The ANALYST

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THE ANALYST

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THE SOCIETY FOR ANALYTICAL CHEMISTRY

BULLETIN

FORTHCOMING MEETINGS

Summer Meeting of the North of England Section, June 14th to 17th, 1963

THE twenty-sixth Summer Meeting of the Section will be held from Friday, June 14th, to Monday, June 17th, 1963, at the Savoy Hotel, **Blackpool.**

At 10.30 a.m. on Saturday an Ordinary Meeting of the Section will be held, at which a lecture will be given by H. Pritchard, M.Sc., F.R.I.C.

London Discussion Meeting of the Microchemistry Group, May 29, 1963

THE **date** of the fortieth London Discussion Meeting of the Group has been **changed** from Wednesday, May 22nd, to Wednesday, **May 29th, 1963,** at "The Feathers," Tudor Street, off Bouverie Street, Fleet Street, London, E.C.4, at 6.30 p.m.

The subject for discussion will be "Kjeldahl Nitrogen—the Digestion Process," and will be opened by P. R. W. Baker, M.Sc., A.R.I.C., and S. Jacobs, M.Sc., Ph.D., F.R.I.C.

Summer Meeting of the Biological Methods Group, June 13th, 1963

THE Summer Meeting of the Group will be held on Thursday, June 13th, 1963, when, by invitation of the United Dairies Ltd., a visit will be paid to their laboratories at Wood Lane, London, W.12.

PROGRAMME

11.15 a.m.	Introductory welcome by R. J. MacWalter, B.Sc., Ph.D., F.R.I.C., M.I.Chem.E.
11.30 a.m.	"Aspects of the Natural Composition and Hygienic Quality Schemes," by R. C. Wright, B.Sc., Ph.D.
12 noon	"Antibiotics in Milk," by J. Tramer, B.Sc., Ph.D.
2.00 p.m.	Conducted tour of the Laboratories.

PRELIMINARY NOTICE OF MEETING

Joint Meeting of the Scottish Section with The Institute of Chemistry of Ireland, September 5th and 6th, 1963

A JOINT Meeting of the Scottish Section with the Institute of Chemistry of Ireland will be held on Thursday and Friday, September 5th and 6th, 1963, in the Rupert Guinness Hall, **Dublin** (by courtesy of Messrs. Arthur Guinness, Son and Co. (Dublin) Ltd.).

The subject of the meeting will be "Modern Aspects of Chromatography." A number of original papers have already been offered, including contributions on Thin-layer and Gas Chromatography.

Tentative bookings for the nights of September 4th, 5th and 6th have been made at several hotels. Those who intend to be present at this meeting should notify the Honorary Secretary of the Scottish Section, Mr. J. W. Murfin, Boots Pure Drug Co. Ltd., Motherwell Street, Airdrie, Lanarkshire, as early as possible.

Full details of the programme, both scientific and social, will be announced as soon as they are available.

BRITISH STANDARDS INSTITUTION

DRAFT SPECIFICATIONS

A FEW copies of the following draft specifications, issued for comment only, are available to members of the Society, and can be obtained from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1.

Draft Specification prepared by a Code Drafting Committee.

D63/1605—Draft B.S. Code of Practice on Lining of Vessels and Equipment for Chemical Processes. Part 2: Lead Linings.

Draft Specification prepared by Sub-Committee INE/9/3—Optical Cells and Colour Filters.

D63/2165—Draft B.S. Specification for Optical Spectrophotometric Cells.

Draft Specification prepared by Sub-Committee PVC/1/12—Organic Pigments.

D63/2280—Draft B.S. Specifications for Organic Pigments for Paints. (B.S. 3599/6—13).

Draft Specifications prepared by Technical Committee NFE/27—Tin and Tin Alloys.

D63/4039—Draft B.S. Methods for the Sampling and Analysis of Tin and Tin Alloys. Part 9: Arsenic in Tin, Solders and White Metal Bearing Alloys.

D63/4040—Draft B.S. Methods for the Sampling and Analysis of Tin and Tin Alloys. Part 15: Copper and Lead in White Metal Bearing Alloys (Electro-deposition Method).

D63/4041—Draft B.S. Methods for the Sampling and Analysis of Tin and Tin Alloys. Part 17: Cadmium in Solders and White Metal Bearing Alloys.

Draft Specification prepared by Technical Committee CHE/8—Process Vessels and Filters.

D63/4324—Draft B.S. Specification for Hard Glass Enamelled Mild Steel Jacketed and Non-jacketed Pressure Vessels and Non-pressure Vessels for the Chemical and Allied Industries.

PAPERS ACCEPTED FOR PUBLICATION IN *THE ANALYST*

THE following papers have been accepted for publication in *The Analyst*, and are expected to appear in the near future. (This list contains titles unavoidably held over from the April *Bulletin* owing to shortage of space.)

" A Sensitive Microbiological Assay Procedure for Determining Magesium in Biological Materials," by K. S. Sastry, G. Padmanaban, P. R. Agida and P. S. Sarma.

"Determination of Trace Amounts of Chloride in Sodium Bromide," by R. B. Rashbrook and S. C. Woodger.

" The Analysis of Geranium Oil by Gas Chromatography," by G. E. Howard.

" Pyrethrum Analysis: A New Method," by J. H. N. Byrne, W. Mitchell and F. H. Tresadern.

" Precipitation of Cuprous Thiocyanate from Homogenous Solution," by E. J. Newman.

" Application of the Uranyl Salt Method to the Determination of Arsenic by the Oxygen-flask Technique," by A. D. Wilson and D. T. Lewis.

" The Volumetric Determination of Antimony in Antimony - Lead and Antimony - Tin - Lead Alloys," by G. Bradshaw.

" The Absorptiometric Determination of Silicon in Water. Part III. Method for Determining the Total Silicon Content," by I. R. Morrison and A. L. Wilson.

" The Determination of Silicon, Zinc and Magnesium in Gallium Arsenide by Neutron Activation Analysis," by D. E. Green, J. A. B. Heslop and J. E. Whitley.

" An Inexpensive Sampling Device for Gas Chromatography," by T. Doran and A. D. Sperrin.

" Precise Micro-determination of Zinc and Cadmium by Photometric Titration with EDTA," by D. B. Scaife.

" The Semimicro-determination of Chlorine in Agricultural Technical Organic Chemicals and their Formulations," a Report by the Chlorine in Organic Compounds Sub-Committee of the Analytical Methods Committee of the Society.

"The Polarographic Determination of Copper, Cadmium, Thallium, Lead, Tellurium and Iron in Selenium," by E. L. Bush.

" The Application of the AutoAnalyzer to the Determination of Zinc in Soils and Sediments," by R. E. Stanton and A. G. MacDonald.

"n-Propyl Gallate as a Gravimetric Reagent for Bismuth and Antimony," by A. D. Wilson and D. T. Lewis.

"The Determination of Antimony in Titanium Dioxide," by J. T. Yardley and D. J. B. Galliford.

" The Determination of Dinoseb in Potatoes," by J. A. Potter.

" A Glucose Oxidase Method for the Rapid Determination of Glucose in Starch Conversion Products," by K. R. L. Mansford and R. K. Opie.

" The Determination of Maltotetraose in Starch Conversion Products," by K. R. L. Mansford.

" Calcium Chloride Starch Dispersing Media," by J. R. Fraser and R. Hoodless.

" Titration of Water in Plasma or Red Cells with Karl Fischer Reagent," by J. D. Pryce.

" The Determination of Magnesium in Calcium Salts," by E. J. Newman and C. A. Watson.

" An Improved Type of Weight Burette for Use in Volumetric Analysis," by H. N. Redman.

" Polythene Wash Bottles for Volatile Solvents," by V. H. Booth.

" The Determination of Tocopherols in Plant Tissues," by V. H. Booth.

" The Volumetric Determination of Iron, Molybdenum and Tungsten in Fluoride Solutions," by J. B. Headridge and M. S. Taylor.

" The Determination of Phosphorus in Different Leathers by Oxygen-flask Combustion," by E. A. Weaver.

" A Rapid Solvent Extraction Sampling Technique for Neutron Activation Analysis," by T. B. Pierce and P. F. Peck.

" The Paper Chromatography of Some Substituted Cinnolines with Aqueous Solvents: Part II," by R. J. T. Graham.

" Detection, Determination and Identification of Furfuraldehyde in Hydrocarbon Oil," by R. B. Harrison.

" Nitrogen Factors for Chicken," a Report by the Meat Products Sub-Committee of the Analytical Methods Committee of the Society.

" The Determination of Selenium in Biological Material by Radioactivation," by H. J. M. Bowen and P. A. Cawse.

" Methods of Separation of Long-chain Unsaturated Fatty Acids," by A. T. James.

THE POLAROGRAPHIC SOCIETY

The Third International Congress of Polarography

THE Polarographic Society will be holding a six-day Congress of Polarography from July 19th to July 25th, 1964, at Southampton University. The Congress will be concerned with all aspects of polarography and will be open to members and non-members of the Society.

Details concerning applications, accommodation, submission and presentation of papers, exhibitions, excursions and other social activities will be published shortly. Further information can be obtained from the Organising Secretary, Dr. D. A. Pantony, Department of Metallurgy, Royal School of Mines, Prince Consort Road, London, S.W.7.

Films on Polarography

THE Polarographic Society has recently obtained new copies of the Czech films "Polarography" and "Oscillographic Polarography." These films provide a unique method of teaching the principles of polarography, and the Society is prepared to hire the films for exhibition to suitable private audiences, such as scientific associations or members of the staffs of individual firms. Details of the films will be sent on application to Mr. R. C. Rooney, c/o Southern Analytical Limited, Frimley Road, Camberley, Surrey.

THIRD INTERNATIONAL CONGRESS OF COSMETIC SCIENCE

THE Third Congress of the International Federation of Societies of Cosmetic Chemists is being organised by the Society of Cosmetic Chemists and will be held in New York from June 21st to 28th, 1964.

Anyone interested in attending this Congress is advised to get in touch with the General Secretary of the Society of Cosmetic Chemists of Great Britain, Mrs. E. Millman, 2 Lovers Walk, London, N.3, without delay. Arrangements are being made for party travel in a special flight by Boeing 707 to New York, at a cost of about £75 per person, subject to sufficient support being forthcoming.

SEVENTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY at OAK RIDGE NATIONAL LABORATORY

Analytical Instrumentation: Design, Development and Utilisation

THE Seventh Conference on Analytical Chemistry in Nuclear Technology will be held at Gatlinburg, Tennessee, U.S.A., from October 8th to 10th, 1963, under the sponsorship of the Oak Ridge National Laboratory.

The scope of the subject matter of the conference this year will differ somewhat from that generally followed in the past in that all sessions will be devoted exclusively to different aspects of a single subject, analytical instrumentation, covering the design, development and utilisation of manual and automatic methods of analysis. Another departure in the conduct of these conferences is that publication of the proceedings is being discontinued.

The conference will be composed of six sessions: (1) Instrumental Methods for the Analysis of Molten Salt Systems; (2) Instrumentation for the Remotely Controlled Analysis of Radioactive Materials; (3) Electroanalytical Instrumentation; (4) A Round-Table Discussion of Recent Developments in Analytical Instrumentation; (5) Analytical Spectroscopy and Gas Chromatography and (6) Instrumentation in Radiochemistry and Nuclear Analysis.

Participation either as a speaker or as a panelist will be on the basis of invited contributions; however, a limited number of papers, up to 25 minutes in length, are solicited and will be accepted provided their subject fits in with the over-all objectives of the conference and meets with the approval of the programme committee. Those who wish to make a contribution are requested to submit an abstract of about 500 words not later than July 10th, giving the name of the intended speaker and the amount of time required for the presentation.

Abstracts of papers and enquiries about the conference should be sent to the Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee, U.S.A., marked "Attention: C.D. Susano." Reservations for lodging should be sent directly to Riverside Hotel, Gatlinburg, Tennessee.

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THE ANALYST

EDITORIAL

Development of *The Analyst*

IN February of this year the Council of the Society received and—except for one matter whose implementation required further consideration—approved a report from the *Analyst* Development Committee. This Committee had, over a period of just on two years, studied criticisms of *The Analyst* and suggestions for changes in its contents and format. It began by inviting members and subscribers, both through a general announcement in the *Bulletin* and by direct personal invitation to members known to hold decided views, to submit their ideas. Thereafter a round dozen were interviewed singly or in small groups, and what they had to say was discussed and recorded in a detailed summary of evidence: this record alone eventually occupied 60 pages of close-spaced typescript.

When the points made at these meetings had been marshalled into some sort of order, a document was drawn up for the Committee to consider in greater detail than had been possible while the ideas were still being put forward. By this stage the Committee had had much valuable discussion with the propounders of the ideas, and it was clear that on some matters there were as many views as critics, and most of them contradictory. But some points of agreement (though never unanimous) had appeared. The members of the Development Committee, too, put forward their own suggestions, and the two written contributions that had been received were also considered. The outcome of the Committee's investigations and deliberations was the presentation to council of 35 recommendations for positive actions that the Committee unanimously believed would enhance the reputation and status of *The Analyst*.

As might be expected, it took longer to consider the criticisms and weigh the suggestions than it had to make them, and during this time some of the less controversial matters were referred to Council, received favourable decisions and were implemented. Already the appearance of the journal has been improved by starting each paper on a new page and by using a modern white paper in place of the older style cream-tinted paper for the text. The second of these changes was made only after the Committee had considered specimen pages printed on eight different papers and had compared them with other journals; even then the final choice was not endorsed until tests by PATRA had shown that the new paper was in many respects technically superior to the old, and inferior in none. But other suggestions, such as changing the size of the page or altering the size of the type, were found to have positive disadvantages and were rejected, and suggestions that the number of pages in each issue should be increased, although they were sympathetically received, can only be implemented when the rate of inflow of papers has permanently increased.

It appeared that some misconceptions might prevail as to the range of subjects considered suitable for publication in *The Analyst*, and as to whether there were any restrictions on authorship. The Committee hoped that removal of these misconceptions would result in more papers being offered, and to this end they have revised the "Notice to Authors." The new version, printed on p. 409, has a preamble intended to convey the information that *The Analyst* caters for all types of paper on the theory and practice of analytical chemistry, provided only that they reach a satisfactory standard of quality. Reviews, fundamental work, descriptions of specialised techniques and applications of existing methods in new contexts—all are essential to a properly balanced journal. *The Analyst* is, too, an international journal—a recent survey showed no less than a third of the contributions to be from overseas—

and the Editors are, when necessary, ready and willing to assist authors whose natural tongue is not English with the presentation of their papers. Nor do authors need to be members of the Society—roughly twice as many papers are accepted from non-members as from members (of course, membership of the Society has many *other* advantages).

Some anxiety had been expressed to the Development Committee about the refereeing system for papers. Much of this proved to be due to a lack of information on the subject; the Committee concluded that not only had the system to be fair (which it was), but that it had to be seen to be fair (which was much more difficult to arrange). Previously, acceptances have been based on a single referee's report, whereas rejections have required two or more adverse reports, obtained seriatim at much expense of time. In future all papers will be sent simultaneously to two referees; if their reports concur, final decisions will be made at once by the Editorial Committee, and if the original reports differ, the Committee will itself select a third referee as arbiter and make its decision only after receiving the third report. The two primary referees will be selected from the existing comprehensive panel of over 200, plus the additions that are constantly being made; this system will be much more rapid, if slightly more mechanical, than hitherto.

The Editorial Committee is, basically, the former Publication Committee. Its functions include the supervision of all aspects of production of *The Analyst*. But the old Publication Committee's responsibility for policy has been transferred to a new Publications Policy Committee. This move is in keeping with the increasing number and scope of the Society's publications, which include, besides *The Analyst* and *Analytical Abstracts*, Monographs, collections of Standard Methods, publications by the Analytical Methods Committee and sundry volumes of Symposium and Congress Proceedings. It is indeed to this Publications Policy Committee that Council has passed, for urgent attention, the question of implementing the excepted recommendation mentioned in the first sentence of this editorial. Although the Development Committee has successfully planned its own demise, it has left a more permanent successor on which will rest the responsibility for further development of *The Analyst*.

Even now, only half of the Development Committee's recommendations have been implemented, and an account of some of the remaining decisions must await a future occasion.

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ANNUAL GENERAL MEETING

THE eighty-ninth Annual General Meeting of the Society was held at 2.15 p.m. on Friday, March 8th, 1963, in the meeting room of the Royal Society, Burlington House, London, W.1. The Chair was occupied by the President, Dr. A. J. Amos, O.B.E., B.Sc., F.R.I.C. The Financial Statement for the year ending October 31st, 1962, was presented by the Honorary Treasurer and approved, and the Auditors for 1963 were appointed. The report of the Council for the year ending March, 1963 (see pp. 334–343), was presented by the Honorary Secretary and adopted.

The Scrutineers, Messrs. P. W. Shallis and K. L. Smith, reported that the following had been elected officers for the coming year—

President—D. C. Garratt, Ph.D., D.Sc., Hon. M.P.S., F.R.I.C.

Past Presidents serving on the Council—A. J. Amos, R. C. Chirnside, J. H. Hamence and K. A. Williams.

Vice-Presidents—S. G. Burgess and R. E. Stuckey.

Honorary Treasurer—D. T. Lewis.

Honorary Secretary—S. A. Price.

Honorary Assistant Secretaries—C. A. Johnson (Programmes Secretary) and D. W. Wilson.

Other Members of Council—The Scrutineers further reported that 143 valid ballot papers had been received. As the number of candidates for election as Ordinary Members of Council had been equal to the number of places to be filled, there had been no ballot for their election.

The President declared the following to have been elected Ordinary Members of Council for the ensuing two years—L. Brealey, A. G. Jones, E. Q. Laws, F. C. J. Poulton, S. G. E. Stevens and C. Whalley.

H. E. Brookes, P. F. S. Cartwright, B. S. Cooper, J. F. Herringshaw, R. M. Pearson and A. A. Smales, having been elected members of the Council in 1962, will, by the Society's Articles of Association, remain members of the Council for 1963.

C. J. House (Chairman of the North of England Section), R. A. Chalmers (Chairman of the Scottish Section), F. H. Pollard (Chairman of the Western Section), W. H. Stephenson (Chairman of the Midlands Section), D. W. Wilson (Chairman of the Microchemistry Group), W. Cule Davies (Chairman of the Physical Methods Group) and W. A. Broom (Chairman of the Biological Methods Group) will be *ex-officio* members of the Council for 1963.

The retiring President, Dr. Amos, thanked the Honorary Officers for their services to the Society during his term of office. He then formally installed Dr. Garratt, who for many years has been Chairman of the Analytical Methods Committee, as President.

After the business outlined above had been completed, the meeting was opened to visitors, and the retiring President delivered his Presidential Address (see pp. 344–351).

ORDINARY MEETING

AN Ordinary Meeting of the Society was held at 6.30 p.m. on Wednesday, May 1st, 1963, at University College, Gower Street, London, W.C.1. The Chair was taken by the President, Dr. D. C. Garratt, Hon.M.P.S., F.R.I.C.

The following paper was presented and discussed: "The Use of Magnetic Resonance Measurements in Chemistry," by Professor R. S. Nyholm, M.Sc., Ph.D., D.Sc., F.R.A.C.I., F.R.I.C., F.R.S.

