H. Tate, F.I.C.

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

"Ancient Egyptian Materials and Industries about 1350 B.C." By A. Lucas, O.B.E., F.I.C.

"Foreign Starch in Arrowroot." By P. H. Jones, F.I.C.

"A Note on Pearl Barley." By P. H. Jones, F.I.C.

"The Examination of 1000 Milks by the Hortvet Freezing-point Process." By J. R. Stubbs, M.Sc., F.I.C., and G. D. Elsdon, B.Sc., F.I.C.

"Note on Nitrates Test in Milk." By W. F. Alvidge, B.Sc., F.I.C.

"The Effect of Certain Salts on Fermentation in Dough." By R. H. Callow, M.Sc., A.I.C.

* Read at the Joint Meeting with the Food Group of the Society of Chemical Industry on February 7th, 1934.

"Note on Freezing-point Determination—Hortvet's Method." By E. V. Jones, F.I.C.

"Some New Applications of the Elaidin Reaction in the Examination of Fatty Oils." By Prof. T. P. Hilditch, D.Sc., F.I.C.

Of the Society's Meetings, one, namely the November meeting, may be mentioned. A discussion on the Chemical (as distinct from Physiological) Tests for Vitamins, opened by Mr. A. L. Bacharach, who was followed by many distinguished speakers, made an interesting and valuable contribution. In recent years it has been the policy of the Council to hold these discussions, and they are tending to increase in number. Without in any way desiring to limit the time available at Ordinary Meetings for the readers of papers, the Council feel that discussions on general analytical problems tend to promote interest and add generally to the usefulness of the Society's Ordinary Meetings.

THE ANALYST.—Although THE ANALYST for 1933 contains a somewhat smaller number of pages than in the previous year (789 as compared with 810) this does not mean any curtailment of the activities of the Journal, but is due to the papers being more concise than in former years. The total number of papers (including those not read before the Society) was 48, and there were also 49 Notes. The catholicity of the interests of the Society is shown by the fact that, of the 48 papers, 18 were concerned with the analysis of food and drugs, 13 with inorganic analysis, 7 with toxicological and forensic work, 5 with organic analysis, 2 with archaeological research, and 1 with micro-analysis. A similar diversity of interest is to be found in the Notes.

Of the papers published, three were the outcome of work under the Society's Analytical Investigation Scheme. Mr. T. H. Pope's valuable compilations of the Bibliography on Heavy Metals in Food and Biological Material have been continued during the year and have since been completed. They have attracted wide attention, and are now being reprinted together as a brochure.

Official and Public Analysts at home and abroad have, as in former years, sent copies of their Annual Reports to the Editor, and these have provided the material for numerous notes of value to analysts. Several reports on legal cases have also been forwarded by the chemists concerned in them, and whenever these have involved certain points of special legal or scientific interest they have been abstracted in a form convenient for reference.

As in the past, papers of direct or indirect analytical interest published in other journals have been abstracted and submitted to the criticism of the Publication Committee, to insure that, so far as is possible, the subject-matter is novel, and that sufficient working details are given to enable the methods described to be tried. Reviews have continued to be a prominent feature of the journal.

TREASURER'S REPORT.—The Honorary Treasurer reports that the accounts for 1933 show that the Society has maintained its usual satisfactory financial position, the income fully meeting the expenditure involved during the year.

STANDING COMMITTEE ON UNIFORMITY OF ANALYTICAL METHODS.—The following reports have been published:

Report No. 1 (Determination of Unsaponifiable Matter in Oils and Fats) of the Sub-Committee on Determination of Unsaponifiable Matter in Oils and Fats and of Unsaponified Fat in Soaps has been received and adopted by the Council, and published in THE ANALYST (1933, **58**, 203). This Sub-Committee has been re-constituted, with Mr. L. V. Cocks as Chairman, and Mr. N. Evers as Honorary Secretary, and Dr. H. E. Cox and Mr. P. L. Bean as new members, Professor Hilditch having resigned.

Report No. 11 of the Essential Oil Sub-Committee has similarly been passed for publication, and it appeared in the February number of THE ANALYST. The work

of these and other Sub-Committees is proceeding, but there are no further reports ready for publication.

The Standing Committee has lost two of its members, E. T. Brewis and W. Partridge, by death; the Milk Products Sub-Committee has also suffered loss by the death of J. D. Roberts.

Mr. A. More has been elected a member of the Standing Committee.

ARTICLES OF ASSOCIATION.—The Council asks that three alterations in the Articles of Association be approved at the Annual General Meeting:—(1) To add, in accordance with the demand of the Board of Trade, the words "if and while unpaid" to the Article relating to the *ex-officio* election of the Chairman and Hon. Secretary of the North of England Section to the Council. (2) That members, who have paid 40 annual subscriptions shall *ipso facto* become life-members of the Society, with full privileges, without payment of further subscription. (3) That the entrance fee of members nominated by the North of England Section be waived.

NORTH OF ENGLAND SECTION.—The Section reports as follows: Five meetings have been held during the past year. A Sub-Committee sat in February and, after discussion, drew up recommendations for obtaining uniformity of design of apparatus and method of procedure for determining the freezing-point of milk.

In April a symposium, at which there was a large attendance, was held on "The Freezing-Point of Milk as a means of Detecting Added Water." After discussion, resolutions were passed for submission to the Council; these were duly sent in and the Council issued a recommendation that, for the present, the Hortvet apparatus and method of procedure should be adopted (ANALYST, 1933, **58**, 318).

A very successful Summer Meeting was held in June at Llandudno. It was well attended and thoroughly enjoyed. We were favoured with the presence, among others, of Dr. and Mrs. Bernard Dyer. A paper read by Mr. A. Lucas was much appreciated; it was afterwards published in THE ANALYST (1933, **58**, 654).

The attendance at meetings has been higher than in any previous year. Eighteen new members have been enrolled. The Section has lost by death two members: James Wood, who served on the Committee and the Council, and William Marshall, who held the office of Auditor from the time the Section was inaugurated (see p. 214).

The Secretary wishes to express his sincere thanks to the Chairman, Mr. John Evans, and all members of the Committee, who have one and all contributed to make every meeting a thorough success.

ANALYTICAL INVESTIGATION SCHEME OF THE SOCIETY.—During the past year two grants were made from the fund. Three researches were completed, and six problems are still under investigation. The Council wishes to call the attention of younger members of the Society to the work that is being carried out under the Scheme, and to assure them that they may rely upon the assistance of individual Members of the Council in overcoming difficulties that may be encountered in the course of an investigation.

BRITISH STANDARDS INSTITUTION.—Conversations have taken place between representatives of the Institution and of the Society directed towards the possibility of establishing co-operation in the matter of standard analytical methods.

PUBLIC ANALYSTS' COMMITTEE.—Several meetings of this Committee have been held during the year, the chief work being carried out at the request of the Malt Vinegar Brewers' Federation. A series of conferences has been held with that body in order to draw up definitions of Vinegar. These definitions are now completed, and have been approved by the Council and the Federation. It is hoped soon to publish these in THE ANALYST, but the Council feels that until the

findings of the Departmental Committee on Food Law are published it would be premature for these definitions to be set out in THE ANALYST.

DEPARTMENTAL COMMITTEE ON FOOD LAW.—This Committee, which was to have met some two years ago, and whose activities were temporarily postponed for reasons of economy, commenced to hear evidence last September. The Society submitted to the Committee a memorandum which they had drawn up in 1931, together with a letter and appendix containing certain important material which was not available at the time the original memorandum was compiled. The Council nominated the President, Mr. Hinks and Dr. Dunn to give evidence before this Committee, and they were heard early in October.

INDUSTRIAL CHEMISTRY CONGRESS AT LILLE.—At this Congress, which was held in September, the Society was represented by Dr. Lampitt, and the Council thanks him for acting as its delegate.

EMPIRE MARKETING BOARD.—The Council notes with regret the dissolution of the Board, which must result in a certain amount of delay in connection with work in the progress of which the Society is particularly interested.

CENTRAL COUNCIL FOR RIVERS PROTECTION.—This Council wrote to the Society, asking that we federate, and that a member be nominated to serve upon this important body. The President, Mr. Arnaud, has consented to serve.

The Biennial Dinner, which the Council has decided to hold this year, marks the 60th anniversary of the foundation of the Society. Although the first general meeting was not held until February 5th, 1875, it is noteworthy that a meeting was held in August, 1874, at which it was agreed that a Society be formed.

The Council extends its hearty congratulations to its Past-President, Dr. J. T. Dunn, on his election as President of the Society of Chemical Industry, and on the fact that he has completed fifty years of membership of the Chemical Society.

The Council again desires to record its thanks to those members who have acted as representatives on various Committees, Federations and Institutions and other organisations during the year, and deeply appreciates the services they have given.

In conclusion, the Council, whilst regretting that the time has come for Mr. Arnaud to vacate the Presidential chair, welcomes the new President, Mr. John Evans, and looks forward to a period of continued prosperity under his guidance.

(*Signed*) F. W. F. ARNAUD, *President.*
G. ROCHE LYNCH, *Honorary Secretary.*

Annual Address of the President

(MR. F. W. F. ARNAUD, F.I.C.)

(Delivered at the Annual General Meeting, held on March 2, 1934)

LADIES AND GENTLEMEN,

It is gratifying to be able again to report that the Society has had a successful year, successful because we record an increase in the number of members, our financial position remains very satisfactory, and our Ordinary Meetings have been well attended. It is not surprising that our Ordinary Meetings have been attractive when the importance of the papers communicated is considered.

Our losses have been unduly heavy, and we mourn the loss of several valued members. The memory of Professor J. Millar Thomson, one of our honorary members, will live for all time with those of us who were privileged to work under him at King's College. His invariable good humour alone was sufficient to endear him to all his students. The list of deaths includes the names of James Wood, E. T. Brewis, A. E. Johnson and William Partridge, who were past or present Members of the Council, and we shall ever have grateful memories of these colleagues.

The Standing Committee on the Uniformity of Analytical Methods and its Sub-Committees have issued further reports during the past year, and your Council has passed a resolution of thanks and appreciation to the Chairman and members of all the Committees for the labours entailed in the production of the reports. The Standing Committee, through your Council, has already supplied information concerning standard processes, etc., to the British Standards Institution, and it is possible that some working arrangement will be made so that the Society will in the future supply methods of analysis when requested by the British Standards Institution.

During July last the Minister of Health and the Secretary of State for Scotland directed that the work of the "Food Law" Committee appointed in 1931, under the Chairmanship of Sir Frederick J. Willis, should be resumed, the terms of reference being "To consider whether it is desirable that the law relating to the composition and description of articles of food should be altered so as to enable definitions or standards to be prescribed, or declarations of composition to be required, for articles of food other than liquid milk; and, if so, to recommend what alterations of the law are required." A Memorandum agreed upon by your Council was presented to the Committee by representatives of the Society. The Committee has not yet completed its task, and evidence is still being heard from various interested organisations.

At the request of the Malt Vinegar Brewers' Federation, definitions of malt vinegar and vinegar were drawn up by one of your Committees, and these were agreed to both by your Council and by the Federation. These definitions may prove extremely useful in the future, and they at least have the merit of being definitions agreed to by the trade and by the chemist.

The Institute of Chemistry has on many occasions very generously placed accommodation at the disposal of the Society for meetings of its Committees, and I express the gratitude of the Society to the President and Council of the Institute for the practical help they are ever willing to extend to us.

This evening I intend to devote my remarks to some aspects of the agricultural industry, and particularly to those to which agricultural chemistry has some relationship and application. Further, my remarks are largely limited to matters within my experience.

Unquestionably everyone appreciates that modern farming involves the application of many scientific principles, some of which are well, but many only very imperfectly, understood. So many different factors have to be taken into account that the solution of some agricultural problems becomes almost impossible, for many of the factors represent unknown quantities. Soil fertility is, perhaps, one.

Examination of Soil.—Having mentioned soil, I will deal with this subject first, as a farmer often seeks advice about what has been termed his raw material.

Frequently a soil is submitted for examination because the farmer wishes to ascertain which fertilisers to apply to the soil, and the most suitable form in which to use them. In brief, he requires to know what quantities of nitrogen, phosphates, potash and lime should be added to his soil to give him the best return. The position with regard to nitrogen is anything but satisfactory, since, even though an examination of a soil may show it to contain a high percentage of nitrogen, yet it can generally be predicted with confidence that the soil will give an increased yield of crops on the application of a soluble nitrogenous salt. Various basic quantities of nitrogen have been suggested from time to time, but the fact remains that soil fertility must for ever be bound up with weather conditions, drainage, position and other considerations. The crop to be grown or manured must also be carefully considered, because the requirements of plants differ, and there may be but little response to anything more than a minimum dressing. Often some indication of probable soil-fertility and response to nitrogen dressings can be obtained by comparing the total nitrogen-content with that present in soil of similar formation and character occurring elsewhere in the neighbourhood, and whose performance and reaction to nitrogen dressings are known. Often the desired information is not easy to obtain. To determine the soil character, a mechanical analysis usually gives the most useful information. The total nitrogen in a soil is determined by means of the Kjeldahl–Gunning process or a similar one, about 10 grms. of the air-dried soil being used. Some information as to availability may be obtained by determining the nitrogen as ammonia and the nitrogen as nitrate in the fresh soil. The nitrogen as nitrate in a cultivated soil is usually higher than in an uncultivated soil, but active plant growth may result in a cultivated soil having but a low nitric nitrogen content.

The small influence of repeated applications of nitrogenous manures on soil composition is well illustrated by some experiments in America. A few years ago the New York Agricultural Experimental Station published the chemical analyses of eight soils which, 17 years before, had been sampled and analysed.

During the intervening years these soils had been variously cropped and manured. All the soils but one had received annual dressings of nitrogen in differing amounts and in differing forms, farmyard manure, dried blood or nitrate of soda having been used. The final analyses of these soils showed that, for practical purposes, the nitrogen in all of the soils had remained constant, despite cropping and treatment. From this it must not be understood that no changes in soil composition, owing either to plant growth or the addition of fertilisers, can be detected, because in some instances changes of great importance have been recorded; there is, for example, the increase in soil-nitrogen in uncultivated land, and also in land under grass and clover, even when the crop is mown. How easily an unwarranted conclusion could be based on the total soil-nitrogen alone is exemplified by a consideration of the Folkestone beds. These beds usually produce little but scrub and heather, and yet often contain about 0·2 per cent. of nitrogen, whereas a good strong wheat soil may contain considerably less.

The difficulty in suggesting a useful addition of nitrogen to a soil from the result of a nitrogen determination will be readily appreciated when the weight of top soil is considered in relation to the percentage effect of a dressing of nitrogen. Assuming a top soil to weigh 1000 tons to the acre, and to contain 0·2 per cent. of nitrogen, it would be necessary, in order to increase the nitrogen to 0·3 per cent., to add at least 1 ton of nitrogen per acre, and this would be equivalent to about 200 tons of farmyard manure.

Determinations of the total phosphates and potash are usually made by treating the air-dried soil with boiling hydrochloric acid, diluting with water and filtering. Obviously, results obtained on such a solution do not really indicate the total phosphates or potash in the soil, but only what is rendered soluble under the conditions of the test.

Of more importance, in judging the fertility of a soil, is knowledge of the amounts of phosphates and potash that are readily available for plant growth. Various solutions have been suggested, and tried, to improve the method devised by Dyer forty years ago, but opinion strongly supports the view that Dyer's original process gives good, and probably the most reliable, information as to the ease with which phosphates or potash in the soil may be taken up by plants. The "available" phosphates are determined by acting on the air-dried soil with a 1 per cent. solution of citric acid either for 7 days or for 24 hours if continuously shaken. Though the method is empirical, the utility of the results is unquestionable. The citric acid solution does not dissolve all the phosphoric acid or potash available for plant-growth, but the amounts dissolved form a basis for comparison with those dissolved from similar soils of known fertility and, therefore, they may indicate manurial requirements. Further, the results indicate when the amounts of available phosphates or potash are so low as barely to support plant life. In America, instead of 1 per cent. citric acid solution, the use of $N/5$ hydrochloric acid or $N/5$ nitric acid has been advocated, and other chemists have favoured the use of a saturated solution of carbon dioxide.

Attention has recently been directed to the ratio of citric-soluble phosphates to "exchangeable" potash. From some published results it would appear useful to pursue this method further as a means of determining soil condition and

requirements. The exchangeable soil bases are determined by liberating them from a soil by means of a neutral salt such as ammonium chloride. Sodium chloride should be used if exchangeable lime is required.

From what has already been said it must be apparent that the mere chemical analysis of a soil does not usually yield information of great practical value, but when the results can be compared with those of soils of known performance, useful conclusions may sometimes be drawn. But even the interpretation of field trials is not an easy matter, and trials should extend over several years at least. In Kent, as in some other counties, a soil survey has been made, and the results have been published, and this survey is of very great utility. Rather more than 20 years ago Hall and Russell published a very comprehensive series of analyses of Kent, Surrey and Sussex soils, and it is to be regretted that this useful volume has long been out of print.

In Kent, information is normally required on soils used for special crops, such as hops and various fruits.

Though difficulty usually exists in the minds of those qualified to advise the farmer of the possibilities of his soil, etc., from a chemical analysis, firms occasionally advertise that they will undertake a soil analysis for a few shillings, and then advise the farmer as to the necessary manures to apply, together with the quantities per acre. One of these reports made on a sample of arable soil was brought to my notice, and may be quoted as an example. It stated that the soil was "somewhat on the poor side in general character," and it advocated, amongst other things, dressings of sewage sludge (which was categorised as a highly organic manure) and 1½ cwts. of sulphate of iron per acre. As the soil in question already contained nearly 3 per cent. of iron (ferric oxide), it was difficult, indeed, to imagine by what reasoning further small quantities of iron were demanded. The suggestion that sewage sludge was a "highly organic manure" was also somewhat strange, as a good dry sewage sludge contains only about 20 per cent. of organic matter.

Iron is often applied to lawns, as it promotes chlorophyll production and, therefore, a green grass. Sulphate of iron has an adverse effect upon some weeds, and particularly on moss, and it is a common constituent, together with sulphate of ammonia, of lawn sand.

Only a very brief reference need be made to some of the other methods directed to indicate the manurial requirements of soils, because I have had no experience with them. For instance, test plants have been used which have an ash containing a known ratio of phosphoric acid to potash. On growing these plants in a soil deficient in phosphoric acid or potash a disturbance of this ratio occurs in the plant ash. Another method involves the use of a specified fungus, which is seeded in a suspension of the soil to which has been added the ingredients necessary to promote the growth of the fungus, but not including the element for which the soil is being tested. After a specified time the mycelium which has developed on the surface is removed, dried and weighed. A principle which has been applied for the cultivation of the sugar cane involves the determination of phosphoric acid and potash in the juice, and minimum limits for both phosphoric acid and potash have been suggested. If either limit is not exceeded, manuring with phosphates or potash is required.

It is of interest to note that at the East Malling Research Station a method has been devised for introducing solutions direct into trees. Experiments have demonstrated that the introduction of potassium nitrate results in a marked increase in vigour, and the research is being continued in connection both with fertilisers and with substances known to have an injurious effect on various plant diseases. Moreover, extracts from varieties of trees which are never infected with certain parasites have been injected into trees that are susceptible to infection, to note whether immunity from attack can be conferred.

Soil classification normally means the classification of soils according to their texture, a soil-texture being dependent on the size of the particles of which it is composed. To determine the texture, a mechanical analysis of a soil is made, the differentiation of the particles of various sizes being effected, first by means of sieves, and then by sedimentation from water. By these means soils can be graded into fractions known as gravel, fine gravel, coarse sand, fine sand, silt, fine silt and clay. Unfortunately, from time to time, the conditions of experiment have been altered, with the result that the soil fractions obtained by the varying processes are by no means identical. Finality may have been reached, however, since the Imperial Bureau of Soil Science has recently issued a report on the dispersion of soils in mechanical analysis, and in it are given details of a recommended procedure. It is to be hoped that the recommendations will be adopted throughout the Empire, so that there will be conformity to a uniform procedure. Many workers in localities where a soil survey has been published will, however, cling to their old methods, because these methods yield results which can be directly compared with those previously published. Mechanical analysis enables a soil to be classified, and thereby a comparison to be made with similar soils, and so classification may lead to a soil-response to fertilisers being foretold. Mechanical analysis also yields information on soil texture, and thus renders apparent the possibilities of cultivation, the water-holding power and other properties of the soil.

In many instances the whole of the soil down to the unweathered material is of importance in crop production. Each soil layer may have a material influence on the movement of water either in a downward or upward direction and, therefore, the mechanical analysis of the top nine inches of soil may give quite a false value to the real water-holding capacity of a soil, particularly where the natural subsoil water level is high. Much attention has recently been given to soil horizons (depth of soil layers), and the differences in fertility of similar soils in a neighbourhood have been thereby explained. Of course, the difference in the performances of similar soils may be due merely to differences in the depth of top soil.

Some success has attended recent endeavours to forecast soil suitability for various crops (particularly fruit) by means of the identification of soil variety and condition in the field. This method involves the classification of soils in "soil series," these being sub-divided into "soil types." The system is dependent on the observer being able to recognise, by inspection, its geological origin and its mode of production. Then its position is noted, whether on a hill, hill-side or valley, and finally its drainage, profile and texture. As a result of this examination, an expert may, with some assurance, express an opinion whether a particular

crop may be grown with success; but the ideal manurial treatment is a problem still awaiting solution.

No laboratory examination of a soil could be considered complete unless it included the determination of lime, and also indicated whether the soil contained sufficient lime to ensure that it did not possess an acid reaction. The restrictions to the deductions that can be drawn from an ordinary soil analysis do not apply to the examination of a soil for lime. The effect of lime on a soil is not only chemical and mechanical, but also biological, as only in its presence can beneficial organisms, such as the nitrifying organisms, flourish. Though there are agricultural plants which will grow in sour soils, these are usually of small economic importance. Some crops are more tolerant of soil sourness or acidity than others; for instance, potatoes and oats may grow well in a sour soil, but clover and barley show less tolerance. A considerable proportion of the superficial area of Kent is covered with chalk, or has chalk immediately below the surface, yet lime-deficient soils are constantly being found, even when the soils are on chalk formations. Soils on the Kentish ragstone, and the result of weathered ragstone, are often seriously lime-deficient, although ragstone contains from 70 to 75 per cent. of carbonate of lime. The figure of 800 lbs. per acre of lime has been suggested as an annual lime loss per acre. Often the need of lime in a soil can be foretold by the absence of worm casts and the presence of certain weeds. Weeds on a sour soil may flourish, not only on account of their ability to grow almost in an absence of lime, but also on account of the agricultural plant being weak and attenuated and unable to smother the weed crop. Various tests have been devised to test soil sourness, including the determination of the p_H value. Often the farmer is recommended to test his soil by adding hydrochloric acid, when an effervescence indicates the presence of calcium carbonate. Aqueous extracts of sour soils have iron in solution; hence, a test frequently applied is that of adding to the dried soil a 10 per cent. solution of sodium salicylate or a saturated solution of thiocyanate in alcohol, when sourness is indicated by a red colour of the solution. Soluble aluminium is also associated with soil sourness, and the aluminium soluble in semi-normal acetic acid bears some relation to lime requirement. The total calcium carbonate in a soil calculated from a carbon dioxide determination does not always give a reliable indication of the probable response of a soil to lime. Russell has recorded instances of soils containing only 0·02 and 0·03 per cent. of calcium carbonate which did not benefit from lime applications, the reason being that the soils were supplied with subsoil waters rich in lime. The total lime soluble in hydrochloric acid includes lime combined as salts as well as lime as carbonate, and it is the latter form of lime which is so important, so far as the free working of the soil and its freedom from acidity are concerned. The lime-magnesia ratio is important, because when magnesia is present in excess of lime, land may respond to lime dressings, even though it contains appreciable quantities of carbonate of lime. On the other hand, Voelcker has shown that, under certain conditions, yields of wheat can be increased by the addition of magnesia. Chlorophyll contains magnesium. In general, the need for lime becomes greater as the amount of clay increases, because of the need of flocculation. The lime-requirement of a soil to correct acidity may be ascertained with some

degree of accuracy by the process devised by Hutchinson and MacClennan, and this process we carry out on all soils (ANALYST, 1914, **39**, 450). However, dressings of lime to-day are largely curtailed by the financial capacity of the farmer to purchase. When a lime-dressing to a sour soil is advised, consideration must be given to the possible amount of organic nitrogen which may have accumulated, because this nitrogen will be largely rendered available. For instance, lime applied to a sour soil before a corn crop may result in a length of straw which will cause the corn to lie. As lime encourages clover, applications to lawns should not ordinarily be made; indeed, in such a case acid manures, such as sulphate of ammonia, tend not only to keep down weeds, but also to promote the growth of the grasses required.

Among some twenty elements, other than those already discussed, invariably present in plants, are sulphur, copper, fluorine, iodine, chlorine, zinc, cobalt, and nickel. Exact information does not exist as to the importance of all of these elements in the plant, and whether certain of them are merely present because they happen to exist in the soil water and become absorbed. Spectrographic methods for the determination of ash constituents are being employed at East Malling Research Station. I have only had occasion to enquire into the presence of two of the above elements in soils, namely, sulphur and copper.

Gypsum applied to soil has been said to increase both the soluble potash and phosphoric acid, but, within my knowledge, little gypsum is now used as a fertiliser. It was advocated at one time as a source of sulphur, but most soils contain ample quantities of sulphur in the form of sulphate from fertiliser residues, such as sulphate of ammonia and superphosphate. Extractions with hydrochloric acid of six different arable soils showed them to contain the following amounts of sulphate:—0·076, 0·074, 0·130, 0·167, 0·126, and 0·086 per cent. Sulphur, itself, has been used as a soil-dressing to provide sulphur, to render plant foods more soluble, and as a preventive of some plant diseases, *e.g.* potato scab.

Copper is often to be found in very appreciable traces in plants and plant-products, but the quantity varies considerably. Determinations made during recent years showed Kent products to contain, for instance: Hay, 1/20, 1/15; clover (dry), 1/10; wheat straw, 1/14; nettles (dry), 1/36; grass, 1/36; thistles, 0; linseed cake, 1/7–1/5; hops, dry (growth 1925–1926), 1/70–1/4; malt, 1/2, 1/2. These results are expressed in grains of copper per pound. Examinations of four samples of beer from different breweries in 1928 revealed copper in amounts varying from 1/15 to 1/10 grain per gallon. Copper is a constituent of various sprays; for instance, it is used on fruit trees for scab, potatoes for blight, and on hops for downy mildew. The sprayed leaves contain considerable amounts of copper, much of which may not be washed from the leaves by rainfall. Summer-sprayed autumn-fallen apple leaves I have found to contain as much as 2·5 grains of copper per pound. The processes used in these determinations were published in THE ANALYST (1926, **51**, 328; 1929, **54**, 650; 1932, **57**, 495). We have found the quinosol process excellent when not less than 5 grms. of material can be taken, and at least 1 grain of copper per pound is present, but with smaller quantities the di-ethyldithiocarbamate process is used. Soils invariably contain some copper; we have determined the following amounts:

Poor grass land	1/14	grain per pound.
Under bush fruit	1/9	,, ,, ,,
Fruit land	1/3	,, ,, ,,
Hop garden	1/14	,, ,, ,,
Grass land	1/10	,, ,, ,,
Apple orchard (arable) ..	1/7	,, ,, ,,

FERTILISERS AND FEEDING STUFFS.—Of fertilisers and feeding stuffs, I have examined considerably more than 15,000 samples during the last twenty years, and the processes mainly used have been those contained in the Regulations issued under the Fertilisers and Feeding Stuffs Acts. These official processes have been well tested throughout the country, and, although they were adopted without any prolonged investigation in different laboratories, they have given extremely satisfactory results. Many of the samples submitted to me have also been submitted to other laboratories, and a comparison of the results shows excellent agreement.

The Kent agriculturist may be said to be noted for his use of rough fertilisers, for almost every form of waste is utilised by him. Foremost among these manures must be placed shoddy, the annual consumption of which amounts to several thousand tons. Shoddy is purchased on a valuation based on its nitrogen-content; a sale may be effected on a nitrogen warranty or at a price per unit of nitrogen. Very little shoddy is now sold without any kind of warranty or stipulation and, therefore, the days when vendors found it profitable to water it before sale are gone. Of necessity, shoddy must vary considerably in quality, as wool and silk refuse contain about 13·5 per cent. of nitrogen, whereas cotton and many fibres used in the textile industries contain less than 1 per cent. However, the composition of truck loads from factories is remarkably uniform, and there has been much exaggeration concerning the difficulties of sampling and the analysis to obtain the true composition of shoddy. We have, on several occasions, had medium-grade shoddy re-sampled, and in every case have obtained extremely concordant results on the duplicate samples. These shoddies have included mixtures of wool with vegetable fibre, and also mixtures in which the loading material has been sandy matter. Truck after truck from a factory may show but little variation, and the accuracy with which sellers determine the nitrogen-content of loads, without chemical analysis, is remarkable. Many different types of "shoddy" are sold; for instance, shearings (wool clippings), carpet waste, wool combings or grey shoddy (rough wool combings often containing many weed seeds), daggings (soiled raw fleece wool), wool dust, etc. There are no stated grades of shoddy, but they are usually classified according to the amount of nitrogen they contain. A high-grade shoddy contains more than 12 per cent. of ammonia, medium-grade between 5 and 12 per cent., and low-grade less than 5 per cent. of ammonia. When a shoddy is sold with a warranty, the warranty invariably states the nitrogen in terms of ammonia, there being no compulsion to refer otherwise to its composition. It is quite possible to adulterate shoddy with sulphate of ammonia, and I have found low-grade shoddy to have been enriched through its addition. Of recent years the unit value of nitrogen in sulphate of ammonia has been below that of nitrogen in shoddy. The value of the nitrogen in

shoddy delivered at a farm station varies from year to year; at the moment it is about 8s. 6d. per unit. Other wastes purchased as a source of nitrogen are rabbit fur, rabbit flick (fur only), rabbit fur waste (contains ears and legs), skin waste (sometimes called fleshings), feathers, feather quills, wings of birds, hairs (pig, calf, goat), silk waste, silk cocoon dust, felt waste (including torn-up waste from gun cartridge wads), ivory dust, casein waste, seal fleshings, chamois dust, etc. All these wastes are of variable composition owing to the possibility of admixture with non-nitrogenous matter, particularly sand or soil. A rabbit fur waste may consist of fur only, or it may contain a large proportion of legs; in the former case the waste will have a high nitrogen-content (about 13 per cent.), whereas the latter will probably not have more than 8 per cent., and it will have a bad spreading value on account of its dense character. The condition of all waste manures is important, because an offered consignment may consist of material in large pieces. For instance, rabbit fur waste may be composed of large pieces of fur and skin or of small clippings, and it must be obvious that the small clippings are not only easier to apply, but also that they can be applied to land more evenly and will possess a greater covering power.

Several materials are used within our county that are but very rarely used in counties with less sea border, such as, for instance, mussels, star-fish, limpets, sprats, and seaweed. These may be termed waste products of sea-fishing and of the sea. Mussels, as they are dredged, contain about 1 per cent. of nitrogen, and star-fish ("five-fingers") double that amount. Recently, attempts have been made to dry limpets and to grind them thoroughly; the dried product contains about 0·5 per cent. of nitrogen and somewhat more than 90 per cent. of carbonate of lime. These shell-fish have only a very small phosphate- and potash-content.

I do not propose to mention the many well-known nitrogenous fertilisers freely sold throughout the country, for their uses and values are well known. This also applies to fertilisers containing phosphates or potash.

Sometimes difficulty is experienced in suggesting the manurial value of nitrogenous manures, and it occasionally happens that there are no published field trials that afford help.

Various methods have been devised for testing the quality of insoluble organic nitrogen, and such methods have received considerable attention in America. One of these methods is contained in the Official Methods of Analysis of the Association of Official Agricultural Chemists. In the processes now recommended by the A.O.A.C. both the water-insoluble organic nitrogen soluble in neutral permanganate solution and the water-insoluble organic nitrogen soluble in alkaline permanganate solution are determined. Originally the method was used to determine the availability of organic nitrogen, but it is now accepted rather as a means of merely distinguishing between good and poor sources of nitrogen. But some of the materials which are accepted as good sources of nitrogen for the soil give poor results, so that results obtained by the processes must be interpreted with caution.

The two chief forms of lime used in farming are the oxide and carbonate. The former may be sold merely as burnt lime or slaked lime or partly slaked lime. In the case of the carbonate, not only is the amount of pure calcium carbonate

important, but also its degree of fineness. According to published experiments, no benefit resulted during two years from an application of calcium carbonate, none of which passed the 100E sieve, and it has been advocated that all limestone or chalk should pass at least the 60-mesh sieve, as coarser particles are of little value. On the sale of ground limestone it is compulsory that a warranty be given of the amount that will pass a prescribed sieve. A slaked lime is often offered for sale, containing variable proportions of lime with upwards of 20 per cent. of water (combined), and the material finds some favour, because, being less dusty than ordinary lime, it is not so dangerous to the farm labourer who applies it to the land. We have found that limes offered to agriculturists vary so much in composition that an analysis is essential for their evaluation, and the material has rightly been included in the Schedules of the Fertilisers and Feeding Stuffs Act. Some experiments have demonstrated that calcium silicate is effective in reducing soil acidity, and that, for instance, even open-hearth fluor spar slags low in phosphates have a value for their lime. In some counties sea-shore sand contains sufficient calcium carbonate to render it a valuable source of lime, and farmers near such coasts have made use of these supplies.