MIDLANDS SECTION

THE Eighth Annual General Meeting of the Section was held at 7 p.m. on Thursday, March 28th, 1963, at the Nottingham and District Technical College, Burton Street, Nottingham. The Chair was taken by Mr. W. T. Elwell, F.R.I.C. The following appointments were made for the ensuing year:—*Chairman*—Mr. W. H. Stephenson. *Vice-Chairman*—Mr. W. T. Elwell. *Hon. Secretary*—Mr. M. L. Richardson, John & E. Sturge Ltd., Lifford Chemical Works, Lifford Lane, Kings Norton, Birmingham 30. *Hon. Treasurer*—Mr. F. C. J. Poulton. *Hon. Assistant Secretary*—Mr. R. Adkins. *Members of Committee*—Prof. R. Belcher, Dr. R. G. H. B. Boddy, Mr. H. E. Brookes, Mr. W. M. Dowson, Mr. G. Ingram, Mr. N. Nix, Mr. D. M. Peake, Dr. H. C. Smith (*ex-officio* for 1 year) and Mr. C. Whalley. Miss M. E. Tunnicliffe and Mr. J. Blenkin were re-appointed as Hon. Auditors.

The Annual General Meeting was followed by an Ordinary Meeting of the Section when the following paper was presented and discussed: "Reactions in Non-aqueous Solutions" by Dr. L. D. Pettit.

Annual Report of the Council: March, 1963

IT has become customary in recent Annual Reports of Council to record and comment on the increasing activities of the Society. During the present year these activities have at least been maintained.

For the second time in recent years the Society's Annual General Meeting—the eighty-eighth—was held outside London. At the invitation of the North of England Section, both the Annual General Meeting and the Bernard Dyer Memorial Lecture were held in Manchester, and Dr. D. W. Hill gave an address entitled "Research and the National Economy." Again, as in Birmingham two years previously, the lecture was well attended, including a substantial proportion of members from outside the North of England Section; the lecture was followed in the evening by the Society's Annual Dinner, again well attended by members from all parts of the country.

Although the report of the Midlands Section, given separately, refers to the Feigl Anniversary Symposium held in Birmingham in April, 1962, it is appropriate to mention it here. The Symposium was held in the Chemistry Department of the University of Birmingham and organised on behalf of the Society by the Midlands Section. Speakers and delegates from 28 countries—to a total of 400—attended to hear lectures, to join the discussions and to pay tribute to Professor Fritz Feigl. The Microchemistry Group, through their Chairman, Mr. C. Whalley, also paid tribute, from the microchemists of the United Kingdom, with the presentation of a magnificent glass vase. This Symposium is yet another in the line of successful Symposia organised at Birmingham by the Midlands Section, and all involved deserve cordial thanks for their work.

The Sections and Groups have again been active and meetings have been as frequent and widespread as in previous years. The Scottish Section organised a meeting, jointly with the North of England Section and at the invitation of the Chemistry Department of Queen's University Belfast, on a range of physico-chemical methods of analysis. In September the Microchemistry Group held a joint meeting with the Dublin and District Section of the Royal Institute of Chemistry in Trinity Hall, Dublin, the title being "Modern Trends in Small Scale Inorganic Analysis." The year was noteworthy in that the Physical Methods Group set up an Atomic Absorption Spectroscopy Discussion Panel with Mr. W. T. Elwell as Chairman and Mr. D. Moore as Honorary Secretary; the Panel held its inaugural meeting on December 12th, 1962, at which a paper entitled "Aspects of Atomic Absorption Analysis" by D. J. David, M.Sc., was read. The Council wishes success to the Physical Methods Group in this venture.

The annual conference of Honorary Secretaries was held somewhat earlier than usual, in January. In addition to the usual meeting, an informal meeting was held under the Chairmanship of Mr. C. A. Johnson, Programmes Secretary, in an attempt to obtain closer liaison with respect to the dates of meetings of the Sections and Groups and with respect to their subject matter. A similar meeting was again held in January, 1963, and further progress was made in this direction.

The Analyst Development Committee, which took the views of a considerable number of people during the course of its investigations, completed its report to Council in January, 1963. The report, which was considered by Council at a special meeting, contains numerous recommendations relating to the constitutions and functions of editorial and policy committees for *The Analyst*, the refereeing system, the contents and format of *The Analyst* and the Proceedings, advice to authors and instructions to referees.

During the year Dr. Evers retired from the Editorship of *Analytical Abstracts*. In considering the future of this publication, Council recorded their considerable debt to Dr. Evers for the part he had played in gaining for *Analytical Abstracts* the high esteem in which the publication was now held in the field of analytical chemistry. It is fully intended that *Analytical Abstracts* will in future be given the support necessary to maintain and to increase its high reputation.

The year 1962 has been busy for the President, Dr. Amos. He spent a week at the Feigl Anniversary Symposium, where, at the invitation of the Midlands Section, he took the Chair at the opening and closing sessions, and he represented the Society at the annual dinners of

other Societies and at the Ramsay Dinner, at which he replied to the toast to the guests. In addition he took an active part in the organisation of the 1st International Congress of Food Science and Technology, serving as a member of the Executive Committee and as Chairman of the Publicity Committee.

The Council records with particular pleasure the award of the C.B. to the Honorary Treasurer of the Society, Dr. D. T. Lewis. Council also records with pleasure the award of the C.B.E. to Professor A. C. Frazer and Professor H. B. Nisbet, and the award of the O.B.E. to Dr. A. M. Smith.

The Society now has 2097 members, an increase of 44 over the membership of a year ago.

LONG MEMBERSHIP—The congratulations and good wishes of the Council are extended to Dr. L. E. Campbell, Major F. K. Donovan, Dr. E. B. Hughes, Dr. D. W. Kent-Jones, Mr. A. W. Starey and Mr. R. W. Sutton, O.B.E., who have completed 40 years of membership.

DEATHS—The Council regrets to have to record the deaths of the following members—

A. Alcock	F. R. Dodd	F. C. B. Marshall
J. J. V. Backes	C. L. Hinton	W. J. S. Pringle
H. W. Christian	H. V. Horton	E. Russell
M. Corner	R. E. Jones	H. B. Salt
C. W. Cornwall	J. King	

SOCIETY MEETINGS—Six meetings of the Society were held during the year; the papers read and discussed were—

April, 1962, in London:

"Square-wave Polarography with Special Reference to the Analysis of Zirconium and Hafnium," by D. F. Wood, B.Sc., A.R.I.C., and R. T. Clark.
"The Determination of Gold by Extractive Titration," by A. W. Titley, B.Sc., A.R.I.C.
"An Automatic Coulometric-titration Assembly," by P. G. W. Scott, B.Sc., A.R.I.C., and T. A. Strivens, B.Sc.

May, 1962, in London, on the Determination of Sterols:

"Determination of Cholesterol for Clinical Purposes," by G. S. Boyd, Ph.D., A.H.-W.C., A.R.I.C.
"Determination of Cholesterol and its 7-Dehydro Derivatives," by J. Glover, M.Sc., Ph.D., A.R.I.C.
"Determination of Vitamin-D Secosterols," by E. Kodicek, M.D., Ph.D.
"Gas Chromatographic Examination of Sterols," by C. J. W. Brooks, Ph.D., A.R.C.S.
"The Determination of Animal Fat in Vegetable Fats by Gas Chromatographic Analysis," by K. R. Beerthuis, Dr. Chem.
"The Determination of Plant Sterols," by Professor T. W. Goodwin, D.Sc., F.R.I.C.
"Determination of Sterols of Wool Wax and Related Materials," by E. V. Truter, Ph.D., A.R.C.S., D.I.C.

October, 1962, in London, on Recent Developments in Polarography:

"Pulse Polarography," by H. M. Davis, B.Sc., A.Inst.P., A.R.I.C.
"Differential Cathode-ray Polarography," by H. I. Shalgosky, B.Sc., A.R.I.C.
"Analytical Aspects of Radio-frequency Polarography," by Dr. H. W. Nürnberg.

November, 1962, in London, on Fluoride, Teeth and the Analyst:

"The Determination of Fluorine in Inorganic Materials by Pyrohydrolysis," by H. J. Cluley, M.Sc., Ph.D., F.R.I.C.
"Fluoridation of Public Water Supplies," by J. Longwell, D.Sc., F.R.I.C., F.R.S.H.
"The Rôle of Analysis in Investigating the Mode of Action of Fluoride in Tooth Decay," by G. N. Jenkins, M.Sc., Ph.D.

December, 1962, in London, on Applications of X-ray Fluorescence:

"The Applications of X-ray Fluorescence Spectrometry in the Steel Industry," by D. F. Sermin, A.Met.
"The Determination of Lead in Air Filters, Vanadium - Nickel Ratios in Oil Ashes, and Strontium in Tap Water by the X-ray Fluorescence Spectrometer," by R. G. Stone, B.Sc., A.R.I.C.
"X-ray Fluorescence in Archaeology at the Museum Laboratory," by E. T. Hall, M.A., D.Phil.

February, 1963, in London, on Particle-size Analysis: Some Methods Used in the Sub-Sieve Range:

"The Size Analysis of Insoluble Drugs," by M. J. Thornton, B.Sc., A.R.I.C.
"Particle-size Analysis in the Formulation of Pesticides," by C. G. L. Furmidge, B.Sc., Ph.D., A.R.I.C.
"Particle Sizing in Aerosol Systems," by D. A. Blyth, B.Sc., J. M. Creasey and N. W. Wootten. B.Sc., A.Inst.P.

Sections and Groups

The present membership of the Sections and Groups, as will be seen from the reports that follow, is—

North of England Section	431
Scottish Section	117
Western Section	123
Midlands Section	372
Microchemistry Group	805
Physical Methods Group	904
Atomic Absorption Spectroscopy Discussion Panel	91
Biological Methods Group	331

North of England section—Membership of the Section totals 431. Because the main concentration is centred round Merseyside and Manchester, Liverpool and Manchester have again been the main centres for meetings. We record with sorrow the death of Mr. A. Alcock, Honorary Secretary during 1955.

In June, 1962, after a very successful period of office, Mr. Brian Hulme relinquished his post as Honorary Secretary and Treasurer, a post he had held since June, 1958. Mr. G. F. Longman was elected by the Committee to act as Honorary Secretary until the next Annual General Meeting.

The papers presented and discussed were—

Liverpool, January, 1962, Annual General Meeting:

"The Work of the Laboratory of the Government Chemist," by D. T. Lewis, Ph.D., D.Sc., M.R.S.H., F.R.I.C.

Manchester, April, 1962, jointly with the Biological Methods Group:

Discussion on "The Assessment of Psychostimulants," introduced by M. W. Parkes, B.Sc., Ph.D.

Llandudno, May, 1962, Summer Meeting:

"Some Experiences in Forensic Science," by G. B. Manning, B.Sc., M.B., Ch.B., F.R.I.C.

Belfast, June, 1962, jointly with the Scottish Section:

"Investigations on the Determination of Noble Metals by Oscillographic Polarography," by I. Beattie and R. J. Magee, M.Sc., Ph.D., F.R.I.C., F.I.C.I.

"Analytical Applications of the Flame Emission Spectra of Lead and Titanium," by C. L. Chakrabarti, M.Sc., A.R.I.C., R. J. Magee, M.Sc., Ph.D., F.R.I.C., F.I.C.I., and Professor C. L. Wilson, Ph.D., D.Sc., F.R.I.C., F.I.C.I.

"An Ultramicrospectrophotometric Method for the Determination of Complex Cyanides," by F. Haba and Professor C. L. Wilson, Ph.D., D.Sc., F.R.I.C., F.I.C.I.

"Differential Cathode-ray Polorography," by H. M. Davis, B.Sc., A.Inst.P., A.R.I.C.

"Instrumental Methods of Continuous Analysis," by G. Jessop, M.Sc., Ph.D.

"Applications of Vapour-phase Infra-red Spectroscopy to the Functional Group Analysis of Propoxy and Butoxy Compounds by Modified Zeisel Reactions," by D. M. W. Anderson, B.Sc., Ph.D.

"Applications of Modern Techniques in Spectroscopy," by R. A. C. Isbell, A.Inst.P.

"The Activation Analysis of High-purity Beryllium Using Penetrating Radiations," by C. A. Baker.

"Some Analytical Applications of Mass Spectrometry," by A. Quayle, M.Sc., A.R.I.C.

"A Modular Gas Chromatograph System for the Analysis of Exit Streams from Reactors and for the Application Work Required for Process Analysers," by C. W. Munday, B.Sc., A.R.I.C., and G. R. Primavesi, B.A.

"The Methylene Insertion Reaction for the Identification of Hydrocarbons by Gas Chromatography," by E. S. Lane, B.Sc., Ph.D., F.R.I.C.

Discussion on "Quantitative Gas - Liquid Chromatography in the Routine and Research Laboratories," introduced by A. F. Williams, B.Sc., F.R.I.C.

Lathom, October, 1962:

"The Analytical Laboratory in the Glass Industry," by F. Hartley, F.S.G.T., F.R.I.C.

Middlesbrough, November, 1962, jointly with the Tees-side Section of the Royal Institute of Chemistry:

"Solvent Extraction of Inorganic Compounds, Some Recent Developments," by Professor H. M. N. H. Irving, M.A., D.Phil., D.Sc., F.R.I.C., L.R.A.M.

Manchester, December, 1962, jointly with the Physical Methods Group:

"Nuclear Magnetic Resonance," by Professor E. R. Andrew, M.A., Ph.D.

SCOTTISH SECTION—Membership of the Section stands at 117 against last year's total of 123.

During 1962, seven meetings have been held, five in Glasgow, one each in Edinburgh and Belfast. The Belfast meeting, a two-day Symposium, was shared with the North of England Section. Two other meetings were held jointly with local Sections of other Societies: the November meeting with the Society of Chemical Industry, and the December meeting, as usual, conjointly by all four Chartered Bodies.

Audience numbers are greater, it seems, when the subject is of a more general nature rather than from a specific part of chemistry. The Annual General Meeting was not well attended, and it has been decided that no lecture will be given in future after the luncheon and business meeting.

The Section Committee records with pleasure the presence of the President of the Society at the Ramsay Dinner, when he ably replied to "The Guests."

The papers presented and discussed were—

Glasgow, January, 1962, Annual General Meeting:

"Applications of Analysis to Research Problems in the Gas Industry," by G. R. Boreham, B.Sc., A.R.I.C.

Edinburgh, February, 1962:

"Death by Poisoning," by A. C. Hunt, M.D.
"Problems in Criminal Investigation," by Det. Supt. J. K. McLellan, M.A., B.Sc., A.R.I.C.

Glasgow, March, 1962:

"The History of Food Technology," by T. McLachlan, D.C.M., A.C.G.F.C., F.R.I.C., M.I.Biol.

Belfast, June, 1962, jointly with the North of England Section:

Details of the papers read at this meeting are given in the report on the North of England Section.

Glasgow, October, 1962:

"The Chemistry of Wines and Spirits," by E. C. Barton-Wright, D.Sc., F.R.I.C., M.I.Biol.

Glasgow, November, 1962, jointly with the Glasgow Section of the Society of Chemical Industry on Cellulose Ethers:

"Applications of Cellulose Ethers," by F. C. Hall, Ph.D., M.Sc., A.M.I.Chem.E., F.R.I.C.
"Analysis of Cellulose Ethers," by A. F. Williams, B.Sc., F.R.I.C.

Glasgow, December, 1962, jointly with the Chemical Society, the Society of Chemical Industry and the Royal Institute of Chemistry:

"Thoughts on Meat," by E. C. Bate-Smith, M.Sc., Ph.D., M.Inst.R.

WESTERN SECTION—The membership of the Section now stands at 123.

During 1962 there have been 6 meetings of the Section, including the Annual General Meeting. The meetings have all been joint meetings, either with the local sections of the Royal Institute of Chemistry or with a Group of the Society.

The papers presented and discussed were—

January, 1962, Newport, Annual General Meeting, followed by joint meeting with the Cardiff and District Section of the Royal Institute of Chemistry:

"Radioactivity Measurements in Monmouthshire," by G. V. James, M.B.E., M.Sc., Ph.D., F.R.I.C.

March, 1962, Swansea, jointly with the Physical Methods Group and the South Wales Section of the Royal Institute of Chemistry:

"Spectrofluorimetry," by C. A. Parker, B.Sc., Ph.D., F.R.I.C.
"X-ray Fluorescence Analysis," by R. J. Otter, B.Sc., Ph.D.

April, 1962, Newton Abbott, jointly with the South Western Counties Section of the Royal Institute of Chemistry:

"The Technique of Sampling," film introduced by W. T. Elwell, F.R.I.C.
"Sampling of Ore," by G. V. James, M.B.E., M.Sc., Ph.D., F.R.I.C.
"Sampling of Soils and Crops," by B. M. Dougall, M.Sc., F.G.S., A.R.I.C.
"Sampling of Fertilisers, Foods and Feeding Stuffs," by F. W. Marston.
"Sampling of Liquids," by G. J. C. Nash, F.R.I.C.
"Sampling for Atmospheric Pollution," by B. T. Commins, M.Sc., A.R.I.C.
"Sampling of Airborne Dust," by N. M. Potter, M.Sc., Ph.D., F.Inst.F., M.I.Min.Ed., F.R.I.C.

October, 1962, Salisbury, jointly with the Mid-Southern Counties Section of the Royal Institute of Chemistry:

"The Rôle of the Analyst in the Food Industry," by Miss M. Olliver, M.Sc., F.R.I.C.

November, 1962, Gloucester, jointly with the Bristol and District Section of the Royal Institute of Chemistry:

Social evening.

December, 1962, Cardiff, jointly with the Cardiff and District Section of the Royal Institute of Chemistry:

"Gem Stones and Jewels, Natural and Synthetic," by R. C. Chirnside, F.R.I.C.

MIDLANDS SECTION—The membership of the Section is 372, consisting of 353 Ordinary Members and 19 Junior Members. This is a total increase of 17 members during the year. There are 9 Honorary Members of the Section.

Twelve meetings were held during the year: 5 in Birmingham, 2 each in Nottingham and Luton, and 1 each in Coventry, Wolverhampton and Northampton.

The Feigl Anniversary Symposium, honouring Professor Fritz Feigl's 70th birthday, was held at Birmingham University during April, 1962. Professor Feigl, an Honorary Member both of the Midlands Section and of the Society, himself chose Birmingham for this function. The Symposium was most successful. Presentations were made to Professor Feigl by delegations from Russia and Japan, and by the Chairman of the Microchemistry Group on behalf of all Microchemists.

Elwell Award, 1962—This annual award was won by Mr. F. J. Wallace, of Foseco International Ltd., for his paper on "The Determination of Magnesium in Aluminium Alloys by Atomic Absorption Spectroscopy."

The papers presented and discussed were—

January, 1962, Birmingham, on Developments in Gas Chromatography as Applied to Polymers:

"Recent Advances in Technique," by D. H. Desty.
"Gas Chromatography and its Use in Polymer Chemistry," by C. A. Finch.
"The Separation of the Degradation Products of Polymers," by R. S. Lehrle.

February, 1962, Birmingham, jointly with the Midland Region of the Association of Clinical Biochemists:

"Automatic Equipment for the Analytical Laboratory," by G. V. R. Mattock, B.Sc., Ph.D., A.R.I.C.
"Automatic Methods in the Analytical Laboratory," by I. D. P. Wotton, M.A., M.B., Ph.D., F.R.I.C.