The chemical examination of feeding stuffs is possibly of more importance than formerly, because owners now generally feed their livestock on scientific principles, and this demands a knowledge of the composition of the foodstuffs used. A dairy cow, for instance, will receive a "maintenance" ration, to cover ordinary daily wastage, and also a "production" ration to compensate for the material contained in her milk. Thus, not only is the kind of food important, but also its composition. A ration is usually stated in terms of starch equivalent and protein equivalent, the latter being a figure half-way between the digestible crude protein and the digestible true protein. In pig-feeding the nutritive or albuminoid ratio is of importance, as the supply of proteins is thereby regulated. The nutritive ratio may be obtained from the digestible oil, carbohydrates, fibre and protein. The amount of digestible oil, digestible proteins, etc., in a feeding stuff is obtained from the total oil and proteins by the use of factors which have been obtained from experiments on livestock.

An examination of a feeding stuff is not complete unless it includes the search for deleterious seeds and other substances. A feeding stuff may contain less than the warranted amount of oil or albuminoids, or it may contain an excess of sand or an excessive quantity of fibre owing to the presence of much husk or shell, but it is important also to ascertain that a food is reasonably safe to give to stock. An adventitious seed liable to occur in feeding stuffs is castor, and, despite the many precautions that are now taken to ensure its exclusion, it is still, from time to time, found in dangerous quantities. As the occurrence of castor in a food is always accidental, it follows that it is generally badly distributed, and, whilst one sample of a cake may contain appreciable quantities, another sample of the same cake may be castor-free. Quite recently I found in a sample of cake three or four almost whole castor beans, but a thorough search in the remainder of the cake failed to reveal a further quantity, and stock were fed on the cake without any resulting injury. Owing to the small quantity of castor that may adversely affect stock, and, perhaps, in particular, milking cows, and also its

uneven distribution, it follows that the sample of cake examined must be large before castor can be certified to be absent. Samples up to one pound in weight may be examined, especially when suspicion attaches to a food.

Inorganic poisons are not frequently encountered in feeding stuffs, but lead or arsenic occasionally occurs.

The possibility of the presence of a cyanogenetic plant must be remembered when injury from a feeding stuff is alleged. For instance, several different beans contain appreciable quantities of a glucoside capable of producing hydrocyanic acid, and for this reason they are useless as food for animals. Linseed invariably gives rise to a quantity of hydrocyanic acid when it is allowed to stand in contact with water, and the possible effect of the hydrocyanic acid so produced has been a subject of some controversy. A few years ago the Government of Northern Ireland thought the matter of sufficient importance to issue a warning that cattle of all ages were liable to be poisoned by the incorrect use of linseed and linseed cake. They were, however, of opinion that no injury could follow the use of linseed if given in a dry state, whether whole or crushed, or after treatment with boiling water. Considerable danger, however, existed if linseed were steeped in warm or even cold water so that enzymic action could proceed, with the consequent production of hydrocyanic acid. During 1910, Lander made several experiments with linseed cake and also with hydrocyanic acid itself. He fed two sheep on cake, which yielded 0·025 per cent. of hydrocyanic acid, one of the sheep receiving one pound of cake for 36 consecutive days, and one for 10 days, during which it received a maximum of 5 pounds per day. No ill-effect resulted. A six-months heifer received 261 pounds of the cake in 67 days, with no adverse effect. Potassium cyanide, itself, was then administered to a heifer, 61·0 grains (HCN) being given in 10 days, the maximum dose being 15·0 grains (HCN), again with no obvious result. A 30-grain dose of potassium cyanide, however, proved fatal within two hours. There is, however, the probability of idiosyncrasy to contend with, and poisoning with linseed has been recorded. In one case which I investigated the veterinary surgeon was of opinion that a linseed cake which I found to yield 0·06 per cent. of hydrocyanic acid was the cause of the death of some bullocks, whilst another veterinary surgeon attributed the death of some calves to soaked linseed cake meal which had been given to them, and which I found to yield 0·028 per cent. of hydrocyanic acid.

Insecticides and Fungicides.—Every year the use of insecticides and fungicides for the control of pests increases, the washing and spraying programme of the fruit and hop farmer, in particular, having been greatly extended. The importance of the amount of the active principle in the preparations used was recognised several years ago, and shortly before 1920 led to a definite demand for legislation. The Chamber of Horticulture and some manufacturers concerned approached the Minister of Agriculture, with the result that a Bill was drafted to ensure that some of the important fungicides and insecticides should be sold only with a guarantee of composition. For certain reasons connected with economy the Bill was never introduced into Parliament. The absence of legislation has led to preparations of varying strength being placed upon the market, and the farmer has, therefore, to take such steps as he may deem desirable to protect

himself and to obtain information about the strength of the spray materials which he purchases. Some years ago the Ministry of Agriculture issued a circular setting out the conditions with which some insecticides should comply, and advised purchasers to stipulate that the materials to be purchased must comply with the published conditions. During 1931 a further meeting was held at the Ministry, and the British Insecticide Manufacturers then indicated their willingness to introduce, as a voluntary system, a scheme which would ensure minimum percentages of certain active ingredients in many products. In connection therewith the Ministry undertook to outline a scheme for the testing of proprietary insecticides. At the close of 1931, questions of finance prevented the development of the arrangements. Recently negotiations have been resumed, and it is possible that in the near future standard specifications will be issued.

The numerous materials used for sprays include lime-sulphur solution, lead arsenate paste, nicotine, tar distillate, petroleum, copper sulphate, lime, derris powder, quassia, soft soap, gelatin, etc.

Lime-sulphur solution is generally sold on the understanding, and often with the warranty, that it shall have a specific gravity of 1·3 at 15° C., and that it shall be free from suspended matter. Lime-sulphur, liver-of-sulphur and ammonium polysulphide are usually assumed to depend on polysulphides for their value, and not infrequently the polysulphide sulphur-content of a wash is specified. Invariably the polysulphide sulphur figure specified refers to the percentage of sulphur by weight of liquid, but occasionally a figure is given without stating whether it is W/V or W/W. It is obvious that in a liquid with a high specific gravity, importance attaches to the method of expressing the result. Lime-sulphur probably cannot be marketed with a higher polysulphide sulphur than 21 per cent. W/W. From time to time supplies are sampled which are very weak, but the products of the best manufacturers are consistently good. Methods of analysis of lime-sulphur are given in the Methods of Analysis A.O.A.C., and a very useful direct process for the determination of polysulphide sulphur will be found in the *Journal of Agricultural Science*, 1925, **15**, 96 (ANALYST, 1925, **50**, 148).

Lead arsenate is usually sold in the form of a paste, and these pastes are of varying, though defined, strengths. A minimum standard of not less than 14 per cent. of total arsenic (as As_2O_5) has been suggested. The maximum amounts of water, water-soluble arsenic and of all other impurities have also been suggested. Arsenate of lead is usually known as a stomach poison, that is to say, it kills when it is eaten with foliage, etc., and it is, therefore, essential that arsenate of lead shall exist in a paste in a very fine condition so that it covers as large a superficial area of the foliage sprayed as possible. A rough method to judge the fineness of the arsenate is to make an aqueous suspension and to note the rate of settlement. A guarantee given by one firm states that 97 per cent. will pass the 300-mesh sieve.

Very considerable quantities of nicotine are purchased, particularly by fruit and hop farmers, for spraying purposes, and it is used especially from the middle of May until the end of June. It is very desirable that nicotine supplies should be examined from time to time to note their purity, a common guarantee in England being 96 or 98 per cent. of pure nicotine. Many dry sprays contain nicotine as the active principle, and nicotine in these sprays varies from about

2 to 4 per cent., the absorbents usually being calcium carbonate, calcium oxide or china clay. For certain uses it is very necessary that these dry sprays should be as free from arsenic as possible, and manufacturers have taken great precautions, so that frequently the arsenic content of a dry spray does not amount to more than 1/100 grain per pound.

I do not intend to comment on the many other substances used in the composition of sprays further than to note that the chemist should give some attention to the soft soap so often used as a "spreader." Soda may partly replace potash in a soft soap, with the result that less soap and more water is present, or the fatty acids may be largely replaced by resin acids. The latter acids are objectionable owing to the nature of the curd formed with hard water. Free alkali may cause damage to foliage.

EXAMINATION OF HOPS.—Hops are an important crop in Kent, the cultivated acreage in 1933 being 9366, whilst all the other English counties only had a total of 7529 acres. Last year's crop was estimated to yield 127,000 cwts. of hops, with a probable value of about one and a half million pounds. Hops are usually submitted to the laboratory for determinations of total arsenic, copper and preservative value. Excessive arsenic in hops is invariably due to the presence of coal-ash, the hops having been dried in oasts with open fires. So long as coal (anthracite) almost free from arsenic is used, there is no danger of hops becoming contaminated, but often coals contain appreciable amounts of arsenic, even though they have been obtained from pits which normally yield good coal. A good coal will contain not more than 1/100 grain of arsenic per pound, and when the amount exceeds about 1/50, danger may be apprehended. However, the passage of coal-ash to the drying hops is connected with the draught in the oast. Many oasts are now provided with apparatus which effects drying without the products of combustion reaching the hops. Mineral oil burned in suitable burners is also under experiment as a source of heat for hop-drying. The preservative value of hops is calculated from the determination of soft resins, and a recent process for the determination of these will be found in the *Journal of the Institute of Brewing*, July, 1932, p. 351. Hops in the past have been sold almost entirely on their appearance, but each year we find an increase in the number of buyers who demand a statement about the preservative value of the hops offered. Some copper occurs normally in hops, but the amount may be largely increased if spraying with copper salts takes place after the cones are well formed. Unfortunately, the hop plant may be attacked by a mildew, particularly in wet seasons, which renders spraying essential; but if copper is not used too late in the season, the quantity of copper in the dried hop is certainly of no consequence.

Time prevents me from outlining other investigations undertaken from time to time on behalf of the farmer, but probably I have covered my subject sufficiently to show the value of the agricultural chemist to the farming community.

In conclusion, I feel I may express the thanks of the Society to the Honorary Secretary, Dr. Roche Lynch, to the Honorary Treasurer, Mr. Hughes, and to the Secretary, Dr. Mitchell, for the manner in which the work of the Society has been

carried out. I certainly owe a debt of gratitude to all the officers for the help so freely given me on every occasion. The consistent consideration extended to me at all times by Members of the Council and the support afforded to me by Members of the Society I have greatly appreciated, and these have largely contributed to the very happy memories that rest with me of the past two years.

Joint Meeting of the Society with the Food Group of the Society of Chemical Industry

(*Held on February* 7, 1934)

THE following papers were read:

THE ANALYSIS OF FRUIT AND FRUIT PRODUCTS

BY E. B. HUGHES, M.Sc., F.I.C., AND A. E. MAUNSELL, B.Sc.

Fruit, in common with all biological materials, is not a standard product, and therefore anyone concerned with the control of fruit or fruit products from the analytical standpoint must depend for the interpretation of his results on certain standard figures.

When such figures are applied to commercial uses, for example, to judge the quality of fruit puree, either sulphited or not, or of canned fruit, it is obvious that the effect of various factors on the figures must be taken into account. We, ourselves, are but rarely called upon to apply our figures to the examination of jams and such products of unknown origin or composition, but usually apply them to control purchases of fruit and manufacturing processes.

We suggest, however, that the figures, which we have determined over a period of some years, and some of which have already been reported, may be of use to those who require to refer to average figures. It is, perhaps, of importance to state that in most cases we have definite knowledge of the origin of the fruit with which we are dealing, for yearly we send chemists to those areas where fruit is being picked and packed for our own use, to ensure that it is not wet or watery fruit, that its condition is satisfactory, and, if necessary, to make sure that the correct variety is supplied. Samples of the fruit, as collected and despatched, are sent to the laboratory for analysis for record purposes, and also for the checking of deliveries. It is particularly necessary to have such analytical data if the fruit is not to be used at once, but is to be preserved with sulphur dioxide in casks, with or without previous cooking, since to such fruit some water must be added, not only as sulphur dioxide solution, but also because some addition is considered necessary for most fruits to ensure adequate contact of preservative. Another source of water is the washing of fruit before packing, *e.g.* strawberries. Furthermore, analytical data are necessary in the control of the use of the fruit as, for example, in the manufacture of jam, where we control the uniformity of the product by boiling to a specified content of total solids of specified ratio of fruit

and sugar. This necessitates the adjustment of the amount of fruit used according to its fruit-content, as determined by analysis, which is particularly necessary when sulphited fruit or canned fruit, such as apricot halves, is used. These requirements indicate that one determination that must be made is the amount of total solids. In addition, knowledge of the amount of sugar is necessary, not only for the obvious reason that it may be an added ingredient, but also because the amount of the natural sugar of the fruits varies (particularly with dry or wet seasons); the amount of sugar in the fruit also may serve as a guide in judging whether or not it had been packed in fresh condition as, if fermentation had taken place to any extent before preserving (in sulphur dioxide or by boiling or processing) this would be indicated by the deficiency in sugar.

The figure which we find to bear the most reliable relationship to the amount of fruit is the difference between total solids and total sugar, *i.e.* the non-sugar solids of the fruit or fruit product; it has also the advantage of not requiring a special determination. In fact, we have found this figure so useful that it may be taken that we do not determine total solids and sugar so much for their direct information as to give us this non-sugar solids result.

Another figure which is so used is, as is well known, the amount of insoluble solids—for which a considerable number of results has been published by Macara (ANALYST, 1931, **56**, 39). We, however, do not make this determination regularly, but such results as we have obtained accord well with Macara's figures. Table I gives the minima, which can be used in determining the amount of fruit in jam, etc.

TABLE I

MINIMUM INSOLUBLE SOLIDS

	A*	B*
Gooseberries	1·66 (7)	1·70 (86)
Strawberries	1·48 (13)	1·30 (47)
Raspberries	4·23 (13)	4·40 (54)
Redcurrants	3·99 (5)	4·05 (9)
Blackcurrants	4·78 (5)	4·70 (20)
Cherries	1·29 (6)	0·95 (12)
Plums	1·00 (14)	0·75 (14)
Greengages	1·07 (8)	0·95 (5)
Blackberries	6·30 (9)	6·60 (11)
Apricots	1·17 (10)	

* Our results, generally fewer, are in column A. * B—Results obtained by Macara (ANALYST, 1931, **56**, 39). Number of samples given in brackets.

The amount of insoluble solids is necessarily much smaller than the non-sugar solids of which it forms part, and it is also more likely to be unevenly distributed in the portioning into jars of a product such as jam. Figures for soluble non-sugar solids would probably be of considerable value to analysts, but we have not sufficient data for statistical selection of such figures.

The methods used for the results given in this paper are described in Appendix A. The only comment here necessary is that, for fruit alone, the method of drying employed gives all the sugar in the total solids in the form of invert sugar, and that, for sweetened fruit products, the method is so modified that the sugars in the total solids remain in the same form as in the sample.

TABLE II

ANALYSES OF SAMPLES OF FRESH FRUITS

Fruit.		Total solids. Per Cent.	Total sugar (as invert sugar) Per Cent.	Non-sugar solids Per Cent.	In-soluble solids Per Cent.	Acidity number (ml. of N/10 per 100 grms.)	Crude calcium pectate Per Cent.	Refracto-meter reading of juice (sugar scale) Per Cent.
Gooseberries	Max.	14·0	7·7	9·0	2·8	415	1·2	10·1
	Min.	7·9 (51)	2·0 (51)	4·4 (51)	1·7 (7)	176 (36)	0·3 (9)	5·2 (9)
	Av.	11·2	4·4	6·8	2·3	235	0·8	7·0
Strawberries	Max.	13·2	8·2	7·4	2·4	200	0·7	10·2
	Min.	8·2 (145)	3·4 (145)	2·9 (145)	1·5 (13)	90 (125)	0·2 (16)	6·1 (74)
	Av.	10·2	5·4	4·8	1·9	145	0·5	6·6
Raspberries	Max.	21·3	8·7	17·7	6·2	390	0·9	12·3
	Min.	11·0 (107)	3·2 (107)	7·4 (107)	4·2 (13)	106 (90)	0·6 (13)	5·3 (57)
	Av.	14·4	4·8	9·7	5·4	203	0·7	7·9
Redcurrants	Max.	20·7	7·9	17·2	7·8	495	1·5	
	Min.	12·7 (26)	2·2 (26)	7·4 (26)	4·0 (5)	275 (13)	0·9 (5)	
	Av.	16·0	5·0	10·9	5·5	375	1·1	
Blackcurrants	Max.	24·4	10·2	17·7	6·3	622	1·8	14·5
	Min.	13·7 (37)	1·6 (37)	10·8 (37)	4·8 (5)	121 (23)	1·4 (5)	8·0 (5)
	Av.	19·0	5·0	14·1	5·7	449	1·6	11·0
Cherries	Max.	24·7	15·3	9·8	3·1	145	0·5	18·3
(Stone-free)	Min.	10·9 (41)	6·4 (41)	3·3 (41)	1·3 (7)	96 (27)	0·2 (5)	10·0 (10)
	Av.	16·3	10·2	6·1	1·9	107	0·3	13·9
Plums	Max.	21·9	13·3	11·7	2·0	386	1·5	22·4
(Various)	Min.	8·1 (91)	2·3 (91)	3·4 (91)	1·0 (14)	25 (70)	0·7 (13)	10·0 (36)
(Stone-free)	Av.	14·0	7·8	6·2	1·4	215	1·2	14·1
Greengages	Max.	21·5	13·9	11·8	2·0	435	1·4	19·7
(Stone-free)	Min.	11·0 (49)	4·1 (49)	5·1 (49)	1·4 (9)	88 (39)	1·0 (7)	10·2 (14)
	Av.	15·6	7·9	7·8	1·5	189	1·2	16·2
Blackberries	Max.	21·2	10·4	16·0	10·5	206	1·2	11·4
	Min.	14·1 (29)	1·7 (29)	8·4 (29)	6·3 (9)	90 (18)	0·6 (9)	6·5 (12)
	Av.	16·8	4·0	12·8	8·4	135	0·8	8·5
Apricots	Max.	18·4	11·8	10·4	2·5	349	1·3	18·5
(Stone-free)	Min.	8·6 (55)	3·0 (55)	4·1 (55)	1·2 (10)	123 (43)	0·7 (11)	8·0 (24)
	Av.	12·4	5·6	6·8	1·7	235	1·0	12·9
Loganberries	Max.	23·3	7·3	22·2	7·3	420	0·7	
	Min.	13·2 (19)	1·1 (19)	7·3 (19)	7·1 (2)	151 (10)	0·6 (2)	
	Av.	16·6	4·5	12·1		315		
Apples	Max.	19·5	13·5	9·8	3·4	410	1·6	17·0
(Whole)	Min.	10·3 (147)	3·2 (147)	1·1 (147)	1·4 (12)	25 (115)	0·5 (16)	9·8 (39)
	Av.	15·1	10·3	4·9	2·2	162	0·8	13·4
Apples	Max.	19·0	14·2	6·9	2·3	450	1·0	17·3
(Edible	Min.	11·5 (80)	6·2 (80)	1·4 (80)	1·5 (5)	20 (75)	0·4 (9)	9·8 (38)
Portion)	Av.	15·2	10·8	4·4	2·0	93	0·6	13·5
Pears	Max.	21·9	12·6	9·9		47		18·6
(Whole)	Min.	14·6 (22)	7·3 (22)	5·6 (22)		10 (23)		12·0 (18)
	Av.	17·9	10·3	7·6		23		16·0
Pears	Max.	20·2	12·8	9·7	1·8	42	0·7	19·2
(Edible	Min.	13·5 (23)	7·8 (23)	5·2 (23)	1·7 (3)	13 (25)	0·3 (3)	12·0 (18)
Portion)	Av.	17·1	10·5	6·6	1·8	26	0·6	13·2

Number of samples in brackets.

The results which are now given are of the same type as those published by Macara, and are further evidence that such values for fruit show some measure of constancy.

Of these results, the values for pectin and for acidity are of only minor importance in estimating fruit-content. It is known that the natural pectin-content and gel strength of some fruits, notably raspberry (Rendle, ANALYST, 1933, **58**, 69) and strawberry—particularly in sulphited fruit—suffer very

considerable depreciation on keeping the fruit, though this change does not occur appreciably if the fruit is first cooked. Moreover, both pectin and acid may be present as added material.

The only results really of direct use in estimating the amount of a fruit present in a sample are the non-sugar solids and the insoluble solids. It would appear at first sight that the insoluble solids figure is the more satisfactory (or rather less varying), but the following Table (III) gives an idea, as an indication of worth, of the relation of the average figure to the minimum. We have no statistical evidence of the spread of values for insoluble solids, so that this ratio of average to minimum is taken as a rough indication of the degree of variation.

TABLE III

Fruit.	A* Non-sugar solids Average/Minimum	B* Insoluble solids (Macara) Average/Minimum
Gooseberries	$\frac{6\cdot8}{4\cdot4}$ = 1·5 (51)	$\frac{2\cdot61}{1\cdot7}$ = 1·5 (86)
Strawberries	$\frac{4\cdot8}{2\cdot9}$ = 1·7 (145)	$\frac{2\cdot14}{1\cdot3}$ = 1·6 (47)
Raspberries	$\frac{9\cdot7}{7\cdot4}$ = 1·3 (107)	$\frac{6\cdot17}{4\cdot4}$ = 1·4 (54)
Redcurrants	$\frac{10\cdot9}{7\cdot4}$ = 1·5 (26)	$\frac{6\cdot02}{4\cdot05}$ = 1·5 (9)
Blackcurrants	$\frac{14\cdot1}{10\cdot8}$ = 1·3 (37)	$\frac{5\cdot69}{4\cdot7}$ = 1·2 (20)
Cherries	$\frac{6\cdot1}{3\cdot3}$ = 1·8 (41)	$\frac{1\cdot88}{0\cdot95}$ = 2·0 (12)
Plums (Various)	$\frac{6\cdot2}{3\cdot4}$ = 1·8 (91)	
(Victoria)		$\frac{1\cdot13}{0\cdot9}$ = 1·3 (14)
(Green and Golden) ..		$\frac{1\cdot03}{0\cdot85}$ = 1·2 (5)
(Red)		$\frac{1\cdot22}{0\cdot75}$ = 1·6 (15)
Greengages	$\frac{7\cdot8}{5\cdot1}$ = 1·5 (49)	$\frac{1\cdot16}{0\cdot95}$ = 1·2 (5)
Blackberries	$\frac{12\cdot8}{8\cdot4}$ = 1·5 (29)	$\frac{9\cdot64}{6\cdot6}$ = 1·5 (11)
Apricots	$\frac{6\cdot8}{4\cdot1}$ = 1·7 (55)	
Loganberries	$\frac{12\cdot1}{7\cdot3}$ = 1·7 (19)	
Apples (Edible portion)	$\frac{4\cdot4}{1\cdot4}$ = 3·1 (80)	

Numbers of samples in brackets. A*—Our results. B*—Macara's figures (ANALYST, 1931, **56**, 39).

The results given in Table III show that the content of non-sugar solids of fruit is of the same order as that of the insoluble solids with regard to the variation in the amount of fruit to be inferred therefrom.

The statistical examination of the figures for non-sugar solids, where we have a sufficient number of results, has been made in our laboratory by Miss B. G. E. Hooke, M.A., and her summarised report is given in Appendix B. Briefly, the examination shows that the distributions for gooseberries and eating-apples (whole) were of symmetrical character, and those for apricots, raspberries and strawberries showed some asymmetry, but gave modal values below the mean values; accordingly, for all these fruits, the distribution of most samples should lie within the limits of mean value ± 2 × standard deviation, and only one sample in 44 would be below the low limit, and only one in 44 above the high limit. Similarly, a value of mean ± 1¼ × standard deviation would give limits of one in ten samples. It is this figure of mean ± 1¼ × standard deviation, the one in ten chance, referred to as probable minimum, which we generally use in calculating fruit-content—chiefly for valuation purposes—but where there is any doubt we use the value for the 43 to 1 chance, which we think sufficiently low, in fact, generously so. The figures for plums and greengages do not come out so well statistically. We think that this is due to bulking varieties of plums and that, for greengages, probably some further separation of varieties is required.

Blackberries require grouping under the headings "wild" and "cultivated." The calculated probable minima for the last-mentioned fruits—plums, greengages and blackberries—are, therefore, apparently somewhat too low.

For currants, the number of analyses is not yet sufficient for satisfactory statistical analysis, but it is reasonably safe to take the probable minima calculated, our evidence having shown that the figure for non-sugar solids of any of the fruits examined has changed but little, as we have been able to add other results from year to year, until the number became really statistically adequate.

TABLE IV

PROBABLE MINIMUM NON-SUGAR SOLIDS

	9 to 1 probability							43 to 1 probability
	1925–7 inc.	1925–8 inc.	1925–9 inc.	1925–30 inc.	1925–31 inc.	1925–32 inc.	1925–33 inc.	1925–33 inc.
Apples—								
Whole	4·0	3·8	3·8	3·0	3·3	3·5	3·5	2·7
Edible portion					3·2	3·2	3·2	2·5
Apricots	6·5	5·1	5·5	5·0	5·0	5·1	5·2	4·3
Blackcurrants ..	12·0	12·2	12·4	12·2	12·3	12·3	12·2	11·1
Redcurrants ..	8·0	7·5	7·9	8·4	8·4	8·4	8·5	7·0
Gooseberries ..	6·0	6·0	5·7	5·4	5·3	5·4	5·5	4·8
Greengages	6·0	5·1	5·3	5·7	5·7	5·9	5·8	4·6
Plums	4·0	4·2	4·2	4·2	4·0	4·2	3·9	2·4
Raspberries	9·5	8·9	8·7	7·6	7·8	7·7	7·9	6·8
Strawberries ..	4·5	4·4	4·3	4·0	3·9	3·7	3·9	3·3

Table IV shows the "probable minima" (9 to 1 and 43 to 1) for the samples of various fruits examined in the years 1925 to 1933.

We use these "probable minima" in calculating the amount of fruit in fruit-products, the result being termed maximum fruit-content. Obviously, 100 is the highest figure that can be accorded, unless there is evidence of concentration.

Fruit-composition is influenced by variation in climate and by district. The figures for raspberries in Table V illustrate this.

TABLE V

ANALYSIS OF SAMPLES OF SCOTTISH AND ENGLISH RASPBERRIES (LLOYD-GEORGE VARIETY)

(1930–1932 inclusive)

English					Scottish				
Total solids Per Cent.	Sugars (as invert) Per Cent.	Non-sugar solids Per Cent.	Acidity No. (ml. of $N/10$ per 100 grms.)	Soluble solids (refract-ometer) Per Cent.	Total solids Per Cent.	Sugars (as invert) Per Cent.	Non-sugar solids Per Cent.	Acidity No. (ml. of $N/10$ per 100 grms.)	Soluble solids (refract-ometer) Per Cent.
15·4	5·8	9·6	185	10·0	11·0	2·7	8·3	258	8·5
15·5	4·0	11·5	241	10·5	12·0	3·3	8·7	302	8·3
16·8	5·1	11·7	272	10·1	11·8	3·5	8·3	271	7·9
15·6	4·5	11·1	282	9·0	12·5	4·2	8·3	302	8·0
14·9	5·6	9·3	197	12·3	11·4	3·7	7·7	225	6·8
20·5	6·6	13·9	234	10·5	14·2	4·5	9·7	271	8·5
12·5	5·1	7·4	159	8·0	13·5	4·3	9·2	261	8·0
	Av.	10·6				Av.	8·6		
English, 1933					Scottish, 1933				
15·5	6·9	8·6	305	11·0	15·3	4·7	10·6	311	8·7
14·7	3·6	11·1	267	8·0	15·3	6·0	9·3	255	9·4
14·9	5·3	9·6	277	7·5	16·5	6·2	10·3	240	9·9
14·2	5·1	9·0	106	9·0	15·7	5·5	10·2	219	8·4
16·3	6·5	9·8	250	10·1	13·8	4·5	9·3	246	7·7
12·0	3·2	9·8	320	6·9	14·4	5·3	9·0	252	8·3
14·6	5·5	9·1	112	9·2	16·1	6·0	10·1	205	9·1
	Av.	9·6				Av.	9·8		

In the years 1930 to 1932, the samples of Scotch-grown Lloyd-George raspberries had, on the average, lower non-sugar solids than the English fruit, but, in 1933, the results for both were about the same, being between the previous results. In 1931 and 1932, samples of canned raspberry pulp from Tasmania contained appreciably higher fruit solids than English fruit; but, in 1933, the figure fell to the average of English fruit (Table VI). Such variations can be quite important to buyers and users of fruit—both in the value of the fruit and in the standardisation of products.

TABLE VI

AVERAGE NON-SUGAR SOLIDS-CONTENT OF RASPBERRIES

Season	Tasmanian Per Cent.	English Per Cent.
1931	10·3 (10)	9·4 (21)
1932	11·1 (10)	9·9 (20)
1933	9·6 (10)	9·8 (21)

Number of samples in brackets.

The Analysis of Fruit Products.—The methods, which differ in some respects from those employed for fruit alone, are described in Appendix A. The chief differences are in the determination of total solids—it being important to avoid any degree of inversion of the sugar, and, in the determination of sugar, to use methods which are accurate for mixed sucrose and invert sugar.

Canned Fruit (with or without added sugar).

Such products are usually simple and contain no other ingredients which might complicate analysis.

The acidity should be in accordance with the fruit-content as calculated from the non-sugar solids. If confirmation of the calculated fruit-content is required, the insoluble solids should be determined, but this is seldom necessary.

TABLE VII

CANNED APRICOTS

	A	B	C
Total solids, per cent.	12·7	8·7	24·0
Total sugars as invert, per cent.	7·4	4·8	—
Invert sugar, per cent.	—	—	10·1
Sucrose, per cent.	—	—	10·0
Non-sugar solids, per cent.	5·3	3·9	3·9
Acidity No. (ml. of $N/10$ per 100 grms.) ..	188	180	181

Interpretation of Results.

Sample A. Maximum fruit-content (9 to 1 probable minimum basis)

$$= \frac{5{\cdot}3}{5{\cdot}2} \times 100, \textit{ i.e. } 100 \text{ per cent.}$$

Sample B. Similarly, maximum fruit-content = 75 per cent.

Sample C. Similarly, maximum fruit-content = 75 per cent.

Sample C contains added sugar.

The natural sugar (as invert) for 75 per cent. of fruit would be, taking the average sugar figure of the fruit (5·6 per cent.), 4·2 per cent.

Hence, there is (10·1–4·2) 5·9 per cent. of invert sugar and 10·0 per cent. of sucrose present not due to the fruit, *i.e.* 15·6 per cent. of added sugar as sucrose.

Hence, the sample contains: maximum fruit-content, 75 per cent.; added sugar (as sucrose), 16 per cent. (approx.); added water, 9 per cent.

It is possible that loss of juice from the fruit may occur if, for example, the fruit should have been heated or cooked in water or syrup before filling into containers.

Examples are given in Table VIII.

TABLE VIII

STRAWBERRIES IN SYRUP

	Strawberries	A	B	C	D
Total solids, per cent.	9·3	39·5	22·9	40·1	23·5
Invert sugar, per cent.	5·4	12·5	7·8	12·5	7·8
Sucrose, per cent.	—	24·4	12·5	24·5	12·5
Non-sugar solids, per cent. ..	3·9	2·6	2·6	3·1	3·2
Acidity No. (ml. of $N/10$ per 100 grms.)	118	78	78	78	78
Insoluble solids, per cent.	1·8	1·2	1·2	1·7	1·8

A made from 600 parts by weight of strawberries
300 ,, ,, ,, ,, sugar
B ,, ,, 600 ,, ,, ,, ,, strawberries
300 ,, ,, ,, ,, 50 per cent. sugar syrup
C = A — 300 ,, ,, ,, ,, its syrup
D = B — 300 ,, ,, ,, ,, ,, ,,

Interpretation of :

Sample A. Fruit-content, calculated from insoluble solids

$$= \frac{1{\cdot}2}{1{\cdot}8} \times 100 = 67 \text{ per cent.}$$

Fruit-content, calculated from non-sugar solids

$$= \frac{2{\cdot}6}{3{\cdot}9} \times 100 = 67 \text{ per cent.}$$

Sugar (as invert), natural to the fruit

$$5{\cdot}7 \times 0{\cdot}67 = 3{\cdot}8 \text{ per cent.,}$$

and added sugar (as sucrose) is 32·7 per cent. (33 per cent.).

Sample B. Similarly, fruit-content, calculated from insoluble solids = 67 per cent.

Fruit-content, calculated from non-sugar solids = 67 per cent.

added sugar = 16·5 per cent.

,, water = 16·5 per cent.

Sample C. Fruit-content, calculated from insoluble solids = 94 per cent.

,, ,, ,, non-sugar solids = 80 per cent.

,, ,, ,, acidity = 66 per cent.

This indicates the presence of not more than 66 per cent. of fruit. Obviously, there has been removal of juice or addition of insoluble solids; the former is the reasonable assumption.

The composition can be calculated as follows:—x = percentage of whole fruit; y = per cent. of insoluble solids, corresponding to juice removed,

$$3{\cdot}9x + y = 3{\cdot}1,$$
$$1{\cdot}8x + y = 1{\cdot}7,$$

so that $x = 67$ per cent. of fruit,

$$y = 0{\cdot}5, \text{ corresponding to } \frac{0{\cdot}5}{1{\cdot}8} = 28 \text{ per cent. of fruit.}$$

This is in accordance with the remainder (33 per cent.) being added sugar; the product contains about 67 per cent. of fruit, the insoluble matter of 28 per cent. of fruit and added sugar (about 33 per cent.).