February, 1962, Luton:

"Analytical Research," by J. Haslam, D.Sc., F.R.I.C.

March, 1962, Birmingham:

Annual General Meeting

March, 1962, Nottingham:

"Application of Radio-isotopes in Analysis," by D. Gibbons, B.Sc., Ph.D., A.R.I.C.

April, 1962, Wolverhampton:

"The Determination of Boron," by R. H. Biddulph, M.A., B.Sc., Ph.D., and H. J. Cluley, M.Sc., Ph.D., F.R.I.C.

May, 1962, Northampton, jointly with the Physical Methods Group and the Birmingham and Midlands Section of the Royal Institute of Chemistry, on Recent Developments in Semi-conductor Analysis:

"The Spectrographic Determination of Some Impurities in Gallium Arsenide," by J. H. Oldfield, F.R.I.C., and D. L. Mack.
"Radioactivation Analysis of Semi-conductors," by D. Hazelby, A.R.I.C.
"The Determination of Carbon and Silicon in Gallium Arsenide," by A. C. Tyrrell, J. M. Page and D. C. Newton, B.Sc.

May, 1962, Luton, jointly with the Microchemistry Group on The Status of Trace Metal Determinations:

"Ferrous Metals," by B. Bagshawe, F.I.M., M.Inst.F.
"Non-Ferrous Metals," by W. T. Elwell, F.R.I.C.
"Distribution in Soils," by H. H. le Riche, Ph.D.

October, 1962, Birmingham: presentation of papers for the Elwell Award, 1962.

"A Method for the Determination and Characterisation of Organic Bases in Pharmaceutical Preparations," by R. E. King, A.R.I.C.
"The Determination of Fluoride by Complexometric Titration," by M.A. Leonard, B.Sc., Ph.D., A.R.I.C.
"The Determination of Magnesium in Aluminium Alloys by Atomic Absorption Spectroscopy," by F. J. Wallace.

October, 1962, Nottingham:

"The Statistical Approach to Analysis," by D. A. Pantony, T.D., B.Sc., Ph.D., A.R.C.S., F.R.I.C.

November, 1962, Coventry:

"Solvent Extraction," by T. B. Pierce, B.Sc., M.A., D.Phil.

December, 1962, Birmingham, jointly with the Microchemistry Group:

"The Determination of Carbon and Hydrogen in Organic Materials," by Miss A. M. G. Macdonald, M.Sc., Ph.D., A.R.I.C.

MICROCHEMISTRY GROUP—The membership of the Group is now 805, an increase of 48 in the past year.

At the Feigl Anniversary Symposium in Birmingham in April, 1962, the Chairman of the Group, Mr. C. Whalley, presented Professor Feigl with a glass vase on behalf of all microchemists.

During 1962 four Ordinary Meetings of the Group were held: in London on February 23rd. (the Annual General Meeting followed by an Ordinary Meeting for the reading of original papers); in Luton on May 11th (jointly with the Midlands Section); in Dublin from September 21st to 23rd (jointly with the Dublin and District Section of the Royal Institute of Chemistry); in Birmingham on December 14th (jointly with the Midlands Sections). The papers read were—

London:

"The Ultra-micro Determination of Halides at Extreme Dilution," by E. Bishop, B.Sc., A.R.C.S.T., A.R.I.C., and R. G. Dhaneshwar, M.Sc.
"Development of a Simplified Spectroscopic Method for Non-routine Solution Analysis of Trace Metals," by C. P. Cole.
"The Ultra-micro Quantitative Determination of Ammonia by Means of Indanetrione Hydrate," by S. Jacobs, M.Sc., Ph.D., F.R.I.C.

Luton:

Details of the papers read at this meeting are given in the report on the Midlands Section.

Dublin:

"Modern Trends in Small-scale Inorganic Analysis," by Professor T. S. Wheeler, D.Sc., F.R.I.C., F.I.C.I., R. C. Chirnside, F.R.I.C., R. A. Chalmers, B.Sc., Ph.D., and D. J. Hingerty, M.Sc., Ph.D., F.R.I.C.

Birmingham:

Details of the paper read at this meeting are given in the report on the Midlands Section.

Five informal discussion meetings were held in London and one in Dublin. The topics discussed and the speakers who introduced them were:

"Determination of Traces of Copper," introduced by E. I. Johnson, M.Sc., F.R.I.C., and D. B. Adams, B.A., B.Sc.
"Do-it-yourself Ideas in Microchemical Apparatus."
"Ion Exchange in Microchemistry," introduced by J. Pilot, B.Sc., and J. A. R. Genge, M.Sc.
"Differences Between Continental and British Practice in the Determination of Elements in Organic Compounds," by W. Schöniger, Dr.ing.
A Review of all Topics Discussed at these Meetings.
"Modern Trends in Analysis."

PHYSICAL METHODS GROUP—The number of Group members is now 904. This is an increase of 60 since the last Annual General Meeting.

The Group has set up an Atomic Absorption Spectroscopy Discussion Panel, under the Chairmanship of Mr. W. T. Elwell, F.R.I.C., and with Mr. D. Moore as Honorary Secretary, with the aim of arranging discussion meetings on applications of this technique.

During the past year the Group has held five Ordinary Meetings; three were held in London and one each in Swansea and Northampton. The Swansea meeting was held jointly with the Western Section and the South Wales Section of the Royal Institute of Chemistry, the Northampton Meeting jointly with the Midlands Section and the Birmingham and Midlands Section of the Royal Institute of Chemistry, and one London Meeting jointly with the Polarographic Society. The papers read and discussed at the Ordinary Meetings of the Group were—

London, November, 1961:

"Electrochemical Methods in Analysis," by G. W. C. Milner, D.Sc., A.Inst.P., F.R.I.C.

London, February, 1962:

"Some Surface Effects in Electro-analytical Chemistry," by Professor H. A. Laitinen.

Swansea, March, 1962:

Details of the papers read at this meeting are given in the report on the Western Section.

Recent Developments in the Analysis of Semi-conductors—Northampton, May, 1962:

Details of the papers read at this meeting are given in the report on the Midlands Section.

Recent Work in Radiochemical Methods of Analysis—London, October, 1962:

"The Use of Charged Particles for Activation Analysis," by T. B. Pierce, B.Sc., M.A., D.Phil.
"Recent Developments in the Use of Radio-isotopes in Analysis," by T. T. Gorsuch, B.Sc., Ph.D., A.R.I.C.
"Recent Uses of Labelled Reagents in Biochemical Analysis," by J. K. Whitehead, M.Sc., Ph.D., A.R.C.S., D.I.C., A.R.I.C.

BIOLOGICAL METHODS GROUP—During the year the membership of the Group has increased from 316 to 331.

In the year ending on October 31st, 1962, the Group has held, in addition to the Annual General Meeting, three discussion meetings and made one laboratory visit. The papers read and discussed were—

December, 1961, London, Annual General Meeting:

Discussion on "The Assessment of Anti-atherosclerotics," introduced by G. S. Boyd, Ph.D., A.H.-W.C., A.R.I.C.

February, 1962, London:

Discussion on "The Assessment of Antibiotics in Animal Feeds," introduced by G. Sykes, M.Sc., F.R.I.C.

April, 1962, Manchester:

Details of the paper read at this meeting are given in the report on the North of England Section.

ANALYTICAL METHODS COMMITTEE—The progress of work during the year has been maintained. The number of committee meetings (73) showed an increase over that for the previous year (64), although the number of active committees and panels had decreased from 22 to 18. The book of Official, Standardised and Recommended Methods of Analysis, compiled and edited by Mr. S. C. Jolly, is due to appear in print early in 1963: this comprises about 350 pages of recommended methods published in Reports of the Analytical Methods Committee since 1927, together with a comprehensive Bibliography of authoritative methods emanating from countries on both sides of the Atlantic. Also with the printer are recommended methods for determining Trace Elements with Special Reference to Fertilisers and Feeding Stuffs: these are being published as a booklet comprising some 40 pages.

A new departure from the usual type of Report by the Analytical Methods Committee is one prepared by the Sub-Committee on Particle Size Analysis: this is a classification of methods of measurement of particles in the sub-sieve range (*i.e.*, below 76 microns), and it is to be published in *The Analyst* as a Review article. This classification represents the first part of the Sub-Committee's work; the second part is intended to be an appraisement of the principles or techniques of the methods listed in the classification, and it is envisaged that this work, which will necessarily involve experimental tests, will take some considerable time.

Other programmes completed during the year include the preparation of a Report on the Determination of Copper, by the Metallic Impurities in Organic Matter Sub-Committee (now

with the printer); a Report on Nitrogen Factors for Beef, by the Meat Products Sub-Committee; a Report on the Determination of Riboflavin in Animal Feeding Stuffs, by the Vitamins (Water-soluble) Panel of the Additives in Animal Feeding Stuffs Sub-Committee; a Report on the Oxygen-flask Method for the Determination of Organically-bound Chlorine in Pesticides and Formulations, prepared by the Chlorine in Organic Compounds Sub-Committee; and a revision of the methods for the Determination of the Capsaicin Content of Capsicum and its Preparations (originally published in *The Analyst* in 1959).

With the completion of most of its programme, the Additives in Animal Feeding Stuffs Sub-Committee has been disbanded: one of its original Panels—on Prophylactics—has now been reorganised as a Sub-Committee in its own right in order to carry on the very lengthy programme originally assigned to it. No new committees or panels have been set up during the year.

LIAISON WITH OTHER SCIENTIFIC ORGANISATIONS—During the year the appointments made were—

Chemical Council:
Dr. D. T. Lewis.

Joint Library Committee, Chemical Society:
Dr. J. G. A. Griffiths.

Parliamentary and Scientific Committee:
Dr. J. H. Hamence.

Royal Institute of Chemistry, Summer School Organising Committee:
Mr. A. N. Leather and Mr. C. Whalley.

International Congress XIX of Pure and Applied Chemistry, 1963, Scientific Committee:
Mr. C. Whalley.

B.S.I. Committees:

Mr. S. A. Price: Chemical Divisional Council.
Dr. C. B. Barrett: Technical Committee on Analysis of Emulsifying Agents etc.
Dr. R. E. Stuckey: Technical Committee on Sampling of Chemical Products.
Dr. R. E. Stuckey: Technical Committee on Bulk Measurement of Chemical Products.
Dr. R. E. Stuckey: Technical Committee on Physical Tests in Chemical Products.
Mr. G. A. Vaughan: Technical Committee on Terminology and Rules for the Expression of Reagent Strengths.
Mr. G. A. Vaughan: Technical Committee on Preferred Ranges of Indicator Solutions.

The Council of the Society thanks all its representatives for the work they have done in the various Committees and at various meetings during the year.

HONORARY TREASURER'S REPORT—The Society's auditors, Messrs. Ridley, Heslop and Sainer, carried out the audit of the Society's accounts, investments, etc., and have provided a balance sheet for the year ended October 31st, 1962. This was submitted to the Finance Committee on Wednesday, December 12th, and approved for submission to Council at their next meeting on Wednesday, January 9th, 1963. Copies of the accounts and balance sheet have been circulated to all members.

The Society continues to possess a strong and vigorous membership, which is still slowly increasing.

It will be remembered that our printers, Messrs. W. Heffer & Sons Ltd., Cambridge, increased their printing charges in 1961 by 10 per cent. for both *The Analyst* and *Analytical Abstracts*. This factor and the reasonable increase in salaries made by the Finance Committee to the permanent staff of the Society have increased expenditure and consequently diminished the excess of income over expenditure. The allocations to the Society's reserves for premises, special publications, etc., were therefore decreased from £1000 to £500. These reserves will be quite heavily depleted in the year 1962–63, by necessary compilation expenses associated with

the Annual Index for 1962 and 1963 and also with the Decennial Index covering the first ten years of *Analytical Abstracts*. The compilation costs of these alone will amount to about £1200, exclusive of printing, publication, etc.

No new investments have been made by the Society during the past year, the bulk of the monies having been allowed to accumulate in the Deposit Account at normal rates of interest.

Full details of the Schedule of Investments are given in the balance sheet, the fall in the market value of the Society's holdings being indicative of the financial fluctuations in share values that have affected both this country and the U.S.A. during the past year.

In financial transactions of this nature, the Society is continually advised by its brokers, Messrs. Chance & Co., and there does not appear to be any reason for any particular change in our investment policy. The position of the Society's finances may thus be regarded as satisfactory, although static, but it must be remembered that the Society is not run for profit but for extending those fields of knowledge embracing the science of analytical chemistry. Nevertheless, it is essential that the financial virility of the Society be preserved by the recruitment of new members and by increasing those revenues obtained by the sales, not only of *The Analyst* and *Analytical Abstracts*, but also of those authoritative publications that it is right and proper that the Society should publish.

PROGRAMMES COMMITTEE—Attendance at meetings during the year has been about average, although one evening, that on which Applications of X-ray Fluorimetry were presented, was seriously marred by fog. The element of chance that attends the traditional meetings devoted to the presentation of original contributions has led to a recent decision to abandon this type of meeting and to replace it, for a trial period, by some meetings arranged for the presentation of researches by workers in Universities and Colleges of Advanced Technology. Much time has been devoted during the past year to a consideration of a proposal that the Society should hold a Conference on Analytical Chemistry; the proposal has been accepted and it seems probable at the moment that such a Conference will be held at Nottingham University during the third or fourth week in July, 1965. It is intended that this Conference should be devoted, in the main, to original work rather than to review papers. The scientific content of the meeting will be organised by the Programmes Committee and a local Committee will be formed to deal with its organisation.

THE ANALYST—The introduction with current volume of a white, calendered, paper in place of the former cream matt paper is probably the most noticeable of recent changes made to improve the general appearance of *The Analyst*. Another is the transformation of the old "Notes" section into a section of Short Papers.

The 1962 volume contained 984 pages, 56 more than the record 1960 volume, and 124 more than last year. This increase was required by a slightly greater number (9 more) of papers and notes describing original work, the total being 160, in addition to five Review Papers and four Scientific Reports prepared by various Committees. There has been a sharp increase in the number of Book Reviews (83 as against 59 last year). Circulation has again increased, and 7300 are now being printed of each issue (7000 last year).

Four of the five Review Papers were concentrated in the first half of the year; it has not proved possible to maintain an even flow, and it must be expected that there will be rather greater numbers in some years than in others. Their value to members and non-members alike is emphasised by the continued steady sale of reprints.

Eleven issues of the Bulletin were distributed with *The Analyst* during the year.

During the year Miss E. R. Prince joined the editorial staff in place of Mr. Harris, who has transferred to *Analytical Abstracts* as Assistant Editor.

ANALYTICAL ABSTRACTS—Several changes of staff took place in 1962, the most important being the retirement, on October 31st, of Dr. N. Evers from the Editorship, which he had held since the inception of *Analytical Abstracts* in 1954. He was succeeded by Mrs. H. I. Fisk, with Mr. Brian Harris, formerly Editorial Assistant in *The Analyst* office, as Assistant Editor. Dr. R. E. Essery, who had been working as a part-time assistant since 1959, retired in June.

In spite of these, and other changes, the total number of abstracts published in 1962 was 5564 on 716 pages; this is the highest in any one year since *Analytical Abstracts* began, the previous record being 5522 abstracts in 1960.

Sales have continued to rise and, as a result of a study by a large industrial group in the U.S.A. on a replacement of their own bulletin with *Analytical Abstracts*, we have now received an order from them for 150 subscriptions in 1963.

In view of this order it was decided that we should try to extend our advertising in the U.S.A., on an exchange basis. Of the several journals approached, favourable replies were received from *Applied Spectroscopy*, *Journal of the Association of Official Agricultural Chemists* and *Cereal Science Today*. Although it is against the policy of the *Journal of Biological Chemistry* to enter into exchange agreements, they have offered to insert an occasional advertisement, free of charge, when convenient to them. The equivalent advertisements from America will appear in *The Analyst*, this being a more suitable medium than *Analytical Abstracts*.

The Decennial Index will be due in 1964, and it has been arranged that Dr. N. Evers will prepare the matter for the Subject section.

Certain changes were made in the constitution of the Editorial Committee. Mr. B. A. Ellis retired from the Chairmanship in July, but agreed to remain on the Committee as an ordinary member, and was succeeded by Mr. B. S. Cooper; Mr. A. G. Jones, Imperial Chemical Industries Ltd., Plastics Division, was co-opted in October as an additional member to deal with the organic chemistry field; and Dr. N. Evers, on his retirement from the Editorship of *Analytical Abstracts*, has agreed to remain on the Committee as an ordinary member.

An abstractors' meeting, followed by a lunch, was held in March. About 40 regular abstractors attended, and many problems, both editorial and abstracting, were discussed.

A. J. AMOS, *President.*

R. E. STUCKEY, *Honorary Secretary.*

Address of the Retiring President

A. J. AMOS, O.B.E., B.Sc., Ph.D., F.R.I.C.

(*Delivered after the Annual General Meeting, March 8th*, 1963)

The Society Yesterday, To-day and To-morrow

WE have reached a stage in the life of our Society when more than ever before in its history we should be forward-looking. The potentialities for extension of the scope of its interests, for expansion of its membership and for enhancement of its status are great, but, if they are to be brought to fruition, our outlook must be more a welcome for the future than a pride in the past. We must give as much thought and supervision to a long-term policy as we do to the planning of our yearly programmes. Before this can be done, we must have clear in mind the direction and the scope of the progress we wish to achieve; we must be agreed upon our goal before we can plan ahead. In this address I shall leave with you my thoughts upon how and to what end we should direct our efforts in the hope that they may prove to be a stimulus that will lead to the preparation and implementation of a planned policy for the future. But although my main concern is to look ahead, I am mindful of the precept of Lord Halifax that—

"The best way to suppose what may come is to remember what is past."

The birth certificate of our Society is to be found in the *Chemical News* for August 14th, 1874, where it is reported that 27 analysts, who were dissatisfied with the Report of a Parliamentary Committee on the Adulteration Act of 1872, met together at a Cannon Street hotel and agreed that "an Association of Public Analysts be formed for the purpose of mutual assistance and co-operation." The name selected for the Association was "The Society of Public Analysts." The reason that prompted the formation of this Association, its inaugural constitution and its adopted title justify the conclusion that the initial interest of our Society was not analytical chemistry, but the analysis of food and drugs. That this was so is clear from the objects of the Society, which were published a few months later. These were—

(*i*) To promote and maintain the efficiency of the laws relating to adulteration.

(*ii*) To promote, and as far as possible to secure, the appointment of competent Public Analysts.

(*iii*) To improve the processes for the detection and quantitative estimation of adulteration and to secure uniformity in the statement of the results by holding periodical meetings for the reading and discussion of original papers on chemical and microchemical analysis, especially with reference to the detection of adulteration.

When a quarter of a century had passed, the Rules of the Society were amended so that membership was not restricted to "analysts in practice," but was open to anyone who had a genuine interest in analytical chemistry. Eight years later, when the Society was incorporated, opportunity was taken to extend its title and to broaden its objects in recognition of the "other analytical chemists" who were then within its ranks. Nevertheless, another 5 years passed and the Society was 38 years old before precedent was broken and the Presidential Chair was occupied by a representative of the "other analytical chemists."