Actually, sample C was obtained from A by draining off 300 parts by weight of syrup from 900 parts of A. A was made from 600 parts of fruit and 300 parts of sugar.

Similarly, sample D is shown to consist of 67 per cent. of fruit and insoluble matter, of 33 per cent. of fruit, and 16·5 per cent. of added sugar. Actually, sample D was obtained from A by draining off 300 parts of syrup (weight) from 900 parts of B.

B was made from 600 parts of fruit and 300 parts of 50 per cent. syrup.

Jam.—For fruits which have no pips, such as "stone" fruits and strawberry, it may be generally sufficient to determine the insoluble solids, though it should be borne in mind that inference of a higher percentage of fruit than required for the grade of the jam should generally result if the fruit-content is calculated

from the minimum insoluble solids of the fruit. Should the result even then be somewhat below standard, the possibility must not be overlooked that, in transferring the jam to jars, there may have been unequal distribution of the fruit, resulting in a sample having low insoluble solids. In such a case a full analysis becomes necessary.

For fruits with pips there is always the possibility that some proportion of these have been removed deliberately or skimmed off the jam, thus reducing the insoluble solids. It is also not impossible that pips could be added. Here, again, any doubt necessitates a full analysis; certainly, for adequate criticism of a jam, such full analysis is required, and for this purpose some or all of the following determinations become necessary:

Total solids; sugar (sucrose, dextrose, laevulose, and perhaps glucose syrup; pectin; acidity (titration); p_H; ash; microscopical examination.

The addition of pectin is very common, and allowance, if necessary, must be made for any extra pectin. Acid or acid juice, such as lemon juice, may also be added, and likewise some allowance must be made if the added amount is appreciable. We have made p_H determinations on over 200 samples of various jams which we knew to be free from added acid; in no case have we found a value below 3·1, though we have found instances of commercial jams having p_H values as low as 2·85.

We do not pretend to be in a position to give detailed methods for the estimation of fruit in any or every sample of jam, but the following examples may be of interest and of use.

TABLE IX

	Fresh raspberries	Pectin concentrate	Raspberry jam I made with 40 per cent of these raspberries		Raspberry jam II made with 40 per cent of raspberries + 10 per cent. of pectin concentrate	
				(Composition calculated from		(Composition calculated from
	A	B	Analysis	A and B)	Analysis	A and B)
Total solids, per cent.	11·8	11·5	70·8		70·7	
Sucrose, per cent.	0·0	0·0	28·2		26·3	
Invert sugar, per cent.	3·5	5·8	39·3		40·6	
Non-sugar solids, per cent. ..	8·3	5·7	3·3	3·3	3·8	3·9
Acidity No. (ml. of $N/10$ per 100 grms.)	257	160	103	103	120	119
Insoluble solids, per cent. ..	5·1	—	2·0	2·0	2·0	2·0
Soluble solids (by refractometer), per cent.	7·9	10·0	70·0		70·1	
Pectin, per cent.	0·7	3·7	0·2	0·3	0·6	0·7

This gives the analyses of two jams and the fruit and pectin used. It will be seen that results accord well.

The composition may be calculated from the "standard" figures as follows (sample II for example).

From insoluble solids, calculated on the basis of the minimum for raspberries:

$$\text{Per cent. of fruit} = \frac{2{\cdot}0}{4{\cdot}4} \times 100 = \text{about } 45 \text{ per cent.}$$

[From the figure for the average insoluble solids (6·2) only 32 per cent. of fruit would be inferred.]

From Non-sugar Solids.

Non-sugar solids less pectin: 3·8 — 0·6 = 3·2.

$$\left.\begin{matrix}\text{Probable minimum}\\ \text{non-sugar solids}\end{matrix}\right\} - \left\{\begin{matrix}\text{Average pectin}\\ \text{of raspberries}\end{matrix}\right\} : 7{\cdot}9 - 0{\cdot}7 = 7{\cdot}2.$$

$$\text{Hence per cent. of fruit} = \frac{3{\cdot}2}{7{\cdot}2} \times 100 = 44 \text{ per cent.}$$

This would indicate added pectin as

$$0{\cdot}6 - 0{\cdot}44 \times 0{\cdot}7 = 0{\cdot}29 \text{ per cent. (0·3 per cent.).}$$

The pectin-content of fruits is small, compared with the non-sugar solids, and, consequently, variation in pectin-content is not of great importance in calculations; moreover, pectin, as determined in jam, tends to be rather less than actually originally present in the ingredients used. The other solids of pectin concentrates are usually not present in amounts of importance, considering the quantities used; the accompanying acid may be of importance, but usually the amount so added to the jam will not increase the acidity beyond the ordinary fruit limits; if it does, it must be taken into consideration. An example of this is seen in Table X.

TABLE X

STRAWBERRY JAMS

	A	B
Total solids, per cent.	73·5	73·5
Sucrose, per cent.	26·9	21·9
Invert sugar, per cent.	44·8	49·6
Non-sugar solids, per cent.	1·8	2·0
Acidity No. (ml. of $N/10$ per 100 grms.) ..	63	140
Pectin, per cent.	0·4	0·4
Insoluble solids, per cent.	0·7	0·4
p_H	3·25	2·85

Analyses of 2 samples of strawberry jam.

Sample A.

Fruit-content, calculated from minimum insoluble solids

$$= \frac{0{\cdot}7}{1{\cdot}3} \times 100 = 54 \text{ per cent.}$$

Fruit-content, calculated from average insoluble solids

$$= \frac{0{\cdot}7}{2{\cdot}1} \times 100 = 33 \text{ per cent.}$$

The analysis shows that this sample obviously contains added pectin. The average pectin of strawberries is 0·5 per cent., so that the probable minimum non-sugar solids, less average pectin-content, becomes 3·9 — 0·5 = 3·4 per cent.

The corresponding figure for the sample is 1·8 — 0·4 = 1·4 per cent. so that the fruit-content is $\frac{1{\cdot}4}{3{\cdot}4} \times 100 = 41$ per cent. This sample would accordingly be passed as in accordance with the Food Manufacturers' Federation standard of 42 per cent. of fruit.

Sample B, which was a commercial product, resembles A in non-sugar solids and in pectin, but differs markedly in insoluble solids, acid number, and p_H.

Calculated from insoluble solids, the fruit-content of the jam is:

Taking the minimum: $\frac{0{\cdot}4}{1{\cdot}3} \times 100 = 31$ per cent.

,, ,, average: $\frac{0{\cdot}4}{2{\cdot}1} \times 100 = 19$ per cent.

The acidity is excessive, and, therefore, the non-sugar solids must be corrected similarly, also, allowance must be made for pectin.

The average acidity of strawberries is 145 ml. of $N/10$ acid per 100 grms., equivalent to approximately 1 grm. of citric acid per 100 grms. of fruit.

The average pectin-content of strawberries = 0·5 per cent. Hence: probable minimum non-sugar solids, less average acid, less average pectin, = 3·9—1·0—0·5 = 2·4 per cent., and, for the sample = 2·0—1·0—0·4 = 0·6 per cent. These results indicate $\frac{0{\cdot}6}{2{\cdot}4} \times 100$, of fruit, *i.e.* 25 per cent. of fruit.

TABLE XI

THE EFFECT OF REMOVAL OF SOME OF THE PIPS FROM RASPBERRY JAM

	A	B
Total solids, per cent.	71·5	71·6
Sucrose, per cent.	33·5	33·7
Invert sugar, per cent.	35·0	35·3
Non-sugar solids, per cent.	3·0	2·6
Acidity No. (ml. of $N/10$ per 100 grms.) ..	—	106
Insoluble solids, per cent.	1·7	1·3
Pectin, per cent.	0·3	0·3

These results indicate:

Sample A. Maximum fruit-content (from non-sugar solids, 9 to 1 basis) = 38 per cent.

,, ,, (from minimum insoluble solids) = 39 per cent.

Similarly, for *Sample B*: Maximum fruit-content (from N-S.S.) = 33 per cent.

,, ,, (from I.S.) = 30 per cent.

Since, in B, the fruit-content, calculated from *minimum* insoluble solids, is less than that for non-sugar solids, there is indication of loss of insoluble solids.

The F.M.F. standard of 38 per cent. of fruit requires 0·38 × 7·9 = 3·0 per cent. of N-S.S., *i.e.* an increase of 0·4 per cent. over the amount found.

Taking this required increase as insoluble solids, then the amount becomes 1·7 per cent., corresponding to 39 per cent. of fruit.

Both of these samples of jam, A and B, were from the same batch which was prepared so as to contain 38 per cent. of fruit, but, for B, some of the pips had been skimmed from the surface of the hot jam.

It may not be possible to state positively that a single sample of jam is below the declared standard, but examination of a number of samples of that jam, preferably obtained from different shops to give greater chance of their being from

different batches of jam, would provide strong evidence for, at least, an intimation to the manufacturer that an explanation is required.

CONCLUSION.—Results have been given of the analysis of a large number of samples of various fruits and, of these results, it is considered that the figures for non-sugar solids are useful in calculating the amount of fruit in such products as canned fruit, jam, etc. For several fruits, sufficient data for non-sugar solids have been obtained to enable statistical examination to be made and probable minima to be calculated. It is suggested that, ordinarily, the probable minima based on: mean $- 1\frac{1}{4} \times$ standard deviation, representing a 9 to 1 chance that any given sample will not have lower non-sugar solids, should be used to estimate the fruit-content of a sample; where there is doubt, the lower probable minimum: mean $- 2 \times$ standard deviation, representing a 43 to 1 chance, might be employed.

This work has been carried out in the laboratories of Messrs. J. Lyons & Co., Ltd., to whom our thanks are due for permission to publish this paper.

METHODS OF ANALYSIS

APPENDIX A

Sampling.—A representative sample of at least 1 lb. is finely minced after fruit stones, stems, etc., have been removed; in the case of the edible portion of apples and pears, the peel and cores are also removed before mincing the sample. The minced sample is finally carefully mixed in a cylinder with a plunger.

Total Solids.—To 1 to 2 grms. of the sample in a nickel dish, hot distilled water is added to distribute the sample evenly over the bottom of the dish. The dish and contents are placed on a water-bath until apparently dry, and finally the remainder of the water is removed by heating in a vacuum-oven at 100° C. for 30 minutes. Experiments have shown that the small quantities of sucrose which may be present in the fruit are inverted during drying. When sucrose is present in appreciable amount, as in jam or canned fruit, the sugars in the dried material are retained in their original form by neutralising (to phenolphthalein) with $N/10$ sodium hydroxide solution before drying. A control determination is made by neutralising citric acid solution of similar acidity with the sodium hydroxide solution and drying in the same way.

Sugar.—Total sugar (as invert sugar) is recorded in the cases of fresh fruit and pulp, since this figure is comparable with the condition of the sugar in the dried solids. Ten grms. of the sample are soaked in hot distilled water for at least 15 minutes, cooled and transferred to a 250-ml. graduated flask. The solution is cleared with 2 to 3 ml. of lead acetate solution (saturated) and 2 to 3 ml. of alumina cream, and made up to the mark and filtered. Any excess of lead is precipitated with solid potassium sulphate and filtered off. Part of the solution is inverted with hydrochloric acid, neutralised, and its copper-reducing power is determined either by the Luff-Schoorl method (*Z. Unters. Lebensm.*, 1929, **57**, 566; *B.C.A.*, 1929, *B.*, 952), or by the Bertrand method. The two methods give identical results.

For jams and fruits to which sugar has been added certain modifications in the method are necessary, as follows:

Ten grms. of the sample are neutralised, and then treated with hot water to dissolve out the sugars, clarified, and made up to 250 ml. Invert sugar is determined, as before, by the Luff–Schoorl sugar method, and laevulose (generally

only before inversion) by the Kruisheer iodine laevulose method (*Z. Unters. Lebensm.*, 1929, **58**, 266). The rotatory power of a solution of suitable concentration is compared with that calculated from the determinations made to ascertain whether commercial glucose is present, but this last complication is seldom found.

The correct determination of the actual proportions of sucrose and invert sugar present in the jam, or other sweetened sample, is most important, as otherwise an erroneous result for non-sugar solids will be obtained. The use of the Bertrand sugar method is not advisable, as the presence of sucrose affects the reducing-sugar figure.

Acidity.—Acidity is determined by boiling 10 grms. of the sample with 300 ml. of water for 15 minutes, cooling and titrating to phenolphthalein with N/2 sodium hydroxide solution. These results in our table are expressed as ml. of *N*/10 sodium hydroxide solution per 100 grms. We have found that this method gives results in good agreement with electrometric titration.

Insoluble Solids.—The amount of the insoluble solids is determined by the A.O.A.C. method (*Methods of Analysis*, 2nd Ed., p. 210), except that the final drying is effected in a platinum dish in an oven at 100° C.

Pectin.—The method either of Carré and Haynes (*Biochem. J.*, 1922, **16**, 60) (more generally), and also that of the A.O.A.C. (*Methods of Analysis*, 2nd Ed., p. 212), have been used. Agreement was found to be satisfactory.

p_H *Value.*—This is determined, where necessary, on a 50 per cent. solution of jam (against *M*/20 potassium acid phthalate solution), with the use of a glass electrode.

Refractometric Reading.—The refractometric reading (on the sugar scale) of the juice, at 20° C., is also recorded (Zeiss refractometer).

Appendix B

A variable is said to be distributed normally when it follows a certain mathematical law, that is, the logarithm of the frequency at any distance, x, from the centre of the distribution is less than the logarithm of the frequency at the centre by a quantity proportional to x^2. Such a distribution is symmetrical, with the greatest frequency at the centre, and, although the range is infinite, the frequency falls off rapidly to very small values. The points of inflexion of the curve occur at distances from the centre equal to the standard deviation of the distribution.*

The ratio of the area of the tail of the curve cut off by an ordinate at any point distant x from the centre of the curve, to the total area of the curve, gives the probability that a deviation as great as, or greater than x, is likely to occur. A negative deviation from the mean equal to twice the standard deviation is likely to occur about once in 44 trials, and a negative deviation of 1·25 times the standard deviation will occur about once in 10 trials.

As a test for normality, two quantities $\pm\sqrt{B_1}$ and B_2-3 of Pearson's notation may be calculated. These are both zero for a normal distribution.

From a calculation of these statistical constants for the various distributions of non-sugar solids it was observed that the distribution with eating apples (whole), apricots, and gooseberries approximated most nearly to the symmetrical, while eating apples (edible portion), raspberries, and strawberries and plums, showed some asymmetry with the modal value invariably less than the mean. Except in the case of plums, this asymmetry is not considerable.

* The S.D. is the square root of the mean square deviation from the mean. Twice the standard error gives the limits of these statistics due to random sampling.

The grouped distributions are shown in Tables, together with their means and standard deviations, the standard errors of these statistics being given also.

The figure obtained by subtracting twice the standard deviation from the mean gives a figure which accords reasonably well with our observations for eating apples (whole), (Table A); eating apples (edible portion), (Table B); apricots (Table C); blackcurrants (Table D); redcurrants (Table E); gooseberries (Table F); loganberries (Table G). The figure for greengages (Table J) is lower than any obtained by analysis; there are 49 observations only, and the distribution is extremely irregular.

Similarly, the figures obtained by this method for pears (whole and edible portion) (Tables L and M) are low. These results are based, respectively, on 21 and 22 observations only.

The distribution for plums (Table N), as mentioned before, shows marked asymmetry, the majority of the observations occurring at the lower end of the distribution, and there being a long tail of high values. An attempt was made, without success, to find a curve which gave a reasonably good fit to this distribution. It may be that there are definite differences in the distribution of certain varieties of greengages and plums, or the irregularities may be partly due to the fact that our selection of fruit for analysis was necessarily arbitrary, and that the distribution cannot be truly said to be random samples.

The figures for cultivated and wild blackberries have been separated (Table O), where the distinction was known. The mean of the former was 11·85, based on 11 analyses, and of the latter, 14·08, based on 10 analyses. Similarly, the mean for red cherries is 5·65 (Table P), as compared with 6·80 and 6·87, respectively, for white and black cherries.

The number of analyses, both of blackberries and cherries, is so few that the calculation of the standard deviation therefrom is of little value.

Non-sugar Solids

Table A. Non-sugar solids	Eating Apples (whole)	Cooking Apples (whole)
1·005–1·505	1	
1·505–2·005		
2·005–2·505	2	1
2·505–3·005	3	
3·005–3·505	5	2
3·505–4·005	14	1
4·005–4·505	20	3
4·505–5·005	31	1
5·005–5·505	24	2
5·505–6·005	13	1
6·005–6·505	5	3
6·505–7·005	3	4
7·005–7·505	3	2
7·505–8·005		
8·005–8·505	1	
8·505–9·005		1
Total	125	21
Mean	4·78 ± 0·09	5·48
Standard deviation	1·05 ± 0·07	
Mean 1·25SD	3·47	
Mean 2SD	2·68	

Table B. Non-sugar solids	Eating Apples (edible portion)
2·505–2·755	1
2·755–3·005	1
3·005–3·255	6
3·255–3·505	5
3·505–3·755	9
3·755–4·005	12
4·005–4·255	10
4·255–4·505	7
4·505–4·755	5
4·755–5·005	7
5·005–5·255	2
5·255–5·505	1
5·505–5·755	5
5·755–6·005	1
6·005–6·255	2
6·255–6·505	1
6·505–6·755	
6·755–7·005	1
Total	76
Mean	4·27 ± 0·10
Standard deviation	0·87 ± 0·07
Mean 1·25SD	3·18
Mean 2SD	2·53

TABLE C. APRICOTS

Non-sugar solids	
4·005– 4·505	1
4·505– 5·005	3
5·005– 5·505	4
5·505– 6·005	5
6·005– 6·505	13
6·505– 7·005	8
7·005– 7·505	7
7·505– 8·005	4
8·005– 8·505	4
8·505– 9·005	3
9·005– 9·505	1
9·505–10·005	1
10·005–10·505	1
10·505–11·005	
Total	55
Mean	6·80 ± 0·17
Standard deviation	1·27 ± 0·12
Mean 1·25SD	5·21
Mean 2SD	4·26

TABLE D. BLACKCURRANTS

Non-sugar solids	
10·505–11·005	1
11·005–11·505	
11·505–12·005	2
12·005–12·505	4
12·505–13·005	2
13·005–13·505	1
13·505–14·005	8
14·005–14·505	7
14·505–15·005	3
15·005–15·505	2
15·505–16·005	4
16·005–16·505	1
16·505–17·005	1
17·005–17·505	
17·505–18·005	1
Total	37
Mean	14·07 ± 0·25
Standard deviation	1·50 ± 0·17
Mean 1·25SD	12·19
Mean 2SD	11·07

TABLE E. REDCURRANTS

Non-sugar solids	
7·005– 7·505	1
7·505– 8·005	1
8·005– 8·505	3
8·505– 9·005	
9·005– 9·505	2
9·505–10·005	2
10·005–10·505	2
10·505–11·005	1
11·005–11·505	4
11·505–12·005	2
12·005–12·505	1
12·505–13·005	3
13·005–13·505	2
13·505–14·005	
14·005–14·505	1
14·505–15·005	1
Total	26
Mean	10·94 ± 0·39
Standard deviation	1·98 ± 0·27
Mean 1·25SD	8·46
Mean 2SD	6·98

TABLE F. GOOSEBERRIES

Non-sugar solids	
4·255–4·505	1
4·505–4·755	1
4·755–5·005	
5·005–5·255	2
5·255–5·505	
5·505–5·755	1
5·755–6·005	5
6·005–6·255	8
6·255–6·505	5
6·505–6·755	4
6·755–7·005	2
7·005–7·255	3
7·255–7·505	6
7·505–7·755	1
7·755–8·005	6
8·005–8·255	2
8·255–8·505	1
8·505–8·755	2
8·755–9·005	1
Total	51
Mean	6·80 ± 0·14
Standard deviation	1·02 ± 0·10
Mean 1·25SD	5·52
Mean 2SD	4·76

TABLE G. LOGANBERRIES

Non-sugar solids	
7·005– 7·505	1
7·505– 8·005	1
8·005– 8·505	
8·505– 9·005	1
9·005– 9·505	1
9·505–10·005	
10·005–10·505	1
10·505–11·005	
11·005–11·505	2
11·505–12·005	2
12·005–12·505	2
12·505–13·005	1
13·005–13·505	3
13·505–14·005	
14·005–14·505	2
14·505–15·005	1
Total	18

Mean	11·58 ± 0·50
Standard deviation	2·13 ± 0·35
Mean 1·25SD	8·92
Mean 2SD	7·32

TABLE I. STRAWBERRIES

Non-sugar solids	
3·005–3·505	1
3·505–4·005	3
4·005–4·505	16
4·505–5·005	21
5·005–5·505	27
5·505–6·005	40
6·005–6·505	17
6·505–7·005	9
7·005–7·505	9
7·505–8·005	1
8·005–8·505	1
Total	145

Mean	4·83 ± 0·06
Standard deviation	0·76 ± 0·04
Mean 1·25SD	3·88
Mean 2SD	3·31

TABLE L. PEARS (whole)

Non-sugar solids	
5·505– 6·005	2
6·005– 6·505	3
6·505– 7·005	4
7·005– 7·505	1
7·505– 8·005	4
8·005– 8·505	3
8·505– 9·005	2
9·005– 9·505	1
9·505–10·005	1
Total	21

Mean	7·43 ± 0·25
Standard deviation	1·14 ± 0·18
Mean 1·25SD	6·00
Mean 2SD	5·15

TABLE H. RASPBERRIES

Non-sugar solids	
6·505– 7·005	1
7·005– 7·505	2
7·505– 8·005	7
8·005– 8·505	14
8·505– 9·005	18
9·005– 9·505	19
9·505–10·005	21
10·005–10·505	8
10·505–11·005	10
11·005–11·505	4
11·505–12·005	7
12·005–12·505	
12·505–13·005	2
13·005–13·505	2
13·505–14·005	4
Total	119

Mean	9·69 ± 0·14
Standard deviation	1·47 ± 0·10
Mean 1·25SD	7·85
Mean 2SD	6·75

TABLE J. GREENGAGES

Non-sugar solids	
5·005– 5·505	2
5·505– 6·005	1
6·005– 6·505	8
6·505– 7·005	4
7·005– 7·505	9
7·505– 8·005	6
8·005– 8·505	2
8·505– 9·005	2
9·005– 9·505	7
9·505–10·005	2
10·005–10·505	3
10·505–11·005	1
11·005–11·505	
11·505–12·005	2
Total	49

Mean	7·75 ± 0·23
Standard deviation	1·59 ± 0·16
Mean 1·25SD	5·76
Mean 2SD	4·57

TABLE M. PEARS (edible portion)

Non-sugar solids	
5·005–5·255	1
5·255–5·505	2
5·505–5·755	2
5·755–6·005	4
6·005–6·255	1
6·255–6·505	2
6·505–6·755	3
6·755–7·005	1
7·005–7·255	1
7·255–7·505	4
Total	21

Mean	6·35 ± 0·16
Standard deviation	0·72 ± 0·11
Mean 1·25SD	5·45
Mean 2SD	4·91

TABLE N. PLUMS.

Non-sugar solids	
3·005– 3·505	1
3·505– 4·005	3
4·005– 4·505	8
4·505– 5·005	16
5·005– 5·505	14
5·505– 6·005	10
6·005– 6·505	10
6·505– 7·005	5
7·005– 7·505	3
7·505– 8·005	4
8·005– 8·505	5
8·505– 9·005	2
9·005– 9·505	1
9·505–10·005	1
10·005–10·505	5
10·505–11·005	2
11·005–11·505	
11·505–12·005	1
Total	91
Mean	6·23 ± 0·20
Standard deviation	1·90 ± 0·14
Mean 1·25SD	3·85
Mean 2SD	2·43

TABLE O. BLACKBERRIES

Non-sugar solids	Cultured	Wild	?
8·005– 8·505			1
8·505– 9·005			
9·005– 9·505			
9·505–10·005	1		
10·005–10·505	1		
10·505–11·005	1	1	
11·005–11·505	2		1
11·505–12·005	3		2
12·005–12·505	1		1
12·505–13·005			
13·005–13·505		1	
13·505–14·005	1	3	
14·005–14·505		1	1
14·505–15·005		2	1
15·005–15·505			
15·505–16·005	1	1	1
16·005–16·505		1	
Total	11	10	8
Mean	11·85	14·08	12·47

TABLE P. CHERRIES

Non-sugar solids	Red	Black	White
3·005– 3·505	1		
3·505– 4·005	2		
4·005– 4·505	1	1	
4·505– 5·005	5		
5·005– 5·505	1	1	4
5·505– 6·005	3	1	1
6·005– 6·505	2		1
6·505– 7·005	2		1
7·005– 7·505	3	1	2
7·505– 8·005		2	2
8·005– 8·505			
8·505– 9·005			
9·005– 9·505	1		2
9·505–10·005		1	
Total	21	7	13
Mean	5·65	6·87	6·80

THE EXAMINATION OF FRUITS AND JAMS BY LEAD PRECIPITATION*

By C. L. Hinton, F.I.C.

Foreword.—At the time the agreed Jam Standards were introduced, the desirability of extending the methods for determining the fruit-content of jams was discussed by a small committee of the chemists engaged in this industry. Arising out of these discussions, the late L. K. Boseley suggested that the quantity of lead precipitate formed, when a lead acetate solution was added to a solution of a jam, might afford a useful indication of the amount of fruit in the sample, and, as preliminary tests showed that there appeared to be some value in the method, it was decided that the Research Association should investigate it.

This investigation has been carried on during the three past fruit seasons in order to put the process on a satisfactory basis and to obtain suitable data for calculating the percentage of fruit in the jam. It will be seen from what follows that the method will not, by itself, indicate the percentage of fruit in a jam with any more certainty than the other methods already employed; it may be particularly useful in the analysis of jams made from a mixture of fruits, the acids of which differ, *i.e.* one fruit containing citric acid and the other malic. It is also sometimes useful in indicating whether a fruit juice or a commercial pectin has been used in making the jam.

By its use it is possible to place the various fruits in three classes, *i.e.* those containing mainly (i) citric acid, (ii) malic acid, (iii) lactic acid, or an acid having similar lead-precipitating properties.

Mr. C. L. Hinton has been responsible for the carrying out of this investigation, and has drafted the report which follows. The Council of the Association has given permission for the publication of any work of this description which may be of assistance to analysts in maintaining the Jam Standards. T. Macara

Boseley's Method.—The method proposed by Boseley, as mentioned in the foreword, was to dissolve 50 grms. of jam, add 100 ml. of 2 per cent. lead acetate solution, make up to 500 ml., and filter off the lead precipitate together with the insoluble matter of the fruit; 100 ml. of the filtrate were heated to boiling, and the unprecipitated lead was titrated with approximately 1 per cent. ammonium molybdate solution, with tannic acid as an outside indicator. A blank titration was also made on 20 ml. of the lead solution diluted with water. The difference was called the "lead number" of the jam. When the molybdate solution was adjusted in strength to be equivalent, volume for volume, to the 2 per cent. lead solution, the "lead number" represented the number of ml. of 2 per cent. lead acetate solution completely precipitated by 10 grms. of jam.

Essentially this is the procedure still used, though various refinements have been made which will be described later. The "lead number," though empirical,

* Communicated by the British Association of Research for the Cocoa, Chocolate, Sugar Confectionery, and Jam Trades.

is quite a convenient mode of expressing results, and, as will be seen, is readily linked up with the chemistry of the precipitation.

THE NATURE OF THE LEAD PRECIPITATE.—Preliminary experiments on strawberry and raspberry jams of known composition soon showed that the "lead number" was not, as Boseley supposed, a measure of any constituents peculiar to the jam fruits, but was directly related to the amount of acid, both free and in the form of salts, in the jam. In further experiments it was found that malic acid gave no precipitate, whilst citric and tartaric acids gave "lead numbers," on 0·05 grm. of acid, of 6·7 and 6·1, respectively.

A simple calculation shows that, for the complete precipitation of 0·05 grm. of these acids as normal lead salts, 6·8 and 6·3 ml. of 2 per cent. lead acetate solution would be required. Thus, practically within the accuracy of the titration (which is not greater than about 0·1 to 0·2 ml.) these acids seemed to be completely precipitated.

The behaviour of malic acid seemed likely to account for the fact noticed by Boseley, that pomace extracts, etc. (in which most of the acid presumably would be malic) lacked the lead-precipitating constituents of the jam fruits. However, further experiments, described later, showed that the matter was by no means so simple.

IMPROVEMENT OF THE LEAD ACETATE REAGENT.—In experiments in which the acidity of the solution from which the precipitation was made was varied, it was found that in more strongly acid solutions (*e.g.* by adding acetic acid to the jam solution to bring it down to a p_H of 2·5), the end-point of the titration of the excess of lead was upset; but addition of sodium hydroxide to give a p_H of 5·7 caused a slight increase in the "lead number," whilst complete neutralisation of the jam before adding the lead acetate raised the "lead number" about 1 ml. Finally, addition of excess of sodium hydroxide had, as its main result, the precipitation of some, or all, of the excess of lead as hydroxide.

In a series of precipitations of citric acid solution first brought to varying p_H (from 2·5 to 8·0) by addition of sodium hydroxide, it was found that the lead equivalent for 0·08 grm. of citric acid increased gradually over the range mentioned from 11·0 ml. to 12·2 ml., even the lowest figure being rather higher than the theoretical. At the same time the p_H values of the filtrates (tested colorimetrically) were different from those of the original solutions; they were all now compressed into the range 4·4 to 5·6.

In view of this tendency to high results, an attempt was next made to keep down the p_H by means of additions of acetic acid. Mixtures of citric acid and sodium hydroxide (from p_H 2·5 to 8·0, with constant amounts of citric acid) were treated with moderate and relatively large amounts of acetic acid before addition of the lead acetate. The lead equivalents, expressed on 0·1 grm. of citric acid, and also the p_H values, are shown in Table I.

Since the theoretical figure for the lead equivalent of 0·1 grm. citric acid should be 13·55 ml., the results showed that an excess of acetic acid prevented complete precipitation, while a lack of it tended to permit the precipitation of too much lead. In view of these experiments it was decided to adopt a modified

reagent prepared by incorporating acetic acid in the lead acetate solution in proportion corresponding with the 2-ml. additions above. Thus the new reagent was composed of:—Lead acetate crystals, 20 grms.; glacial acetic acid, 2·5 grms. per litre.

TABLE I

CONTROL OF LEAD CITRATE PRECIPITATION WITH ACETIC ACID

		2*N* acetic acid added (per 500 ml. of mixture)					
		0 ml.		2 ml.		20 ml.	
Citrate mixture	p_H (before addition of acetic acid	p_H filtrate	Lead equiv. 2 per cent. lead acetate	p_H filtrate	Lead equiv.	p_H filtrate	Lead equiv.
I	2·5	4·4	13·8	4·1	13·5	3·6	12·8
II	5·0	5·2	14·3	4·9	13·7	3·9	12·8
III	8·0	5·6	15·2	5·0	13·8	4·0	12·9

DEPENDENCE OF RESULTS ON TOTAL AMOUNT OF PRECIPITABLE ACID.—In tests with the improved reagent it was found that the amount of lead precipitated per unit of acid varied slightly, but definitely, according to the total amount of citric acid present; or, what is almost the same thing, according to the total amount of lead precipitated. Thus, when amounts of citric acid from 0·2 grm. to 0·6 grm. (per 100 ml. of lead solution) were used in the test, the lead equivalents were slightly higher than expected for the smaller amounts of acid, and slightly lower for larger amounts. For the intermediate amounts the precipitation agreed with the theoretical values. Table II gives the actual figures. In preparing the mixtures for precipitation, sodium hydroxide was added to neutralise about one-third of the citric acid, so as to correspond with conditions in fruit extracts.

TABLE II

DEVIATION FROM CORRECT LEAD PRECIPITATION WITH TOTAL AMOUNT PRECIPITATED

Citric acid used (per 100 ml. lead solution) ml.	Calculated titration difference ml.	Titration difference found ml.	Difference ml.
0·20	5·4	5·6	+0·2
0·30	8·1	8·3	+0·2
0·40	10·85	10·9	+0·05
0·50	13·55	13·55	0
0·60	16·25	15·9	−0·35

A few experiments on varying quantities of fruit extracts showed, as was anticipated, that discrepancies were even greater than with citric acid solutions. The results are given in Table III, where the lead equivalents for the varying amounts of fruit extract taken have been calculated in the last column to a common basis of 10 grms., to correspond with the fixed 10 grms. of Boseley's original method.

TABLE III

VARIATION OF LEAD NUMBER OF FRUITS WITH AMOUNT OF FRUIT EXTRACT TAKEN

Fruit	Amt. of 50 per cent. extract represented in titration	Lead titration diff.	Lead number per 10 grms. of fruit
	ml.	ml.	ml.
Raspberry	6	7·7	25·7
	8	10·0	25·0
	10	12·0	24·0
	12	14·3	23·8
Gooseberry	4	5·1	25·5
	6	7·3	24·3
	8	9·5	23·8
	10	11·6	23·2
	12	13·7	22·8
Blackcurrant	2	6·7	67·0
	3	9·6	64·0
	4	12·5	62·5
	5	15·1	60·4

In view of these results it seemed necessary to study further the conditions governing the precipitation of the pure fruit acids themselves, both separately and in admixture, and thus establish conditions for correct precipitation when applied to fruit and jam solutions.

CONDITIONS FOR SATISFACTORY PRECIPITATION OF LEAD CITRATE.—It was found more convenient to work with solutions of twice the concentration of those previously used, *i.e.* with 250 ml. instead of 500 ml., and with 50 ml. of filtrate for titration instead of the former 100 ml. In further tests on the precipitation of varying quantities of lead citrate under these conditions, a mono-sodium citrate was used (the total citric-content of which had been determined by titration of free acidity and alkalinity of ash). As before, there was a high result, compared with theory, for the smallest amount of citrate precipitated, and a low result for the largest amount (Table IV). For the intermediate amount, with a lead titration difference of 12 ml., the correct precipitation figure was obtained.

TABLE IV

DEVIATION FROM CORRECT LEAD PRECIPITATION FOR DIFFERENT AMOUNTS OF CITRATE

Monosodium citrate used (per 100 ml. lead solution)	Calculated titration diff.	Titration diff. found	Difference
grm.	ml.	ml.	ml.
0·30	8·0	8·2	+0·2
0·45	12·0	12·0	0
0·60	16·0	15·8	−0·2

These figures are similar to those of Table II, except that the deficiency of precipitation at 16 ml. was not so great. This may have been due to the fact that the doubling of the concentration had had some effect.

However, it seemed that correct results were obtainable with citric acid if the total precipitation were such that a lead titration difference of about 12 to 14 ml. was obtained.

BEHAVIOUR OF MALIC ACID IN PRECIPITATION OF MIXTURES.—In preliminary experiments on the precipitation by lead of citric acid, when mixed with malic

acid (so as to simulate the conditions in fruit juices), a co-precipitation of part of the malic acid was found, about 40 to 50 per cent. of the theoretical amount of lead being thus precipitated by the malic acid; but the amount was dependent, to an appreciable extent, on the total amount of malic acid present, as well as on the total amount of lead precipitated.

For a more complete investigation, mono-sodium citrate and malic acid of analysed composition were used, and sodium hydroxide was added to the mixtures to keep the p_H in the ordinary range for fruits, *viz.* about 3·5.

In the first series, the citric acid was kept constant, and the amount of malic was varied. In calculating the amount of precipitation due to the malic acid, the effect due to the citric was deducted, with a suitable small allowance for the deviations from correct precipitation already established for that acid. In Table V the effect of the malic acid has been calculated as a percentage of the full amount theoretically precipitable.

TABLE V

PRECIPITATION OF MALIC ACID IN ADMIXTURE WITH CITRIC ACID : CITRIC ACID CONSTANT

Per 100 ml. of lead solution					
Amt. of mono-sodium citrate Grm.	Malic acid Grm.	Lead titration diff. ml.	Amt. due to malic acid ml.	Theor. for complete pptn. ml.	Per cent. precipitated
0·35	0·104	10·9	1·5	2·94	51
"	0·208	12·15	2·8	5·89	48
"	0·312	13·35	4·0	8·83	45
"	0·416	14·15	4·8	11·76	41
"	0·520	14·95	5·65	14·72	38

From these results it appeared that the precipitation of the malic acid was relatively less when the total amount of malic (or of malic + citric) was increased; or, looking at it in another way, there was less precipitation of the malic acid as the amount of excess of lead acetate available for its precipitation was reduced.

A second series was tried in which the malic acid was kept constant, but the citrate was varied. Again, in calculating the amount of precipitation due to the malic acid, allowance was made for the slight variation in the citric acid effect (Table VI).

TABLE VI

PRECIPITATION OF MALIC ACID IN ADMIXTURE WITH CITRIC ACID : MALIC ACID CONSTANT

Per 100 ml. of lead solution					
Amt. of mono-sodium citrate Grm.	Malic acid Grm.	Lead titration diff. ml.	Amt. due to malic acid ml.	Theor. for complete pptn. ml.	Per cent. precipitated
0·20	0·298	8·85	3·35	8·43	40
0·30	"	11·75	3·75	"	45
0·40	"	14·35	3·75	"	45
0·50	"	16·4	3·2	"	38

Under these conditions the malic acid precipitation again varied, reaching a maximum when the lead titration difference was from 12 to 14 ml., or under

about the same conditions (as regards excess of lead) as for the correct precipitation of citric acid.

In a third series the total amount of precipitation was kept approximately constant (by varying the proportions of citrate and malic acid) at about this point of correct citric and maximum malic precipitation (Table VII).

TABLE VII

PRECIPITATION OF MALIC ACID IN ADMIXTURE WITH CITRIC ACID : TOTAL LEAD PRECIPITATION CONSTANT

Per 100 ml. of lead solution					
Amt. of mono-sodium citrate	Malic acid	Lead titration diff.	Amt. due to malic acid	Theor. for complete pptn.	Per cent. precipitated
Grm.	Grm.	ml.	ml.	ml.	
0·40	0·178	13·2	2·55	5·04	51
0·35	0·296	13·2	3·9	8·38	46
0·30	0·415	13·2	5·2	11·75	44
0·25	0·543	13·15	6·5	15·36	42
0·20	0·661	13·0	7·7	18·71	41
0·15	0·780	12·8	8·8	22·08	40

This series showed again the effect of increasing quantities of malic acid, as in Table V, so that this effect is manifested over and above the effect noted from Table VI, since it occurs when all the lead precipitations are at what should be the point of maximum malic acid precipitation.

The practical outcome of these experiments was that, if the quantity of malic and citric acids were kept within suitable limits, the malic acid precipitated could be taken as a fixed percentage. In particular, if the malic acid used in the test (per 100 ml. of lead solution) amounted to at least 0·3 grm., and the citric acid was from about 0·2 grm. to 0·3 grm., about 40 to 45 per cent. of the malic acid was precipitated. A mean figure of 43 per cent. can be taken to cover all such cases correctly, within the limits of experimental error.

Subject to these restrictions, we have a means of determining the proportion of malic acid in a mixture of the two acids (or their salts). For this purpose it is convenient to reckon all the acid as citric acid (this total acid is ascertainable directly from titrations of free acidity and of ash, when salts are present). Then the theoretical amount of 2 per cent. lead acetate solution, equivalent to each 0·1 grm. of acid (as citric), is 13·55 ml. But whilst all the citric acid is precipitated, only 43 per cent. of the malic acid accompanies it.

Thus, if T be the grms. of total acid present in the solution used for the test; D the lead titration difference (*i.e.* on one-fifth of T); and M the grms. of malic acid (reckoned as citric) contained in the T grms. of total acid,

$$D = \frac{13{\cdot}55}{0{\cdot}1}\left[\frac{1}{5}M \times \frac{43}{100} + \frac{1}{5}(T - M)\right]$$

$$= 27{\cdot}1\,[T - 0{\cdot}57\,M],$$

whence $M = 1{\cdot}75\,T - 0{\cdot}065\,D$ .. .. (I).

To take an illustration, suppose the total of the two acids in a solution taken for the test is 0·75 grm., reckoned as citric, and that the lead titration difference is 12·8 ml., then

$$M = 1{\cdot}75 \times 0{\cdot}75 - 0{\cdot}065 \times 12{\cdot}8 = 0{\cdot}48 \text{ grm.}$$

and the citric acid would be $0{\cdot}75 - 0{\cdot}48 = 0{\cdot}27$ grm.

The actual malic acid, as malic, would be $0{\cdot}48 \times \frac{67}{70} = 0{\cdot}46$ grm.

It will be noted that the quantity of each of the acids conforms to the restrictions previously set out. It may sometimes happen that this is not so. In that case, in order to obtain a more accurate result, the determination should be repeated, with suitable additions of either citric or malic acid, as the case may require, and, if necessary, also an accompanying alteration in the amount of the mixture taken for the test.

The titration difference may fall outside the range of 12 to 14 ml. required for correct precipitation of the citric acid. In that case a small correction, based on the data of Tables II and IV, may be applied before calculating the proportions of malic and citric acids. These corrections are given in Table VIII.

TABLE VIII

CORRECTIONS TO BE APPLIED TO LEAD TITRATION DIFFERENCES

Lead titration diff. ml.	Correction ml.
8·5– 9	−0·2
9·1–11	−0·1
11·1–14	0
14·1–15	+0·1
15·1–16	+0·2

Titration values outside the range shown here are less reliable, and, when obtained, a fresh determination on an altered quantity of original solution should be made.

BEHAVIOUR OF PECTIN IN THE LEAD PRECIPITATION.—Before applying the method elaborated for pure acids to fruit extracts it was thought desirable to examine the behaviour of pectin when precipitated by lead.

A solution of orange pectin, containing 0·82 per cent. of pectin as calcium pectate, was used. The free and combined acidity of the pectin, expressed on the calcium pectate basis, was equivalent to 13·6 per cent. as citric acid. Thus, for theoretical precipitation of the pectin as the lead salt, 100 ml. of pectin solution would require $13{\cdot}55 \times 0{\cdot}136 \times 0{\cdot}82$ ml. = 15·1 ml. of 2 per cent. lead solution.

In a first experiment, in which 100 ml. of the pectin solution were treated alone by the usual procedure, the titration difference was 2·9 ml. This was, as usual, on one-fifth of the total volume, so that the theoretical lead equivalent should have been $\frac{15{\cdot}1}{5} = 3{\cdot}02$ ml. Within ordinary limits, therefore, the precipitation result was in agreement with the theoretical value.

In a subsequent experiment, 125 ml. of pectin solution were mixed with a known amount of citric acid solution (partly neutralised with sodium hydroxide

to correspond with conditions in a fruit juice). The titration difference was 12·8 ml., whilst a control test of the citric acid solution, without the pectin, gave 10·6 ml., or a difference of 2·2 ml., due to the pectin. The theoretical lead equivalent should have been $15{\cdot}1 \times \frac{1{\cdot}25}{5} = 3{\cdot}8$ ml., so that, in presence of citric acid, the precipitation of lead by the pectin was reduced considerably.

The amounts of pectin used above were four or five times as large as would be present in the test as carried out on an ordinary fruit or jam, but, in order to prevent any possible interference, and also to improve the filtration, which tended to be sluggish in the presence of the pectin, a preliminary treatment with acetone was introduced into the procedure to remove the pectin. A fruit or jam extract was made up to double its volume with acetone, being meanwhile swirled round to avoid entangling too much air, and then filtered, with precautions against evaporation. A suitable amount of this pectin-free filtrate was taken for the test, and, after removal of the acetone by evaporation, the solution was cooled, and the lead test proceeded with as usual. The free and combined acidity of the fruit were also determined on the pectin-free filtrate, so that all results should be on the same basis.

Effect of Phosphates on Lead Number.—In view of the effect of the possible (though doubtful) presence of small amounts of phosphates in fruit extracts or jams, known amounts of a solution of acid potassium phosphate (KH_2PO_4) were added to citric acid solutions, and the mixtures were treated by the usual lead process. In Table IX the quantities taken, and lead titration differences found, are shown; and the effect due to the phosphate, obtained by deducting that of the citric acid, is compared with the theoretical amount required for the complete precipitation of triplumbic phosphate [$Pb_3(PO_4)_2$].

Table IX

Precipitation of Lead by Phosphate in Admixture with Citric Acid

Citric acid taken Grm.	KH_2PO_4 taken Grm.	Lead titration diff. ml.	Amt. due to phosphate ml.	Theoretical for phosphate ml.
0·10	0·30	15·9	13·3	12·54
0·20	0·20	13·7	8·3	8·36
0·30	0·10	12·2	4·1	4·18

The precipitation was close to the theoretical value. It should be noted that any phosphate present in a fruit extract would behave, in the determination of free and combined fruit acids, as though it were the salt of a dibasic acid, *e.g.* $KH(HPO_4)$, whereas the lead salt precipitated is the tribasic salt. Thus, any part of the apparent "total fruit acid" which may be present as phosphate would appear to precipitate 3/2 times the amount of lead that would be precipitated by its equivalent of citric acid. Thus, whilst 0·1 grm. of citric acid (equivalent weight = 70) has a 2 per cent. lead acetate equivalent of 13·55 ml., 0·1 grm. of phosphoric acid (virtual equivalent in fruit analyses = 49) has a lead equivalent of

$$13{\cdot}55 \times \frac{70}{49} \times \frac{3}{2} = 29{\cdot}0 \text{ ml.}$$

The phosphoric acid in the ash of a large number of samples of fruit has been found to be usually between 0·03 and 0·06 per cent. of the fruit. Since the lead number of the fruit, by Boseley's scheme, is expressed on 10 grms. of sample, that portion of it due to this phosphoric acid would be $29 \times \frac{0{\cdot}003}{0{\cdot}1} = 0{\cdot}9$ to 1·8 ml, if it were present as phosphate in the fruit extract. This, however, is doubtful, at least as regards the whole of it; so that the effect of any phosphate in this way would not be great, and certainly very much less than the natural variations in lead number from one sample of fruit to another.

Behaviour of Other Acids in the Lead Precipitation.—Although the evidence discussed later indicates that citric and malic acids are the principal acids occurring in jam fruits, at least in quantity sufficient to affect significantly the amount of lead precipitate, the effect of a few other acids has been studied.

Tartaric Acid.—This is, of course, a prominent acid in the grape, but does not occur to any extent in most jam fruits. A few experiments with a solution of cream of tartar of known composition showed that this acid was precipitated as neutral lead tartrate when submitted to the standard "lead number" process (see Table X).

Table X

Lead Precipitation of Tartaric Acid

Tartaric acid* taken (per 100 ml. of lead solution) Grm.	Calculated titration diff. ml.	Titration diff. found ml.	Diff. ml.
0·298	7·5	7·7	+0·2
0·447	11·3	11·4	+0·1
0·596	15·0	14·7	−0·3

* *i.e.* equivalent to the amount of cream of tartar taken.

The slight differences from the theoretical values are very similar to those of citric acid, so that, in the event of tartaric acid being present, the corrections given for citric acid (Table VIII) would apply. There would be no interference with the calculation of the malic acid present in a mixture of the three acids.

Succinic Acid.—Tests carried out on succinic acid in admixture with varying proportions of mono-sodium citrate showed that there was no more lead precipitated than would be due to the citrate alone.

Thus, any succinic acid present in a mixture of fruit acids would cause the amount of malic acid, as given by the calculation earlier, to be too high. However, no definite evidence has so far been found that succinic acid occurs in any appreciable quantity in jam fruits.

Fumaric Acid.—This acid has been stated to occur as a natural constituent of some fruits.

Experiments on the lines of those already carried out with malic and succinic acids showed that fumaric acid, when citrate was also present, precipitated lead to the extent of about 55 per cent. of the amount required to form the neutral lead salt. Thus, any fumaric acid present would appear as malic acid in the calculation of the latter.

However, attempts to identify fumaric acid in extracts of plums and greengages, in which its presence was at first suspected for other reasons, gave negative results.

Lactic Acid.—This acid is not supposed to occur naturally in fruits, though it may be considered as a natural "food" acid, and is in some countries officially recognised as a permissible substance in food preparations. It is used in the manufacture of some commercial pectin preparations, which, therefore, introduce it into jams containing them.

Experiments on lactic acid alone, and also in admixture with citrate solutions, showed that there was no precipitation of lead whatever by the lactic acid. Thus, any lactic acid present in fruit products would considerably increase the apparent amount of malic acid, as given by the calculation from the lead precipitation. Since the calculation depends on the fact that 57 per cent. of the malic acid is unprecipitated, whereas the whole of the lactic acid remains so, the latter would cause the malic to appear too high by $\frac{100}{57}$ times its equivalent weight as malic acid. In the presence of lactic acid, therefore, the method of calculating malic acid breaks down, unless there is some means of determining the former and allowing for it.

AN EXTENSION OF THE LEAD PRECIPITATION PROCESS: PRECIPITATION FROM 50 PER CENT. ACETONE SOLUTION.—Auerbach and Weber (*Z. anorg. Chem.*, 1925, **147**, 68), in the course of a general study of the solubility of the lead salts of fruit acids, found that the lead salts (of citric, malic, tartaric, and succinic acids) were only very slightly soluble in 50 per cent. alcohol. This seemed to hold out the possibility of more definitely characterising the individual acids and the fruit extracts, etc., in which they were present, and an extension of the lead-precipitation process was accordingly devised.

Acetone seemed to offer advantages over alcohol as a medium for the new form of precipitation, and a few preliminary experiments showed that the lead salts were just as insoluble in a 50 per cent. (by vol.) acetone medium as in the alcohol mixture of Auerbach and Weber. The amount of lead precipitated by citric acid was, however, about 10 per cent. more than the theoretical, whilst malic acid now gave practically the same precipitation as citric acid, also about 10 per cent. more than the theoretical. It is possible that this extra precipitation of lead is connected in some way with a shift of p_H caused by the acetone (as shown when an indicator was added). It was found in the experiments of Table I that when the p_H is not controlled in the aqueous precipitation, excess lead, up to at least 12 per cent., was precipitated.

In the aqueous precipitations it was found that correct precipitation of lead by citric acid was obtained when about 0·5 grm. of citric acid was taken per 100 ml. of 2 per cent. lead acetate (see Tables II and IV). The precipitation in the acetone medium was more arbitrary, and there was no point at which it could be said that "correct" precipitation was obtained. Hence, for the purpose of comparisons and practical work, it was decided to assume that the precipitation given by 0·5 grm. of citric acid (per 100 ml. of lead solution) was a "correct" one for the

acetone medium. This was found to average 15·0 ml. of lead-titration difference. On this basis the actual results found for citric acid and a number of mixtures of malic and citric acids, in the acetone medium, are compared in Table XII with the calculated "correct" values. In these tests, as in previous ones, the citric acid was used in the form of mono-sodium citrate, and the malic acid in the partially neutralised condition, to correspond with the conditions in fruit products.

TABLE XII

DEVIATION FROM ASSUMED CORRECT LEAD PRECIPITATION IN 50 PER CENT. ACETONE MEDIUM

Per 100 ml. of lead solution				
Mono-sodium citrate Grm.	Malic acid Grm.	Calc. lead titration diff. ml.	Titration diff. found ml.	Difference
0·30	—	8·85	9·15	+0·3
0·45	—	13·26	13·35	+0·1
0·60	—	17·7	17·2	−0·5
0·35	—	10·3	10·7	+0·4
0·35	0·104	13·6	13·65	+0·05
0·35	0·208	16·8	16·5	−0·3
0·20	0·298	15·25	15·05	−0·2
0·30	0·298	18·2	17·4	−0·8
0·40	0·074	14·1	14·2	+0·1
0·35	0·123	14·15	14·3	+0·15
0·30	0·173	14·25	14·3	+0·05
0·25	0·222	14·3	14·3	0
0·20	0·271	14·35	14·4	+0·05
0·15	0·321	14·45	14·45	0

The precipitation due to the malic acid in the mixtures has been assumed to be the same as for the equivalent amount (*i.e.* $\times \frac{70}{67}$) of citric acid.

It can be seen that the lead equivalents of the acids present are subject to the same sort of slight fluctuations as in the aqueous precipitations. The deviations increase rather sharply with titration differences above about 16 ml., probably owing to insufficient excess of lead.

It should be noted that the deviations shown by the solutions containing malic acid were similar to those of citric acid alone. This means that the malic acid is precipitated as completely from the 50 per cent. acetone medium as is citric acid.

In Table XIII the deviations are expressed in the form of corrections which can be applied to the titration differences to bring them all to the same basis of assumed correct precipitation.

Titration differences falling outside the above range are not very reliable; in such cases it would be advisable to repeat the test with a different amount of the solution.

When the titration differences have been corrected in this way, the sum of the citric and malic acids (both expressed as citric) in a mixture of the two can be found by taking a titration difference of 15·0 as representing 0·10 grm. of acid (as citric) precipitated; or, what is the same thing, 0·50 grm. of acid in the full quantity of solution taken for precipitation by the 100 ml. of 2 per cent. lead acetate solution.

TABLE XIII

CORRECTIONS TO BE APPLIED TO LEAD TITRATION DIFFERENCES (PRECIPITATION IN 50 PER CENT. ACETONE)

Lead titration diff. ml.	Correction ml.
9·0—11	−0·3
11·1—13	−0·2
13·1—14	−0·1
14·1—15	−0
15·1—15·7	+0·1
15·8—16·2	+0·2
16·3—16·5	+0·3
16·6—16·8	+0·4
16·9—17·1	+0·5

Thus, suppose 25 ml. of a solution are treated with 100 ml. of 2 per cent. lead acetate, and the mixture is made up to 250 ml. with acetone and filtered; 50 ml. of the filtrate are then titrated and found to give a difference from the blank of 12·5 ml. The correction on this, from Table XIII, brings it to 12·3 ml. Hence, the amount of combined citric and malic acids in the 25 ml. of solution initially taken is $0{\cdot}5 \times \frac{12{\cdot}3}{15{\cdot}0} = 0{\cdot}41$ grm. (expressed as citric acid).

BEHAVIOUR OF OTHER ACIDS IN THE 50 PER CENT. ACETONE MEDIUM.—Tartaric acid, which, it was seen, is precipitated completely, like citric acid, from aqueous solution, is precipitated similarly to citric acid from the 50 per cent. acetone, *i.e.* a slight excess of lead being thrown out (about 15 per cent.). As this acid is not present to any extent in jam products, no significant error arises if the lead equivalent of the citric acid is used to cover both acids. Thus, the acid precipitated in acetone includes tartaric with the citric and malic acids.

Phosphoric acid (used in the form of KH_2PO_4) was found to precipitate from the 50 per cent. acetone medium just the theoretical amount of lead required for the triplumbic phosphate. There was no excess precipitation as with the organic acids. However, it must be remembered that the same consideration holds good as in the aqueous precipitation of phosphate; any of the fruit acidity due to phosphoric acid, as given by titration to the phenolphthalein end-point, has 3/2 times the lead-precipitating power of the organic acids. Consequently, if phosphoric acid is present in a mixture, the total lead precipitation from acetone will be higher than it would be if all the acids were organic.

Fumaric acid (examined in admixture with citrate), precipitated practically the theoretical amount of lead from the acetone medium, but there was a slight solubility effect, as a slight further precipitate came out from the filtrate, on standing overnight. In any case, this acid would be included with sufficient accuracy in the total of the other acids.

Lactic acid, both alone and in admixture with citrate, was found to be unprecipitated from the acetone medium. This was a fact of special importance. It was shown earlier that, when present, this acid, owing to its non-precipitation from aqueous solutions, invalidates the calculation of malic acid. In the acetone

medium, however, it was alone among the acids considered here in not being fully precipitated. Hence, we have a ready means of estimating its amount with some exactness, and so allowing for its effect in calculating the malic acid.

If T be the grms. of total acid in the solution used (obtained as before mentioned by titration of the free acidity and of the ash), D′ the lead titration difference for the 50 per cent. acetone medium (*i.e.* on one-fifth of T), and K the grms. of lactic acid (reckoned as citric) in the T grms. of total acid, then we have

$$D' = \frac{15{\cdot}0}{0{\cdot}1} \times \frac{1}{5}(T - K),$$

since 0·1 grm. of citric acid (or its equivalent in malic, tartaric, etc.) precipitates 15·0 ml. of 2 per cent. lead acetate solution. From this equation,

$$K = T - \frac{D'}{30} \quad .. \quad .. \quad .. \quad .. \quad .. \quad \text{(II)}$$

Reverting to the earlier equation (I) for the calculation of the malic acid from the aqueous lead titration difference, the T in that equation must now be replaced by (T–K), since the lactic acid was completely inert in that determination also. So we have $M = 1{\cdot}75\,(T - K) - 0{\cdot}065\,D$,

or, substituting for K the value given by equation (II) above,

$$M = 1{\cdot}75\,(T - T + \frac{D'}{30}) - 0{\cdot}065\,D$$

$$= 0{\cdot}058\,D' - 0{\cdot}065\,D \quad .. \quad .. \quad .. \quad \text{(III)}$$

Thus, the malic acid can now be obtained by a simple calculation from the two lead titrations. It may be noted that, for the purpose of determining the malic acid only, it is not necessary to know the total acidity of the solution; this is only required if the lactic acid, or the total acid (citric + tartaric + phosphoric) are required in addition.

It should be pointed out that the preceding calculation includes any phosphoric acid with the citric acid, and assumes that it precipitates lead similarly to the latter. Actually, as was shown earlier, this is not the case. The effect of the assumption is to make the calculated amounts of lactic and malic acids slightly low, whilst the remaining acid (*i.e.* citric + tartaric + phosphoric) is made slightly high. The errors, even supposing that all the phosphorus found in the fruit ash is derived from phosphates, are not very large—not more than 0·02 per cent. (expressed on the fruit) for the malic, and 0·035 per cent. for the (citric + tartaric + phosphoric) acids.

The above method for determining the malic acid breaks down, of course, if there are appreciable amounts of other acids present which are differently precipitated in aqueous and in acetone medium. From other evidence it seems likely that such is not the case with many fruits, including most of the soft jam fruits and apples. With regard to stone fruits there is more doubt. In any case, for the purpose of the analysis of fruit products there seems no objection, in the first instance, to classing empirically as malic acid all the acid material which behaves like it in the lead tests. This device, while ignoring the slight errors

that may be caused by traces of phosphoric or other acids, has the advantage, from an analytical standpoint, of separating the acid constituents of the fruits into three groups:

(i) Citric acid, and acids which behave similarly (*e.g.* tartaric acid); (ii) malic acid, and acids which behave similarly (if any); (iii) lactic acid, and acids which behave similarly (if any).

Since it will be shown later that the acids of apples and of the stone fruits consist chiefly of malic acid (or of acids behaving like it), it is clear that a means of discriminating between the different groups of acids affords useful information in the analysis of mixed products.

DETERMINATIONS OF LEAD NUMBER ON FRUIT EXTRACTS.—In the course of the past two or three seasons a considerable number of determinations of lead number has been made on extracts prepared from fresh fruits. At first the aqueous extracts were used for the precipitations without removing the pectin, but it was found later that the results with stone fruit were more reliable if the pectin was removed. Later determinations were, therefore, always carried out on the filtrate from the precipitation of pectin with acetone, the acetone being removed by evaporation prior to the aqueous lead precipitations. It was found that results on this pectin-free filtrate were practically identical with those on the original extract of soft fruits and apples, but were sometimes different (usually higher), and certainly more reproducible, with the stone fruits. Later, when the lead precipitation from 50 per cent. acetone was worked out, the procedure was arranged so as to take advantage of the preliminary precipitation of the pectin with the acetone, as will appear in the description of the full method of working eventually adopted.

A further modification introduced when the acetone lead precipitation came into use was a fivefold increase in strength of the lead acetate solution (including the contained acetic acid); in place of the former 100 ml., only 20 ml. of the stronger solution were, of course, used. This permitted of the use in the test of sufficiently large amounts of the rather weakly acid extracts obtained from some samples.

Also, for stone fruits and apples, the practice was adopted in the aqueous precipitations of adding a suitable amount of citric acid (in the form of monosodium citrate solution or of the free acid) in order to ensure the proper co-precipitation of the malic acid (see BEHAVIOUR OF MALIC ACID, p. 251). A still later improvement was the addition to some extracts, where the natural malic acid was believed to be deficient (as in strawberries, raspberries, etc.), of small amounts of malic acid, also for the purpose of securing the right degree of co-precipitation. Appropriate allowance was made for these additions of citric or malic acid in calculating the lead numbers of the fruits.

In Table XIV is given a summary of the results of determinations of the aqueous lead number on most of the ordinary jam fruits. For stone fruits and apples only the later results, obtained on pectin-free extracts, and with additions of citrate as above mentioned, are included. The extracts of the fruits were prepared by boiling the samples with an equal weight of water for an hour, cooling, replacing the water lost by evaporation, and filtering. In calculating results back to the original fruit, correction has been made for the amount of insoluble matter, and

also for the fact that the extracts were made up by weight, whilst the amounts used for analysis were pipetted. The lead numbers are expressed according to Boseley's original scheme, *i.e.* the number of ml. of 2 per cent. lead acetate solution precipitated by 10 grms. of the sample.

In addition to the lead numbers, the table shows the average total acid-content of each kind of fruit (from the free acidity and ash titrations). Finally, the value obtained by dividing the lead number of each sample by its total acidity is shown. This is really the lead equivalent (2 per cent. lead acetate solution) of each 0·1 grm. of acid (as citric acid). It is also numerically equal to the "lead number per 1 per cent. of acid" in the sample. If all the acid were citric acid, this figure would be 13·55. The deviation from this is a measure of the proportion of non-precipitated or partly-precipitated acids (probably chiefly malic acid) present.

The figures for "highest" (and "lowest") values of lead numbers and of lead number per 0·1 grm. of acid do not necessarily belong to the same sample.

TABLE XIV

LEAD NUMBERS OF JAM FRUITS (AQUEOUS PRECIPITATION)

Fruit	No. of samples		Lead number ml.	Total acidity, as citric acid Per Cent.	Lead number per 0·1 grm. acid ml.
Gooseberries ..	17	Highest	29·9	—	11·7
		Lowest	17·3	—	9·5
		Average	25·5	2·44	10·4
Strawberries ..	15	Highest	22·7	—	13·3
		Lowest	9·8	—	10·5
		Average	16·3	1·31	12·4
Raspberries ..	11	Highest	34·2	—	14·3
		Lowest	19·0	—	12·1
		Average	26·8	2·02	13·3
Redcurrants ..	7	Highest	43·1	—	14·3
		Lowest	34·8	—	12·0
		Average	37·6	2·81	13·4
Blackcurrants ..	10	Highest	64·8	—	14·4
		Lowest	39·5	—	12·2
		Average	52·7	3·92	13·5
Apples	4	Highest	10·9	—	7·4
		Lowest	6·9	—	6·3
		Average	9·4	1·33	7·1
Plums	5	Highest	18·0	—	7·6
		Lowest	6·9	—	2·5
		Average	10·2	2·14	4·8
Greengages ..	2	1.	12·0	—	5·9
		2.	8·1	—	5·5
		Average	10·1	1·77	5·7
Damsons ..	4	Highest	19·4	—	7·0
		Lowest	9·4	—	3·0
		Average	13·0	2·77	4·7
Blackberries ..	12	Highest	22·5	—	10·2
		Lowest	7·2	—	8·1
		Average	13·9	1·51	9·2
Apricots ..	2	1.	20·8	—	11·0
		2.	14·7	—	9·6
		Average	17·8	1·72	10·3

From these results it appears that the acid of raspberries, redcurrants and blackcurrants is almost entirely citric acid (or belongs to that type). Strawberries contain a slight proportion of other acid, gooseberries, blackberries, and apricots

rather more, whilst apples and the stone fruits probably contain very little citric acid.

In a few analyses of raspberries and currants the value for the lead number is even slightly higher than should be obtained if all the acid precipitated its full equivalent of lead. Part of this excess may be due to difficulty in determining the end-point of the titration, which is sometimes found in the more strongly coloured fruits; but part may be also due to traces of phosphates, which, it will be remembered, precipitate lead more strongly than their titratable acidity warrants.

The results of lead-number determinations in the 50 per cent. acetone medium are summarised in Table XV. The data are fewer, as this method was only brought into use during the 1932 season. This accounts for the slightly different average figures for acidity compared with those of the preceding Table.

TABLE XV

LEAD NUMBERS OF JAM FRUITS (50 PER CENT. ACETONE PRECIPITATION)

Fruit	No. of samples		Lead number ml.	Total acidity, as citric acid Per Cent.	Lead number per 0·1 grm. acid ml.
Gooseberries ..	2	1.	40·9	—	15·4
		2.	39·8	—	15·4
		Average	40·4	2·62	15·4
Strawberries ..	3	Highest	27·0	—	15·6
		Lowest	15·8	—	15·3
		Average	21·4	1·39	15·4
Raspberries ..	3	Highest	37·4	—	15·6
		Lowest	35·0	—	15·0
		Average	36·6	2·38	15·4
Redcurrants ..	2	1.	51·8	—	17·1
		2.	50·7	—	16·7
		Average	51·3	3·04	16·9
Blackcurrants ..	2	1.	78·2	—	17·3
		2.	74·1	—	16·3
		Average	76·2	4·53	16·8
Apples	4	Highest	22·2	—	15·1
		Lowest	16·5	—	14·9
		Average	19·9	1·33	15·0
Plums	3	Highest	34·4	—	14·6
		Lowest	19·0	—	12·3
		Average	26·1	1·88	13·9
Greengages ..	3	Highest	28·6	—	13·0
		Lowest	15·0	—	10·3
		Average	20·3	1·68	12·1
Damsons ..	2	1.	43·3	—	15·6
		2.	34·9	—	14·6
		Average	39·1	2·59	15·1
Blackberries ..	2	1.	34·4	—	15·6
		2.	22·2	—	15·2
		Average	28·3	1·84	15·4
Apricots ..	2	1.	25·9	—	15·3
		2.	23·5	—	13·6
		Average	24·7	1·72	14·4

In most of the fruits it is evident that the lead number in the acetone medium was very close to that corresponding to complete precipitation of the acids. That is to say, the acids fall into the citric or malic acid groups. Most of the results were a little higher, in fact, as can be seen by comparing the "lead number per

0·1 grm. of acid" with the theoretical figure of 15·0. With currants the precipitation was appreciably higher than this; so far a satisfactory explanation has not been found, but it is possible that phosphates partly account for the excess.

The most interesting results were from plums and greengages. The few samples of these examined all gave incomplete precipitations, showing the presence of some acid not belonging to either the malic or citric acid groups. The behaviour of this acid in the lead tests, according to the scheme elaborated in an earlier section, was similar to that of lactic acid. Whether it is lactic acid or not is a matter as yet undecided. Unfortunately, its amount is apparently very variable, so that it does not offer very much prospect of assistance in discovering the fruit-content of products containing these fruits.