Reference to the volumes of *The Analyst* published in that and the other years of the fourth decade of the Society's existence provides supporting evidence that the interests of the Society were becoming less sharply focused on food and drugs and were coming more into line with its revised objects, which were "to encourage, assist and extend the knowledge and study of analytical chemistry and of all questions relating to the analysis, nature and composition of natural and manufactured materials." Critical surveys of advances in methods of analysing cellulose and rubber were commissioned for *The Analyst* and the subjects of original papers in the journal included dyestuffs, paper, turpentine, mineral oils, rubber, disinfectants, metallic ores and alloys, detergents, coal, gases, blood stains and documents.

Diversification of its interests material-wise continued to increase as the Society veered numerically towards a Society of Other Analytical Chemists and Public Analysts. At the same time, because of the progressive discovery of new analytical tools, a cross segregation of members based on methodology tended to develop. Eventually this trend reached a stage that warranted official recognition and support, and these were provided in 1943 by the decision of Council to permit the formation within the Society of Groups for the furtherance of specialised branches of chemical analysis. In less than 2 years, three Groups were in existence—a Microchemistry Group, a Physical Methods Group and a Biological Methods Group.

At the time the formation of the first Group was imminent, which fell in the 70th year of the Society's existence, the number of papers dealing with food and drugs appearing in any volume of *The Analyst* was little more than one-third of the total. The preponderance of papers on analysis in other contexts tended to become even greater as papers read at meetings of the three active Methods Groups began to flow into the journal, because very few of them dealt with food and drugs. This pronounced shift of emphasis in the themes of the papers in the Society's journal was paralleled by a change in the structure of its membership; by the time the Society was 75 years old its "other analytical chemists" outnumbered its Public Analysts by more than 15 to 1. From a small group of Public Analysts absorbed in the problems of food and drug analysis the Society had grown into a large band of chemists whose collective interests covered the fundamental principles of analytical chemistry, methodology, the application of analytical techniques in a wide range of contexts other than food and drugs, and the teaching of analytical chemistry.

The name of the Society, which in any event was too long and cumbersome, was no longer apposite, and, indeed, was misleading. Some progressively minded members of Council who subscribed to Bernard Shaw's dictum that "all progress is initiated by challenging current conceptions and executed by supplanting existing institutions" began to press for a change of title, but they met considerable opposition; they found it easy enough to "challenge current conceptions" but a very uphill task to "supplant existing institutions." However, eventually good sense prevailed and at the close of 1953 the Society became "The Society for Analytical Chemistry" and entered the fold of learned societies.

Some Public Analysts took the view that with this change they were losing their birthright, whereas their emotion should have been pride in the fact that the vision and the efforts of their enthusiastic forbears who founded an Association in 1874 and nurtured it in its early years had culminated in a learned Society of nearly 2,000 members that catered for all aspects of theoretical and applied analysis. I am sure that those early Public Analysts to whom we owe so much—men like Redwood, Muter, Allen, Hehner and Dyer, to mention but a few—would have been proud indeed had they had a foresight of the outcome of their labours.

With this change of name, the Society of yesterday became the Society of to-day. We are now in the last year of our first decade as a learned Society and it is an opportune time to review our achievements and our policies—to decide whether our resources, our plans and our activities have been so directed that we are serving analytical chemistry in general and our members in particular to the best of our capabilities.

It is much to the credit of the Society that when British Chemical Abstracts were discontinued, an event that occurred about the time the Society changed its name, Council decided to repair the loss to analytical chemists by publishing monthly a journal of abstracts of analytical papers. This was particularly a laudable action because it called for additional and specialised staff and it was undertaken at a time when the Society was experiencing an annual loss on its journal. Council's faith in this venture to serve analytical chemistry was vindicated, and to-day the sales figure for *Analytical Abstracts* is over 7500. The international reputation of these abstracts, which are the only ones relating to analytical chemistry that can be purchased independently of abstracts of other branches of science, is deservedly high, but I believe that neither in status nor sales has this publication yet reached its zenith.

At the time the Society of yesterday became the Society of to-day it was making an annual loss of about £2000 on *The Analyst*, and within 3 years the deficit in the annual accounts of *Analytical Abstracts* was a similar sum. These losses were made good—as were the publication losses of other scientific societies—by grants from the Chemical Council, but the situation was a frustrating one. Before the Society could hope to progress, it had to become self-supporting,

and it achieved this target in 1958, being the first of the four beneficiary Societies to dispense with the aid of the Chemical Council. It has consolidated its financial position in the intervening years, and, although it has been and will again be faced with unavoidable rises in expenditure, I am confident that we shall never again go back on the dole.

Another innovation made since the Society changed its names is the Programmes Committee. Before its appointment, the paper-reading meetings were planned by the Publication Committee and with few exceptions they consisted of papers selected from those submitted for publication in *The Analyst*. This practice served well enough yesterday, but in the face of the quickening tempo of scientific research its retention would have made the Society a historian instead of a pioneer of analytical developments.

The planning of the Programmes Committee has been based upon the sound premise that in selecting topics for meetings of the Society priority should be given to those subjects that are currently of widespread interest. In place of the old type of meeting in which several already submitted papers on widely divorced subjects were read—a type of meeting well suited to the earlier days of the Society of Public Analysts—it favours the meeting at which invited specialists present papers on a common theme, particularly the principles and practice of a modern analytical technique. Reference to the 1962–63 programme of the Society reveals that four of the six paper-reading meetings are of this type, the subjects, for each of which a series of papers was commissioned, being polarography, X-ray fluorescence, particle size analysis and magnetic resonance. The 1961–62 programme had a similar pattern, three of the five meetings having as their respective themes, the oxygen flask combustion technique, new analytical reagents and the application of infrared spectroscopy to analytical problems. In giving the programmes of the Society this new look, the Committee did not at first eliminate the older type of meeting, but in the light of later experience it has decided not to retain it as a regular feature.

The meeting arranged for April resembles the old type of meeting in that the programme embraces a number of topics, but there the similarity ends; the papers have not been chosen from those submitted to *The Analyst*, but will be contributions from research students in universities and colleges of advanced technology. This is a new venture and if it is successful it might well be repeated in future years. Even if these meetings for research students attract only the relatively small audiences that tended to become characteristic of our traditional multi-subject meetings, there is a good case for their continuance; they will have a missionary impact by bringing the Society to the notice of potential members, whereas at the old type of meeting we only preached to the converted.

Because of the trend of advance in applied analysis, the topic of a one-theme meeting will more often than not be a physical method of analysis. Not infrequently the method warrants periodical discussion over a number of years because its devoted band of followers introduce modifications into the technique, make improvements in an instrument or discover new applications of the analytical procedure. However, there is a limit to the number of meetings the parent Society can hold each session, and it may well be that the only way it can keep pace with the advance of analytical chemistry is to relegate the organisation of more meetings to specialist panels.

The creation of a Sub-Group, Panel—call it what you will—to provide a forum for the discussion of a new specialised analytical technique may have an insurance value by arresting the formation of what has been called a "splinter group," since the best way of ensuring that the exponents and adherents of a new technique conduct their discussions and reviews under the aegis of the Society is to give them a niche within our constitution. I am sure that Council took a step in the right direction when last year it approved the precedent of permitting non-members of the Society to join the recently formed Atomic Absorption Spectroscopy Discussion Panel. By thus fostering in a practical manner the interests of specialists outside the Society, we effect a liaison that may in the course of time bring some of them into our ranks. Had we been sufficiently forward-looking in this respect in the past the Society might have become the centre for discussions and reports of activities and progress in a newer technique by specialists whose desire to foregather urged them to form organisations of their own.

As long ago as 1884 the Council then in office appointed a Committee to examine the various methods of milk analysis in use and to report upon their respective accuracies. Forty years later, the need for standardisation of analytical methods had extended to other fields

of work and had become sufficiently pressing to prompt the Council to appoint a standing Committee to advise when and in what direction a study of the applicability and reliability of competitive methods was desirable. This was the forerunner of the present Analytical Methods Committee. Within a short time, the standing Committee of 1924 had advised and Council had approved the formation of two working Sub-Committees, one to deal with the analysis of condensed and dried milk and the other with essential oils. Last year, its offspring, the Analytical Methods Committee, was supervising 18 Sub-Committees and Panels, each of which was either guiding or conducting research on specific analytical problems.

This notable expansion of the work of the original Standing Committee was made possible by an action taken soon after we became the Society of to-day, a progressive action of "supplanting existing institutions." This was an appeal to industry to provide the funds that would enable the Analytical Methods Committee to maintain a paid Secretariat. Until then, not only the collaborative analytical work but all the necessary ancillary secretarial work had been performed free of charge by members of the Sub-Committees and Panels. They were all busy men whose professional duties had first call on their time and accordingly the consideration of the outcome of a practical exercise and the issue of a final report were often seriously delayed because the associated not inconsiderable volume of paper work could not be done quickly.

Following industry's avowed interest in and financial support for the work it was doing, the Analytical Methods Committee widened its activities and published a "Bibliography of Standard, Tentative and Recommended or Recognised Methods of Analysis," a book of 34 sections that contained well over 6000 references. Encouraged by the sale of 1500 copies of this book, the Committee has produced a second edition on more ambitious lines; it is wider in scope and reproduces in full instead of by reference all the Committee's recommended methods. This book, which bears the title "Official, Standardised and Recommended Methods of Analysis" was published at the beginning of March. Between these two editions, the Analytical Methods Committee published a book of recommended methods for the analysis of trade effluents, based on an investigation made jointly with the Association of British Chemical Manufacturers, and, in a few weeks, will have on a sale a book on the determination of trace elements.

The parent Society also has added to what are termed "other publications" in the Annual Accounts by initiating what will become a series of Monographs. It is planned that these Monographs shall be books for the bench rather than for the reference library. The series began with "Methods for the Analysis of Non-Soapy Detergent Products" and this will shortly be followed by "The Determination of Sterols."

Supplementary publications edited by the parent Society or by its Analytical Methods Committee can and undoubtedly will enhance the status and benefit the finances of the Society, but we must never lose sight of the fact that *The Analyst* and *Analytical Abstracts* are its life blood. We cannot afford, therefore, to be complacent about sales of *The Analyst* and *Analytical Abstracts*, but must periodically review our publication policy. The wisdom of so doing is proved by the fact that in its recent report the specially appointed Analyst Development Committee saw fit to make 30 recommendations.

In comparing the Society of to-day with the Society of yesterday I have made no reference to number of employees, size of office accommodation, annual income and expenditure, number of pages in *The Analyst*, and the like because retrospective comparison of these and other material items are not a true measure of progress. Our concern should be whether we are doing more than we did to stimulate and to sustain the march of analytical chemistry, whether the contributions we may make to this end take heed of the ever-widening horizons of this branch of science, and whether we give adequate coverage to each of the multitudinous interests of those concerned with the teaching, the theory and the practice of analysis. And particularly we should ask ourselves whether we cater too much for the expert and the experienced and serve too little the embryo and newly fledged analysts, because there is truth in Franklin Roosevelt's observation that the test of progress "is not whether we add more to the abundance of those who have too much; it is whether we provide enough for those who have too little."

Looking back as we have done at the Society of yesterday enables us to gauge the soundness and the success of the plans adopted as measures of development. That we have made progress is beyond doubt: now the scope of the Society's interests extends, as it should do,

over the whole realm of analytical chemistry viewed from the standpoint of techniques or contexts; the meetings of the parent Society are supplemented by meetings organised by specialist Groups and by new Sections, thereby providing greater opportunity for members to keep pace with new work; the old type of meeting comprising papers on unco-ordinated subjects has been replaced by a single-subject meeting that attracts an audience with a keen interest in all the papers in the programme; the work of the Analytical Methods Committee has been intensified and accelerated and has earned the interest and financial support of industry; the programme of each Society meeting is judiciously planned and planned well in advance by a specially appointed Committee instead of remaining a matter of chance; finances have been put on a sound basis; and the Society has undertaken the task of making available throughout the world abstracts of analytical literature. In the light of these and other developments it cannot be denied that to-day the Society, through its meetings, through its journals, through its "other publications" and through its Analytical Methods Committee, is serving analytical chemistry and analysts to better effect than did the Society of yesterday.

Having looked from to-day into the past, it is time to turn to the future. What of the Society of to-morrow? Its control will not be in our hands, but the success that attends the efforts of those who will be in charge may be much influenced by the course we pursue —what they reap will spring from what we sow.

Our first endeavour must be to ensure that in our meetings and in our journal we give complete coverage in the field of analytical chemistry no matter how greatly or how rapidly the field extends. To achieve this, we must maintain a keen, active and well-balanced Programmes Committee. The primary function of this Committee, which, I believe, may well become the most important of the Society's Committees, will be to keep constant watch for promising new techniques, for new applications of existing techniques, and for industrial and legal developments that create new problems for the analyst, and then to arrange meetings at which specialists will speak on these subjects. A secondary duty of the Committee might well be to remedy the absence from *The Analyst* of papers on a subject that is of widespread interest or of growing importance by arranging a Symposium on the subject.

The possibility and desirability of arranging joint meetings with other organisations should also be frequently reviewed by the Committee. Such meetings not only assist the Society to extend its sphere of influence, but may engender interest in it and thereby initiate recruitment among those who have never enquired what it has to offer because they do not regard themselves as analysts. There are many in this category and we should not neglect any measure that will attract them to our ranks. A chemist who is occupied in making quantitative determinations of one or more constituents of a parent material is still an analyst, even if the identification and separation are performed by an instrument and his final measurement that completes the assay involves only the taking of a reading on this same or an ancillary instrument. He may be termed a physicist or a physical chemist, but he is just as much an analyst as his predecessor who made the same determinations by classical analytical procedures, and we should take positive steps to bring to his notice the fact that there is a place for him in our Society.

There is need also to forge a link between the Society, perhaps through specialised groups, and organised bodies of those who are interested in the construction and performance rather than the application of specialised analytical tools. Such liaison benefits both bodies; it enables the analyst to understand better the performance, the sources of error, the specificity and the sensitivity of the instrument and it suggests to the instrument specialist possible new analytical uses of the tool.

During the investigation made by the Analyst Development Committee, it became clear that despite our graduation from a professional body to a learned Society, *The Analyst* had not acquired the status of a learned journal throughout the academic world. It is understandable that in days gone by the channel of publication sought for a paper on some fundamental principle of analysis was one of the recognised learned journals rather than one devoted mainly to papers on food and drugs with special reference to adulteration. The justifiable hope that this attitude would be abandoned in the light of the change in the status of the Society and in the contents of its journal was not realised. No longer do papers on food and drugs predominate in *The Analyst*, but academic research workers are still loth to see their papers surrounded by papers on "applied" analysis. This is not the time nor

place to delineate upon the line of demarcation between or the relative importances of applied analysis and what has been variously qualified as fundamental, pure or basic analysis, but the issue is clear. Our policy for the future must be to eradicate misconception about the Society and its interests and to preach the interdependence of pure and applied analysis until *The Analyst* is accepted in academic circles as an appropriate journal for the analytical papers that at present they send elsewhere.

In the first place, we may have to go out and seek such papers, relying upon personal appeal and persuasion by members of Council and of the Publication Committee. If these efforts are successful, other papers will follow and the inflow will become self-expanding. But we can do more than this. We can plan to bring the Society more frequently and more closely to the notice of academic institutions. Notices of meetings on notice boards can help, but a closer contact is required; we need to bring the Society itself and not merely records and announcements of its activities into the universities and technical colleges. We are making a start in this direction in the meeting that is arranged for April at the Chelsea College of Science and Technology, but we should plan others that are not designed specifically for post-graduate students.

April's meeting brings the Society to the notice particularly of young analysts still in training—potentially Society members of to-morrow. It is better that they should have first-hand knowledge of the Society before and not after they go into industry or teaching, and we should strive to make this type of meeting a regular feature of our annual programme. We should look upon these meetings as "bread upon the waters" and accordingly not be disheartened if at first they do not attract large audiences.

If we achieve what should be our aim—to have the Society of to-morrow recognised as all-embracing in its interests in the field it serves—then its meetings and its journals will be considered to be appropriate for contributions upon not only basic analytical procedures, the application of analysis in specific contexts and the potentialities of specialised analytical tools, but also upon the theory, history, philosophy and teaching of analytical chemistry. As this aim approaches realisation, a venture worthy of consideration would be the publication of two journals rather than a considerably enlarged *Analyst*. *The Analyst* would be devoted to papers on analytical problems and procedures particular to the application of analysis in specific contexts, and a new journal, which might be entitled "The British Journal of Analytical Chemistry" would be the site of theoretical and practical papers on fundamental analytical chemistry and papers on the history, philosophy and teaching of analytical chemistry. In my opinion, this would be a development worthy of mature consideration. I realise that it would involve various administration and financial problems, but I believe that they could be solved without great difficulty.

Analytical Abstracts has made and will continue to make the Society more widely known, and now produces an income in excess of the cost of production. These are sound, albeit material, reasons why the publication should have a major call upon the Society's resources, but there is an ethical reason why we should be prepared to make special efforts to ensure its continuation. Having voluntarily undertaken the task of providing this service for analysts, we are under a moral obligation to do all that is within our power to give it permanency. And our pride as a learned Society and our desire to stimulate the advancement of analytical chemistry should preclude lack of financial support or inadequate supervision of administration ever causing *Analytical Abstracts* to fall short of the high standard they have attained.

The existing Group structure of the Society had much to commend it when it was introduced 20 years ago, but its retention unchanged in the Society of to-morrow might become a sign of old fashioned thinking. To-day, very many analysts who are unconversant with filter sticks and other specialised and elegant equipment dear to the heart of the earlier microchemists are working with samples or determining amounts much smaller than those that were the topics of discussion in the early meetings of the Microchemistry Group. As micro-analysis becomes progressively more commonplace, the retention of a major specialist Group devoted to microchemistry will be difficult to justify. The wisdom of retaining the Biological Methods Group as a major Group is arguable for a different reason. Biological methods are still a specialised branch of analysis, but because it is so very specialised its application is limited and advances of note are few and far between. Accordingly, the stage has been reached when the Group Committee finds itself at a loss each year how to build

a programme. The reverse holds good in the Physical Methods Group. Developments in and extension of the applications of physical methods have been so great that physical techniques warranting discussion far exceed the number of Group meetings that can be held. Moreover, the methods and their uses are of such general interest that many of the meetings of this Group might well be meetings of the parent Society and *vice versa*. I believe, therefore, that the days of the existing Groups are numbered; the interests of two of them are insufficiently specialised and those of the other too highly specialised for them to remain as major Groups in the Society of to-morrow—the segregation of interests would be too artificial and unrealistic. Rather do I see a series—and a changing series—of Panels or Discussion Groups that will look after the interests of specialists and ensure that the main and subsidiary meetings of the Society between them give ample coverage to the latest developments and trends in analytical chemistry. Some of these Panels or Groups will be longer lived than others, but whenever a stage is reached at which it becomes an onerous task to scrape together sufficient papers to build what has previously been a customary programme, the function of a Group should be relegated to a watching brief for a new discovery or a resurgence of interest in its specialised field.

Thought will have to be given to the place and function of the Analytical Methods Committee of the Society of to-morrow. It has been suggested that the work performed by this Committee and its Sub-Committees and Panels, although in keeping with the interests and the activities of the Society of yesterday, does not come within the purview of a learned Society. This is not my view. I believe it right and proper for a learned Society concerned with analytical chemistry to initiate and sponsor investigations designed to evaluate or to improve the reliability of existing or to devise new methods of analysis. But it is also my belief that the investigations it sponsors should extend over a wide area of analytical chemistry and embrace both fundamental and applied problems. The work of the Analytical Methods Committee in the Society of yesterday and to-day has not done this; it has been limited to a narrow field and, in view of the too slowly disappearing impression that the Society's interests are still only those of the Public Analysts, it is unfortunate that the narrow field is that of food and drugs.