DISTRIBUTION OF THE ACID GROUPS IN FRUITS.—If the equations (II) and (III) given earlier are applied to the two sets of lead numbers obtained from the fruits, approximate figures for the amount of each of the three acid types are obtained. This has been done for all those samples for which determinations of both lead numbers were available, and the apparent amounts of the malic acid and lactic acid types, expressed as percentages of the total organic acid, are shown in Table XVI. Many of the percentages so found, especially of "lactic acid," are slightly negative. This may possibly arise from the presence of traces of phosphate,

TABLE XVI

APPARENT PROPORTIONS OF ACIDS OF DIFFERENT TYPES IN FRUIT SAMPLES

Fruit	Total acid Per Cent.	Per cent. of total acid: Malic acid group	Per cent. of total acid: Lactic acid group
Gooseberry	2·65	41	— 3
	2·58	35	— 3
Strawberry	1·76	15	— 2
	1·39	8	— 3
	1·01	14	— 4
Raspberry	2·39	— 5	— 4
	2·48	— 2	0
	2·27	12	— 3
Redcurrant	2·97	16	—14
Blackcurrant ..	4·54	5	— 9
	4·51	14	—15
Apple	1·47	78	0
	1·42	81	0
	1·31	77	0
	1·10	92	0
Plum..	1·75	93	5
	1·55	70	18
	2·35	70	3
Greengage	2·20	80	13
	1·38	70	17
Damson	2·78	90	— 4
	2·39	97	2
Blackberry	2·21	67	— 4
	1·46	47	— 1
Apricot	1·54	53	— 2
	1·90	15	9

which would affect the calculation of both the malic and lactic acid types in a negative direction (see p. 259). Larger negative results are shown by currants, which, it was seen, had a tendency to give lead numbers above the theoretical in the aqueous precipitation, and quite notably above it in the acetone precipitation.

Apple and the stone fruits appear as predominantly "malic acid" fruits, whilst gooseberries, blackberries and, perhaps, apricots, appear to have a more even distribution of the acids in the citric and malic groups.

Some of these findings, so far as relative proportions of citric and malic acids are concerned, are similar to the results of Nelson (ANALYST, **1924, 49**, 592; **1925, 50**, 191, 295), who made a direct determination of the acids by an ester distillation method. He found in strawberries 10 per cent., raspberries 3 per cent., blackberries 17 per cent., and apricots 70 per cent. of the total acid to be malic acid. Franzen and Helwert (*Z. physiol. Chem.*, see *Canning Age*, 1925, June, p. 562) reported the acids of apples to be chiefly malic, with some citric; whilst currants contained chiefly citric, with some malic acid. This, again, is confirmed by the present results.

THE LEAD NUMBER OF JAMS.—We return, finally, to the motive behind Boseley's original idea of the lead-precipitation process, namely, the desire for a means of arriving at the approximate fruit-content of jams.

It has been shown that the lead number is due certainly (within experimental limits of accuracy) to the acid constituents of the fruits; further, that the acid constituents themselves can, by means of the lead precipitation, be separated into groups, and that the fruits fall broadly into classes containing a preponderance of citric or malic acid. Thus, it should be possible, within certain rough limits, to discover whether the acid constituents of a jam are normal to the class of fruit used, provided that any foreign fruit or fruit juice added belongs to a different class. In particular, the addition of apple pulp or juice, or pomace extract, to strawberry, raspberry, etc., jam, should make itself evident by disturbing the normal citric acid preponderance of these fruits. On the other hand, such additions to stone fruit jams would not appreciably alter the proportions of the acid groups (unless use can ultimately be made of the "lactic acid" group).

For the present the discussion will be confined to the former case. For this purpose it is not necessary to calculate from the lead number the actual quantities of citric and malic acids present. The lead numbers themselves can be used and compared with established data for the several kinds of fruits concerned, with due allowance for the natural variations. It should here be pointed out, what is evident from Tables XIV and XV, that it is not the lead number itself that is specially characteristic of a particular fruit. Thus, a lead number of 6·5 found for a jam might be given by 40 per cent. of strawberries alone, or by 25 per cent. of strawberries and 26 per cent. of apple pulp, or by 60 per cent. of apple alone. The characteristic property which makes it possible to gain some idea of the proportions of the constituents in such mixtures is the lead number *relative to the acid content*, or, according to the empirical method adopted above for expressing this property, the "lead number per 0·1 grm. of acid." (It should be remembered that *total* acid is always meant here, as obtained from the free acidity and ash titrations.) Hence, from a consideration of the average values for this figure

for the fruits concerned, their respective proportions in an unknown mixture, or rather, the proportions of their acids, can be approximately determined.

The matter may be made clearer by an example. Suppose the "lead number" of a strawberry and apple jam to be 6·4, and the percentage of total acid in the jam was found to be 0·61, then the acid in the 10 grms. of jam equivalent to the 6·4 ml. of 2 per cent. lead acetate solution is 0·061 grm., and the "lead number per 0·1 grm. of acid" is $\frac{6{\cdot}4}{0{\cdot}61} = 10{\cdot}5$. Now the averages for strawberries and apples are, respectively, 12·4 and 7·1 (Table XIV). Hence the proportion of the acids due to strawberries is $\frac{(10{\cdot}5 - 7{\cdot}1)}{(12{\cdot}4 - 7{\cdot}1)}$ 100 per cent. of the total, = 64 per cent. Thus, the percentage of acid in the jam due to strawberries is $0{\cdot}61 \times \frac{64}{100} =$ 0·39 per cent.; and that due to apples will, therefore, be 0·61 − 0·39 = 0·22 per cent. Taking the average total acid contents of strawberries and apples as 1·31 per cent. and 1·33 per cent., respectively (Table XIV), the amounts of the two fruits in the jam are:

$$\text{Strawberry: } \frac{0{\cdot}39}{1{\cdot}31} \times 100 = 30 \text{ per cent.}$$

$$\text{Apple } = \frac{0{\cdot}22}{1{\cdot}33} \times 100 = 17 \quad ,,$$

The same method can be applied to other mixtures, provided the characteristic figures for the fruits concerned, "lead number per 0·1 grm. of acid," are sufficiently far apart. Thus, the method breaks down for such mixtures as raspberry and redcurrant, plum and apple, etc., and is of doubtful value for blackberry and apple, or strawberry and gooseberry (see Table XIV).

The calculation can be expressed in the form of a simple formula.

Let F_1 and F_2 be the respective percentages of two fruits in a mixed product,

L_1 and L_2 the average values of the "lead number per 0·1 grm. acid" (Table XIV),

A_1 and A_2 the average values for total acid in the two fruits (Table XIV),

l the actual "lead number per 0·1 grm. of acid" found in the sample,

and a the actual per cent. of total acidity found,

$$\text{Then } F_1 = \frac{100a(l - L_2)}{A_1(L_1 - L_2)} \quad .. \quad .. \quad .. \quad .. \quad \text{(IV)}$$

$$\text{and } F_2 = \frac{100a(L_1 - l)}{A_2(L_1 - L_2)} \quad .. \quad .. \quad .. \quad .. \quad \text{(V)}$$

JAMS CONTAINING POMACE EXTRACTS OR PECTINS.—Most jams now on the market contain added pectin, which is used either in the form of a direct extract

from pomace, or a specially-prepared proprietary "fruit pectin" (usually prepared from apple residues), or as a dry powdered pectin prepared from citrus fruits or apple residues. The latter preparations, which are more or less pure pectin, should introduce no lead-precipitating acids but themselves into the jam; and, as they can be removed along with the natural fruit pectins by a preliminary precipitation with acetone, they should cause no complications.

The case is different with pomace extracts, etc. These, when they are aqueous extracts, may be considered as apple extracts deprived of a portion of their natural acids. The remaining acids, however, will still have the same lead-precipitating properties as the acids of the whole fruit (apart from the pectinous constituents, which can be removed before the lead test is made). Thus, the formulae of the preceding section can still be applied, though the apparent percentage of apple juice indicated will be low because of the removal of part of its acid. There will be no interference with the calculation of the amount of the main fruit constituent (F_1).

Some commercial pectins, however, appear to have been prepared by an extraction of pomace with lactic acid. Two of the most popular "fruit pectins" on the market in this country, for instance, on examination by the lead process, both in the aqueous and the 50 per cent. acetone medium, showed a large proportion of lactic acid (or an acid of closely similar type) among their acid constituents. Table XVII shows the essential parts of the analysis of these products, and the proportions of citric, malic, and lactic acid groups calculated from the lead numbers by the formulae already given.

TABLE XVII

COMPOSITION OF ACID CONSTITUENTS OF COMMERCIAL PECTINS AS CALCULATED FROM THE LEAD NUMBERS

Sample	Total acid (as citric) Per Cent.	Lead number (per 10 grms. of sample)		Acids (expressed as citric)		
		Aqueous medium	50 per cent. acetone medium	"citric" acid Per Cent.	"malic" acid Per Cent.	"lactic" acid Per Cent.
A.	2·04	3·0	6·9	0·05	0·41	1·58
B.	1·09	3·7	8·7	0·05	0·53	0·51

Thus, in one case about half, and in the other case three-quarters of the acid was lactic acid, the remainder being, presumably, the natural acids of the apple still remaining in the pomace or apple residues used.

Clearly the calculation of the fruit-content from the aqueous lead number by formula (IV) would be erroneous in jams containing such pectin preparations. The effect of the lactic acid would be to depress the "lead number per 0·1 grm. of acid," making the proportion of apple acids appear too high. The solution of the difficulty is afforded by the second, or "acetone" lead number. This gives a value for the total acids excluding the lactic acid, so that a corrected value can be obtained for the "lead number per 0·1 grm. of acid," which refers only to the malic and citric types of acid. Formula IV can then be applied to these corrected values for a and l.

This calculation is of use only for those fruits which themselves show no appreciable amount of the lactic type of acid, *viz.* the soft fruits and damsons (see Table XVI). But, as plums and greengages have an aqueous lead number so similar to that of apples as to preclude its use in calculating fruit-content in their case, the restriction is not a material one.

It is desirable to point out here, in connection with the calculation of fruit-content in mixtures containing commercial pectins, that experience in the analysis of a large number of jam samples of various origin has shown the figure of 7·1 for the "lead number per 0·1 grm. of acid" of apples (Table XIV) to be rather high for general application. This was the average from four samples only. A figure giving results more in accordance with other analytical indications is 6·5. This, too, is about the figure given by the commercial pectins of Table XVII, when due allowance is made for the extraneous lactic acid.

Hence, for the fruit-content of jams with added "pectin" (from apples), formula IV may be simplified to:

$$F_1 = \frac{100a(l - 6{\cdot}5)}{A_1(L_1 - 6{\cdot}5)} \quad .. \quad .. \quad .. \quad \text{(VI)}$$

The a and l of this formula should be suitably corrected for any lactic acid shown to be present by the "acetone" lead number. Values of A_1 and L_1 appropriate to the various fruits may be obtained from Table XIV.

Details of Analytical Procedure.—The details of the procedure adopted for the various determinations involved in applying the lead-precipitation method to the analysis of jams are as follows:

Preparation of Extract.—Weigh 250 grms. of the sample into a beaker, and add 250 ml. of water. Mix well to break up the jam, then heat to boiling with continual stirring, and boil gently for an hour, with occasional stirring, keeping the beaker covered, and maintaining the volume by adding water, if necessary. Cool, transfer to a 500-ml. measuring flask, make up to volume, shake well, and filter through a coarse filter.

Preparation of Pectin-free Filtrate.—Transfer 250 ml. of the aqueous extract to a 500-ml. flask, and add acetone (while swirling round without entangling too much air) to the mark. Mix well, and filter through a large dry filter, with precautions to avoid loss by evaporation.

Titration of Free Acid.—Pipette 40 ml. of the pectin-free filtrate into a large beaker, add about 500 ml. of boiled and cooled distilled water, and titrate with $N/10$ sodium hydroxide solution, using phenolphthalein as indicator. Carry out a blank titration of 500 ml. of the water similarly, and deduct this from the jam titration. The difference, multiplied by 0·07, gives the percentage of free acid (expressed as hydrated citric acid) in the jam.

Ash of Jam.—Evaporate 50 or 100 ml. of the pectin-free filtrate to dryness in a platinum dish on a water-bath, char over an Argand burner (protecting the contents of the dish from the gas fumes), and ash at a dull red heat, preferably in an electric muffle. Cool and (if required) weigh.

Titration of Combined Fruit Acid.—Dissolve the ash in a measured 15 ml. of $N/10$ hydrochloric acid, filter into a 175-ml. conical flask, and wash through

thoroughly. Boil for a few minutes. Cool, add a drop of methyl orange solution, titrate to yellow with $N/10$ sodium hydroxide solution, and then to the neutral tint with $N/10$ hydrochloric acid. Calculate the amount of acid consumed by the ash to the number of ml. of $N/10$ acid per 100 grms. of jam; this is the "methyl orange alkalinity" of the ash. (Pfyl, *Z. Nahr. Genussm.*, 1922, **43**, 313.)

Next acidify the titrated solution with about 2 ml. of $N/10$ hydrochloric acid, and evaporate to about 15 ml. (It is sometimes advisable to boil on a sand-bath, on account of bumping.) Cool, and neutralise carefully to methyl orange with $N/10$ sodium hydroxide solution. Add a few drops of phenolphthalein solution and 10 ml. of a strong neutral calcium chloride solution. Boil again for a few minutes, and titrate to the phenolphthalein end-point with $N/10$ sodium hydroxide solution. Calculate the number of ml. of $N/10$ sodium hydroxide solution per 100 grms. of jam, and multiply by 3/2. This gives the phosphoric acid in the ash as its equivalent of $N/10$ sodium hydroxide solution. Then find the "total alkalinity" of the ash, equivalent to all the alkali and alkaline earth metals present, by adding to the "methyl orange alkalinity" one-third of the phosphoric acid equivalent. Finally, multiply this total alkalinity by 0·007 to obtain its value as percentage of combined fruit acid as citric acid.

Total Fruit Acid.—The total fruit acid (including any phosphates present in the extract) is the sum of the free acid and combined acid found as above, and is expressed as the percentage of total citric acid (hydrated).

Aqueous Lead Number.—Take an amount of pectin-free filtrate (to the nearest 5 or 10 ml.) containing approximate amounts of total fruit acids according to the following scheme:

	Grm.
(i) Gooseberry, apricot, or blackberry jams	0·50
(ii) Strawberry, raspberry, redcurrant, or blackcurrant jams ..	0·35
(iii) Apple, cherry, plum, greengage, or damson jams	0·65

Remove the acetone by distillation, transfer the residue to a 250-ml. measuring flask, and cool. Then add, in the case of groups (i) and (ii), 3·0 ml. of 10 per cent. malic acid solution, or, in the case of group (iii), 3·0 ml. of 5 per cent. citric acid solution (pipetted accurately). (The strength of the acid used should be correct to within 1 per cent. of the total.) Dilute to about 200 ml. Ensure that the temperature of the solution is at about 16° to 20° C., then add from a pipette, while rotating the flask, 20 ml. of lead acetate solution (containing 100 grms. of normal lead acetate pure crystals, and 12·5 grms. of glacial acetic acid, per litre), and make up to volume with water. Shake well, and filter without delaying more than a few minutes. Titrate 50 ml. of the filtrate (diluted with 50 ml. of water) at or near the boiling-point, with ammonium molybdate solution (9·3 grms. per litre), using a 0·5 per cent. solution of tannic acid as an outside indicator (by spotting on a tile). The first appearance of a distinct yellow colour in the test drop (or a definite increase in a slight existing yellowish colour) marks the end-point.

For a blank titration, dilute 20 ml. of the lead acetate solution to 250 ml., and titrate 50 ml. of this + 50 ml. of water in the same way. Correct the difference between the two titrations for any lack of correct strength in the lead or molybdate

solutions. If the difference so corrected is not in the range 11–14 ml.. make a further correction according to Table VIII. (Should the difference lie outside the range there allowed for, repeat the determination on a larger or smaller quantity, as the case may require, of pectin-free filtrate.)

From the corrected titration difference deduct 3·6 ml. (when malic acid was initially added) or 4·1 ml. (when citric was added). Calculate the remainder back to the number of ml. of 2 per cent. lead acetate solution, which would be completely precipitated by 10 grms. of the original sample (or 40 ml. of the pectin-free filtrate). This is the "lead number" (aqueous) of the jam, according to Boseley's original definition; that is, if the amount of pectin-free filtrate taken for the test be P ml., and the corrected titration difference D, then

$$\text{Lead number (aqueous) } L = \frac{200D}{P}$$

The "lead number per 0·1 grm. of acid" is then found by simply dividing L by the percentage of total fruit acid (a) in the sample

$$l = \frac{L}{a} \qquad .. \quad .. \quad .. \quad \text{(VII)}$$

Acetone (50 Per Cent.) Lead Number.—Take an amount of pectin-free filtrate (to the nearest 5 or 10 ml.) containing approximate amounts of total fruit acid as follows:

	Grm.
(i) Gooseberry, strawberry, raspberry, redcurrant, blackcurrant, apricot, or blackberry jams	0·50
(ii) Apple, cherry, plum, greengage, or damson jams	0·40

(If more than 200 ml. would be required, the amount must be restricted to this figure.)

Place the required amount in a 250-ml. measuring flask, and in the case of jams of group (ii) add 3·0 ml. of 5 per cent. citric acid solution (measured accurately). (Should it have been necessary to limit the amount of pectin-free filtrate taken to 200 ml., the deficiency of fruit acid may be made up by a suitable addition of 5 per cent. citric acid solution, its effect being allowed for later.)

Add acetone, while rotating the flask, to make up the total amount of acetone present to 125 ml. Then add from a 20 ml. of 10 per cent. lead acetate solution (as in the aqueous test), and make up to volume with water. Mix, and filter, taking precautions to avoid loss by evaporation. Titrate 50 ml. of the filtrate, diluted with 50 ml. of water, as in the aqueous test.

Correct the difference between the titration and the blank (that obtained earlier will suffice) for any factors of the lead or molybdate solutions. If the difference so corrected is not approximately 14–15 ml., make a further correction according to Table XIII.

From the corrected titration difference deduct 1·5 ml. for each 1 ml. of added 5 per cent. citric acid solution, if any.

Calculate the remainder, as before, back to the number of ml. of 2 per cent. lead acetate solution completely precipitated by 10 grms. of the sample. This is

the "lead number" (acetone) L′ of the jam. The lead number per 0·1 grm. of acid is then obtained as before,

$$l' = \frac{L'}{a} \quad .. \quad .. \quad .. \text{ (VIII)}$$

Interpretation of Results.—If l' is appreciably less than 15, and plums or greengages are not present, lactic acid from a commercial pectin is probably present, and its amount can be approximately found by a formula adapted from the equation (II) given earlier:

$$k = a - \frac{L'}{15} \quad .. \quad .. \quad .. \text{ (IX)}$$

where k is the percentage of lactic acid in the sample. A corrected value for l (see VII) is then obtained by deducting the lactic from the total acid:

$$l \text{ (corrected)} = \frac{L}{a - k} \quad .. \quad .. \quad .. \text{ (X)}$$

The value for l, corrected or not as required, and the total acidity a, with any lactic acid deducted, are then used in formula VI to find the fruit-content of the sample.

For mixed jams coming within the scope of the method, formulae IV and V may be used, though it should be noted that if pomace extract or liquid pectin is present, it will be included with the fruit of lower lead number.

Discussion

The President remarked that all would agree with him that they had had very interesting papers read to them, and that the methods described were extremely ingenious, and the results of unquestionable utility. They had now agreed standards for the fruit-content of jam, and also the National Mark Standards were in existence, and it was, therefore, very essential that any proposed methods of analysis by means of which the true fruit-content of jam could be determined should be closely studied. He himself had had practically no experience of the examination of fresh fruits, and this must be the case with many other analysts, and, therefore, the results which Mr. Hughes and Miss Maunsell had given would be of great value. He admired the ingenuity those authors had displayed in the method of calculation. They had concluded their paper by observing that it was really necessary to examine a number of jams before coming to any definite conclusion. The Public Analyst usually had to draw his results from one sample, and this was perhaps unfortunate. He was particularly pleased to hear Mr. Hinton's paper because, as Mr. Hinton had mentioned, Boseley had experimented with a lead process, and almost on the last occasion on which he was present at a meeting of the Society he had referred to his process which he enthusiastically believed would enable the fruit-content of jam to be accurately determined.

Mr. T. Rendle congratulated the Society on having such an excellent evening, and the authors on papers containing such useful information. All who handled fruit and fruit products had felt the lack of satisfactory methods of analysis, and every fresh figure was a considerable help. He would like to know whether the figures for apricots referred to the fresh, dried or canned fruit. He believed that Macara's published figures for insoluble solids showed very considerable differences for different varieties of the same fruit, and for the same variety grown

in different districts. Mr. Hughes and Miss Maunsell had put forward figures for one variety only of raspberries—"Lloyd George." He felt that it would add to the value of the paper if further information on other varieties could be given, and if the maximum and minimum figures, as well as the average, were included. He would also like to know whether there was less variation between the maximum and minimum values for non-sugar solids than with the figures for insoluble solids on the same samples.

With regard to Mr. Hinton's paper, it was customary in the manufacture of pectin from pomace to adjust the final acidity by the addition of citric or tartaric acid. Would the use in a jam of pectin containing these acids influence the lead number?

Mr. G. N. GRINLING referred to a pamphlet issued by the Research in Canning Section of the University of Bristol, whereby the ingredients of canned fruit were calculated.

Mr. J. R. NICHOLLS queried how accurate the figure for non-sugar solids was likely to be. Presumably, when one got differing total solids and sugars, all the errors would be thrown on the non-sugar solids.

Mr. YOUNG asked what was the possibility of the action of sulphites on the lead number.

Mr. WILSON (from California) said what a great pleasure it had been to him to be present at that meeting. He had done some work on these lines himself, and certainly, in California, they found that many factors, such as degree of ripeness, variety and district, affected these natural products. It was always a pleasure to him to attend such a meeting, and he extended a hearty welcome to any member who could attend one of their meetings in America.

Dr. L. H. LAMPITT said that when a mass of figures, such as those they had had that evening, was shown upon the screen it was practically impossible, at the time, seriously to consider them and put forward any useful criticism. He did not know whether Mr. Hinton had considered the large number of other acids which occurred in small quantities and how far they were likely to affect his results of mixed acids when found in jams. Knowing how interested Mr. Boseley had been, Dr. Lampitt thought that it would be a very good thing if chemists in the fruit trade could try this method on a large number of samples. It was only by gradual accumulation of a large number of figures that they were likely to get satisfactory information of a biological nature. He would like to thank Mr. Hinton for putting forward another possible tool which might prove of great use.

Mr. T. MACARA congratulated Mr. Hughes and his colleague on the very ingenious way in which they had worked out the value of the non-sugar solids in fruits and applied the results to the analysis of jams. He had given figures in his own paper on the "Composition of Fruits" (ANALYST, 1931, **56**, 39), from which the non-sugars could be calculated, and although these figures were not obtained by the same methods, they could be used in the way indicated by Mr. Hughes and Miss Maunsell. It was a pity that the Society had not found it possible to publish all the tables of analyses of fruits which he had submitted, as the results for individual fruits were frequently helpful in dealing with difficult cases. He hoped that the new results would prove helpful to others. He was pleased to hear the authors stress the necessity for the examination of more than one sample before coming to a decision. This was necessary to meet cases of bad distribution of the fibre and seeds in filling the jam into jars. There were also occasions when a manufacturer was obliged to skim off seeds or pips when these floated too freely to the surface of the jam. There were, of course, other cases where pips might be deliberately added, and it was then necessary to consider other constituents of the fruit, *e.g.* the acid. In this connection he referred to the

case of a sample of gooseberry and raspberry jam submitted to him for analysis. This contained sufficient pips to represent 100 per cent. of raspberries, but he had reported it as containing only 10 per cent. At first the manufacturer professed indignation at this result, but afterwards admitted that he had purposely "faked" the jam to see whether it could be detected. He stated that he had added 12 per cent. of raspberries. The result reported was arrived at after a consideration of the figures for constituents other than that for insoluble matter, particularly the acid figure, in conjunction with a microscopical examination. It must be recognised, however, that it was possible to make a report of this sort for commercial purposes, when a Public Analyst might naturally hesitate to do so. He was not quite sure that the authors fully realised the Analyst's position in this respect.

Mr. Hinton's paper described another very useful method. Like all other methods proposed, it could not, by itself, give the true fruit-content of a jam. It was, however, another tool which did help, especially with jams made from a mixture of fruits containing different acids.

Mr. A. L. BACHARACH said that he would like to add his tribute to the ingenuity of the calculations. During the last few years he had become increasingly impressed by the practical value of statistical methods. Mr. Hughes and Miss Maunsell that evening had done one extremely useful thing (among others) by showing that, in fact, these methods could be employed to give certain figures and results that were perfectly intelligible, and gave one the only really sound basis for the control of many manufacturing processes.

Miss MAUNSELL, replying to Mr. Rendle, said that the apricots referred to in the tables were fresh fruit, except in Table VII, where canned apricots provided the data for an example of calculation. For all fruits, the analyses of many varieties were included, and the non-sugar solids figures for each kind of fruit fell into the statistical distribution calculated. The fruit was obtained from England, Scotland, Holland, Germany, Belgium, France, Italy, and (in the case of apricots) Spain. South African apricots also contained non-sugar solids in agreement with the figure for English and Spanish fruit. The same applied to South African and American apples and pears. With regard to the question about varieties of raspberries, and whether they varied according to district, "Lloyd George" raspberries had been selected to illustrate the difference between those grown in England and those grown in Scotland. Different varieties of this fruit did not vary very much; one obtained, possibly, high results for one season, but all the varieties would give high results for that district. All varieties of raspberries fell within the limits given, and so varieties could not be differentiated by chemical analysis. The pamphlet mentioned by Mr. Grinling was of interest, but the results were based on physical data; it might be helpful to use both sets of figures.

As to limits of accuracy: in Table IX the calculated composition of the jam was given, as well as the actual analysis, and it would be seen there that the greatest difference in non-sugar solids was 0·1 per cent., *viz.* non-sugar solids, 3·9 per cent. calculated and 3·8 per cent by analysis.

Mr. HINTON, replying, said that the citric or tartaric acid used in extracting pectin had no appreciable disturbing effect. He did not think that, bearing in mind the small amounts used, the amounts of acid would fall outside the range of natural variations in the fruits. Mr. Young mentioned the possibility of disturbance by sulphites. Sulphite was quite easily dealt with by boiling the sulphur dioxide off. If oxidised, it might cause a small amount of lead precipitation; but if much sulphate had been formed, the effect on the p_H value would be so enormous that the sample would be detected as abnormal at once. Dr. Lampitt had mentioned traces of other acids. They had never found them to occur in sufficiently large quantities to disturb the results. In any case, any traces of unusual acids fell into one of the three groups shown.

The Separation and the Determination of Traces of Lead in the Presence of Traces of Bismuth

Part II. Organic Compounds

By J. HUBERT HAMENCE, M.Sc., A.I.C.

In a previous paper (Analyst, 1933, **58**, 461) a method for the colorimetric determination of traces of lead in the presence of traces of bismuth was described. This method, however, is not applicable to compounds with organic acid radicles such as tartrates, which would inhibit the precipitation of the ferric hydroxide by ammonia. A slightly modified method has now been devised which is suitable for such compounds, and which may also be employed to determine the lead in phosphates and in the solution obtained after the destruction of organic compounds by wet oxidation, when traces of bismuth are also present.

Co-precipitation of Lead and Ferrous Sulphides.—When hydrogen sulphide is passed through a solution containing ferrous ammonium citrate and traces of a lead salt, made alkaline to a p_H of 8 by the addition of ammonia, the lead is quantitatively precipitated with ferrous sulphide. The colloidal lead sulphide with which we are familiar in the lead test, and which is often so difficult to coagulate, is carried down with the ferrous sulphide.

The mixed sulphides are filtered off, washed, dissolved in dilute nitric acid, and the iron is separated from the lead by the thiocyanate process (Hamence, Analyst, 1932, **57**, 622). The efficacy of this method for the separation and determination of lead was tested in the following manner:

Five grms. of the compound to be tested were dissolved in about 20 ml. of water, 10 mgrms. of crystalline ferrous sulphate and 1 grm. of lead-free citric acid were then added; when solution was complete, ammonia was introduced until the p_H was about 8, two drops of universal indicator being added to the solution in order to ascertain this, and then hydrogen sulphide was passed into the liquid for 15 minutes. The precipitate was filtered off and washed with saturated hydrogen sulphide water made just alkaline with ammonia. This precipitate was dissolved in dilute nitric acid, and the iron was separated by the thiocyanate process.

The following results were obtained with lead-free compounds to which known amounts of lead had been added:

Compound	Lead added Mgrms.	Lead found Mgrms.
Citric acid	0·20	0·20
Rochelle salt ..	0·20	0·21
Sodium acetate ..	0·05	0·06
Sodium phosphate ..	0·15	0·15

Separation of Bismuth and Lead.—This method of separation by the co-precipitation of the lead as sulphide with ferrous sulphide provides a process

by which lead and bismuth may be precipitated from a solution containing organic acid radicles and phosphates; then, having been separated from the large quantities of interfering salts, they may themselves be separated by the pyridine thiocyanate process.

METHOD.—Five or 10 grms. of the compound, 10 mgrms. of ferrous sulphate, and 1 grm. of citric acid, are dissolved in about 25 ml. of water, ammonia is added until the p_H is 8, and hydrogen sulphide is passed into the liquid for 15 minutes. The solution is filtered through a small (No. 31) Whatman paper, and the precipitate is washed well with hydrogen sulphide water made just alkaline with ammonia; it is important that the precipitate should be washed free from citrates. The filter paper and the precipitate are then boiled with 25 ml. of water and 0·6 ml. of concentrated nitric acid. When the sulphides have completely dissolved (which is indicated by the absence of the black sulphide colour) the solution is filtered through the original filter and washed with water. No trouble has been experienced through the separation of sulphur. The filtrate and washings (which should amount to 30 ml.) are then transferred to a separator, and 2 ml. of saturated ammonium thiocyanate solution are added. Pyridine is added until a turbidity is produced, the red thiocyanate colour not being completely bleached (0·9 ml. to 1·0 ml. should be required), and the solution is extracted twice with a mixture of 15 ml. of ether and 15 ml. of amyl alcohol. The aqueous layer is then filtered, the filter-paper being washed once with water and the lead in the filtrate being determined colorimetrically by the sulphide method.

The following results were obtained with 5-grm. portions of different compounds to which known amounts of bismuth and lead had been added:

Compound	Lead added Mgrms.	Bismuth added Mgrms.	Lead found Mgrms.
Rochelle salt ..	0·05	1·0	0·055
Sodium phosphate	0·30	2·0	0·27
Sodium acetate ..	0·10	1·5	0·10
Tartaric acid ..	0·40	0·50	0·38

VISCERA AND ORGANIC COMPOUNDS.—The organic matter is destroyed by the wet oxidation method, nitric acid being added, drop by drop, until the sulphuric acid in the Kjeldahl flask is completely colourless. When all the nitrous fumes have been driven off, the solution is allowed to cool and 20 ml. of water are added; the flask is heated again until white fumes of sulphuric acid are visible. When cold, the contents of the flask are diluted with a small quantity of water and poured into a beaker. The flask is then boiled out twice with 10 ml. of 20 per cent. ammonium acetate solution, and finally washed out with a little water. Two grms. of lead-free citric acid and 10 mgrms. of ferrous sulphate are added to the sulphuric acid solution and washings from the flask, the mixture is heated until any undissolved calcium sulphate has dissolved, and the p_H is adjusted to 8. The process is then continued as described in the previous section. In some cases it may be necessary to add more citric acid in order to dissolve all the calcium phosphate.

The following table shows the results obtained by this process:

Substance	Lead added Mgrms.	Bismuth added Mgrms.	Lead found Mgrms.
Ox-liver, 25 grms. ..	Nil.	Nil.	0·01
Ox-liver, 25 grms. ..	0·05	10·0	0·06
Ox-liver, 25 grms. ..	0·50	0·5	0·45
Ox-kidney, 25 grms. ..	0·40	0·5	0·35
Sardines, 10 grms. ..	—	—	0·07
Sardines, 10 grms. ..	—	5·0	0·065

The lead in the first sardine experiment was determined by a dilute sulphuric acid and alcohol precipitation method, after wet oxidation of the organic matter. Bismuth nitrate was added to another portion, and the lead in the mixture was determined by the method previously described.

Since the publication of the first paper on the separation of lead and bismuth, the method has been tested with larger amounts of bismuth than had been used before. Some of the results obtained are given below:

	Lead added Mgrms.	Bismuth added Mgrms.	Lead found Mgrms.
Calcium chloride, 5 grms. ..	0·25	5·0	0·22
Calcium chloride, 5 grms. ..	0·08	10·0	0·06

Two extractions with the amyl alcohol and ether mixture were made in each case.

When larger quantities of bismuth, such as these, are added, the greater part of the bismuth is precipitated as an insoluble basic bismuth thiocyanate. This remains in the interface between the ethereal layer and the aqueous layer after extraction, and any traces remaining in the aqueous layer are removed when the solution is filtered.

The following results were obtained by treating a solution containing traces of lead and bismuth with ammonium thiocyanate and pyridine, and filtering off the bismuth compound:

To 30 ml. of a neutral solution of lead and bismuth nitrates were added 0·5 ml. of concentrated nitric acid and 2 ml. of saturated ammonium thiocyanate solution. One ml. of pyridine was then added and, after standing for some minutes, the solution was filtered and the precipitate washed once with water. The lead in the filtrate was determined by the sulphide method.

Lead added Mgrms.	Bismuth added Mgrms.	Lead found Mgrms.
Nil.	5·0	Less than 0·01
0·05	5·0	0·05
0·20	5·0	0·19

I wish to thank Dr. A. M. Ward for his helpful advice and criticism during this investigation.

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Notes

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

THE EXTRACTION OF QUININE

IN a case recently heard in Birmingham (ANALYST, 1934, 174) it was contended that if ether were used for extracting the quinine from a solution of quinine sulphate, the weight of the residue of anhydrous quinine left on evaporation of the extract would be too high after being dried at 100° C., whereas correct results would be obtained if chloroform were used for the extraction.

To test this statement I weighed out two portions of 0·120 grm. each of anhydrous quinine sulphate (obtained by drying the B.P. salt at 100° C. until constant in weight), and dissolved each of these in 50 ml. of slightly acidulated water. One portion was rendered alkaline with ammonia and extracted four times with chloroform, and the other was similarly extracted with ether. The residue from each extraction was dried at 100° C. and weighed, then placed in the steam-oven for another two hours and again weighed. There was no further loss in weight. The actual weight of anhydrous quinine, both from the ether and chloroform extractions, was 0·104 grm.

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THE DETERMINATION OF QUININE

IN the report of a case on the dispensing of quinine sulphate given in the Legal Notes of the last issue (ANALYST, 1934, 173) it is contended that high results are obtained when quinine is determined by extraction with ether. The residue is stated to contain water which is difficult to drive off at 100° C., but that extraction with chloroform yields anhydrous quinine.

On more than one occasion we have shown that identical results are obtained by extraction of quinine with ether and with chloroform, and that after the residues have been dried at 100° C. no loss in weight occurs on further drying at 125° C. It may also be mentioned that with several preparations the British Pharmacopoeia directs ether to be employed for the extraction of quinine and the residue to be dried at 100° C. In the case of quinine tannate it states "evaporate the mixed ethereal solutions, dry the residue at 100°, and weigh the anhydrous quinine."

In order again to check the point, a re-examination has been made of the sample referred here in connection with the case in question. Chloroform was used to extract the quinine, and the amount found was 0·21 grm. per 100 ml., an identical result with that obtained when ether was used for the extraction.

The alkaloid extracted by ether in the original analysis was checked against a standard sample of quinine by comparing the fluorescences of dilute sulphuric acid solutions under the mercury lamp. The purity of the extracted quinine was thus established.

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NOTE ON THE DETERMINATION OF ALUMINIUM IN NICKEL ALLOYS

In a recent issue of The Analyst (**1934, 16**), Nickolls has described a method for the separation and determination of aluminium in magnesium alloys.

The aluminium and iron, together with comparatively large amounts of manganese, zinc, or nickel, are separated from the magnesium by the addition of sodium sulphide. From the solution of this precipitate the aluminium, iron, and manganese are precipitated with ammonia, and the nickel and zinc are determined in the filtrate.

For the analysis of nickel alloys containing moderately small amounts of aluminium I have not found this method of separating aluminium from nickel, etc., to be satisfactory.

Blum (*Sci. Papers*, No. 286, Bureau of Standards) has stated that aluminium cannot be satisfactorily separated from nickel, zinc, cobalt and manganese by precipitation with ammonia and ammonium chloride, owing to co-precipitation of the hydroxides of these metals at the p_H value most suitable for aluminium.

Lundell and Knowles (*J. Amer. Chem. Soc.*, **1923, 45**, 676) state that, by following Blum's directions, moderate amounts of manganese and nickel can be separated equally well by precipitation with ammonia and ammonium chloride as by the basic acetate process, but they find that the method breaks down in the case of manganese if phosphorus and vanadium are present, and that the separation of aluminium from zinc, copper, and cobalt is incomplete.

Kling and Lassieur (*Compt. rend.*, **1924, 178**, 1551) found that, in the basic acetate process, aluminium could be precipitated completely at p_H 5·2, zinc and manganese at p_H 6·0 and 6·5, respectively, and that complete separation of aluminium from these elements is possible at p_H 5·2. Although nickel does not precipitate until p_H 6·1 is reached, yet no satisfactory separation from aluminium could be obtained.

In the case of the nickel aluminium alloy mentioned above, the amount of nickel was large compared with that of aluminium. The basic acetate method was found less effective than the ammonia and ammonium chloride separation. With this, a reasonably complete separation of the aluminium could rarely be achieved in less than three precipitations, and the ignited precipitate of alumina was frequently slightly coloured.

The following method has been found to give a satisfactory separation with one precipitation only:—To the cool, weakly acid solution of the nickel alloy, a strong solution of potassium cyanide is added until the precipitate at first formed re-dissolves, to form potassium nickelocyanide, $K_2Ni(CN)_4$. The solution is then poured slowly, and with constant stirring, into an excess of ammonia. The precipitated aluminium hydroxide is allowed to settle and is then filtered off, washed with 2 per cent. ammonium nitrate solution, dried, ignited and weighed. The precipitate obtained in this way is invariably white.

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NOTE ON THE DETERMINATION OF SULPHUR IN ALLOY STEELS

Evolution methods which depend on the solution of a sample of steel in hydrochloric acid and the absorption of the hydrogen sulphide formed in a suitable medium are usually not applicable to alloy steels. Gravimetric methods are generally long and tedious and not suitable for routine tests. A combustion method affords a rapid and convenient means for the determination.

The method described by Holthaus (*Stahl u. Eisen*, 1924, **44**, 1514) consists in the combustion of the sample in a stream of oxygen, absorption of the oxides of sulphur produced in a measured volume of a standard solution of sodium hydroxide containing hydrogen peroxide, and titration of the excess of alkali with a standard solution of sulphuric acid, sodium alizarin sulphonate being used as indicator.

This method necessitates very rapid combustion of the sample (2 grms. in about 1 minute) at a temperature of about 1200° C. Wear and tear on the combustion tube is, therefore, very considerable, especially as the molten oxide of iron sometimes penetrates through the boat and adheres to the walls of the tube. Considerable spurting of oxide also occurs during the combustion period. In order to minimise the deleterious effects of the oxide, a layer of alundum powder was placed in the combustion zone of the tube and in the bottom of the boat underneath the sample. This procedure certainly increased the life of the tube, but low results were obtained whenever alundum was used in this manner. It was also noticed that when the combustion tube was slightly tilted the boat was frequently perforated by the molten oxide. Maintaining the tube in a horizontal position lessened this effect very considerably. Morgan combustion tubes and boats of a similar composition were found to be fairly resistant to the attack of the molten oxide.

Another difficulty in the Holthaus method is the detection of the end-point. The colour change is very sensitive, and much experience is necessary to obtain consistent results. The weight of sample that can be used in a determination is limited, and this means that the titration must be carried out very carefully. The use of an incandescent lamp screened by means of an opalescent glass plate is recommended by Holthaus for the titration. The use of a lamp of the daylight type (tinted blue) is a decided improvement.

No.	Sample Type	Sulphur	
		Combustion Method Per Cent.	Gravimetric Method Per Cent.
1	Standard Steel ..	0·028	0·027
2	Cr 18, Ni 8, W 1 ..	0·016	0·016
3	,, ..	0·016	0·018
4	,, ..	0·017	0·015
5	,, ..	0·020	0·017
6	,, ..	0·018	0·015
7	,, ..	0·020	0·021
8	,, ..	0·021	0·024
9	Cr 1, Mo 0·5	0·033	0·032
10	Cr 18, Ni 8	0·016	0·015
11	,, ...	0·018	0·019
12	,, ...	0·016	0·019

The employment of glass wool as a filter for retaining iron oxide carried over during the combustion requires caution, as glass wool is frequently alkaline and absorbs sulphur dioxide from the gas stream before it reaches the absorption vessel. Iron oxide fume is usually produced when the combustion takes place under pressure, the pressure being due to the smallness of the jet in the absorption vessel. If the size of the jet is so adjusted that very rapid combustion can be obtained without the undue accumulation of pressure in the apparatus, the amount of iron oxide fume produced is negligible, and a glass wool filter is, therefore, not necessary. Also the accumulation of pressure in the apparatus during combustion usually results in low values for the percentage of sulphur.

A temperature of 1150° C. appears to be ample for the combustion of ordinary carbon steels, but for chrome-nickel steels of the 18·8 type a temperature of 1350° C. is necessary. There is no advantage in using too high a temperature. The rate of combustion, however, is very important; the sample should be burnt as rapidly as possible.

The results of sulphur determinations on a number of steels by the combustion method and by a gravimetric method are given in the subjoined table. Some experience and considerable care are required in order to realise, in practice, the accuracy claimed for this method.

I wish to thank Messrs. Stapleton, King and Jenkins who carried out the experimental work.

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THE INVESTIGATION OF ATMOSPHERIC POLLUTION

REPORT AND OBSERVATIONS IN THE YEAR ENDING MARCH 31, 1933*

THE present publication is the 19th of the series, and consists of the Report of the Standing Conference to the Co-operative Bodies for the Year 1932 to 1933, p. 1–3; the Report of the Atmospheric Pollution Research Committee for the year, p. 4–7; the Report of the Superintendent of Observations, p. 8–45; Appendices I and II; and the General Deposit Tables, p. 51–99.

SULPHUR GASES IN AIR.—Regular observations of sulphur dioxide concentration by the "lead peroxide" method, developed by the Building Research Station of the Department (ANALYST, 1933, **58**, 284), have been extended to 22 stations, and the close correspondence of readings obtained with 2 cylinders placed close together shows the reliability of the procedure. The method is still in the experimental stage, but seems likely to be a valuable supplement to the volumetric method.

PHOTO-ELECTRIC METHOD OF MEASURING OPTICAL INTENSITY OF SMOKE ISSUING FROM A CHIMNEY.—Existing methods of estimating smoke pollution are based on eye observations only, or eye observations aided by the Ringelmann chart or a similar standard of comparison. An apparatus is now being developed which uses a photo-electric cell so arranged as to measure the amount of light received from a definite area of the smoke, as compared with that from an equal area of sky. The light from the smoke consists of both transmitted and reflected light, and this modifies the direct relationship between measured "optical density" and pollution in the case of dense smokes. To minimise the errors likely to arise from the reflected light, which varies with different types of smoke and under different conditions of illumination, an ultra-violet filter may be used with the apparatus, but, even so, it is necessary to determine the general form of the relation between apparent brightness of the smoke and the amount of pollution. Further, allowance should be made for the effect of light scattered by the air between the smoke and the instrument by making observations not only on the sky and the smoke trail, but also on the tops of the chimneys. During the preliminary work with the apparatus the smoke under observation was classified by eye into one of

* Published 15th February, 1934, pp. 99. Obtainable at Adastral House, Kingsway, W.C.2. Price 5s. net.

the six classes very light, light, light medium, medium, medium excessive, and excessive, and analysis of the readings recorded showed that there is a well-defined reading for each class of smoke, so that the instrument may be used to determine when the chimney smoke is of a greater density than the prescribed limit. It is hoped soon to be able to make the instrument the basis of rough measurements of the relative total amounts of pollution emitted by the chimney in a given period.

JET DUST COUNTER.—It is now established that this apparatus provides a satisfactory measure of the number of insoluble particles usually present in the air.

DAYLIGHT MEASUREMENT.—Daylight estimations by the potassium iodide method have been made throughout the year at two stations at Halifax, and it was found that the more heavily polluted of the two stations lost, in 1931 to 1932, as much as 20 per cent. of sunlight as recorded by the amount of iodine liberated, and in 1932 to 1933, 17 per cent., the proportionate loss being much greater in winter than summer. The corresponding figures for deposited impurity at the two stations were for 1931 to 1932, 281 and 133 tons per sq. mile, respectively, and for 1932 to 1933, 297 and 121 tons. A similar series of figures was obtained at Salford, but more figures are needed for other places.

RECORD OF OBSERVATIONS.—The total number of deposit gauges in use throughout the year was 91, together with 3 automatic filters. The maximum and minimum monthly deposits, as metric tons per sq. km. (conversion tables are given, and the figures also tabulated as English units) were: *Tar:* London (South Kensington), 147; Salford (Ladywell Sanatorium), 19; *Other insoluble carbonaceous matter:* Edinburgh, (Princes Street), 130; Marple, 32; *Insoluble ash:* Edinburgh (Princes Street), 145; Salford (Ladywell Sanatorium), 62; *Ash of soluble matter:* London (Ravenscourt Park), 154; Rochdale (Town Hall), 58; *Total solids:* Birmingham (West Heath), 144; Marple, 64; *Rainfall:* Leicester (Western Park), 129; Rochdale (Town Hall), 75. The recorded figures show that although, on the whole, improvement has continued, in that there was a decrease of 11 per cent. in the average total solids, this improvement has not been so great as in the last 2 years (20 and 24 per cent., respectively). Sulphate deposits have markedly decreased during the year, but the increase during the last 2 years at Ravenscourt Park has again been maintained. Attention is called to the unique distribution of suspended impurity at Cardiff, where some unusually heavy output occurs about 2 or 3 p.m. Cardiff is also remarkably free from sulphur pollution, and throughout the year there was not a single observation with over 0·2 part per million.

APPENDIX I deals with the sunlight and ultra-violet light measurements at Salford, and gives a description of Dr. Ashworth's method (ANALYST, 1933, **58**, 690).

APPENDIX II discusses atmospheric corrosion as related to atmospheric pollution. The effects of minute quantities of polluting substances on metals are sometimes represented by preponderating amounts of sulphates or basic sulphates in the final products. Thus, the green patina on copper after prolonged exposure to the air has been shown to consist essentially of basic copper sulphate, not basic copper carbonate, as it was previously assumed to be. Any effect due to large amounts of carbon dioxide has been shown to be quite undetectable in the presence of excessively smaller concentrations of sulphur dioxide.

D. G. H.

REPORT OF THE WATER POLLUTION RESEARCH BOARD

FOR THE YEAR ENDED 30TH JUNE, 1933*

THIS is the Sixth Annual Report of the proceedings of the Water Pollution Board, and there is an accompanying Report of the Director of Water Pollution Research (Dr. H. T. Calvert).

WATER-BORNE DISEASE.—The need for even greater vigilance than in recent years is occasionally emphasised by outbreaks of water-borne disease, such as the outbreaks of enteric fever at Malton and at Denby Dale, in 1932, and the outbreak of paratyphoid in Epping during 1931. Part of the Epping sewage effluent discharges into Cobbin's Brook, which enters the River Lea above the Metropolitan Water Board's intake from that river. Samples of the sewage effluent still contained paratyphoid bacilli at the end of June, 1933. Disinfection of Cobbin's Brook by means of chlorine was begun in February, 1931, and has since been continued. After chlorination the water does not contain *B. coli* in 100 ml., or paratyphoid bacilli in 500 ml. In addition the filtered water from the waterworks has been disinfected by treatment with ammonia and chlorine, and for a short period the River Lea was not used for the supply.

BEET SUGAR EFFLUENTS.—The investigations described in the last Annual Report (ANALYST, 1933, **58**, 282) have been continued. Several hundred strains of bacteria were isolated from the percolating filters at the factory at Colwick, and have now been examined in Rothamsted Laboratories. From the results of the examination it appears, that, in general, those species of bacteria most active with carbohydrates also most readily attack the salts of organic acids. In experiments on the effect of adding phosphate to solutions of sucrose prior to treatment on the percolating filters, it was found that active biological films were deposited on the filtering media, and that under certain conditions the biochemical oxygen demand of the treated effluent was less than 2 per cent. of that of the original solution.

MILK FACTORY EFFLUENTS.—Experiments at Rothamsted have shown that milk diluted with water to contain 1·3 per cent. of milk can be readily oxidised biologically by filtration through gravel at the rate of 100 galls. per day per cb. yard of filtering medium. To prevent clogging of the filters, the effluent must be treated in two stages (*cf.* Richards and Cutler, *Water Pollution Research Technical Paper*, No. 3, 1933).

BIOLOGICAL OXIDATION OF CELLULOSE.—Experiments showed that aqueous suspensions of cellulose in the form of wood pulp are hardly oxidised by the activated sludge process, but with percolating filters about 70 per cent. of the cellulose is oxidised in a suspension of 50 parts per 100,000 by filtration at the rate of 100 galls. per day per cb. yard of filtering material.

SURVEY OF THE RIVER TEES.—The comprehensive scientific survey of the River Tees has been completed, and will shortly be published in a final report. The factors influencing the self-purification of the river from *sewage* pollution have been systematically studied. Of these factors, temperature is the most important, the rate of self-purification increasing rapidly as the temperature is raised from 10° to 20° C. A survey of the comparatively unpolluted Estuary of the River Tay has been made, and the results have been compared with those for the River Tees.

METHYLENE BLUE TEST FOR STABILITY OF SEWAGE.—As a result of the various experiments the following method of testing a sewage or sewage effluent with methylene blue has been proposed. Two Thunberg tubes are each supplied with

* H.M. Stationery Office, Kingsway, London, W.C.2. 1934. Price 1s. net.

the same quantities of a washed sewage sludge, a hydrogen donator such as formate, 1 ml. of a 0·02 per cent. solution of methylene blue, and buffer solution of a p_H value of 7·4. To one of the tubes, 3 or 4 ml. of the sewage to be examined are added, and a similar volume of water is added to the second tube to serve as a control. The tubes are then evacuated and incubated at 45° C. In the control the methylene blue is usually decolorised in less than an hour. If the sample under examination in the other tube is crude domestic sewage, the time required for reduction of the methylene blue is usually rather less than with the control, whereas it is much greater with samples of a well-purified sewage effluent. Examples of the results obtained with crude sewage and treated sewage from three purification works are given in tables.

BASE-EXCHANGE PROCESS OF WATER SOFTENING.—A new type of apparatus has been devised for examining the softening powers of various base-exchange materials for water containing varying amounts of different salts of calcium and magnesium.

PLUMBO-SOLVENT WATERS.—The summary of existing knowledge on this subject has been revised and enlarged and is to be published as *Water Pollution Research Technical Paper*, No. 4. Preliminary experiments on the possibility of contamination of water by lead through the leakage of electric current through service pipes have indicated that, unless the leakage of current is exceptionally large, appreciable increase in the quantity of lead in the water is unlikely.

COLLOIDS OF SEWAGE AND BEET SUGAR EFFLUENTS.—An account is given of the further investigations carried out at University College, London, under the direction of Professor Donnan. Samples of sewage from the Birmingham area and of effluent from the beet sugar factory at Colwick have been examined by ultra-filtration, gravity sedimentation and centrifuging at different speeds. A beginning has also been made in a study of the electrical properties of sewage colloids.

Hong-Kong

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1932

MR. V. C. BRANSON, the Government Analyst, refers in his report to the great loss suffered by the Department by the death of his predecessor, Mr. E. R. Dovey.

The number of analyses made during the year was 2706, as compared with 2720 in 1931.

FORENSIC CHEMISTRY.—Of the 146 examinations made, 115 were in connection with toxicological work, arising out of 91 cases. No poison was found in 54 cases, opium was found in 21, adalin in 3, alcohol in 2, lysol in 2, veronal in 2, barbituric acid in 2, and potassium cyanide, hydrochloric acid, morphine, formaldehyde and mercury in 1 case each.

Poisonous Sweets.—Several children showed symptoms of poisoning after eating sweetmeats made locally. It was ascertained that an excess of synthetic essences had been used, and that the wrapping paper contained aniline dyestuffs which had contaminated the sweets.

FOOD AND DRUGS.—Of the 268 samples examined, 56 consisted of milk, 27 of bread, 13 of butter, and 6 of tea. The only samples found to be adulterated were 3 of milk and 1 of tea, which contained exhausted leaves. There is no doubt that the number of samples normally submitted for examination is very much too low, considering the population of the Colony. The reason for the low figures

is due, possibly, to the state of the Regulations covering the sale of Food and Drugs. There is at present only one standard for foodstuffs laid down, *i.e.* that for fresh milk. Draft definitions or standards for the most important foodstuffs were submitted by the late Mr. E. R. Dovey in August, 1927, and embodied in a new Food and Drug Bill printed in November, 1930. Until this Bill becomes law, the present unsatisfactory state of affairs will remain.

COLOURING OF PETROL.—At the end of the year an investigation was carried out for the Roads Department, to ascertain whether it would be possible to colour petrol, issued to Government lorries, so that unauthorised use of this petrol could be detected. The best concentration of a suitable dye was found, and a trial is to be made during the early part of 1933.

United States Pharmacopoeia Vitamin Standards*

THERE being only a limited amount of the International Vitamin *A* and *D* Standards available, the U.S.P. Vitamin Advisory Board undertook the preparation of a sufficient quantity of a cod-liver oil of known vitamin potency to be used as the basis for the standardisation of American medicines and foods claiming "A" or "D" vitamin potency. The Vitamin Board secured the co-operation of the Bureau of Fisheries at Washington—who supplied a sufficient quantity of authentic cod-liver oil collected and de-stearinated under the supervision of the Government Laboratory in Gloucester, Massachusetts. This oil was immediately placed in 30-ml. amber-colour glass containers under rigid conditions involving the drying of the container and oil, the exclusion of all air by the use of a vacuum, the introduction of carbon dioxide, and hermetic sealing of the containers. The containers of oil were placed immediately in cold storage below 15° C. The Board then arranged with seventeen vitamin laboratories to assay this bottled oil, following exactly the assay methods adopted by the large vitamin committee. All laboratories reported only by code number, the Chairman of the Board alone holding the key.

Fifteen of the seventeen laboratories have already reported, and the other two have the assays in hand. The Vitamin Board has painstakingly studied and evaluated the reports and has recommended the following standards for the official cod-liver oil:—

Minimum Standard for Vitamin A for U.S.P. Cod-liver Oil.—The minimum Vitamin *A* standard for U.S.P. Cod-liver Oil shall be not less than 600 International Units.

Minimum Standard for Vitamin D for U.S.P. Cod-liver Oil.—The minimum Vitamin *D* standard for U.S.P. Cod-liver oil shall be not less than 85 International Units.

Note.—The new "U.S.P. Vitamin Units" and "U.S.P. Vitamin D Units" are identical with the corresponding "International Units." In expressing on labels the potency of vitamin-containing products, it is recommended that the term "U.S.P. Vitamin *A* Units" or "U.S.P. Vitamin *D* Units" be employed. To indicate the adoption of the *new* standards the statement "U.S.P. X—Revised 1934" may be used.

RELATIONSHIP OF VITAMIN UNITS.—For the benefit of manufacturers or others who wish to know the approximate relationship between units they are now using and International Units of vitamins *A* and *D*, the following information is provided:—

One U.S.P. X Sherman or A.D.M.A. unit of vitamin *A* equals 1·4 International or new U.S.P. Units.

One Steenbock Unit of vitamin *D* equals 2·7 International or new U.S.P. units.

One International or U.S.P. unit of Vitamin *D* equals 3·25 A.D.M.A. units.

The U.S.P. Board of Trustees has also announced the release of the "Reference Cod-liver Oil," prepared under the supervision of the Vitamin Board, for use in the standardisation of medicinal or food products claiming vitamin potency, and already many laboratories in the United States have secured this official vitamin standard. These new U.S.P. Standards of vitamins *A* and *D* will be the basis for the evaluation by the Food and Drug Administration of all products in U.S.A. claiming vitamin *A* or *D* potency.

* *Amer. J. Pharm.*, 1933, **105**, 583–587.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Colouring Matter in American Red and Purple Tomatoes. M. B. Matlack and C. E. Sando. (*J. Biol. Chem.*, 1934, **104**, 407–414.)—Previous work by various investigators on the red pigment "lycopene" of the tomato (*Lycopersicum esculentum*) is briefly summarised. Most of the work was carried out on the pigment from Italian-grown varieties. These tomatoes are smooth, plum-shaped, approximately three inches long and one inch in diameter, have firm flesh and practically no core, and usually have a more brilliant and more uniformly distributed red colour than the average tomato grown in the United States. American-grown tomatoes are large and globular, and generally more juicy. In America, two distinct types of red tomatoes are recognised. One type is carmine-red with a purplish cast. Tomatoes of this type are characterised by purplish-red flesh and transparent skin, and are sometimes described as purple tomatoes. Typical examples are Livingston Globe and Cooper Special. In the second type the colour approaches scarlet-red. These tomatoes are characterised by purplish-red flesh and yellow pigmented skin, which points together cause the colour to appear more nearly true red. The Stone, Indiana Baltimore and Santa Clara Canner are examples of this type. It was decided to isolate and study the pigment from American red and purple tomatoes, and to determine whether it is identical with that isolated from Italian varieties. The results of such an investigation would definitely answer the question often raised by canners as to whether the pigments are the same in American red and purple varieties. Four varieties of tomatoes were used, namely Fiaschetti (Italian-grown red), Indiana Baltimore (American-grown red), Santa Clara Canner (American-grown red) and Cooper Special (American-grown purple). The method employed for the isolation of the crude pigment was essentially that of Willstätter and Escher (*Z. physiol. Chem.*, 1910, **64**, 47). It was found that the pigment obtained from the American-grown red and purple varieties was identical with lycopene isolated from the Italian variety (Fiaschetti). P. H. P.

Further Observations on Factors which influence the Component Fatty Acids of Butter. H. K. Dean and T. P. Hilditch. (*Biochem. J.*, 1933, **27**, 889–897, *cf.* ANALYST, 1930, **55**, 702.)—Further work has now been carried out on the butter-fats from milks of various cows (in many cases the same cows as were used previously) belonging to the typical herd of the National Institute for Research in Dairying, Shinfield. The samples represented the period 1928 to 1932, and the data now presented, taken in conjunction with the earlier work, afford means for detecting two characteristic changes in the composition of the fatty acids. The first is the seasonal change occurring when the cows return to pasture; and the second, which appears to be a function of the age of the cow, consists in a gradual augmentation in the proportion of unsaturated components of the fat. The facts that the analyses cover four seasons, and are concerned chiefly

with the same cows throughout, enable safe conclusions to be drawn. The seasonal change consists in an abrupt and relatively immediate increase in the proportion of oleic and linolenic acids, with a simultaneous decrease shared almost wholly by the butyric and stearic acids. The same change has been observed in each of the four seasons involved, and the increase in unsaturated acids amounts to 4 per cent. (mols.) and takes place within 2 to 3 weeks, or even less, after the cows are put out to grass. In addition to the abrupt seasonal rise in iodine values, there is a definite tendency for the iodine values of the pasture milk fats to rise throughout the series, and this increase is probably a function of the age of the cow. Whilst the Reichert-Meissl values tend to vary inversely with the iodine values, the alteration is not so regular or abrupt. In studying the gradual augmentation of C_{18} acids, in the progressive analyses of milk fat from a given cow with the corresponding diminution of palmitic acids, seasonal factors were eliminated, so far as possible, the comparison being based on the fats from pasture-fed animals of the seasons 1928 to 1932, and the conclusion is arrived at that the increase corresponds with the increasing age of the cow. It is suggested that a similar range of variation observed by Banks and Hilditch (ANALYST, 1931, **56**, 816) for beef-tallows may be connected in the same way. D. G. H.

Body Fats of the Pig. III. Influence of Body Temperature on the Composition of Depôt Fats. H. K. Dean and T. P. Hilditch. (*Biochem. J.*, 1933, **27**, 1950–1956.)—In order to ascertain whether the respective layers of fat in the pig on either side of the "streak" are homogeneous, or whether there is a progressive alteration as the skin is approached, the central portion of the whole of the back fatty tissue from a very fat sow was divided into five layers of approximately equal thickness, two from the "outer" portion between skin and streak, and three from the inner portion beneath the "streak." The fat was extracted by means of acetone, and the component acids present were determined as in previous studies (ANALYST, 1932, **57**, 531). Unsaturated acids of lower molecular weight than oleic acid were specially looked for in the fat of the Inner III sample, but, if present, they were estimated to be less than 1 per cent. of the total fatty acids. The molar distribution of the individual acids was as follows:

Fat	Myristic	Palmitic	Stearic	Oleic	Linolic	C_{20-22} unsaturated
Outer I ..	3·1	25·6	9·8	45·0	14·8	1·7
Outer II ..	3·4	25·1	12·6	41·8	15·3	1·8
Inner I ..	3·5	26·6	14·0	41·4	13·6	0·9
Inner II ..	3·3	27·2	14·0	40·1	14·2	1·2
Inner III ..	3·6	26·2	14·0	41·6	13·4	1·2

The component acids of the three "inner" layers were thus almost identical, but the outermost contained slightly less palmitic and about 4 per cent. less stearic, and correspondingly more oleic acid. The detailed analytical figures confirm the conclusion of Henriques and Hansen (*Skand. Arch. Physiol.*, 1901, **11**, 151), that there is a close relationship between increase in saturation of the fat and increasing body-temperature. At the same time the greater part of the fat beneath the streak was evidently completely homogeneous. The high proportion of linolic acid and of 1 to 2 per cent. of highly unsaturated acids of the C_{22} and C_{22} series is

probably characteristic of pigs of considerable age, and not due to the diet (maize meal, thirds and whey). The statement that warm-blooded animals and plants of tropical origin produce more solid saturated fats than cold-blooded animals or plants from cooler regions, is shown to be only partly true. D. G. H.

Kernel Fats of Some Members of the Palmae. G. Collin. (*Biochem. J.*, 1933, **27**, 1366–1372.)—A quantitative estimation of the component fatty acids has been made for five more kernel fats of the *Palmae* order. In the case of *Acrocomia sclerocarpa* Mart, *Manicaria saccifera*, Gaertn, and *Astrocaryum Tucuma* Mart, the quantity of fat available was sufficient for the attainment of the normal standard of accuracy; for *Maximiliana caribaea* Griseb, and *Attalea excelsa* Mart, only a rough estimation of the component fatty acids was possible. In the first case a single fractionation only was possible, the general composition being deduced from the analytical constants of the primary fractions, and in the second case the primary fractionation was so controlled as to correspond closely in size of fraction and range of boiling-point with an average primary fractionation of a Palmae kernel fat, and, by comparison, a general idea of the composition was obtained. The methods of Collin and Hilditch (*J. Soc. Chem. Ind.*, 1928, **47**, 261T; ANALYST, 1929, **54**, 243; 1930, **55**, 291) were followed, except that special precaution was taken to guard against loss of low b.pt. esters during the vacuum distillation. In each case the general composition of the fatty acid mixture followed the usual arrangement found in the kernel-fats of this order.

	Acrocomia sclerocarpa Gru-gru	*Manicaria saccifera*	*Astrocaryum tucuma*	*Maximiliana caribaea* (immature nuts)	*Attalea excelsa*	*Coconut* refined (commercial sample)
Kernel, per cent. of nut ..	26·0	15·0	—	59·0	3·0	—
Kernel fat, per cent. ..	44·4	57·7	39·8	48·0	62·6	—
M.pt. of fat	24·0° C.	27·1° C.	30·3° C.	—	25·5° C.	—
Saponification equivalent ..	222·3	221·8	218·9	236·8	231·7	217·2
Iodine value	17·1	10·7	15·8	22·7	18·2	9·7
Unsaponifiable matter, per cent.	0·45	0·05	0·4	0·23	—	—
Acid value	0·6	0·6	1·8	20·2	—	0·3
Fully-saturated glycerides, per cent.	69·0	82·0	73·0	—	—	—
Mono-unsaturated di-saturated, per cent. mols.	21·0	11·0	18·0	—	—	—
Di-unsaturated mono-saturated, per cent. mols.	10·0	7·0	9·0	—	—	—
Caprylic acid, per cent. ..	11·5	7·8	1·9	—	broadly as	11·2
Capric acid ,, ..	6·9	8·0	5·6	6·0	*Acrocomia*	9·2
Lauric acid ,, ..	47·6	49·9	53·1	50·0	*sclerocarpa*	46·5
Myristic acid ,, ..	12·2	17·4	20·6	21·0	,,	16·5
Palmitic acid ,, ..	6·3	6·7	5·5	8·0	,,	7·7
Stearic acid ,, ..	1·8	1·8	1·3	?	,,	1·8
Oleic acid ,, ..	12·5	7·3	10·1	} 15	,,	6·0
Linolic ,, ..	1·2	1·1	1·9		,,	1·1
Association ratio	1·29 to 1	1·16 to 1	1·25 to 1	—	—	1·3 to 1·4 to 1

D. G. H.

Unsaturated Acid in the Kernel Fat of "Akarittom" (*Parinarium laurinum*.) II. M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, 1934, **36**, 673–675.)—A further study has been made of the acid isolated from akarittom fat (ANALYST, 1933, **58**, 351) and supposed to be an isomer of elaeostearic

acid. The fat obtained on this occasion had an iodine value (Wijs) of 193·6, as compared with the previously obtained value of 214·1. The new acid was prepared from the fat as before, and, when further refined, melted at 85–86° C. The chief product of decomposition on treating the acid by the ozone method was azelaic acid, with probably some azelaic semi-aldehyde. Oxidation by the permanganate method also yielded azelaic acid with an indication of sebacic acid, judging by the higher m.pt. of the latter fractions. It is now considered possible that the acid is identical with couepic acid, and the previously assigned provisional constitutional formula is withdrawn. D. G. H.