Restriction of all but two or three of the Committee's investigations to food or drugs has not been a matter of choice, because the investigations are prompted by requests put to the Committee, not infrequently by other bodies. The reasons why requests for investigations have not come to the Committee from industries other than those concerned with food or drugs should be investigated in the hope that the situation can be rectified, because the scope of the Committee's researches in the Society of to-morrow must be much wider. It must be much wider not only to preclude its giving a misleading picture of the Society's interests and status, but also to safeguard the essential financial support it receives from industry. It is unrealistic to expect organisations whose business is in petroleum, heavy chemicals, engineering, rubber, metals and the like to be willing to subsidise heavily researches that rarely extend beyond problems in the analysis of food and drugs. If these industries cannot or do not submit analytical problems to the Committee, then the scope of the investigations should be widened by initiating or sponsoring research of a fundamental nature. I am convinced that if in the Society of to-morrow the work of the Analytical Methods Committee continues to be confined within the present narrow limits, the scheme will have an adverse effect upon the reputation of the Society and, moreover, is likely to become but a shadow of its former self through lack of financial support.

In planning for the Society of to-morrow, we should not be content to fix our sights at the national level. The Society has 255 overseas members representing 47 nationalities and non-member subscriptions to the Society's journals come from over 90 countries. This should serve as an incentive for us to formulate our policy for the future with not only the national but the international reputation of the Society in mind. To-day, many of the non-member subscribers to *The Analyst* and *Analytical Abstracts* know the Society only as a name that appears on those journals; we should not rest until they and all other analysts throughout the world recognise it as an authoritative body in the field of analytical chemistry that is contributing significantly to the advancement of that branch of science. One means to this end is to make the Society periodically the focal point of a gathering of analysts from all parts of the world. I welcome, therefore, the approval by Council of a plan to hold a Conference on analytical chemistry in 1965. I believe that with dedicated determination

on the part of Council, with an enthusiastic Conference Committee and with the experience of the highly successful conferences that have been held at Oxford, St. Andrews, Edinburgh and Birmingham, this meeting can achieve a success that will be an assurance that the goal of international acceptance of the Society as an organisation of high standing in the field of analytical chemistry is realistic and attainable.

The universe of analytical chemistry is expanding at a fascinating speed; so great has been progress in the recent past that looking ahead we can expect to see, in the words of Alexander Pope, "New distant scenes of endless science arise." The opportunities before us are therefore great, but unless our outlook is continuously anticipatory, the time will come when we shall begin to lose the status we have won. We should be constantly on the watch for developments that attract increasing attention or are likely to do so because of their potentialities so that at an appropriately early stage they can be the subjects of papers in our meetings or journals. If we wait until a new trend in analysis has been established before we provide a platform for it, we shall be too late. On more than one occasion in the past we have thus lost a great opportunity, and specialist groups that might have been part and parcel of the Society have arisen as independent bodies. This should never happen again —the Society should be in the van of the advance and not a camp follower.

In bringing to a close this review of the prospects that lie before the Society and steps we can take to bring them to fruition, I would remind you of those lines from Lowell—

> "New times demand new measures and new men;
> The world advances, and in time outgrows
> The laws that in our fathers' day were best."

Let us hope then that the succession of members through whose hands will pass the formulation and the implementation of policy will be men of vision, men who look from the plains of to-day to the heights of to-morrow. And let us be firmly resolved not to be bound by the shackles of tradition, but ever ready to prune, to reconstruct and to explore.

Anniversary Dinner

In the evening following the Annual General Meeting, a Dinner to celebrate the eighty-ninth anniversary of the Society was held, by kind permission of the Court of Assistants of the Grocers' Company, at Grocers' Hall, Princes Street, E.C.2. The members and guests, numbering 155, including all the living Past Presidents of the Society, were received by the President, Dr. A. J. Amos, O.B.E., F.R.I.C. and Mrs. Amos. The President afterwards took the Chair at the Dinner.

The Guests of the Society and of the President included The Right Honourable the Lord Todd, F.R.S., (Past President of The Chemical Society) and Lady Todd; The Honourable Mr. Justice Lloyd-Jacob, M.A., D.C.L., (Chairman of the Analytical Methods Trust); E. Le Q. Herbert, Esq., B.Sc., F.H.-W.C., F.R.I.C., M.I.Chem.E., F.Inst.P., F.Inst.F., (Past President of The Royal Institute of Chemistry) and Mrs. Herbert; S. I. Levy, Esq., Q.C., M.A., Ph.D., F.R.I.C., and Mrs. Levy; D. D. Moir, Esq., M.Sc., F.R.I.C., (President of The Association of Public Analysts) and Mrs. Moir; Mrs. B. Lamb, B.Sc., F.R.I.C., (Chairman of The Polarographic Society) and Mr. Lamb; M. A. T. Rogers, Esq., B.Sc., Ph.D., F.R.I.C., (Research Controller, Imperial Chemical Industries Ltd.) and Mrs. Rogers.

The Loyal Toast was proposed by the President.

Lord Todd, proposing the toast of The Society for Analytical Chemistry, recalled his undergraduate course in inorganic analysis—gravimetric determinations, by text-book methods, of elements in simple solutions, starting with silver nitrate and progressing through the classical qualitative analytical groups of metals. Perhaps this hardy beginning had led him away from analytical into other kinds of chemistry; it certainly had led him to appreciate the skills required of practising analysts. But unless a proper training was given, which included arousing an interest in the subject, the profession of analytical chemistry was likely to be short of recruits. This was not simply a task for the Universities or Colleges of Technology, but was one that the Society was particularly well fitted to tackle. He concluded with a tribute to *Analytical Abstracts*, and to the Society for starting when *British Abstracts* had stopped and thereafter developing *Analytical Abstracts* into the world's foremost single-subject abstracting journal.

Dr. Amos replied by recalling that in his Presidential Address he had dwelt on the Society's past, present and future. The Society was as concerned as Lord Todd at the difficulty of getting sufficient analysts, and it intended to show that it had much to offer to those engaged in teaching analytical chemistry, doing fundamental research into the subject and working to solve the analytical problems of industry, commerce and legislation. To this end it was planning closer liaison with the Universities and Technical Colleges, and was reorganising its specialist panel system to cater for all advances in technique as soon as they appeared. Success in this depended on those who gave their time to serve as Members of Council and as Honorary Officers, both of the parent Society and of the Sections and Groups. There was no lack of such voluntary workers and, in paying tribute to them, he felt that the Society's success was assured.

Dr. D. T. Lewis, the Government Chemist and Honorary Treasurer of the Society, proposed the toast of The Guests. Besides the representatives of other Societies, there were present Mr. Justice Lloyd-Jacob—a Bernard Dyer Memorial Medallist of the Society as well as Chairman of the Analytical Methods Trust—and Dr. S. I. Levy, an eminent Queen's Counsel, who had served in the Ministry of Munitions in the first World War and was Assistant Director of the Ministry of Supply in the second. Also all the living Past-Presidents of the Society were present, making this a unique occasion.

Dr. S. I. Levy, Q.C., in reply, alluded to the days when he and Dr. Amos had been Officers of the Chemical Club. He had left chemistry to make himself a career in the Law. He was particularly pleased that Mr. Justice Lloyd-Jacob, Her Majesty's Special Judge appointed to deal with Patent cases, was present. It had been his privilege and pleasure to appear many times before his Lordship. On behalf of all the guests he thanked the Society for its hospitality.

The proceedings concluded with Dr. Amos calling on Dr. D. C. Garratt, the incoming President and Chairman of the Analytical Methods Committee, and investing him with the Presidential Badge. Dr. Garratt presented Dr. Amos with a replica of the Society's Badge to wear as Past President.

Applications of Infrared Spectroscopy

Part X.* The Zeisel Determination of t-Butoxyl Groups, and the Anomalous Reactions of t-Butylphenols†

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Zeisel determinations on t-butoxyl compounds give non-quantitative and variable results. t-Butyl iodide decomposes thermally to isobutene, the equilibrium involved being affected by the reaction variables and by the addition of phenolic compounds. The over-all effect is therefore particularly complex for aromatic t-butoxyl compounds, since phenolic compounds are formed within the reaction medium as de-alkylation occurs.

Results are presented showing that more satisfactory analyses can be obtained when hydrobromic acid is used in place of hydriodic acid. t-Butyl bromide suffers $\not>2$ per cent. decomposition to isobutene when boiled under reflux with constant-boiling hydrobromic acid; moreover, this decomposition is reproducible under given reaction conditions, and correction factors can therefore be applied. Since t-butoxyl compounds are de-alkylated almost as quickly in hydrobromic acid as in hydriodic acid, the reaction periods required are not significantly longer; the period required varies from 2 to 3 hours, and is dependent on the nature of the sample.

Boiling under reflux with constant-boiling hydrochloric acid offers a method of differentiating between true t-butoxyl compounds and those t-butyl compounds that react anomalously in hydriodic and hydrobromic acids.

The utilisation of t-butyl and t-butoxyl compounds has increased greatly in recent years, *e.g.*, in antioxidants,[1,2] perfumery chemicals,[3] free-radical reactions,[4,5] graded oxidants[6,7] and in chromatographic separations.[8] The relatively easy removal[9,10] of t-butyl and t-butoxyl groups makes them useful in reaction intermediates[11] and as protective groups in syntheses, *e.g.*, of peptides.[12] Steric effects,[9] rearrangements[13] and instability[14,15] are factors that combine with the property of ease of removal to complicate the functional analysis of t-butoxyl groups. t-Butylphenols react anomalously in Zeisel determinations,[16,17] and some of the attendant analytical difficulties have been indicated.[18]

Only a few papers have discussed the application of the Zeisel reaction to butoxyl compounds in general. Of these, only two—so far as we are aware—have quoted results for the tertiary isomer. Houghton and Wilson[19] reported, without comment, a recovery of only 18·8 per cent. of the theoretical yield of t-butyl iodide from t-butyl alcohol; under different reaction conditions, Kirsten and Nilsson[20] obtained 60 to 70 per cent. recoveries, and stated that "tertiary butanol appears to give a fairly stable volatile iodide, although the reproducibility of recovery is not good."

It has long been known that t-butyl iodide is unstable at its boiling-point (103° C), the equilibrium—

$$C_4H_9{}^tI \rightleftharpoons C_4H_8 + HI$$

being established.[21] Some decomposition must therefore occur in Zeisel determinations (compare Campbell and Chettleburgh[16]), in which the reaction temperature is 127° C. In view of the discrepancies between the recoveries reported,[19,20] a spectroscopic[22] study of the recovery of t-butyl iodide from reflux in hydriodic acid was undertaken in an attempt to improve the accuracy of determining t-butoxyl groups.

It became clear that the use of hydriodic acid was analytically unsatisfactory when it was found that: (*i*) variation of the reaction conditions gave recoveries of t-butyl iodide ranging from 19 to 80 per cent.; (*ii*) under standardised reaction conditions, the yields of t-butyl iodide were affected by the presence of phenolic compounds in the reaction medium.

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t-Butoxyl compounds react rapidly[23,24] with aqueous hydrobromic and hydrochloric acids, and t-butyl bromide and chloride are more stable thermally than is the iodide; the possibility of basing analytical reactions on boiling under reflux with those acids was therefore investigated.

Experimental

Compounds—

(*a*) Samples of t-butyl alcohol[25] and t-butyl halides conforming to literature description were obtained by redistillation under reduced pressure of reagent-grade commercial samples. Since t-butyl iodide quickly develops a dark colour, small amounts were redistilled daily. Isobutene was prepared by dehydration (with concentrated sulphuric acid) of purified t-butyl alcohol.

(*b*) *t-Butyl ester*—t-Butyl 3,5-dinitrobenzoate was prepared; the specimen conformed to literature description.

(*c*) *t-Butyl ethers*—t-Butyl phenyl ether, t-butyl-*p*-tolyl ether and t-butyl-1-naphthyl ether were prepared by Grignard reactions with t-butyl perbenzoate[26,27]; the specimens gave satisfactory elemental analyses (Weiler and Strauss, Oxford). Dark colours developed on storage, and these specimens were redistilled under reduced pressure as required.

(*d*) *t-Butylphenols*—Samples were supplied by Dr. R. L. Williams, Messrs. Kodak Ltd. and Messrs. I.C.I. (Dyestuffs Division) Ltd. Liquids were purified by redistillation. Most of the samples, however, were low-melting solids not readily purified by recrystallisation; these were purified by zone-melting.

Apparatus, reagents and procedure—

These have been described,[28,29] together with details of (*i*) the technique for trapping volatile reaction products and (*ii*) the infrared vapour-phase method for their subsequent identification and determination. Particular care is necessary when transferring the contents of the trap to the gas-cell; t-butyl iodide decomposes so readily that direct warming of the trap over a flame is inadvisable. Satisfactory results were obtained by immersing the trap in water at 80° to 90° C, the sodium chloride cell windows being suitably protected (with plastic covers) during this operation.

A slight reaction occurred between t-butyl halides (particularly the iodide) and the sodium chloride cell windows, so that the windows "fogged" much more quickly than usual. The validity of calibration curves had therefore to be checked more frequently than in previous investigations.

Use of solid scrubbers—

Aqueous solutions hydrolyse t-butyl halides to t-butyl alcohol; hydrolysis of the iodide occurs extremely rapidly.[30] It is therefore essential (compare Campbell and Chettleburgh[16]) to use a solid scrubber in determinations of t-butyl halides. Soda asbestos[31] has given satisfactory results throughout our studies.

Results

Experiments with constant-boiling hydriodic acid—

(*a*) *Rate of reaction of t-butoxyl compounds*—Zeisel determinations were conducted on t-butyl alcohol, t-butyl 3,5-dinitrobenzoate and t-butyl-1-naphthyl ether under standard conditions. The conditions were: volume of hydriodic acid, 6 ml (sp.gr. 1·70, pre-conditioned[28]); nitrogen flow rate, 6 to 8 ml per minute; weight of phenol added, 30 mg. Sample weights yielding 2 to 4 mg of t-butyl iodide were taken. The yields of t-butyl iodide at the reaction times stated were as shown in Table I. Burwell, Elkin and Maury[32] have already commented on the fact that ethers are not always less reactive than alcohols.

(*b*) *Recovery of t-butyl iodide*—Samples of t-butyl iodide (in small weighing bottles fitted with ground-glass stoppers—see Anderson and Duncan[28]) were placed in the Zeisel reaction flask; the recovery from boiling under reflux in hydriodic acid was investigated, the reaction conditions being the same as those outlined in (*a*) above. The maximum recovery varied from 58 to 80 per cent.; about 80 per cent. of the total recovery in each determination distilled within 20 minutes. For fixed weights of samples of t-butyl iodide, small variations in recovery

TABLE I: YIELD OF t-BUTYL IODIDE FROM DIFFERENT COMPOUNDS

Compound	Yield of t-butyl iodide (as percentage of theoretical) After reflux for 1 hour	After reflux for 2 hours	After reflux for 3 hours
t-Butyl 3,5-dinitrobenzoate	76·0	80·8 (max.)	—
t-Butyl-1-naphthyl ether	40·5	66·6 (max.)	—
t-Butyl alcohol { 1st determination	42·5	48·7	56·6 (max.)
t-Butyl alcohol { 2nd determination	39·5	45·0	60·9 (max.)

resulted when: (*i*) the volume of hydriodic acid was decreased from 6 to 1 ml, (*ii*) the flow rate was varied from 4 to 12 ml per minute and (*iii*) the weight of phenol was varied from 0 to 100 mg. Little variation in the rate of recovery was found when the temperature of the condenser water was increased (compare Belcher, Fildes and Nutten[33] and Inglis[34]).

(*c*) *Production of isobutene*—In all these determinations some isobutene was produced, the sum of the molar recoveries of t-butyl iodide and isobutene accounting for the t-butyl iodide taken.

A time - recovery experiment with 2,6-di-t-butyl-4-methoxyphenol in which Campbell and Chettleburgh's[16] experimental conditions were used gave results agreeing well with those reported[16]; boiling under reflux for 1 hour gave the theoretical yield of methyl iodide, together with isobutene and a yield of t-butyl iodide that, calculated as methyl iodide, gave an apparent methoxyl content of 21 to 22 per cent. The ratio of the molar yields of isobutene and t-butyl iodide was, however, constant over the whole reaction period, *e.g.*, boiling under reflux for 10 minutes gave approximately 70 per cent. of the total yield of isobutene and also approximately 70 per cent. of the total yield of t-butyl iodide. This does not support Campbell and Chettleburgh's implication[16] that the isobutene results from decomposition of some t-butyl iodide that does not distil in the earlier stages of the reflux period.

The molar ratio of isobutene to t-butyl iodide (*i.e.*, the extent of decomposition of the t-butyl iodide) was also much greater than in any of our previous experiments. It was suspected that this resulted from the changes made in the reaction conditions in order to duplicate Campbell and Chettleburgh's experiments.[16] These workers, in testing scrubber effects, determined the total apparent methoxyl content of 2-t-butyl-4-methoxyphenol under four different reaction conditions, and found four different values ranging from 18·06 to 22·56 per cent. This range was confirmed when these experiments were repeated with a solid scrubber. Changes in reaction conditions, and not scrubber hydrolysis effects, therefore cause the variable results. This effect was further investigated as described below.

(*d*) *Variation in yield of t-butyl iodide with reaction conditions*—In a series of experiments, a constant weight of t-butyl-4-hydroxyanisole (mixed 2 and 3 isomers) was allowed to react under different conditions; these are shown, together with the yields of t-butyl iodide obtained, in Table II. Further experiments showed that cresols and other phenolic compounds caused similar variations in the results. The conjoint addition of other solubilisers, such as propionic anhydride and hypophosphorous acid, further complicated the effect.

Other experiments indicated that phenolic compounds, formed in the reaction medium during the de-alkylation reaction, contributed to the decomposition of t-butyl iodide. (1) t-Butyl-4-hydroxyanisole (5 mg) was allowed to react in hydriodic acid (6 ml), with no added phenol. The recovery of t-butyl iodide was 80 per cent., in agreement with the result

TABLE II: YIELD OF t-BUTYL IODIDE FROM 5-mg SAMPLES OF BUTYLATED HYDROXYANISOLE UNDER DIFFERENT REACTION CONDITIONS

Nitrogen flow rate, ml per minute	Hydriodic acid (sp.gr. 1·70) used, ml	Phenol added, mg	Yield (as percentage of theoretical)
4	1	30	19
4	6	30	51
6 to 8	1	10	53
6 to 8	6	0	80
6 to 8	6	10	72
6 to 8	6	30	62
6 to 8	6	60	50
12 to 15	1	30	45
12 to 15	6	30	73

in Table II. (2) The reaction medium was boiled for a further 4 hours to eliminate all traces of alkyl iodides, and the mixture was then cooled. A further 5 mg of sample and 30 mg of phenol were added; the recovery of t-butylphenol was 52 per cent., compared with 62 per cent. (see Table II) for the corresponding "straight" reaction with 30 mg of phenol. (3) The reaction medium was again boiled for 4 hours, and then cooled; a further 5 mg of sample and 30 mg of phenol were added. The recovery of t-butyl iodide was then only 42 per cent., compared with 50 per cent. for 60 mg of phenol in Table II. Thus the effect of the total phenol added (60 mg) was apparently augmented by the sum (approximately 6 mg) of the weights of phenolic compounds formed in determinations (1) and (2).