Fatty Oil of *Parinarium Macrophyllum* (Neou Oil). A. Steger and J. Van Loon. (*Rec. Trav. Chim. Pays-Bas.*, 1934, **53**, 197–204.)—The edible nuts of *Parinarium macrophylla* (N.O. *Rosaceae*) of average weight 14 grms., consisted of 91 per cent. of shell and 9 per cent. of kernel, the latter yielding, on extraction with petroleum spirit, 65·2 per cent. of a colourless, pleasant-smelling oil possessing the following characteristics: Sp. gr. at 78° /4°C., 0·8901; n_D^{70}, 1·4741; saponification value, 190·0; iodine value (Wijs) about 162; thiocyanogen value, 78·2; Reichert–Meissl value, 0·33; acid value 0·25; unsaponifiable matter 0·9 per cent.; saturated fatty acids (Bertram) 10·3 per cent.; unsaturated fatty acids 83·8 per cent.; glycerol (as C_3H_2) 4·3 per cent.; and volatile matter 1·6 per cent. The total fatty acids (94·1 per cent., of the oil) showed n_D^{70} 1·4651; a true iodine value of 169·3; acid value 200·2; and mean molecular weight 280·2. The true iodine value of the oil cannot be found by the usual Wijs procedure, and the oil somewhat resembles tung oil and oiticica oil in this respect. Complete saturation with halogen takes a long time, and unsaturation cannot be determined by hydrogenation, since the more unsaturated acids undergo slight polymerisation very rapidly, and this lowers the power of taking up hydrogen. The unsaturation of the oil, as expressed by the iodine value over a period of 168 hours, is 162·3 and partial unsaturation (by means of thiocyanogen solution) is taken as 134. The unsaturated fatty acids were examined by re-crystallisation, bromination, separation by Twitchell's method, elaidinisation, ozonisation, and oxidation with alkaline permanganate solution. The percentage composition of the oil is worked out as:—fatty acids 94·1 per cent., consisting of saturated acids 10·3, elaeostearic 30; linolic 32; and oleic acid 21; unsaponifiable matter, 0·9; glycerol 4·3; and volatile constituents 1·7. D. G. H.

Oil of "Karasumi." M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1934, **36**, 676B.)—"Karasumi" is the salted and dried ovary of the grey mullet (*Mugil japonicus*), and a sample of the orange-yellow, flat, elliptical substance from Formosa yielded, on extraction with ether, about 32 per cent. of a brownish oil, which deposited an appreciable amount of solid at ordinary temperature, and had the following characteristics:—Sp.gr. at 20°/4° C., 0·8818; n_D^{20}, 1·4695; saponification value, 120·1; iodine value (Wijs), 130·6; unsaponifiable matter, 40·64 per cent.; and acid value, 16·0. The fatty acids were semi-solid at 20° C., and had m.pt. 25° to 26° C.; neutralisation value, 196·0; and iodine value, 186·1. They yielded 52·3 per cent. of ether-insoluble bromide, containing 70·09 per cent. of bromine. The unsaponifiable matter was bright orange-yellow, rather hard and crystalline,

and contained 9·62 per cent. of cholesterol, as determined by the digitonin method. Fractional distillation of the acetyl derivatives showed that the solid part consisted, besides cholesterol, mainly of cetyl alcohol with a small proportion of octadecyl alcohol. The liquid part consisted of octadecenol, (possibly oleyl alcohol), and hexadecenol also appeared to be present. Karasumi oil is, therefore, to be regarded as a liquid wax, resembling sperm oil and inguandarame oils, except in the higher unsaturation of the fatty acids and the large content of cholesterol. The occurrence in appreciable quantity of cetyl alcohol and octadecenol in the reproductive organs of fish is noteworthy. D. G. H.

Methods for the Determination of Lead in Foods. H. J. Wichmann and others. (*J. Assoc. Off. Agric. Chem.*, 1934, **17**, 108–135.)—In this paper six methods are described in considerable detail for the determination of small quantities of lead, with particular reference to spray residues present on fruit, such as apples and pears. The methods, which are adaptations of existing processes, involve the following steps: (*a*) *Preparation of sample:*—Wet oxidation of the whole sample (A.O.A.C., *Methods of Analysis*, 1930, 306), or ashing at a temperature not greater than 500° C., or removal of the spray residue by solvents is employed. The solvent treatment is as follows:—The stem and sepals of the weighed fruit are removed by cutting, and are placed in a funnel inserted in a flask. The fruit is impaled on a glass rod, and immersed in a boiling mixture of 25 ml. of 30 per cent. sodium hydroxide solution, 25 ml. of 10 per cent. sodium oleate solution and 200 ml. of water (which is sufficient for treating a sample lot of 10 fruits) until the skin begins to "check"; it is then removed to the funnel, and rinsed with a stream of hot dilute nitric acid (1 + 49), particular attention being paid to washing out the stem and calyx ends. The alkaline solution is cooled and mixed with the acid solution in the flask. It is claimed that in this way 95 per cent., or more, of the lead is removed "even with the most refractory fruit." (*b*) *Preliminary separation of lead*:—This is either dispensed with, or precipitation as sulphide (*cf.* Fairhall, *J. Ind. Hyg.*, 1922, **4**, 9), or sulphate, or extraction of the lead salt of diphenylthiocarbazone (*cf. inter alios* Allport and Skrimshire, ANALYST, 1932, **57**, 440), is employed. (*c*) *Determination*:—The methods include precipitation as chromate and titration of the chromate ion (*cf.* Fairhall, *loc. cit.*), anodic deposition of lead peroxide, and iodimetric determination of this (Jones, ANALYST, 1933, **58**, 11), colorimetric determination as sulphide (Hamence, ANALYST, 1932, **57**, 622), and colorimetric determination with diphenylthiocarbazone (Fischer, *Z. anal. Chem.*, 1933, **46**, 442). S. G. C.

Derris Roots from New Guinea. (*Bull. Imp. Inst.*, 1933, **31**, 469.)—Samples of fine and coarse roots have been tested for their content of rotenone by a method (recently published by the United States Department of Agriculture) which depends on extraction with carbon tetrachloride. Fine roots from New Guinea contained 3·2 per cent., coarse roots 2·1, and a commercial sample of Malay roots 2·2 per cent. The rotenone-content varies considerably, both with the species and with the age of the plant from which the roots are obtained. A number of commercial samples of derris root, examined by the carbon tetrachloride method, have been found to contain from nil to 6·9 per cent. of rotenone (*cf.* ANALYST, 1932, **57**, 782). R. F. I.

Biochemical

Presence of Oxalates in Plants from the Point of View of Oxaluria. A. Goudswaard. (*Pharm. Weekblad*, 1934, **71**, 114–118.)—It has been stated that, with a few exceptions (*e.g.* mushrooms), oxalic acid does not occur in plants in the free state, but it is of greater importance, from the point of view of the study of oxaluria, to know whether oxalates are present in plants in the soluble or insoluble state. Calcium oxalate crystals are not dissolved by 0·4 *N* hydrochloric acid (although soluble in higher concentrations of acid), and this corresponds with an acidity greater than that existing in the stomach. The solubility of oxalates from cooked foods will also depend on the method of cooking; thus, for instance, addition of alkali (*e.g.* to rhubarb or sorrel) increases the solubility by formation of the sodium salt, which is stated to be more harmful (*cf.* Molisch, *Mikrochemie der Pflanzen*). The Table below gives the total oxalate-content, determined by the author's modification of the Van Itallie-Lemke method (*vide infra*), and the soluble oxalate-content per kilo of raw material (+ indicates present, and 0 absent).

Material	Total oxalate-content (French results) per kilo. mgrms.	Total oxalate-content (German results) per kilo. mgrms.	Soluble oxalates by author's method per kilo. mgrms.	Calcium oxalate	Soluble calcium salts
Potatoes	—	400	0		—
Endive	+	100	0	+	+
Beans	310	300	0		+
Chocolate	900	900	—		
Cabbage	+	—	0		
Purslane	—	—	6000 to 7500	+	—
Red beet	390	400	1800	+	—
Spinach	1910 to 3300	3300	Doubtful trace		
Celery	+	+	0	+	+
Tea	3750	3700	Large quantity		
Coffee	120	100	—		
Tomatoes	+	5	0	—	—
Strawberries ..	—	60	0		+
Plums	120	120	—		
Rhubarb	2460	2400	6440		
Onions	—	—	0	—	—
Carrots	+	—	0	—	+
Sorrel	2740 to 3600	3600	—		
Leeks	—	—	0	+	+
Asparagus	+	—	—		
Pepper	3250	—	—		
Amarantus spec. ..	—	—	3900	+	—

For comparison, results obtained by French and German chemists are also given.* In the author's method the finely-minced sample (50 grms.) is boiled for 10 minutes with 150 ml. of water, and the mixture is filtered. The filtrate is not decolorised, but to one portion is added calcium chloride solution, and the non-occurrence of a precipitate after 24 hours is taken to indicate the absence of oxalic acid. If any precipitate is produced, it is removed in the centrifuge, washed, and identified

* No references to the original papers are given.

microscopically. Ammonium oxalate solution is added to another portion, and, if no precipitate is formed, the absence of calcium salts is indicated; any precipitate is examined as described above, the crystals being then converted into the characteristic crystals of calcium sulphate by means of sulphuric acid. Soluble oxalates are determined by diluting the clear, cold filtrate from an extract of 10 grms. of sample in 150 ml. of hot water (*cf. supra*) to 250 ml., and neutralising 5 ml. of the dilute solution with 0·1 *N* hydrochloric acid, with neutral red as indicator; if a precipitate results, a fresh extract is made, and this is acidified, diluted to 250 ml., and filtered. The filtrate (5 ml.) is treated with calcium chloride, and any resulting precipitate is separated, washed in the centrifuge, and titrated with a 0·01 *N* solution of potassium permanganate (by Kolthoff's method). J. G.

Isolation of Heteroxanthine from Yeast. P. W. Wiardi and B. C. P. Jansen. (*Rec. Trav. Chim. Pay-Bas*, 1934, **34**, 205–208.)—Brewer's yeast was digested with water containing 0·1 per cent. of benzoic acid, with the addition of hydrochloric acid to give a p_H value of 4·5, and 100 litres of extract were obtained from 40 kilos of yeast. To this extract were added 6 kilos. of fuller's earth, followed, after separation had occurred, by baryta and ice. To the alkaline filtrate, acidified with hydrochloric acid to give a p_H value of 4·8, a solution of sodium silicotungstate (p_H 4·8) was then added until precipitation was complete. The precipitate, when decomposed with baryta in the presence of ice, gave an alkaline solution, and this was acidified with nitric acid to give a p_H value of 2 and then treated with an excess of silver nitrate. The resulting precipitate, containing no vitamin *B*, was decomposed with hydrochloric acid, the solution was filtered and evaporated to dryness, and the residue was extracted with dilute sulphuric acid. By repeating the silver nitrate purification, together with concentration and re-crystallisation from 0·5 *N* hydrochloric acid, 1·2 grm. of a pale yellow crystalline mass was obtained. A consideration of the behaviour of this substance on heating in a tube, and with sodium; the positive murexide, and negative xanthine test; the absence of precipitate with picric acid or sodium picrate, together with a determination of the nitrogen-content, indicated that the substance was a mono-methylxanthine. Further reactions showed that it was heteroxanthine, *i.e.* 7-methylxanthine. Three-quarters of the nitrogen present was in the form of a volatile ammonium base, and one-quarter as amino acid, and the methyl group was shown to be present in the amino acid. The general reactions closely resembled those of heteroxanthine prepared from theobromine. If lead acetate and silicotungstic acid were used in the preparation before addition of fuller's earth, adenine hydrochloride, not heteroxanthine, was eventually isolated. D. G. H.

Isolation and Detection of Bilirubin. C. E. May, R. Martindale and W. F. Boyd. (*J. Biol. Chem.*, 1934, **104**, 255–257.)—The authors have been working over a prolonged period on the isolation and detection of small amounts of bilirubin. Recently, Daddi (*Riv. clin. med.*, **32**, No. 2; *Pathologica*, 1933, **25**, 215) and Laemmer and Beck (*Compt. rend.*, 1933, **113**, 166) reported work along similar lines, and the authors decided to publish the results they had obtained. They state that many substances were tried as bilirubin precipitants, and it was found that bilirubin is

best precipitated from a dilute aqueous solution by means of a mixture of barium chloride and di-sodium phosphate, or a mixture of barium chloride and tri-sodium phosphate. For the detection of bilirubin, diazo chlorides were tried other than *p*-sulphobenzene-diazo chloride, first suggested by Ehrlich (*Z. anal. Chem.*, **1883, 23**, 275; *Centr. klin. Med.*, 1883, 721), and, later, used for the detection of obstructive jaundice, and it was found that in neutral alcoholic solution bilirubin reacted only with *p*-sulphobenzene-diazo chloride to give a highly coloured product. In an alkaline-alcoholic solution of bilirubin, both *p*-sulphobenzene-diazo chloride and *p*-nitrobenzene-diazo chloride reacted. In an acetic acid solution of bilirubin, *p*-nitrobenzene-diazo chloride yielded a highly coloured product. The colours produced were pronounced, and were stable for several days. Biliverdin showed no evidence of reacting with diazo chlorides. While the work was in progress, Greco (*Diagnostica e technica di Laboratorio*, Naples, 1931, **2**, 925) published a method which the authors have used with very good results. They were unable, however, to duplicate that part of his work in which he matched the resulting coloured solutions with solutions of mixed indicators, but describe modifications which were found to be satisfactory. P. H. P.

Relative Concentration of Esterase and Lipase in Adipose Tissue. J. S. Hepburn and H. McDuffy Moore. (*Amer. J. Pharm.*, **1934, 106**, 14–15.) The tissue was obtained from well-nourished subjects within 24 hours of death (15 days in the case of refrigerated carcases), and 50 grms. were chopped, ground with sand and triturated several times with water. The extract was filtered successively through wire-gauze and cotton-gauze, and the residue was washed until the total volume of filtrate was 500 ml. Two 100-ml. portions were then placed in separate flasks (one being boiled and cooled to serve as a control), and 1 ml. of substrate (ethyl butyrate for esterase and tributyrin for lipase) and 0·3 ml. of a 1 per cent. solution of phenolphthalein in alcohol were added. Each mixture was shaken, neutralised with 0·1 *N* sodium hydroxide solution, and preserved with 1 ml. of toluene, and the acidity was determined after 72 hours at 37·5° C. by titration with the 0·1 *N* alkali. Results for esterase and lipase, respectively, expressed as the difference between the titration values of the butyric acid produced by the sample and control were:—Chicken (3 samples), 2·10 to 2·65, 9·25 to 10·10; turkey (2), 4·40 and 4·50, 9·90 and 11·20; goose (2), 9·55 and 9·25; 8·60 and 9·00; lamb (2), 44·35 and 47·50, 19·25 and 17·80; man (2), 7·15 and 7·80, 5·50 and 5·95. J. G.

Comparative Studies of the Nutritive Value of Raw and Pasteurised Milk. J. C. Drummond. (*J. Soc. Chem. Ind.*, **1933, 52**, 400–403T.)—It is pointed out that a large proportion of papers on the nutritive value of milk in relation to pasteurisation, the conclusions of which are frequently quoted, are almost valueless when assessed in the light of the methods of scientific investigations. A series of experiments has been carried out on young rats with raw and commercially pasteurised milk. These experiments have failed to detect any evidence that pasteurisation adversely affects the nutritive value of milk. Raw milk, supplemented by biscuit prepared from white flour, has been found to be insufficient to enable a young female rat to produce and rear a normal litter of

young. So far as the experiments go, they suggest that additional vitamin *B* (yeastrel) may adjust the balance of this diet so that satisfactory reproduction can occur, and it is thought that amounts of copper and iron above those required to maintain a normal blood picture may influence reproduction beneficially. It has not been determined to what extent other substances present in the yeast extract (*e.g.* manganese) may be responsible for the results observed. These results are not in agreement with those of Mattick and Golding, and no satisfactory explanation of the curious divergences from their results can be suggested; samples of the same milk and white flour employed by Mattick and Golding were used in the investigation. P. H. P.

Plant Colouring Matters. LV. Occurrence of α- and β-Carotene in various Natural Products. P. Karrer and W. Schlientz. (*Helv. Chim. Acta*, 1934, **17**, 7–8.)—According to Kuhn and Lederer (*Z. physiol. Chem.*, 1931, **200**, 246), preparations which appear to be pure β-carotene may be obtained from various plants, *e.g.* grass, ordinary nettles, spinach and paprika; also, the carotene of cows' ovaries is stated to consist of the β-form with not more than 1 per cent. of the α-modification. These results have now been tested by chromatographic adsorption with lime (Karrer and Walker, *Helv. Chim. Acta*, 1933, **16**, 641; Karrer, Walker, Schöpp and Morf, *Nature*, 1933, **132**, 26). The results show that the preparations named consist mainly of β-carotene, but are not quite free from the α-form. This accumulates in the calcium hydroxide chromatogram in a narrow, bright yellow zone below the β-carotene adsorption layer and, after solution, gives absorption spectra indicating the presence mainly of α-carotene. The small proportions of the α-form occurring in the non-fractionated, crystallised carotene preparations from spinach, paprika, nettles, and corpus luteum are insufficient to impart to them any measurable optical activity, and, for practical purposes, such preparations may be regarded as almost pure β-carotene. T. H. P.

Carotene. VII. Physical Properties of Carotenes from Different Plant Sources. J. H. C. Smith and H. W. Milner. (*J. Biol. Chem.*, 1934, **104**, 437–447.)—It has recently been shown that carotene derived from different leaves and from carrot roots possesses the same degree of unsaturation. On the basis of optical activity, however, it is clearly evident that at least two isomeric carotenes exist, namely, α-carotene, which is optically active, and β-carotene, which is optically inactive. Carotene isolated from plant sources is often a mixture of these two forms. In order to define the composition of such carotene samples in terms of their components it is necessary to know the physical properties of the mixtures, as well as of the pure components. For this reason several of the physical properties of carotene samples, varying in composition from pure α- to pure β-carotene, have been measured and compared with their optical activities. The methods of procedure for the determination of optical rotations, melting-points, solubilities and absorption spectra are described in detail. It is shown that the m.pts. of carotenes with zero optical activity average about 180·5° C. The highly rotatory α-carotene melts at 182·5° C. All the leaf carotenes examined were β-carotenes, but other workers have shown that tea leaves contain almost

pure α-carotene, and that carrot leaves, in common with carrot roots, contain a mixture of α- and β-carotenes. The m.pts. of different samples of carrot root carotene were found to vary, probably depending on the relative proportions of the α- and β-forms. A series of measurements of the m.pts. and optical rotations of these samples gave a curve resembling the typical melting-point diagram for a two-component system in which solid solutions but no compounds are formed. The optically inactive carotenes from carrot root and sunflower leaf are shown to be identical. The solubility data show that solid solutions exist, that α-carotene is slightly less soluble than β-carotene, that mixtures of the two are much more soluble than either form separately, and that leaf and carrot-root carotenes have one component in common. P. H. P.

Sterols of Molluscs. W. Bergmann. (*J. Biol. Chem.*, 1934, **104**, 317–328.)—From the unsaponifiable matter of the oyster, *Ostrea virginica*, a new zoo-sterol, which closely resembles cholesterol, has been isolated, and has been given the name *ostreasterol*. The purest ostreasterol obtained melts at 142–143° C. and has $[\alpha]_D^{20} = -43{\cdot}57°$. It gives the Liebermann-Burchard and the Salkowski reactions, and its solubility in different solvents is about the same as that of cholesterol. Under the microscope the crystals of ostreasterol obtained from 96 per cent. alcohol appear in the form of flat needles. From methanol it crystallises occasionally in the form of well-shaped long needles. The acetate, even after one re-crystallisation, has a higher m.pt. than cholesteryl acetate. It adds bromine rapidly, giving a difficultly soluble bromide (m.pt. 122° C.). The purified bromide is reduced with zinc dust to the acetate (m.pt. 134·5° C.; $[\alpha]_D^{20} = -45{\cdot}94°$). From the purified sterol the benzoate and the propionate were prepared. The propionate melted at 113–114° C., whilst the benzoate (like cholesteryl benzoate) showed a double melting-point. At 145–147° C. it melted to a turbid liquid, which, on further heating, exhibited a play of colours, and became clear at 152° C. From the mother liquors of ostreasteryl acetate, after long standing, a crystalline acetate separated, which, after several recrystallisations and purification, melted at 104° C., and had an optical rotation of $[\alpha]_D^{21} = -15{\cdot}9°$. The sterol obtained from the acetate melted at 122° C. Until it has been more thoroughly investigated it will be referred to as ostreasterol II. Ostreasterol has been shown to replace cholesterol in all organs of the oyster. The author has also found ostreasterol in the unsaponifiable matter of the common round clam, *Venus mercenaria*, and in the mussel, *Modiola*. The investigation has been extended to members of the class of gastropods, for the common whelk and the common snail have each been shown by other workers to contain cholesterol. The sterols of the large gastropods, *Fulgur carica* and *Fulgur canaliculata*, have now been shown to contain small amounts of cholesterol and larger amounts of ostreasterol. It should be mentioned that the gastropods of the genus *Fulgur* feed largely upon oysters and other bivalves, from which food they may have acquired the ostreasterol present in their unsaponifiable matter. The analysis of ostreasterol agrees with the formula $C_{27}H_{46}O$ or $C_{27}H_{44}O$. Titration of the acetate with perbenzoic acid indicated the presence of two double bonds, which makes $C_{27}H_{44}O$ the more probable formula. P. H. P.

Behaviour of Vitamin *C* (Ascorbic Acid) and other Reductors towards Catheptic and other Enzymes. H. v. Euler, P. Karrer and F. Zehender. (*Helv. Chim. Acta*, 1934, **17**, 157–162.)—It was noted by Karrer and Zehender (*ibid.*, 1933, **16**, 701) that ascorbic acid is able to activate catheptic enzymes from the liver previously freed from their natural activators. As a result of further experiments, various explanations seem possible for the mechanism of this action: (1) Such activation may depend on the fixation of traces of heavy metals, particularly copper, which inhibit the action of the enzymes; ferrous, ferric and calcium salts accelerate the activity of these enzymes. Activation of the inactive catheptic enzymes is also caused by substances, such as potassium cyanide, hydrogen sulphide, and cysteine, which are able to fix copper. (2) The action of ascorbic acid may consist in fixation of oxygen by the acid, the enzymes being thus protected from the action of oxygen. This effect would be similar to the activation of arginase by cysteine, ferrous salts, or the system cupric salt–ascorbic acid. (3) The ascorbic acid may give rise to the formation of a labile oxido-reduction system necessary for the enzymic processes. T. H. P.

Vitamin *E*. I. Some Chemical and Physiological Properties. H. S. Olcott and H. A. Mattill. (*J. Biol. Chem.*, 1934, **104**, 423–435.)—The only published systematic investigation of vitamin *E* is that of Evans and Burr (*Mem. Univ. California*, 1927, 8). Various aspects of the chemical and physiological problems concerned with vitamin *E* have been examined by the authors during the course of four years. The most striking function of vitamin *E* is to provide for a normal gestation in a pregnant rat, in that it prevents the resorption of the embryos which invariably occurs in its absence. A curative method of assay which was developed by Evans and Burr, based upon this physiological property, was used in the experiments described. It is shown that a single large dose of vitamin *E* given to female rats may secure fertility for two gestations, but not for three. Mothers on a diet deficient in vitamin *E* require more than 8 per cent. of yeast in the diet for normal lactation. The paralysis in the young cannot be cured by the administration of vitamin *E* after the symptoms have appeared; spontaneous recoveries have been observed. An active concentrate was prepared from lettuce by methods of fractional crystallisation and distillation, and a shortened method is described for the preparation of concentrates from wheat-germ oil by similar procedures. Some of the properties of these concentrates are tabulated. Vitamin *E* is destroyed by bromination, but not by acetylation, benzoylation, mild oxidation with silver nitrate, or hydrogenation. The concentrates strongly resist saturation with hydrogen. Potassium permanganate destroys the vitamin. Concentrates of vitamin *E* are stable for as long as four weeks in a rancid food mixture at room temperature. When injected subcutaneously, vitamin *E* has no effect on the ovaries, uterus, opening of the vagina, or cornification in the immature rat. It is also shown that there is no immediate relationship between xanthophyll and vitamin *E*. P. H. P.

Bacteriological

Significance of True *Bacillus Coli* (*B. coli communis*) and *Bacillus lactis aerogenes* in Samples of Milk. C. H. Chalmers. (*Zentr. Bakt.*, 1934, **89**, 459–474.)—These two organisms are widely distributed in nature, and have been shown to be present in samples of milk in about equal numbers. The true *B. coli* is the predominant coliform organism in fresh faeces and gains entrance to milk from this source. *B. lactis aerogenes*, on the other hand, is the predominant coliform bacillus in the dust from grains and in soil and water, these being mainly responsible for the presence of the organism in milk. During the summer of 1930 an investigation was made into the cause of the persistent contamination with *B. lactis aerogenes* of samples of "certified" milk from the two farms of a single producer. Two sources of the organism were found, namely, the outside of the udder, and, intermittently, the milk duct. Owing to the capsulated nature of the organisms, ordinary methods of washing did not appear to remove them from the udder, and washing with a mild disinfectant became necessary; a mixture of Izal (0·5 fluid oz. per gallon of water) and soft soap (3 oz. per gallon of water) proved satisfactory. Rejection of the normal amount of fore-milk did not overcome the contamination of the milk.

B. lactis aerogenes does not seem, at least when present in water, to be deleterious from the dietetic aspect, little danger accruing from the ingestion of the organism in large numbers. Moreover, Gray (*J. Hyg.*, 1932, **32**, 132) regards a preponderance of this bacillus over *B. coli* in a water-supply as an indication of freedom from pathogenic organisms, including *B. typhosus* and *B. para-typhosus B.* As the sources of contamination of water and of milk with coliform organisms are fundamentally the same, Gray's conclusion seems applicable also to milk.

From a study of the literature on *B. lactis aerogenes*, it seems desirable that the presumptive *B. coli* test should be modified to show to what separate extents true *B. coli* and *B. lactis aerogenes* are present in milk. Such modification exhibits difficulties, primarily because the different strains of coliform organisms which ferment lactose are numerous and their differences small. Help is, however, obtainable from the use of telluric acid and Brilliant Green. True *B. coli* (those which are V.P.* and Koser† negative and M.R.§ positive) resist telluric acid in certain concentrations, but are inhibited by Brilliant Green, whereas those organisms which tolerate Brilliant Green (*i.e. B. aerogenes*) do not withstand telluric acid. The concentration 0·0013 per cent. of telluric acid in bile salt solution, appears to produce the minimum inhibition of true *B. coli* coincident with prevention of the growth of *B. aerogenes*, provided that this is not present in excessive numbers. Moderately satisfactory results have been given on examination of milk samples in this way, but certain of the factors involved, concerned chiefly with the rates of growth of the two organisms, require further investigation. T. H. P.

* Voges-Proskaner test for acetal-methyl-carbinol. † Test for decomposition of citric acid.
§ Final reaction in glucose broth rendered acid to methyl red.

Organic Analysis

Determination of the Position of the Double Linking. R. Frognier and F. van Goetsenhoven. (*Bull. Soc. Chim. Belg.*, 1933, **42**, 391–409.)—The conditions governing the determination of the double linking in derivatives of the butenoic acids have been investigated. The readiness with which a double linking is saturated is influenced in varying degree by the nature and proximity of certain functional groupings. It is, for instance, possible to determine $\beta\gamma$-unsaturated compounds in presence of $\alpha\beta$-compounds by measuring their bromine absorption. Methods applicable to nitriles cannot, however, be used for acids, since the reactivities of these two classes of compounds are quite different. The rate at which bromine (in carbon tetrachloride solution) is added in the dark to the following compounds (also in carbon tetrachloride) diminishes in the order: vinylacetic acid, ethyl vinylacetate, vinylacetonitrile, crotonic acid, *trans*-crotononitrile, *cis*-crotononitrile. Conditions have been determined in which the numbers of molecules of bromine added per molecule of substance are for: ethyl vinylacetate, 0·99; vinylacetonitrile, 0·99; *trans*-crotononitrile, 0·016; *cis*-crotononitrile, 0·006; ethyl crotonate, 0·02.

On the basis of these results, the following modification of Heim's method (ANALYST, 1931, **56**, 129) is given for the determination of $\beta\gamma$-unsaturated esters or nitriles in presence of $\alpha\beta$-compounds. Use is made of an Erlenmeyer flask with a hollow ground-in stopper, through which passes the stem of a separating funnel. The bulb of this funnel is connected with the stopper by a second tube provided with a stop-cock. Bromination is effected by means of a solution containing 2·7835 grms. of potassium bromate and 9·918 grms. of potassium bromide per litre. The nitrile or ester (0·01 molecule) to be determined is dissolved in carbon tetrachloride (100 ml.). About 40 ml. of the bromide-bromate solution and 10 ml. of the ester or nitrile solution are run into the flask, which is at once fitted with the separating funnel and covered with a black cloth. After addition of 25 ml. of 10 per cent. sulphuric acid solution, the flask is shaken vigorously for two minutes, after which, by suitable manipulation of the two taps, 20 ml. of 10 per cent. potassium iodide solution are introduced. After further shaking for one minute, the flask is uncovered and the liberated iodine is titrated with 0·1 *N* sodium thiosulphate solution. Variations in the temperature between 0° and 30° C. do not influence the results. The amount of bromine absorbed (expressed as ml. of the thiosulphate), when multiplied by 5, gives the percentage of $\beta\gamma$-nitrile or ester in the liquid tested. Hundreds of determinations made in this way have given results reproducible to within about 0·2 per cent.

A second procedure, in which a solution of bromine (6 grms. per litre) in carbon tetrachloride is used, is also described. With this solution the vapour pressure of the bromine is much less than in aqueous solution, so that a simple Erlenmeyer flask with a ground stopper may be employed. Results reproducible to within about 0·5 per cent. are thus obtainable. T. H. P.

Detection of Nitrobenzene and of Phenol by the Formation of Resorufin. H. Eichler. (*Z. anal. Chem.*, 1934, **96**, 21–22.)—The fact that, when heated with resorcinol (or phenol) in concentrated sulphuric acid solution, nitrobenzene

yields resorufin, may be utilised for the detection of either nitrobenzene or phenol. To detect nitrobenzene, a very small amount of the substance to be tested is heated with resorcinol and sulphuric acid (a solution of 0·5 to 0·6 grm. of resorcinol in 100 grms. of the concentrated acid is suitable) until the liquid becomes violet or emits sulphur trioxide vapour. After being cooled, the solution is diluted with water, made alkaline with sodium carbonate, and filtered if necessary; the appearance of the yellowish-red fluorescence accompanying the formation of resorufin indicates the presence of nitrobenzene in the substance. Phenol is tested for by heating with nitrobenzene in concentrated sulphuric acid solution. A number of nitro-compounds are specified which do not give resorufin when treated with resorcinol as described above. T. H. P.

Determination of Pyruvic Acid. G. Carpeniseanu. (*Compt. rend.*, **1934, 198**, 272–274.)—Simon's colorimetric determination of pyruvic acid, based on the green colour given with acetic acid, sodium nitroprusside, and ammonia (*Comp. rend.*, 1897, **125**, 534; *Bull. Soc. Chim. Biol.*, 1924, **6**, 477), is capable of greatly increased sensitiveness if the conditions are suitably adjusted. The author uses a wide range of standards prepared from a solution (*P*) containing either 0·25 grm. of sodium pyruvate or 0·2 grm. of pyruvic acid per litre. The quantities measured out are run from burettes calibrated to 0·5 ml., and the colour comparisons are made in test-tubes (about 25 ml.) free from striae and of the same dimensions. The standard tubes contain: 1 ml. of water; 0·95 ml. of water and 0·05 ml. of solution *P*; 0·09 ml. of water and 0·1 ml. of solution *P*; . . . 1 ml. of solution *P*. A tube with 0·1 ml. of the solution to be tested is also prepared. To each tube are added, in order, 0·25 ml. of acetic acid (40 vols. of glacial acetic acid + 60 vols. of water), 0·5 ml. of fresh sodium nitroprusside solution (1 per cent.) and 0·75 ml. of ammonia solution (1 vol. of 0·880 ammonia + 1 vol. of water). After the lapse of 30 to 60 minutes for the more concentrated tubes, or 60 to 90 minutes for the others, the tubes are compared by looking through them at a piece of white paper. T. H. P.

Tung Oil. Chemical Studies and Specification. L. A. Jordan. (*J. Soc. Chem. Ind.*, 1934, **53**, 1–11T.)—The chemical work carried out by the Paint and Varnish Research Association in connection with the plans for Empire development, as co-ordinated by the Tung Oil Committee of the Imperial Institute, has involved, in addition to the examination of chemical and physical properties of tung oils as related to the country of origin, species, manurial and cultivation factors, methods of crushing, etc., concurrent work, which has been carried on for 3 years with a view to a better understanding of such matters as the state of polymerisation, and the present paper gives an account of this work. Tung oil has been shown to consist mainly of the glycerides of the triply unsaturated elaeostearic acid, the singly unsaturated oleic acid, and the saturated stearic acid, the elaeostearic glyceride being mainly responsible for the characteristic properties of the oil. This glyceride has now been determined, together with the relative proportions of the other glycerides, the total unsaturation being measured by means of complete hydrogenation, and partial saturation by the addition of halogen to the oil in various ways.

Complete saturation determination involved the examination of the method used for finding the iodine value. Although the quantity of hydrogen used to effect saturation of a quantity of tung oil can be determined within 1 per cent., the experimental refinements preclude the method being adopted in commercial specifications. For the measurement of partial saturation a modification of Kaufmann's mixed halogen method has been followed. Gelation effects are discussed in detail. For the evaluation of the degree of polymerisation of a tung oil it is emphasised that the past of a treated tung oil determines its present and future possibilities, so that the manner of expressing the degree of polymerisation can only be a statistical average. However, a definite proportion of the gel is insoluble in acetone, the proportion increasing with the time of heating, up to an uncertain limit, approximately 75 per cent. of the mass. The measurement of the amount and state of the polymerisable content of tung oil at any time can be followed by studying the changes in the amount of acetone-insoluble material, or disperse phase in the polymerised oil, and the refractive index and viscosity of the oil and its component phases. The "heat tests," which in some form comprise a feature of every specification for tung oil, involve either heating small quantities of oil in a hot bath or the direct heating of large quantities of oil. Small quantities are preferable, so that the start of the polymerisation change may be a well-defined instant. The "polymerisable matter" was found to vary with the condition of the test, and it was considered desirable to select a precise period for after-heating of the gel, at the end of which the rate of change with time is small, and within an ordinary degree of experimental error. A period of 20 minutes was selected, at which, with a polymerising temperature of 290° C., the percentage extract is at a minimum. The following is the final "Heat Test and Determination of Polymerisable Matter in Tung Oil" recommended for inclusion in the British Standard Specification; it has been in use for some time at the Paint Research Station:—The oil (5 ml.) is placed in a thin test-tube (not over 0·04 in. in thickness, 6 in. by $\frac{5}{8}$ in. internal diameter), fitted with a grooved cork through which a glass rod, $\frac{1}{8}$ in. in diameter, may freely pass. The tube is placed in an oil-bath previously heated to 295° C., which causes the temperature to drop to 290° C., at which point it is kept ($\pm 1°$) by regulating the source of heat. The oil-bath consists of an 800-ml. glass beaker (4 in. diameter, 5 in. high), filled to a height of 3 in. with soya bean, cotton-seed or mineral oil (approx. 500 ml.), and heated by means of a gas burner (on a gauze); the oil is not stirred. The beaker is provided with a loose metal cover with two $\frac{3}{4}$-in. holes symmetrically placed $\frac{3}{4}$ in. from the centre. The tube, with the tung oil, is supported through one hole by a cork collar arranged to keep the bottom of the tube 1 in. above the bottom of the bath, and the second hole carries a cork holding the thermometer (of a limited range pattern) immersed to within 1 in. above the reading 290° C. (a detailed specification for a suitable thermometer is given), and with its bulb 1 in. above the bottom of the bath. Seven minutes after the insertion of the sample the glass rod is raised to test for gelation, and this test is repeated every $\frac{1}{4}$ minute until the tube is lifted with the rod. This stage should be reached within 10 minutes with a genuine tung oil. The sample is then left undisturbed in the bath, with the temperature at 290° C., for 20 minutes from the outset of gelation, and is then

withdrawn, left to cool in a vertical position in air with the cork removed, after the outside of the tube has been wiped free from oil. The oxidised top surface ($\frac{1}{4}$ in. in depth) is cut off, the remainder roughly crumbled, and a 2-grm. portion is weighed into a mortar, ground with a little sharp sand, extracted in a Soxhlet extractor for 1 hour with petroleum spirit (60°–80° C.), after which the solvent is evaporated, and the residue weighed. Results obtained by independent workers agreed well. An example of results is as follows:—Gelation time (*a*), extractive per cent. (*b*) and $n_D^{25°C}$ (*c*). Pure American *A. Fordii* oil, (*a*) $8\frac{1}{4}$ mins., (*b*) 16·3, (*c*) 1·5187; ditto +5 per cent. soya bean oil, (*a*) $8\frac{1}{2}$, (*b*) 20·3, (*c*) 1·5167; commercial tung oil, (*a*) $9\frac{1}{2}$, (*b*) 21·8, (*c*) 1·5172; oil of *A. montana*, (*a*) 11, (*b*) 27·9, (*c*) 1·5145; ditto +10 per cent. of soya-bean oil, (*a*) $12\frac{1}{2}$, (*b*) 36·9, (*c*) 1·5112. It has been found that the extent of change in results due to experimental variations can be approximately foreseen. The temperature of 290° C. is taken because the effect of temperature variations on the extractive determination is least at this point. The possibility of establishing an empirical connection between extractive-content and commercial valuation of the oil is suggested. The newer grades of orchard-grown tung oil, characterised by quick gelation and high insoluble-content, appear to yield slightly superior varnish media when the tung oil is first adulterated with about 5 per cent. of a semi-drying oil, such as soya-bean oil. D. G. H.

Analysis of Nitrocellulose Lacquers. H. Anderson. (*J. Soc. Leather Trades Chem.*, 1934, **18**, 88.)—The lacquer (10 to 15 grms.) is treated with a large excess of benzene, added slowly and with vigorous stirring. The precipitated nitrocellulose is collected on a tared filter paper, washed with benzene, dried and weighed. This mixture of nitrocellulose and pigment is digested with 200 ml. of acetone, and the pigment collected on a tared filter paper, washed, dried and weighed. A pigment consisting of a lake colour leaves a white ash, if any. The benzene solution (*supra*) is dried in a steam-oven. Boiling it with dilute borax solution will remove any shellac; and extraction with cold alcohol removes plasticisers, such as synthetic or formaldehyde-phenol resin, but not gum dammar. Phosphorus in the plasticiser may indicate tricresyl phosphate; phthalic acid would suggest dibutyl phthalate; acetic acid, triacetin; and benzoic acid, glyceryl tribenzoate. Oxalic acid would point to "Barkite," and adipic acid to "Sipalin." Alternatively, plasticisers and gum may be differentiated by adding 20 ml. of water to 20 grms. of the lacquer, evaporating the mixture to dryness, and heating the residue for at least 3 hours in a steam-oven to remove solvents of high b.pt., and then digested with cold alcohol or dilute borax solution, as described above. The type of solvent may be ascertained by steam-distillation, and drying and fractionating the distillate. R. F. I.

Inorganic Analysis

Detection of Cations by means of Resorufin. H. Eichler. (*Z. anal. Chem.*, 1934, **96**, 22.)—With solutions of the salts of certain elements, alkaline solutions of resorufin give characteristic, coloured precipitates which appear dark in the deep yellowish-red fluorescent solution in incident light (especially when a black background is used), and are hence detectable in small quantity. The

neutral or faintly acid solution of the salt is treated with a few drops of a solution of 0·2 grm. of resorufin in 5 ml. of ammonia solution and 100 ml. of water. Solutions containing $Cu^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ba^{\cdot\cdot}$ or $Sr^{\cdot\cdot}$ give precipitates, and solutions containing $Mg^{\cdot\cdot}$, $Ag^{\cdot}$, or $Pb^{\cdot\cdot}$ and free from ammonium salts yield violet precipitates. Ferrous salts (or hydrosulphites) reduce the resorufin and must be oxidised (or destroyed by treatment with acid) prior to the test. Freshly precipitated ferric or aluminium hydroxide also reacts with resorufin. T. H. P.

Determination of Uranium in Ores. W. R. Bennett. (*J. Amer. Chem. Soc.*, 1934, **56**, 277–280.)—*Swedish Kolm.*—The method involves removal of iron by electrolysis over a mercury cathode, precipitation of titanium with cupferron, and volumetric determination of uranium with permanganate. To a 3·5-grm. sample of the ignited ore, contained in a platinum dish, are added 10 ml. of concentrated sulphuric acid and (drop by drop) 15 ml. of hydrofluoric acid, the mixture is digested on a steam-bath for half an hour, and then heated for two hours at a temperature sufficient to cause the evolution of sulphur trioxide fumes. After cooling, 100 ml. of water are added, the mixture is heated to dissolve soluble material, then filtered, and any residue is given a second treatment with sulphuric and hydrofluoric acids. If a little residue still remains, it is brought into solution by fusion with potassium bisulphate. The combined solution is diluted to 500 ml., and the elements of the ammonium hydroxide group are precipitated by the addition of ammonia in the usual way. The precipitate, which contains the uranium, is filtered off and dissolved in 18 ml. of 6 *N* sulphuric acid, and the solution is diluted to 50 ml., giving an acid concentration of 2 to 3 per cent. by volume. The solution is electrolysed over a mercury cathode with a current of 2 to 3 amps. at 8 volts for 2½ hours (*cf.* Smith, "Electroanalysis"). After electrolysis, sulphuric acid is added to the solution to give an acid concentration of about 10 per cent. by volume, and the uranium is oxidised to the sexavalent condition by the addition of a slight excess of potassium permanganate. Titanium is then precipitated by cupferron in the usual way, and the precipitate, after being washed, is rejected. The filtrate is evaporated with nitric acid to destroy the cupferron, the evaporation being continued until only 5 ml. of sulphuric acid remain. This residue is dissolved in 100 ml. of water, and sufficient potassium permanganate is added to the warm liquid to yield a permanent pink colour. The solution is cooled, passed through a Jones reductor; air is bubbled through this reduced solution for 5 minutes to oxidise any tervalent uranium to the quadrivalent form, and the solution is finally titrated with standard permanganate. The addition of a few drops of 0·5 *M* barium diphenylamine sulphonate indicator is recommended to render the end-point readily detectable in the green-coloured uranium solution.

Canadian Uraninite.—This mineral contains rare earths, *e.g.* cerium, and metals of the hydrogen sulphide group; a modified method was, therefore, adopted. A 0·5-grm. sample is heated with 10 ml. of concentrated nitric acid and 10 ml. of concentrated sulphuric acid; the mixture is evaporated to 3 ml.; this is taken up in 100 ml. of water and saturated with hydrogen sulphide at 60° C. The resulting sulphide precipitate is filtered off, washed and rejected, and the filtrate is boiled to expel hydrogen sulphide. The rare earths are precipitated from the solution

by the addition of hot saturated oxalic acid solution, the oxalate precipitate being kept overnight and then filtered off. The solution is electrolysed as above, and the solution is evaporated with nitric acid to destroy any oxalic acid which remained undecomposed after the electrolysis. The residue is dissolved in water. The method from this point is the same as for Swedish Kolm. S. G. C.

Direct Determination of Iron in Presence of Vanadium by the use of a Silver Reductor. G. H. Walden, L. P. Hammett and S. M. Edmonds. (*J. Amer. Chem. Soc.*, 1934, **56**, 350–353.)—Iron and vanadium in dilute hydrochloric acid solution are reduced by finely divided silver to the bi- and quadrivalent states, respectively; in this reduced solution, rendered 5 *M* acid with sulphuric acid, the ferrous iron may be quantitatively oxidised with ceric sulphate, whilst the vanadium remains unoxidised. The silver reductor is of the Jones reductor type, employing a column (12 cm. by 2 cm.) of silver, precipitated from a solution of 29 grms. of silver nitrate in 400 ml. of water by means of sheet copper; the silver column is supported in a glass tube over a plug of glass-wool and no suction is required. In the course of use the silver is converted into silver chloride, which blackens; the blackening gradually extends down the column in successive determinations, thus affording an indication of the behaviour of the reductor; when the blackening extends over three-quarters of the length of the column, the silver should be regenerated by inserting a zinc rod into the reductor tube, so that it touches the contents, thus reducing the silver chloride back to silver without loss. *Method.*—The test-solution (50 ml.; *M* in hydrochloric acid) is poured through the reductor at the rate of 30 ml. per minute; the column is then washed through with 150 ml. of *M* hydrochloric acid. To the combined liquids are added 200 ml. of 10 *M* sulphuric acid; after cooling, 1 drop of 0·025 *M* "phenanthroline-ferrous ion" indicator is added, and the solution is titrated with 0·1 *M* ceric sulphate solution. Accurate results were obtained in test experiments with about 0·1 grm. of iron in presence of approximately equal amounts of vanadium, manganese, titanium and chromium, and also with about 13 mgrms. of iron alone and in presence of a similar amount of vanadium; molybdenum interferes. Good results were obtained with solutions of ferrovanadium after removal of the molybdenum, which involved separation of the iron and vanadium by double precipitation with ammonia. As much as 0·2 grm. of nitric acid may be present in 50 ml. of the solution to be reduced, since, unlike the zinc reductor, the silver reductor yields no reduction products of nitric acid capable of being oxidised by ceric sulphate. S. G. C.

Detection of Nitrates, Nitrites, and Nitrosylsulphuric Acid by the Formation of Resorufin, Orcirufin, and Indophenols. H. Eichler. (*Z. anal. Chem.*, 1934, **96**, 17–21.)—Small proportions of nitrites and nitrates may be detected, even in presence of coloured substances, by means of the reaction between resorcinol (or orcinol) and nitrosylsulphuric acid, which gives, first, nitroresorcinol and the corresponding indophenol, and then, by ring-closure (in presence of hot, concentrated sulphuric acid), resorufin. This is characterised by the violet colour of its solution in concentrated sulphuric acid and by the yellowish-red fluorescence of its violet-red alkaline solution. Use is made of a solution of 0·5 to 0·6 grm. of

resorcinol in 100 grms. of concentrated sulphuric acid free from the nitrosyl-acid (*cf.* Atkins, *Nature*, 1932, **129**, 98); a blank test must be made on each fresh batch of this solution. From 1 to 2 ml. of this solution is poured as a layer on to a little of the substance to be tested; any reaction—such as evolution of carbon dioxide, sulphur dioxide, etc.—is allowed to finish, and the liquid is then heated until either a violet colour indicative of nitrite or nitrate appears or sulphur trioxide vapour is evolved. After being cooled, the solution is diluted with 5 to 10 ml. of water and neutralised with sodium carbonate. Any precipitated carbonate or hydroxide is either filtered off or allowed to settle, the yellowish-red fluorescence of the resorufin being then readily visible either in sunlight or in front of a dark background. The solution must not be made alkaline with sodium hydroxide, which decomposes resorufin. The resorcinol solution used may be replaced by a solution of 0·4 to 0·5 grm. of orcinol in 100 grms. of concentrated sulphuric acid, which gives a red colour with nitrite or nitrate when heated on the water-bath.

The formation of resorufin is prevented if iron, sulphides, or comparatively large proportions of oxidising agents, such as chromates, manganese dioxide, iodates, or nitrates, are present. Such interference may be avoided by heating the substance for a long time with concentrated sulphuric acid, cooling the liquid, adding sufficient solid resorcinol to produce a blue colour, and then heating until the solution becomes violet.

When both nitrite and nitrate are present, the nitrite may be removed, prior to the test, by evaporating a faintly acid or faintly alkaline solution of the substance. A suitable procedure is to bring the solution to p_H 3 by addition of acetic acid, or to add ammonium chloride or sulphate before evaporation. Another method consists in destroying the nitrite by treatment with urea in slightly acid solution. In any of these ways nitrate may be detected in presence of nitrite, but nitrite can be detected only in absence of nitrate. The method is easily adapted to the detection of nitrosylsulphuric acid or oxides of nitrogen. As little as 0·000015 grm. of sodium nitrite is detectable by this reaction with resorcinol. T. H. P.

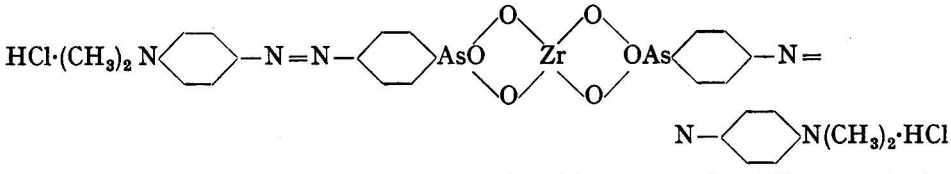
Use of Magdala Red for the Detection of Nitrites. H. Eichler. (*Z. anal. Chem.*, 1934, **96**, 99–100.)—The reagent is a 0·1 per cent. solution of the dye in water containing a little acetic acid. A minimum quantity of the reagent is added to 5 or 10 ml. of water, which is treated in the cold with hydrochloric acid until fluorescence ceases and the liquid turns violet. The solution is heated to boiling, which causes strong yellow-red fluorescence, and the neutral or feebly alkaline solution is added. If nitrite is present, the fluorescence again disappears, while the colour changes to blue. Cupric and ferrous salts favour the reaction; nitrates do not interfere with the fluorescence, even on long boiling, but sulphites and thiosulphates destroy it. Formaldehyde is without effect. W. R. S.

Microchemical

Collected References. Micro-methods of Determination of Proteins in Medicine and Biology. A. Wasitzky. (*Mikrochem.*, 1934, **14**, 81–112.)—Details of the more important methods are given under the following headings:—(i) Gravimetric methods. (ii) Kjeldahl methods. (iii) Refractometric, interferometric,

and combined refractometric and viscometric methods. (iv) Diaphanometric and nephelometric methods. (v) Colorimetric methods. (vi) Sedimentation methods. (vii) Volumetric methods. (viii) Other methods. There are 102 references to original papers. J. W. B.

"Spot" Test for Fluorine. F. Feigl and E. Rajmann. (*Mikrochem.*, **1933, 12,** 133–136.)—The *p*-dimethyl-amino-azo-phenyl-arsenic acid test for zirconium, in which the following yellow-brown acid insoluble compound is formed:



is used as a test for fluorides, which decolorise this compound and liberate the free azo-phenyl arsenic acid, which is red. The reagent consists of a 0·025 per cent. solution of *p*-dimethyl-amino-azo-phenyl-arsenic acid in 9 parts of alcohol and 1 part of concentrated hydrochloric acid. Quantitative filter paper (Schleicher and Schull, 589) is immersed in this solution for a few minutes, dried in air, and then immersed in a solution of zirconium oxychloride (containing 0·01 per cent. of zirconium) in *N* hydrochloric acid, which turns the red paper brown. After ten minutes the paper is washed for five minutes with cold 2 *N* hydrochloric acid, then for five minutes with 2 *N* hydrochloric acid at 50° C., and finally with water, alcohol and ether, and dried *in vacuo*. For the test, three drops of neutral or alkaline test solution are acidified on a spot plate or in a micro-crucible with a drop of 2 *N* hydrochloric acid, and one drop of this mixture is placed on the impregnated paper. In the presence of fluorides a colourless centre appears surrounded by a red circular fleck. As little as 0·25 γ of fluorine can be detected in a dilution of 1:200,000. In the presence of phosphates, arsenates, sulphates and thiosulphates, which interfere, and also with minerals and insoluble fluorides, the fluorine is first converted into hydrogen silicofluoride. Feigl's closed test-tube (Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, Leipzig, 1933, p. 121) is used; the solid substance under examination is placed at the bottom of the tube and covered with a few drops of concentrated sulphuric acid; a few drops of dilute hydrochloric acid are placed on the dropper on the underside of the stopper, and the apparatus is gently heated on an asbestos plate. To prevent distillation of the sulphuric acid, owing to too prolonged heating, a crystal of tartaric acid may be placed in the sulphuric acid. After one or two minutes' heating the drop of hydrochloric acid under the stopper is tested for fluorides by placing it on the reagent paper, as before. In this way as little as 0·2 γ of fluorine in the presence of 80,000 times the amount of foreign matter can be detected. J. W. B.

Micro-Volumetric Analysis with Diphenylcarbazide and Diphenylcarbazone as Indicators in Mercury Titrations. J. V. Dubský and J. Irtílek. (*Mikrochem.*, **1933, 12,** 315–320.)—Both diphenylcarbazide and diphenylcarbazone are used as indicators in 2 per cent. alcoholic solution, rendered colourless, if necessary, by a few drops of 0·2 *N* nitric acid. Metallic salts other than

those of mercury (with the exception of chromates and molybdates) do not react with the reagents in 0·2 *N* nitric acid, so that the indicators may be used in the presence of other heavy metals. Diphenylcarbazone is the more sensitive reagent; it gives an intensive violet-blue colour with the first micro-drop of excess of mercuric nitrate in a chloride titration. For a chloride determination, a few mgrms. of the substance to be analysed are dissolved in a few ml. of water, and 1 ml. of 0·2 *N* nitric acid and 3 drops of diphenylcarbazide (or carbazone) are added. For the titration, 0·01 *N* mercuric nitrate is run in from a micro-burette. Results of test determinations agreed with the calculated values within less than 0·3 per cent. J. W. B.

α-α′-Dipyridyl as a Reagent for the Determination of Ferrous and Total Iron in Natural Waters. H. Müller. (*Mikrochem.*, 1933, **12**, 307–314.)—*Reagents*: A 1 per cent. solution of α-α′-dipyridyl in 0·1 *N* hydrochloric acid; hydrochloric acid 0·1 *N*, solid (A.R.) crystallised sodium sulphite; a 10 per cent. solution of sodium sulphite; dilute hydrochloric acid (1 : 1). *Iron standard solution*: A solution of 0·4318 grm. of ferric ammonium sulphate with 10 ml. of concentrated hydrochloric acid, diluted to 1 litre. This is used in two dilutions: (i) consists of 160 ml. of the standard solution, and 2 ml. of 5 per cent. mercuric chloride solution diluted to 1 litre, and (ii) consists of (i) diluted 10 times. These solutions contain 8·0 γ and 0·8 γ per ml., of iron respectively. The colour formed is permanent; hence a series of permanent standard colours are made up and kept in stoppered tubes of colourless glass, 14 cm. high and 1 cm. in diameter, graduated by means of a ring at a height of 10 cm. The standard colours are made up from volumes of 0·2 to 6 ml. of dilution (ii) and 0·65 to 1 ml. of dilution (i), mixed with 2 ml. of α-α′-dipyridyl solution, followed by a few ml. of the sodium sulphite solution and 0·1 ml. of dilute (1 : 1) hydrochloric acid, and are made up to the mark with sodium sulphite solution. After shaking, two drops of the mercuric chloride solution are added, and the mixture is shaken again. The ferrous iron in the solution under examination, after the same treatment, is compared directly with the standard colours. The total iron may be determined afterwards in the same solution, after adding about 0·6 grm. of solid sodium sulphite and about 0·1 ml. of hydrochloric acid. The standard solutions are similarly treated, and the colours are matched after about 5 minutes. The smallest determinable amount of iron in 8 ml. is 0·1γ. Results for the water of a number of lakes are given. J. W. B.

Physical Methods, Apparatus, etc.

Mercury-in-Glass Thermo-regulator. C. C. Coffin. (*Proc. Nova Scot. Inst. Sci.*, 1933, **18**, 213–214.)—A closely-wound helix (16 turns) of flattened, thin-walled glass tubing, filled with distilled mercury, is placed in the bath in such a way that the ends project vertically above the surface of the liquid. One end contains a stop-cock (below the liquid surface) and, below it, a pointed platinum or tungsten contact, whilst the other is sealed to a capillary tube (0·3 mm. in diameter), in which is fixed a second contact also below the surface; on the latter contact is fused a glass bead which serves to maintain a central position. The

stop-cock regulates the amount of mercury in the system and, consequently, the setting; the capillary may be open to the air, except in cases where a high current causes sparking to occur, when it may be used to fill the system with an inert gas. The mercury in such an apparatus should form a column about 160 cm. long, 0·8 cm. wide and 0·15 cm. thick, and it would then have a volume 20 times, and a surface-volume ratio 3 times those of an ordinary Beckmann thermometer. Advantages are: ease in filling, a wide temperature-range (since mercury is used), efficient integration of temperature over the whole volume of liquid in the bath, elimination of inflammable liquids, simple adjustment, and the fact that little room is occupied in the bath. The dv/dT ratio is much less than for toluene, but this is offset by the greater rate of change of volume; and in a steel spiral this would probably be even greater. The accuracy of regulation is 0·001° C.

J. G.

Examination of Rye-Grass Seed by Means of Ultra-Violet Light. L. François. (*Ann. Falsific.*, 1934, **26**, 34.)—In order to distinguish the seeds of English rye grass (*Lolium perenne L.*) from the Italian species (*Lolium italicum* Al. Br., *Lolium multiflorum Lam.*), especially in cases in which the distinguishing prolonged awn of the inferior glumule in the Italian species has been broken off, the samples of seeds are germinated, and the young radicles are examined under ultra-violet light. The Italian seed shows a brilliant silver-blue fluorescence, but the English remains dull, with no trace of fluorescence. D. G. H.

Rapid Photometric Method for the Determination of Small Quantities of Lead. B. L. Samuel and H. H. Shockey. (*J. Assoc. Off. Agric. Chem.*, 1934, **17**, 141–146.)—The method, which involves the photometric determination of lead sulphide in suspension by means of a photo-electric cell, has been adapted to the determination of lead in foodstuffs, with special reference to sprayed apples.

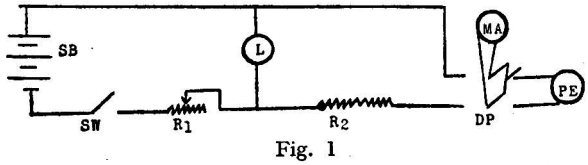


Fig. 1

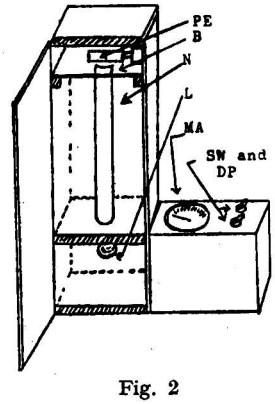


Fig. 2

The photometer (Fig. 2), which the authors constructed themselves at small cost, consists of a wooden box, the front of which opens on hinges, with the parts mounted as shown. The Nessler tube, N, stands over a hole in the lower shelf, and the top of it fits into a hole in the upper removable shelf, B. The light-bulb, L, is mounted about ½ inch directly under the Nessler tube, and the photo-electric cell,

PE, is fixed above the Nessler tube. In the compartment on the right are contained the other components of the apparatus, of which the electrical connections are shown in Fig. 1: SB is a 6-volt accumulator; SW, switch; R1, 1-ohm 5-amp. variable rheostat; R2, 100,000-ohm resistance; L, 6-volt 32-candle-power electric bulb; DP, double pole-double throw switch; MA, 0 to 100 micro-ammeter; PE, Weston photronic cell, Model 594. *Method*:—The organic matter of a sample of convenient size is destroyed by digestion with nitric and sulphuric acids. The nitric acid having been removed by evaporation, the residue is cooled, dissolved in 25 ml. of water, 25 ml. of hydrazine sulphate reagent [20 grms. of hydrazine sulphate and 20 grms. of sodium bromide, dissolved in 1 litre of hydrochloric acid (1+4)] and 20 grms. of sodium chloride are added, and any arsenic is removed by distillation. The remaining liquid is transferred to a 200-ml. volumetric flask, the original vessel being washed out with 10 ml. of hot ammonium acetate solution (20 per cent.) followed by water; 10 ml. of nitric acid are added, and the liquid is made up to volume. Forty ml. of the filtered liquid are transferred to a separating funnel, and shaken with 2 ml. of ammonium thiocyanate solution (saturated) and 15 ml. of ether, to extract the iron. The aqueous bottom layer, which should be practically colourless, is drawn off, 25 ml. of ammoniacal ammonium citrate and potassium cyanide solution (a mixture of 12·5 grms. of citric acid, neutralised with ammonia, in 50 ml. with 125 ml. of 10 per cent. potassium cyanide solution and 1 litre of "ammonium hydroxide") are added, the mixture is transferred to the Nessler tube and diluted to the mark, and the tube is placed in position in the photometer. The light in the photometer having been turned on for at least 1 minute, the rheostat is so adjusted that the micro-ammeter reading is 100. Four drops of sodium sulphide solution (10 per cent.) are added, the solution is mixed by making three gentle strokes with a glass plunger, and the micro-ammeter reading is at once noted. The reading obtained is referred to a curve connecting the photometer cell current with the amount of lead present, which has been established experimentally by working under similar conditions with known amounts of lead. The instrument is sensitive to 0·013 mgrm. of lead; the agreement with the theoretical results in test experiments was within 0·06 mgrm. Phosphates and calcium do not interfere. The only common metals which interfere are bismuth, mercury and tin. The interference of tin can be overcome by the addition of 1 ml. of concentrated potassium hydroxide solution before the addition of the sodium sulphide. S. G. C.

Reviews

SOLVENTS. By T. H. DURRANS, D.Sc., F.I.C. Monographs on Applied Chemistry. Third and revised edition. Pp. xiii + 205. London: Chapman & Hall, Ltd. 1933. 10s. 6d.

Little beyond what has already been said in this journal about the first and second editions of this book needs to be added. The addition of a further 26 pages to the book, again without any increase in price, reflects the increasing scope of the subject, with the resulting potentially wider public for the book, as well

as the deserved increase in circulation of the series of monographs, of which this is volume four, produced under the editorship of Dr. E. Howard Tripp.

The reviewer's comments on the second edition have, in so far as they were critical, been largely met, but the emphasis still lies heavily on the employment of solvents in the manufacture and use of cellulose lacquers. The reviewer is still of opinion that a sub-title indicating the restricted, albeit increasingly important, scope of the book, would prevent possible misunderstanding and disappointment.

A table of plasticiser proportions has been added as a third appendix, and the chapter on "vapour-pressure" includes new sub-sections on "blush numbers" and on evaporation rates. Apart from these specific additions, an increase in the number of solvents discussed, consequent on the introduction of new ones into the industry, is mainly responsible for the additional pages. A. L. BACHARACH

NATURAL VARNISH RESINS. By T. HEDLEY BARRY. Pp. xii and 294. London: Ernest Benn, Ltd. Price 42s. net.

This work, as its title implies, is restricted to the study of only those resins which are used in the varnish and allied trades.

It is divided into two parts, the first, covering 43 pages, being devoted to the history, botanical origin, physical characters, and general methods of analysis. This part of the work is of considerable interest, and includes a good deal of information not hitherto to be found, except in a scattered form in periodicals, etc. The second part, which forms the bulk of the work, deals with individual resins, including the copals, kauri, dammar, acaroid, sandarac, mastic, dragon's blood, kino, natural lacquers, rosin and shellac. The systematic account of these resins is well done, and forms very interesting reading. The pure chemistry of such bodies as rosin and shellac is brought well up to date, and the only section one would like to see expanded is that dealing with analysis. In any future edition this could easily be extended without interfering in the slightest degree with the groundwork of the book. Dealing with the Wijs method for the determination of the iodine value of resins, the author states that it "owing to its rapidity, is frequently adopted, and in the case of shellac has become firmly established as the standard method." Since the reviewer, in 1901, showed that the then existing published figures for shellac were hopelessly incorrect, as they were obtained from, in many cases, grossly adulterated samples, the standard method for the determination of rosin in shellac in this country has not been the Wijs, but the Hübl process. The latter is far less influenced by slight changes of conditions, and is only an additive reaction, giving about half the value given by the Wijs solution. It is true that the Wijs process is official in the United States.

Four papers on shellac, which are merely referred to in two lines on page 263, contain a great deal of analytical information which is absent from the present work. No reference is made to the influence of orpiment on the iodine value of shellac, which was first established in one of the papers referred to, and which caused so many pure samples of fine orange shellac to be condemned in the United States as containing rosin. To-day this influence is well recognised in India and in America, as well as in this country. The author appears to have lost sight of the terms on which shellac is marketed in London—a matter to which he devotes

some space. One illustration will suffice. TN shellac contracts for delivery, which constitute the bulk of the trade, provide for 3 per cent. only of adulterating matter: parcel to be accepted with fair allowance up to 10 per cent.: over 10 per cent. entitles to rejection.

The book will be found of considerable value to all interested in the varnish resins, but it is to be hoped that more information of value to the analyst will be forthcoming in any future edition. ERNEST J. PARRY

A TEXTBOOK OF INORGANIC CHEMISTRY. By Dr. FRITZ EPHRAIM. Second English Edition, Revised and Enlarged, by P. C. L. THORNE, M.A., M.Sc., Ph.D. Pp. xii+873. London: Gurney & Jackson. 1934. Price 28s. net.

The first English edition of this excellent treatise was reviewed in the ANALYST (1926, **51**, 651). The plan there outlined has remained unaltered; the text-matter is subdivided into seven sections, each of which has been brought up to date so as to include the most recent discoveries and theories. These additions to chemical knowledge are responsible for an increase of 68 pages.

The most interesting new-comers in the new edition are: The elements rhenium and masurium, both higher homologues of manganese; illinium (or florentium), the elusive member of the cerium group; alabamine, homologue of iodine; and virginium, homologue of caesium. It must be added that the individuality of the last two requires confirmation. We are also introduced to the binary compounds, fluorine monoxide (obtained by the action of fluorine upon caustic soda) and sulphur tetroxide (formed in the fluorination of sulphuric acid).

Throughout the book the reader is made aware of the steady progress of chemical science during the brief interval which has elapsed between the appearance of the two English editions. To name only a few advances, we are presented with the most recent views on the structure of atoms, ions, molecules, and crystals; on ionic volume and the parachor; on the constitution of the boron hydrides; on the properties of the rare earths and the lanthanide contraction. A considerable advance in our knowledge of the structure of silicates has been realised as the result of Bragg's *X*-ray analysis and the investigations of Goldschmidt on isomorphism. The conclusions arrived at by these two chemists are summarised in Chapter XXVII.

In these times of rapidly increasing knowledge and unavoidable specialisation, a textbook, such as the one under review, has become indispensable. It enables students and professional chemists to survey and retain their grasp of general chemistry, while reference books, such as Dr. Mellor's monumental work and the German handbooks (*e.g.* Gmelin-Kraut), record all that is known about the individual compounds. Of textbooks of the former type, a new edition is necessarily required at intervals of less than ten years. English-speaking chemists are fortunate to possess in this attractive volume Dr. Thorne's masterly translation of the fourth German edition. It is to be hoped that Ephraim's work will continue to appear in both languages whenever the need for a revised edition arises.

W. R. SCHOELLER

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