EXPERIMENTS WITH CONSTANT-BOILING HYDROBROMIC ACID—

(*a*) *Recovery of t-butyl bromide*—When 6 ml of hydrobromic acid, 30 mg of phenol and a nitrogen flow rate of 6 to 8 ml per minute were used, the recovery of samples (2 to 5 mg) of t-butyl bromide after boiling under reflux for 1 hour was 90·7 per cent. and, after 2 hours, 98·4 per cent. (maximum yield). An equilibrium of the form—

$$C_4H_9{}^tBr \rightleftharpoons C_4H_8 + HBr$$

must exist,[35] but under the stated reaction conditions (reflux temperature 115° C) the extent of decomposition to isobutene does not exceed 2 per cent. Indeed, only traces of isobutene were detectable in the infrared spectrum of the reaction products; some polymerisation[35] of isobutene may occur. The recoveries of t-butyl bromide were reproducible and were not strongly influenced by small changes in reaction conditions or in the amounts of phenol added.

(*b*) *Rate of reaction of t-butoxyl compounds*—With use of the same reaction conditions as in (*a*) above, the rate of evolution of t-butyl bromide from some t-butoxyl compounds was determined. The results are shown in Table III. The reaction time required varies from 2 to 3 hours, depending on the compound being analysed. When these results are corrected by +1·6 per cent. (the percentage loss of t-butyl bromide during recovery), only the results for two of the ethers are slightly low; this may well reflect the state of purity of these specimens.

(*c*) *The anomalous reaction of t-butylphenols*—Some t-butylphenols were boiled under reflux in constant-boiling hydrobromic acid for 2 to 3 hours. Nearly quantitative yields of t-butyl bromide were produced. Such compounds cannot therefore be distinguished from t-butoxyl compounds by this reaction.

TABLE III: YIELD OF t-BUTYL BROMIDE FROM t-BUTOXYL COMPOUNDS

Compound	Yield of t-butyl bromide (as percentage of theoretical)		
	After reflux for 1 hour	After reflux for 2 hours	After reflux for 3 hours
t-Butyl alcohol	95·4	98·3 (max.)	—
t-Butyl 3,5-dinitrobenzoate	97·0	98·6 (max.)	—
t-Butyl phenyl ether	86·5	91·1	96·2 (max.)
t-Butyl-p-tolyl ether	86·8	93·3	95·6 (max.)
t-Butyl-1-naphthyl ether	90·8	93·6	97·5 (max.)

EXPERIMENTS WITH CONSTANT-BOILING HYDROCHLORIC ACID—

Under the reaction conditions specified in "(*a*) Recovery of t-butyl bromide" above boiling under reflux with constant-boiling hydrochloric acid for 2 hours gave the results listed below.

(*a*) Recovery of added t-butyl chloride was nearly quantitative (>98 per cent.) (compare Kistiakowsky and Stauffer[36]).

(*b*) t-Butyl alcohol and t-butyl 3,5-dinitrobenzoate gave 98 per cent. of the theoretical yields of t-butyl chloride.

(*c*) t-Butyl ethers gave 60 to 65 per cent. of the theoretical yield of t-butyl chloride.

(*d*) The reactions of the t-butylphenols were—

(*i*) No t-butyl chloride formed—
2,4-di-t-butylphenol;
5-methyl-2-t-butyl-4,6-dinitroanisole;
4-t-butylphenol.

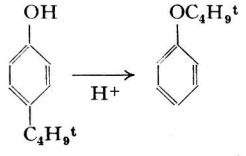
(*ii*) <10 per cent. of t-butyl chloride formed—
5-methyl-2-t-butylphenol;
t-butylated-4-hydroxyanisole (mixed 2 and 3 isomers);
2,6-di-t-butylphenol.

(*iii*) <20 per cent. of t-butyl chloride formed—
2,4-dimethyl-5-t-butylphenol;
3-methyl-4,6-di-t-butylphenol.

Conclusions

Boiling under reflux with constant-boiling hydrobromic acid is a satisfactory method of analysis for t-butoxyl groups. Under the reaction conditions described, decomposition of t-butyl bromide does not exceed 2 per cent., and the appropriate correction factor can be applied to the analytical results. The reaction period varies from 2 to 3 hours, depending on the compound being analysed. When the infrared method of determination[22] is being used, prolongation of the reaction period is not critical, although this might be inadvisable for volumetric or gravimetric determinations of the t-butyl bromide. Boiling under reflux with constant-boiling hydrobromic acid does not distinguish between true t-butoxyl compounds and t-butylated phenols.

Boiling under reflux with constant-boiling hydrochloric acid, however, offers a method of making this distinction. The yields of t-butyl chloride vary from 60 to 98 per cent. for t-butoxyl compounds, and from 0 to 20 per cent. for the range of t-butylphenols studied. It is possible that a rearrangement[27] of the form—



occurs in acid solution, the extent of the rearrangement depending on the concentration of acid and the nature of the substituent groups and substitution pattern in the phenolic compound.

The results presented show clearly that boiling under reflux with hydriodic acid does not give a satisfactory analytical reaction for t-butoxyl groups. The equilibrium—

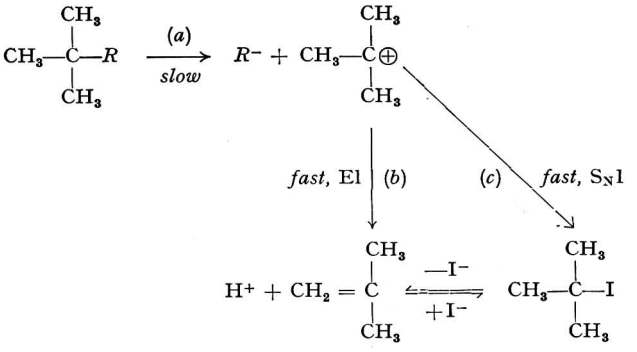
$$C_4H_9{}^tI \rightleftharpoons C_4H_8 + HI$$

is clearly dependent on the ratio of sample weight to volume of acid used, on the flow rate of scavenging gas and on the amounts of phenolic compounds added as solubilisers or formed within the reaction medium during the de-alkylation reaction.

Our results indicate that production of isobutene does not increase markedly in the latter stages of a determination; there is no extensive decomposition of undistilled portions of t-butyl iodide. Two effects must be distinguished. In the recovery of t-butyl iodide, the yield varied from 58 to 80 per cent. and was not strongly dependent on changes in flow rate or on the addition of phenolic compounds. The rate of distillation was rapid (approximately 80 per cent. in 15 minutes), and the recovery of added t-butyl iodide appears to be mainly dependent on the thermal decomposition equilibrium. In the formation of t-butyl iodide from t-butoxyl compounds, however, several striking differences are apparent. (*a*) The relative yields of t-butyl iodide vary much more widely (19 to 81 per cent.); (*b*) the rate of distillation (now dependent on the rate of formation) is much slower (approximately 50 per cent. in 1 hour); (*c*) the relative amounts of t-butyl iodide and isobutene formed are strongly dependent on the reaction conditions, and, particularly, on the presence of added compounds.

Mechanisms of the reactions of t-butyl compounds have been extensively studied,[37,38] and the relative stability of the t-butyl carbonium ion is well known. Olefine-forming

elimination reactions involving butyl compounds proceed via competitive S_N1 and E1 unimolecular reactions, in which the rate of formation of the carbonium ion (step (*a*) below) is rate-determining.



It appears that the relative extent to which reactions (*b*) and (*c*) occur in Zeisel determinations is dependent on the reaction conditions and additives employed.

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References

1. Rosenwald, R. H., Hoatson, J. R., and Chenicek, J. A., *Ind. Eng. Chem.*, 1950, **42**, 162.
2. Kim, D. H., and Kummerow, F. A., *J. Amer. Oil Chem. Soc.*, 1962, **39**, 150.
3. Ferrero, C., and Helg, R., *Helv. Chim. Acta*, 1959, **42**, 2111.
4. Cook, C. D., and Gilmour, N. D., *J. Org. Chem.*, 1960, **25**, 1429.
5. McGowan, J. C., and Powell, T., *J. Chem. Soc.*, 1960, 238.
6. Cook, C. D., Depatie, C. B., and English, E. S., *J. Org. Chem.*, 1959, **24**, 1356.
7. Menini, E., and Norymberski, J. K., *Biochem. J.*, 1962, **84**, 195.
8. Mazur, R. H., Ellis, B. W., and Cammarata, P. S., *J. Biol. Chem.*, 1962, **237**, 1619.
9. Bell, F., *J. Chem. Soc.*, 1958, 120.
10. Ireland, R. E., and Chaykovsky, M., *in* Roberts, J. D., *Editor-in-Chief*, "Organic Syntheses," John Wiley and Sons Inc., New York, 1961, Volume 41, p. 5.
11. Klee, W., and Brenner, M., *Helv. Chim. Acta*, 1962, **44**, 2151.
12. Beyerman, H. C., and Bontekoe, J. S., *Rec. Trav. Chim.*, 1962, **81**, 691.
13. Roberts, J. D., McMahon, R. E., and Hine, J. S., *J. Amer. Chem. Soc.*, 1950, **72**, 4237.
14. Smutny, E. J., and Bondi, A., *J. Phys. Chem.*, 1961, **65**, 546.
15. Howe, J. H., and Morris, L. R., *J. Org. Chem.*, 1962, **27**, 1901.
16. Campbell, A. D., and Chettleburgh, V. J., *Analyst*, 1959, **84**, 190.
17. Anderson, D. M. W., and Duncan, J. L., *Chem. & Ind.*, 1959, 457.
18. ——, ——, *Talanta*, 1962, **9**, 661.
19. Houghton, A. A., and Wilson, H. A. B., *Analyst*, 1944, **69**, 363.
20. Kirsten, W. J., and Nilsson, S. K., *Mikrochim. Acta*, 1960, 983.
21. Jones, J. L., and Ogg, R. A., *J. Amer. Chem. Soc.*, 1937, **59**, 1943.
22. Anderson, D. M. W., *Analyst*, 1959, **84**, 50.
23. Gerrard, W., and Whitbread, E. G. G., *J. Chem. Soc.*, 1952, 914.
24. Norris, J. F., and Rigby, G. W., *J. Amer. Chem. Soc.*, 1932, **54**, 2088.
25. Maccoll, A., and Stimson, V. R., *J. Chem. Soc.*, 1960, 2836.
26. Frisell, C., and Lawesson, S., *in* Roberts, J. D., *Editor-in-Chief*, *op. cit.*, p. 91.
27. Beringer, F. M., Forgione, P. S., and Yudis, M. D., *Tetrahedron*, 1960, **8**, 49.
28. Anderson, D. M. W., and Duncan, J. L., *Talanta*, 1960, **7**, 70.
29. ——, ——, *Ibid.*, 1961, **8**, 1.
30. Moelwyn-Hughes, E. A., *J. Chem. Soc.*, 1962, 4301.
31. Anderson, D. M. W., and Duncan, J. L., *Chem. & Ind.*, 1959, 1151.
32. Burwell, R. L., Elkin, L. M., and Maury, L. G., *J. Amer. Chem. Soc.*, 1951, **73**, 2428.
33. Belcher, R., Fildes, J. E., and Nutten, A. J., *Anal. Chim. Acta*, 1955, **13**, 16.
34. Inglis, A. S., *Mikrochim. Acta*, 1957, 677.
35. Howlett, K. E., *J. Chem. Soc.*, 1957, 2834.
36. Kistiakowsky, G. B., and Stauffer, C. H., *J. Amer. Chem. Soc.*, 1937, **59**, 165.
37. Ingold, C. K., "Structure and Mechanism in Organic Chemistry," Bell and Sons, London, 1953.
38. Dostrovsky, I., and Klein, F. S., *J. Chem. Soc.*, 1955, 791.

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A Cryoscopic Method for assaying Pyridine

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A method is described suitable for the routine assay of pyridine. Water present in the original sample or absorbed during the assay has an abnormal effect on the freezing-point, and errors arising from this source are overcome by applying a correction based on the water content of the sample at the end of the test.

The depressions of the freezing-point of pyridine caused by additions of up to 6 moles per cent. of α-picoline, β-picoline, γ-picoline, 2,6-lutidine and benzene have been measured; these substances include all the major impurities likely to be present in pyridine derived from natural or synthetic sources. For each of the compounds added the depression of the freezing-point was linear over the range examined, and the values of the cryoscopic constant were identical within the limits of error of the experimental procedure.

Within the range of our experiments, therefore, the accuracy of the method is not dependent on the composition of the sample, and the single equation presented relating freezing-point to purity can be used with confidence for the assay of pyridine from natural or synthetic sources.

Results of an inter-laboratory co-operative programme for determining the precision of the method are reported.

In 1959 Adey and Cox[1] described a method, based on solution temperature in aqueous potassium chloride, for determining small amounts of α-picoline in pyridine. If the assumption is made that α-picoline and water are the only contaminants of commercial pyridine, the procedure affords a precise and accurate measure of the purity of this chemical. However, there is always the possibility that other bases may be present. It is known, for example, that one synthesis of pyridine also yields β-picoline, and we have found that the depression of the solution temperature of pyridine is 1·09° C per 1 per cent. w/w of β-picoline fraction compared with 0·70° C per 1 per cent. w/w of α-picoline present. Further, the effect of benzene, which may be used in the azeotropic dehydration of pyridine, is some 10 times as great as that of α-picoline (6·9° C per 1 per cent. w/w of benzene).

Later, a simple cryoscopic method for assaying β-picoline, γ-picoline and 2,6-lutidine was reported.[2] During this work it was found, as might be expected, that the bases formed ideal solutions in so far as there were no significant differences in the depression of the freezing-point of a given base by several different basic impurities. Thus, for example, the separate depressions of the freezing-point of γ-picoline produced by 1 mole per cent. of each of four different impurities (α-picoline, β-picoline, 2,4-lutidine and 2,6-lutidine) ranged from 0·537° to 0·550° C. It was concluded, therefore, that the freezing-point was a better criterion of purity in that it was less sensitive to the nature of the basic impurities present. The adaptation of the method to pyridine posed various problems, among them the necessity to work at a much lower temperature, about −42° C, than with the picolines, and the inability to use a mercury thermometer at this temperature, but these were solved more easily than was at first expected. Thermometers having the mercury - thallium eutectic as the indicating liquid were readily obtained to special order, and unqualified assistants found no difficulty in working with a cooling bath at −48° to −50° C.

Experimental

Purification of bases—

Samples of β-picoline, γ-picoline and 2,6-lutidine were purified by slow fractional freezing as described by Biddiscombe, Coulson, Handley and Herington,[3] the process being repeated until no further rise in freezing-point was observed.

The freezing-points of the purified bases were within 0·1° C of the values reported by these authors for the pure bases. This we considered adequate for our purpose.

The freezing-points of pyridine (−42° C) and α-picoline (−67° C) were too low for the same procedure to be adopted with the apparatus at our disposal. These bases were therefore purified by high-efficiency fractional distillation of the commercially pure products.

The pyridine submitted to this treatment was assayed at 99 per cent. purity by the solution-temperature method.[1] The α-picoline used had a boiling range of 1·7° C (drop to dry).

A glass fractionating column was used; this was 5 feet long by 1 inch internal diameter. It was packed with 1/16-inch × 1/16-inch Dixon gauze rings and surrounded by an air jacket with electric heaters for temperature compensation. Take-off was controlled by an electronically operated vapour-dividing still head and boil-up was measured with a conventional boil-up meter interposed between the still and the column.

Two litres of α-picoline were placed in the still and distilled at a boil-up of 1000 ml per hour and a reflux ratio of 50 to 1. The first 20 per cent. by volume of distillate was rejected and the next 60 per cent. by volume collected for use. Analysis by gas - liquid chromatography showed no compounds other than α-picoline.

The pyridine was distilled in a similar way. The final product had a freezing-point of −41·8° C. Its purity as determined by the solution-temperature method was 99·7 moles per cent.

DEPRESSION OF FREEZING-POINT BY WATER—

Because of our experience with the picolines and 2,6-lutidine, which we found to be extremely hygroscopic,[2] no attempt was made to prepare solutions of known amounts of water in pyridine. Instead a suitable amount of water was added to pyridine, and the freezing-point of the mixture was determined. The concentration of water present at the end of the determination was measured by the Karl Fischer method.

In one series of experiments the mixtures used contained approximately 0·05, 0·1, 0·2, 0·4 and 0·6 per cent. of water in pyridine. Their freezing-points and water contents were measured by the procedure described below.

The determinations were repeated on a second series of samples containing 0·02 to 0·9 per cent. of water. As with the picolines, a graph of water content against depression of freezing-point was linear within the range examined.

DEPRESSION OF FREEZING-POINT BY BASIC IMPURITIES AND BENZENE—

Weighed amounts of each impurity in turn were added to weighed amounts of pyridine (see Table I). The water contents of all the substances used were determined, and the molar concentration of dry impurity in the total dry mixture was calculated for each mixture in turn. The freezing-points were converted to a dry basis by determining the water content at the end of the test and applying the appropriate correction from the graph described above. Water contents were kept as low as possible in order to minimise the correction, and were in every instance less than 0·1 per cent.

TABLE I

CONCENTRATIONS OF IMPURITIES IN PYRIDINE

Impurity	Range of concentration, moles per cent.
α-Picoline	0·0 to 4·9
β-Picoline	0·0 to 5·3
γ-Picoline	0·0 to 5·9
2,6-Lutidine	0·0 to 3·9
Benzene	0·0 to 4·9

METHOD

APPARATUS—

The freezing-point apparatus is of the conventional type and consists of an inner test-tube, 150 mm × 25 mm, fitted concentrically by means of a cork inside a wider tube, 150 mm × 40 mm, that acts as an air-jacket. The inner tube is closed by a cork fitted with a suitable thermometer (see below) and a glass stirrer. The stirrer is a glass rod about 3 mm in diameter bent at its lower end into a loop at right angles to the axis of the rod. This loop is of suitable diameter (about 18 mm) to surround the stem of the thermometer and move easily up and down the inner tube. The thermometer is centrally placed in the cork and so positioned that the bottom of its bulb is about 1 cm above the bottom of the inner test-tube.

The cooling liquid is contained in a Dewar jar, internal diameter about 100 mm, to minimise absorption of heat from the atmosphere.

Apparatus for the determination of water content by the Karl Fischer method is also required.

THERMOMETERS—

Two thermometers have been used. Both were calibrated for 100-mm immersion, subdivided to 0·1° C and had N.P.L. certificates or the maker's Works Certificates quoting corrections with an error of 0·1° C for temperatures above −45° C.

(*i*) Range −46° to −34° C and −0·5° to +0·5° C, made by Short & Mason Ltd., London.

(*ii*) Range −55° to −25° C, made by H. J. Elliott Ltd., E-Mil Works, Pontypridd, Glamorgan.

PROCEDURE—

Place in the Dewar jar an amount of cooling mixture such that, when the apparatus is assembled, the level of liquid in the jar is at least as high as the level of the sample in the inner test-tube. Adjust the temperature of the mixture, immediately before use, to between 6° and 8° C below the expected freezing-point of the sample. A suitable cooling mixture can be prepared from solid carbon dioxide and ethanol. Place approximately 25 ml of the sample to be tested in the inner test-tube. Fit the stirrer and thermometer in the inner test-tube, and pre-cool the sample, with stirring, to about 5° C above the expected freezing-point. Rapidly dry the outside of the test-tube, and fit it centrally inside the air-jacket already in place in the cooling bath. Stir gently and continuously, and read the thermometer at 30-second intervals (estimate the temperature to 0·01° C). When the temperature has fallen to the expected freezing-point, introduce a seed crystal as rapidly as possible, and continue the test. (The seed crystal can be conveniently introduced by raising the stirrer to its highest extent, without removal of the cork from the inner test-tube, and depositing a crystal from a glass rod as low as possible on it. The stirrer is then replaced in the liquid and stirring is continued). The freezing-point corresponds to the first set of four consecutive readings during which the temperature remains constant. If supercooling occurs, the constant temperature will be observed after the temperature rise. A temperature rise of 1° C is the maximum permissible; if it exceeds this value, repeat the determination on a fresh portion of the sample.

Record the observed freezing-point, F, corrected for any scale error of the thermometer.

Remove the inner test-tube, complete with thermometer and stirrer, without delay, and heat rapidly, with stirring, until the temperature rises to between 14° and 16° C. By pipette, preferably with use of a pipette filler, withdraw 20 ml of sample, and determine its water content (per cent. w/v).

Calculate the corrected freezing-point, F_0, for the dry substance by adding an amount 2·30 w, where w is the water content (per cent. w/v).

Calculate the purity of the dry sample, P_0, from the expression—

$$P_0, \text{ mole per cent.} = 100 - \frac{(-41{\cdot}62 - F_0)}{0{\cdot}594}$$

Alternatively, if the impurities are known to be picolines, the percentage w/w purity, P_w, can be calculated from—

$$P_w, \text{ per cent. w/w} = 100 - \frac{(-41{\cdot}62 - F_0)}{0{\cdot}505}$$

If many samples are to be tested, it is much more convenient to prepare graphs from these expressions and also of 2·30 w.

RESULTS

The depression of the freezing-point of pyridine by water was calculated by the method of least squares for each series of mixtures.

The equations for the regression lines are—

(*i*) $F_0 = -41{\cdot}82 - 2{\cdot}321\,w$; $s = 0{\cdot}091$

(*ii*) $F_0 = -41{\cdot}77 - 2{\cdot}284\,w$; $s = 0{\cdot}074$

where F_0 = observed freezing-point, °C, corrected for scale errors of the thermometer,

w = water content at the end of the test, per cent. w/v, and

s = standard error of the regression coefficient.

The effects of basic impurities and benzene on the freezing-point of pyridine are shown in Table II.

TABLE II

DEPRESSION OF FREEZING-POINT OF PYRIDINE BY OTHER BASES AND BENZENE

Impurity	Depression of freezing-point (θ) caused by 1 mole per cent. of impurity,* °C	Standard error of θ	Number of observations
α-Picoline	0·5824	0·012	8
β-Picoline	0·5963	0·016	8
γ-Picoline	0·5880	0·015	6
2,6-Lutidine	0·5534	0·022	7
Benzene	0·5613	0·013	6

* Mixture consists of 99 moles per cent. of dry main component and 1 mole per cent. of dry impurity.

DISCUSSION OF RESULTS

A statistical examination of the values of the depression of the freezing-point (θ) and its standard error, S.E. (θ), for the bases in Table II, showed that the values of θ did not differ significantly from each other. The over-all regression coefficient for bases and its standard error were therefore calculated and, in addition, the over-all regression coefficient for the three picolines, *i.e.*, excluding the value for 2,6-lutidine. The results of the calculations are shown in Table III.

TABLE III

VALUES OF THE OVER-ALL REGRESSION COEFFICIENTS

	θ	S.E. (θ)	Number of observations
All bases	0·5954	0·0070	23
Picolines only	0·5943	0·0055	18

Although the regression line for 2,6-lutidine has the lowest value of slope, the inclusion of the results for this base increases rather than decreases the regression coefficient for the combined results. The difference between the values of the slopes is, however, without significance; it arises from the reduction in weight given to the freezing-point of pure pyridine (which is common to all the regression lines) when the several sets of results are combined.

The value for benzene ($\theta = 0{\cdot}5613$) was not included in the calculation of the over-all coefficient, since benzene is not a usual contaminant of pyridine, but may occur, *e.g.*, through malfunctioning of an azeotropic dehydration unit. The results show that the presence of small amounts of benzene will not vitiate an assessment of the purity of a sample of pyridine from its freezing-point. The method described here does not therefore suffer from the disadvantages of the solution-temperature method in this respect.

Biddiscombe, Coulson, Handley and Herington,[3] who used iso-octane as the impurity, obtained a value of 0·607° ± 0·017° C for the depression of the freezing-point of pyridine by 1 mole per cent. of impurity. The results given here agree closely with this figure. The same workers reported a freezing-point of −41·55° ± 0·05° C for 100 per cent. pyridine. A later personal communication from Dr. Herington gave −41·62° ± 0·0° C as the best estimate for the pure base, and this value has been used in the expression on p. 361 for calculating the molar purity from the freezing-point.

It will be noted that the denominator of this expression is 0·594, that is, the value of θ corresponding to the picolines only. Although there are theoretical reasons for preferring this value to the over-all value of 0·595, the difference is, as stated above, without significance,

and substitution of the latter value does not give rise to a significant difference over the range of purity under discussion. A freezing-point of −44·59° C, for example, corresponds to 5·00 moles per cent. of impurity when $\theta = 0{\cdot}594$ and to 4·99 moles per cent. when $\theta = 0{\cdot}595$.

This method has been adopted by the Standardisation of Tar Products Tests Committee in its handbook[4] and the Tar Bases Panel of that Committee has carried out an inter-laboratory co-operative programme to determine the precision of the method. They found a repeatability of 0·20° C, corresponding to 0·34 moles per cent. of pyridine, and a reproducibility of 0·50° C, corresponding to 0·85 moles per cent. of pyridine. These are 95 per cent. confidence limits, and in the long run of properly conducted tests the majority of pairs of results will differ by much less than these amounts. The repeatability and reproducibility are expected to improve further as the operators become more familiar with the test.

Results obtained in the laboratories of the Midland Tar Distillers show good agreement between the solution-temperature[1] and freezing-point methods, as the results in Table IV show.

TABLE IV

COMPARISON OF SOLUTION-TEMPERATURE AND FREEZING-POINT METHODS

Sample No.	Solution temperature (S.T.), °C	Freezing-point (F.P.), °C	Purity calculated from— S.T., % w/w	Purity calculated from— F.P., % w/w	Difference S.T. − F.P.
1(*a*)	26·64	−41·85	99·49	99·54	−0·05
1(*b*)	26·72	−41·78	99·60	99·68	−0·08
1(*c*)	26·58	−41·86	99·40	99·52	−0·12
2(*a*)	26·48	−42·10	99·26	99·05	+0·21
2(*b*)	26·40	−42·08	99·14	99·09	+0·05
3	26·15	−42·16	98·79	98·93	−0·14
4	26·11	−42·19	98·73	98·87	−0·14
5	26·27	−42·14	98·96	98·97	−0·01
6	26·45	−42·03	99·21	99·19	+0·02
7	26·56	−41·98	99·37	99·29	−0·08
8	26·19	−42·19	98·84	98·87	+0·07

I acknowledge the help of Mrs. S. Walker and Mrs. M. MacIntyre, by whom most of the practical work was done, and thank the Directors of The Midland Tar Distillers Ltd., Oldbury, for permission to publish this paper.

REFERENCES

1. Adey, K. A., and Cox, J. D., *Analyst*, 1959, **84**, 414.
2. Adey, K. A., *Ibid.*, 1959, **84**, 560.
3. Biddiscombe, D. P., Coulson, E. A., Handley, R., and Herington, E. F. G., *J. Chem. Soc.*, 1954, 1957.
4. Watkins, P. V., *Editor*, "Standard Methods for Testing Tar and its Products," Fifth Edition, Standardization of Tar Products Test Committee, Gomersal, Leeds, 1962.

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Determination of Particulate Acid in Town Air

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A method for measuring particulate acid in town air by titration was investigated and found to be suitable. Particulate matter of the air was collected by filtration, and the amount of acid determined by immersing the collected sample in a known excess of 0·01 N sodium tetraborate in de-ionised water at pH 7 and titrating back to pH 7 with 0·01 N acid. The particulate acid in the air of the City of London appeared to be mainly sulphuric.

Various workers have studied the acidity of urban air since regular observations of atmospheric pollution began in 1913. They all recognised that the main gaseous acid, apart from the carbon dioxide, in air was sulphur dioxide, but they also identified sulphuric acid in the suspended matter.

Ellis[1] measured the total acid in London air by titration after absorbing both sulphur dioxide and particulate acid in hydrogen peroxide; he determined the sulphur dioxide alone by an iodine method and the concentration of particulate acid by subtraction. Goodeve[2] used sintered-glass discs to filter out the acid, and Coste and Courtier[3] devised a technique in which the acid droplets were made to grow before collection. The general conclusion at that time was that the amount of particulate acid present in urban air was extremely small in comparison with the amount of sulphur dioxide. With the advent of "smog" in Los Angeles, interest in acid droplets was revived, and Mader, Hamming and Bellin[4] used washed filter-papers to collect acid droplets there. All these investigators found significant amounts of acid only in fog.

In the London fog of December, 1952, sulphur dioxide but not particulate acid was measured; this episode revived interest in the subject.

When suspended matter in London air is collected by impaction on glass slides coated with gelatin containing thymol blue and viewed under a microscope, strongly acidic droplets can be seen as pink spots.[5] This method is, however, only qualitative, and, of the various procedures for determining acid, the titration of air solids collected on a filter-paper was found to be the most suitable.

Method

Determination of particulate acid—

Samples for analysis are collected on 4·25-cm circles of Whatman No. 1 filter-paper held in a Perspex holder so that a 1-inch circle of the filter-paper is exposed. Air-flow rates of up to 30 litres per minute are used, and samples are usually taken over periods of up to 6 hours. At times of high pollution, a one hour sample representing 1 cu. metre of air was adequate for analysis.

The method involves titration of filter-papers to pH 7. A solution of bromothymol blue in de-ionised water is prepared by adding 4 ml of a 0·1 per cent. solution of the indicator in alcohol to 100 ml of de-ionised water. To this solution sufficient 0·01 N sodium tetraborate is added to make it a stable apple-green colour (pH approximately 7). After the outer unexposed edges of the filter-paper have been cut off, the sample is cut into two exactly equal portions, one portion being added to 1 to 2 ml of the solution and titrated with 0·01 N sodium tetraborate to the original green colour. A similar beaker containing the same volume of the solution is kept as a control, since this liquid absorbs any sulphur dioxide from the air and slowly changes colour. During titration the solution is agitated by vigorous swirling, and it is found that the end-point is reached after about 5 minutes. This end-point is shown by a stable green colour identical to that of the control solution.

The amount of acid indicated by this method is too low, since some of the acid reacts with water-insoluble bases present in the sample. The true amount of acid is found by adding a known excess of 0·01 N sodium tetraborate (at least 0·1 ml more than the amount

indicated above) to 1 to 2 ml of the pH 7 solution and then immersing the second portion of the filter-paper in it and titrating the excess with 0·01 N sulphuric acid. Then the concentration of acid (calculated as sulphuric acid) in μg per cu. metre of air $= 98{,}000 \times \frac{Nv}{V}$, where

N = normality of sodium tetraborate (0·01 N),

v = equivalent volume (in ml) of 0·01 N sodium tetraborate used to neutralise the acid during back titration of half the sample filter-paper, and

V = volume of air sampled (cu. metres).

STORAGE OF SAMPLES—

Samples become neutralised when left in air, and they should therefore be titrated as soon as possible after collection. Samples are neutralised more readily indoors than outdoors and only slowly when sealed in polythene bags. Tests have shown that, outdoors, losses of acid varied between 0 and 30 per cent. over 5 days. For the same period indoors, losses up to 70 per cent. occurred owing no doubt to greater amounts of ammonia being present. Samples kept in polythene bags showed a loss of about 50 per cent. over a period of one year.

DISCUSSION AND JUSTIFICATION OF METHOD

Many substances other than sulphuric acid are present in air. Possible interferences in the method were examined and are discussed below.

INTERFERENCE BY ACIDIC GASES—

Carbon dioxide, nitrogen dioxide and sulphur dioxide are all present in polluted air. Carbon dioxide is an extremely weak acid, is not appreciably absorbed by filter-paper and therefore does not interfere with the method. Nitrogen dioxide, even if it were absorbed by filter-paper during collection, is insufficiently absorbed by water to affect the measurement of sulphuric acid. To assess the interference by sulphur dioxide, 200 p.p.m. of the gas at high humidity was passed for 2 hours through a filter-paper loaded with various amounts of smoke collected from the air; no additional sulphuric acid was detected on the filter-papers, and thus sulphur dioxide can be assumed not to interfere significantly with the method.

INTERFERENCE BY BASIC GASES—

When particulate acid can be detected in town air, small amounts of free basic gases (ammonia and amines) can be found also. The co-existence of these two pollutants can be explained by the acidic particles being covered by carbonaceous, tarry or other solid material that hinders neutralisation with ammonia. In order to find out whether ammonia neutralises the acid during sampling, it was removed before the acid was collected. This was done by impinging the air approximately 2 cm above the surface of the concentrated sulphuric acid, a flow rate of 20 litres per minute being used. Preliminary experiments showed that ammonia gas mixtures of between 0·2 and 10 p.p.m. in air are absorbed with efficiencies of between 70 and 95 per cent., and that, when a prepared mist of sulphuric acid (2·5 mg per cu. metre, mass median diameter 0·50 μ), was used, losses in the impinger did not exceed 6 per cent. Acidic particles of this size are found in the polluted air of London during fog; at other times the acid particles are smaller and the loss by impingement would be even less than that found in these experiments (there are also larger acidic particles, but these represent only a small fraction of those found in the polluted air of London). Several samples of acid were collected on filter-papers after ammonia had been removed in this way. These filter-papers were titrated and the results compared with those from samples collected without prior removal of ammonia. Sixteen pairs of samples were collected, each for 8 hours, in the City of London. Comparison of individual results showed in some instances small differences, but the average of the sixteen samples was 3·96 μg per cu. metre of acid, after the removal of ammonia, compared with 3·67 μg per cu. metre of acid for normal collection. This small difference (7·5 per cent.) between the results indicates that there is not enough ammonia present in the air of the City of London to invalidate this method of collecting the sulphuric acid.

INTERFERENCE BY OTHER PARTICULATE ACIDS—

Particulate acids other than sulphuric may be present in town air. These are hydrochloric, nitric, phosphoric, sulphurous and nitrous acids; these acids may be wholly or partly caught on a collection filter-paper. Sulphuric acid can be efficiently filtered from air.[4] Only extremely small amounts of nitrate, phosphate, sulphite and nitrite can be detected in samples collected on filter-paper, and the concentrations of the acids corresponding to these anions must therefore be extremely small. Solids collected from the air of the City of London contained from 0·2 to 2·4 mg of hydrogen ion per g (measured by titration). The chloride content varied between 15 and 150 mg per g, and if this chloride were all hydrochloric acid it would correspond to between 0·4 and 4·2 mg of hydrogen ion per g of solids, so that all the indicated acidity could be due to hydrochloric acid. However, there was no correlation between chloride and acidity in fifty samples collected during two prolonged periods of high pollution, whereas sulphate (present in concentrations between 40 and 200 mg per g of solids) and acidity were highly correlated. Sulphate was always present in amounts greater than could be accounted for by sulphuric acid alone. These findings suggest that the predominant acid present in air is sulphuric acid.

INTERFERENCE BY PARTICULATE BASES—

Organic bases are produced when coal is distilled, and thus they would be expected to be present in town air. The aliphatic bases and some aromatic bases are readily volatile at ordinary temperatures, but some of the less volatile aromatic bases may be expected to be present in particulate pollution. The latter bases are extremely weak and will not interfere with the titration of sulphuric acid if the pH is carefully chosen. Titration of known mixtures of a 10-fold excess of the aromatic base, aniline, in sulphuric acid, when an extraction solution of low initial pH was used that was titrated back to this pH after the mixture had been added, gave a low result for the acid present; for pH values less than 5·4 a negative amount of acid was indicated. For extraction solutions at pH 7, the true amount of acid was indicated when titrated back to this pH, and therefore such a procedure was chosen for titration of the acid collected from air. For procedures in which solutions of pH >7 were used, spuriously high amounts of acid were indicated. Samples of collected air solids behaved in a similar way to the aniline - sulphuric acid mixture.

Soluble basic particles, such as lime or other metallic oxides or hydroxides, would, if present, interfere with the determination of acid by the titration of filter-paper samples. To find out if such bases are present, the acid in the samples can be neutralised with ammonia gas, and the unaffected bases, if present, determined by titration. This procedure was applied to collected air solids, and the samples were neutralised with ammonia over a period of 2 minutes, after which they were left in the laboratory for 2 hours before being titrated. Samples collected in London were neutralised by exposure to ammonia for 2 minutes and, after being left in laboratory air for 2 hours, were placed in water at pH 7; they were never alkaline but were neutral or slightly acid. This indicated that only negligible amounts of soluble bases were present in the samples. Insoluble bases, such as calcium carbonate, may also be present; their presence can be detected by titrating with sodium tetraborate the "ammoniated" sample after a known excess of acid has been added. Results of these experiments have shown that many samples of solids collected from the air in London contain appreciable amounts of insoluble bases.

In order to overcome the interference by insoluble bases, an amount of 0·01 N sodium tetraborate greater than the equivalent amount of acid (determined first by titrating a portion of the sample at pH 7) is added to 1 to 2 ml of water at pH 7, in which another portion of the sample is immersed; the solution is then titrated with 0·01 N sulphuric acid. This titration procedure allows the sodium tetraborate to neutralise the acid before the insoluble base has a chance to do so. It has been found that the results of the determinations of acid by this method are 10 per cent. higher at times of high pollution and up to 30 per cent. higher at times of low pollution than those obtained by direct titration.

Although the method described above has been found to be suitable for determining acid in town air, two other methods have been considered. In one, the total particulate sulphate is taken to be an indication of the total particulate acid. This "sulphate index" has, however, proved unreliable for use in the City of London, since the acid content has been shown to vary from 20 to 80 per cent. of the amount of sulphate present. In the other

method, the acid is neutralised by adding excess of ammonia to the air before the air solids are collected on the filter-paper. The amount of ammonium ion present on the filter-papers was determined with Nessler's reagent 2 hours later, after which time the ammonia not used for neutralisation had come off the filters. The ammonium ion content of an untreated sample of air solids was also measured and the amount of particulate acid calculated from the difference between the two results, it being assumed that all the acid had been converted to ammonium sulphate. This method takes longer than the titration method and the results are not as reproducible, but it has the merit that reactions on the filter-paper between the acid and other material present are minimised.

Results

Range of concentration of particulate acid in town air—

The concentrations of particulate acid correspond to those of other pollutants. Concentrations of particulate acid are especially high at times of fog and have reached levels of 678 μg (calculated as sulphuric acid) per cu. metre of air in the City of London. Typical winter daily concentrations are 18 μg per cu. metre of air, compared with 7 μg per cu. metre for summer in the City. The sulphuric acid content of the air in the City of London can be up to 10 per cent. of the total sulphur.

Conclusions

The procedure developed for the measurement of particulate acid was suitable for its determination in urban air. Interference by other pollutants can be avoided by the use of a back titration technique. The particulate acid appears to be mainly sulphuric acid.

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References

1. Ellis, B. A., The Investigation of Atmospheric Pollution 17th Report, H.M. Stationery Office, 1931, p. 38.
2. Goodeve, C. F., *Trans. Faraday Soc.*, 1936, **32**, 1218.
3. Coste, J. H., and Courtier, G. B., *Ibid.*, 1936, **32**, 1198.
4. Mader, P. P., Hamming, W. J., and Bellin, A., *Anal. Chem.*, 1950, **22**, 1181.
5. Waller, R. E., *J. Roy. Met. Soc.*, in the press.

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Iodimetric Determination of Milligram Amounts of Rubber Hydrocarbon

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An iodimetric method is described for determining rubber hydrocarbon; it is based on the bromination of the rubber molecule, and is sensitive to 2 mg of rubber dissolved in benzene. By comparing it with a standard procedure, it has been shown that the proposed method will determine accurately the rubber hydrocarbon content of field latex. The precision with which solutions of pure rubber in benzene can be determined by the method corresponds to a coefficient of variation of about 0·5 per cent., and rubber hydrocarbon in latex can be determined with a precision of about 1·5 per cent.

The chemical determination of rubber hydrocarbon may be based either on its property of forming a stable tetrabromide, as in early volumetric methods[1,2] and in more recent gravimetric methods,[3,4,5] or on its ability to produce titratable volatile acids on oxidation with chromic acid.[6] Volumetric methods are rapid and sensitive, but, although it has been claimed[7] that rubber hydrocarbon can be satisfactorily determined by bromination, such procedures have not been found generally satisfactory. Their unsatisfactory nature may have been caused by faulty analytical techniques, and in the work described here an improved analytical procedure has been used for determining rubber hydrocarbon, after bromination of the rubber molecule under carefully controlled conditions.

Bromination methods assume that the rubber hydrocarbon tetrabromide is formed by the addition of bromine at double bonds, as summarised in the equation—

$$(C_{10}H_{16})_n + 2nBr_2 = (C_{10}H_{16}Br_4)_n$$

Attempts have been made to allow for any extra bromine taken up through substitution by applying the McIlhiney correction,[1,2] but according to Bloomfield[8] the simultaneous absorption of halogen by cyclisation makes this impracticable. Substitution can, however, be suppressed by using a polar reagent; for example, bromine in glacial acetic acid, as in the work of Kemp and Mueller.[9]

For volumetric methods involving determination of the excess of bromine remaining after bromination, it is essential that a quantitative addition of the halogen should be made initially. Preliminary work had shown that such addition is extremely difficult when, as in the methods referred to above,[1,2] solutions of bromine in a volatile solvent, such as carbon tetrachloride, are used. Solutions of this kind quickly lose bromine on exposure to the air; this is also true for solutions of bromine in acetic acid. Quantitative introduction of bromine can be readily made, however, by using bromide - bromate mixtures,[10] and a polar reagent of this type has been used in the method of determining rubber hydrocarbon described below.

The proposed method is designed for rubber that is completely soluble in benzene, since Willits, Swain and Ogg[3] have shown by a gravimetric procedure that such a method can be applied to the determination of rubber in plant tissue. This application, which involves problems of extraction and of interference by other substances, is not discussed in this paper, but it is intended to show in a later publication how the proposed method can be used for determining rubber in plants.

Experimental

Before its determination rubber may be dissolved in carbon tetrachloride,[1,2] chloroform[7] or benzene.[3] Benzene has been found most suitable for extracting rubber from plant tissue[11] and, since one object of this paper is to describe a method also applicable to the analysis of plant material, the use of solvents other than benzene has not been studied.

Bromination of solutions of rubber in benzene—

Preliminary work had shown that both commercial and analytical-reagent grades of benzene absorbed appreciable amounts of bromine; further, when the same sample of benzene was repeatedly brominated, the amount of bromine absorbed each time rapidly decreased

with successive brominations. Purification of benzene by distillation alone did not reduce the amount of bromine absorbed, but washing with concentrated sulphuric acid produced a large decrease. These results suggested that much of the bromine was absorbed by an impurity such as thiophen, which would be removed by sulphuric acid but not easily by distillation, as it boils at about the same temperature as benzene.

The amount of bromine absorbed by rubber in solution must be obtained by subtracting the amount absorbed by the solvent from the total amount taken up by the solution, and for accurate work, therefore, purified benzene should be used. In Fig. 1 values obtained by subtraction in this way show the rate at which bromine is absorbed by rubber dissolved in purified benzene; the corresponding absorption of bromine by the solvent is also shown.

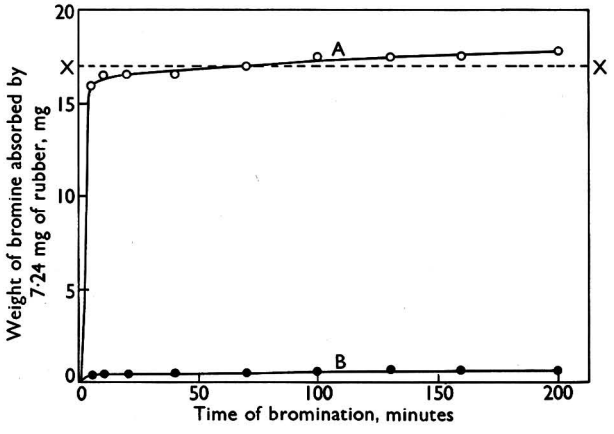

Fig. 1. Effect of time on the bromination of benzene and rubber hydrocarbon: curve A, purified rubber; curve B, purified benzene

The effect of external conditions on the absorption of bromine was also investigated; rubber dissolved in purified benzene was brominated for 100 minutes, in clear bottles in both subdued and bright light and also in opaque bottles in a dark cupboard at various temperatures between 6° and 28° C. The results are shown in Table I, and indicate that the effect of light on the bromination of benzene is sufficiently pronounced to make it essential that, in the proposed procedure, bromination is carried out in the dark. The results also show that the effect of temperature on the bromination of both benzene and rubber in the dark is small compared with its effect in subdued or bright light.

TABLE I

EFFECT OF LIGHT AND TEMPERATURE ON THE BROMINATION OF BENZENE AND RUBBER

The results are expressed as milligrams of bromine absorbed by 10 ml of purified benzene and by 8·92 mg of purified rubber

Temperature, °C	Bromine absorbed					
	In the dark by—		In subdued light by—		In bright light by—	
	benzene	rubber	benzene	rubber	benzene	rubber
7	0·32	21·5	—	—	—	—
20	0·54	22·4	17·6	23·9	—	—
27	0·74	23·9	32·8	14·1	72·6	1·1

METHOD

REAGENTS—

The reagents should be prepared from pure chemicals and distilled water.

Sodium molybdate solution, 0·1 per cent. w/v in 10 per cent. v/v hydrochloric acid and 10 per cent. v/v acetic acid.

Potassium bromate solution, 0·55 per cent. w/v in 10 per cent. w/v potassium bromide solution.

Sodium borate solution, 2·5 per cent. w/v, aqueous.

Sodium thiosulphate solution, 2·5 per cent. w/v, aqueous.

Sodium thiosulphate solution, 0·04 N, aqueous.

Iodine solution, 0·01 N in 4 per cent. w/v potassium iodide solution.

Benzene—Purify by shaking with concentrated sulphuric acid and washing four times with water. Filter the benzene, and then distil at 80° C; discard the first and last 50 ml of distillate from 2 litres.

PROCEDURE—

Put a 25-ml portion of a benzene solution containing 5 to 10 mg of rubber hydrocarbon into an opaque stoppered bottle, and add 5 ml of sodium molybdate solution and then 5 ml exactly of potassium bromate solution. Replace the stopper tightly, mix the aqueous and benzene phases thoroughly, and place the bottle in a dark cupboard. After 100 minutes have elapsed record the temperature of the cupboard, remove the bottle, and quickly add 2 g of potassium iodide to the contents. Replace the stopper tightly, shake the solution thoroughly, and after 5 minutes quickly add 100 ml of sodium borate solution. (A 100-ml calibrated flask with a spout permits rapid addition of sodium borate to be made; it is essential that this flask and all glass apparatus used in the bromination should be free from grease.) Again shake the solution thoroughly, and add 25 ml of sodium thiosulphate solution with continuous swirling. After 5 minutes, filter about 20 ml of the solution through a Whatman No. 1 filter-paper (previously moistened with distilled water to ensure that only the aqueous phase passes through), and discard. Filter the remainder of the aqueous phase into a clean dry flask, and titrate a 50-ml portion with the standard iodine solution and starch as indicator. Carry out a blank determination on 25 ml of benzene only by the same procedure. The volume of standard iodine solution corresponding to the bromine absorbed by the hydrocarbon is obtained by multiplying the difference between the two titres by the total volume of the aqueous phase (135 ml) and dividing by the volume of the portion taken (50 ml). The amount of rubber present can then be calculated by multiplying this result by a factor, corrected for temperature as described below.

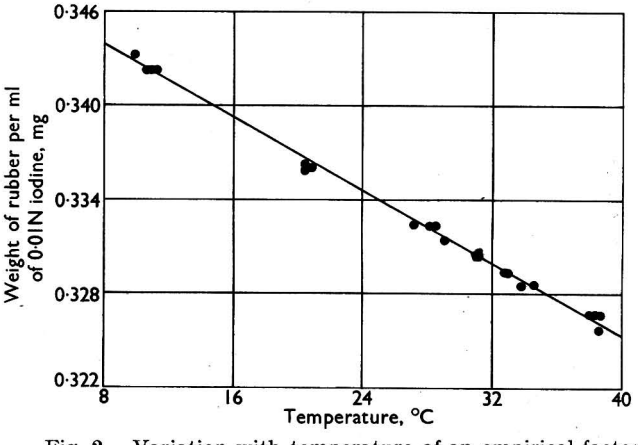

Fig. 2. Variation with temperature of an empirical factor for calculating rubber hydrocarbon

CALIBRATION OF THE METHOD—

Fig. 1 indicates that there is a rapid initial absorption of bromine by rubber hydrocarbon, caused mainly by addition of the halogen at double bonds; subsequently there is a much slower absorption that may be caused partly by substitution of hydrogen. If this is so, bromination will not always produce the tetrabromide quantitatively, but it can be experimentally shown with considerable precision that at a given temperature the amount of

bromine absorbed per milligram of rubber is nearly constant over the range 2·5 to 12·5 mg; an empirical factor can therefore be used to relate the weight of rubber to the amount of bromine absorbed. It was clear from the results shown in Table I that the factor would vary with temperature, and the nature of this variation is shown in Fig. 2; these results were obtained by brominating in accordance with the proposed procedure 8 mg of purified rubber in 25 ml of purified benzene. A highly significant linear regression of an empirical factor (expressed as mg of rubber per ml of 0·01 N iodine) on temperature is shown, with a negative slope corresponding to the equation—

$$\text{Factor at } t^\circ \text{ C} = 0{\cdot}3339 - 0{\cdot}000589\ (t - 25).$$

A similar calibration, carried out with synthetic *cis*-polyisoprene as the standard substance, gave a slightly different factor with a more pronounced temperature gradient corresponding to the equation—

$$\text{Factor at } t^\circ \text{ C} = 0{\cdot}3345 - 0{\cdot}00126\ (t - 25).$$

Comparison with a standard method for analysing latex

The dry rubber content of field latex, which includes rubber hydrocarbon together with small amounts of other materials,[12] was determined by a standard method,[13] and rubber hydrocarbon was determined by the proposed method, after non-rubber substances capable of absorbing bromine had been removed by means of the pre-treatment described below.

Weigh 0·15 to 0·20 g of latex into a 250-ml beaker, and spread by adding 1 ml of water and rotating. Evaporate to dryness on a steam-bath at 90° C, when an extremely thin translucent film should form on the bottom of the beaker. Extract three times with 100 ml of boiling ethanol, 15 minutes being taken for each extraction. After the final extract has been removed by decantation, heat on the steam-bath until free from ethanol. Add 150 ml of purified benzene, stir thoroughly at intervals, and, when all the rubber has dissolved, make up to 250 ml in a calibrated flask. Determine the content of rubber hydrocarbon in a 25-ml portion by the procedure described above.

The results of the comparison were plotted (see Fig. 3) and reveal a highly significant regression of rubber hydrocarbon on dry rubber content.

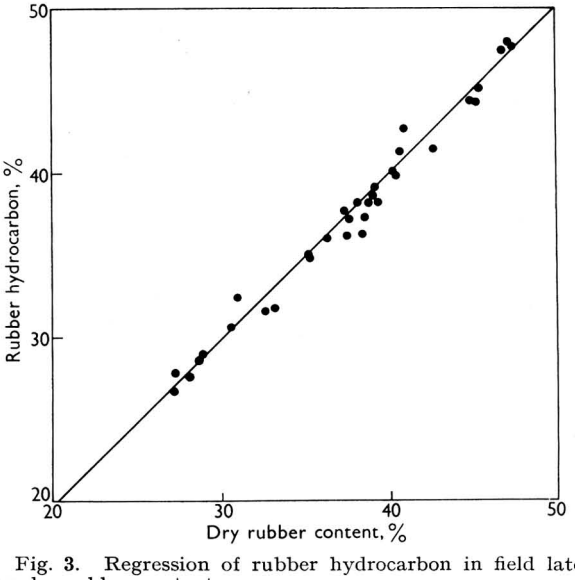

Fig. 3. Regression of rubber hydrocarbon in field latex upon dry rubber content

Discussion of the method

The amount of bromine absorbed, by both hydrocarbon and solvent, is equal to the difference between the amount added and the amount remaining at the end of the reaction; an excess of potassium iodide converts the latter into an equivalent amount of iodine, which can then be titrated with thiosulphate.

The presence of three phases (aqueous, benzene and rubber bromide) had made the direct titration of liberated iodine difficult, the more so when bromination was carried out in opaque bottles. Moreover, as pointed out by Fisher, Gray and Merling,[2] traces of excess of bromine, occluded in the precipitated bromide, may not be released during the titration. These difficulties are avoided in the proposed method by adding a measured excess of thiosulphate and by waiting until its reaction with the halogen is complete; the aqueous phase is then filtered off, a portion of it is taken and the excess of thiosulphate is titrated with standard iodine solution. Thiosulphate is however unstable in contact with the amount of acid needed to release bromine from bromide - bromate mixtures, and for accurate titrations a definite pH is needed, depending on the concentrations of iodine and thiosulphate used.[10] In the proposed procedure the acid is partly neutralised with sodium borate before the addition of thiosulphate, and a borate - acetate buffer giving a final pH of 5·5 is thus formed.

Another difficulty had arisen when a strong acid only was used to liberate bromine from bromide - bromate mixtures; this acid (hydrochloric) produced an excessive amount of heat when neutralised by sodium borate. The problem was eventually solved by replacing part of the hydrochloric acid by acetic acid, which liberates less heat on neutralisation, and by adding sodium molybdate, which strongly catalyses the release of bromine under such conditions.[10]

In Fig. 1, the line $\times - \times$ marks an absorption of 17 mg of bromine by 7·24 mg of rubber; this amount corresponds to a quantitative formation of rubber hydrocarbon tetrabromide, which contains 70·13 per cent. of bromine, and the minimum bromination time required to form it appears to be about 70 minutes. The rate of absorption of bromine seems, however, to fall off appreciably after 100 minutes, and since this time has been used by other workers[5] it has been adopted as the bromination time in the proposed procedure.

ACCURACY AND PRECISION OF THE METHOD—

The calibrations recorded above show that similar results are obtained when purified rubber and *cis*-polyisoprene are used, although the effect of temperature on bromination is not exactly the same for both substances. It is, however, accepted that there are definite differences in structure between *cis*-polyisoprene and natural rubber.[14] Moreover, recent work[15] has suggested the presence of aldehyde and other abnormal groups in the natural rubber molecule; both these variables might be expected to cause a difference in bromination between the two materials, when the procedure described above is employed. The *cis*-polyisoprene is considered to have a rubber hydrocarbon content of between 99·5 and 100 per cent.; the purified natural rubber, from which inorganic matter, proteins and fatty materials had been removed by treatment with an aqueous detergent and alcohol, should be of similar purity. The fact that calibrations made by using the two standards have given similar results can therefore be taken as an indication of the satisfactory accuracy of the method.

The accuracy of the method can also be judged by comparing it with a standard procedure[13] for determining the dry rubber content of field latex. The results of the comparison are recorded in Fig. 3, in which mean rubber hydrocarbon values (obtained from duplicate brominations on each of two sub-samples of latex) are plotted against the means of two determinations of dry rubber content on the same samples of latex.

The linear correlation between rubber hydrocarbon (R.H.C.) and dry rubber content (D.R.C.) is highly significant (correlation coefficient + 0·989), and the corresponding regression equation is—

$$\text{R.H.C.} = \text{D.R.C.} \times \underset{\substack{\text{(standard error} \\ \pm\ 0{\cdot}0268)}}{1{\cdot}0134} - \underset{\substack{\text{(standard error} \\ \pm\ 1{\cdot}013)}}{0{\cdot}580}$$

The deviations of the slope (1·0134) and the intercept (−0·580) from unity and zero, respectively, are not statistically significant, and the least squares regression differs only insignificantly from the relation R.H.C. = D.R.C.; this can be readily shown in terms of the total variation among the 34 samples—the least squares regression accounts for 97·81 per cent. of the variation, whereas the alternative relation (R.H.C. = D.R.C.) accounts for 97·78 per cent. This implies, but does not establish, that in this comparison of methods R.H.C. is equivalent to D.R.C.; but it should be noted that the regression equation given above has been worked out for field latex only—when other lattices are involved, for example, skim or

concentrate, it may be necessary to re-determine the equation, but the same method would seem to be applicable.

Table II summarises the statistical examination of the rubber hydrocarbon results obtained in the comparison of methods. The components of variance show that considerably more error is associated with sub-sampling and pre-treatment (which are confounded) than with bromination and titration (which are also confounded). By combining components for these sources of variation, the standard error of a single determination of rubber hydrocarbon, on any given sample of latex, can be estimated as $\pm 0{\cdot}5712$, which corresponds to a coefficient of variation of 1·53 per cent. The coefficient of variation associated with duplicate brominations is, however, 0·48 per cent. and this figure agrees well with a value of 0·35 per cent. computed for duplicate determinations, the means of which are plotted in Fig. 2.

TABLE II

STATISTICAL ANALYSIS OF RUBBER HYDROCARBON DETERMINATIONS ON 34 SAMPLES OF LATEX

Source of variation	Degrees of freedom	Mean square	Component of variance
Between samples of latex	33	140·7858***	$\sigma_2^2 = 35{\cdot}0412$
Between sub-samples within samples of latex	34	0·6210***	$\sigma_1^2 = 0{\cdot}2948$
Between duplicate brominations on sub-samples of latex	68	0·0315	$\sigma_0^2 = 0{\cdot}0315$
Total	135	—	—

Mean rubber hydrocarbon content = 37·296 per cent. by weight.

Standard error of a single determination on a given sub-sample = $\pm\sigma_0 = \pm 0{\cdot}1775$; coefficient of variation = 0·48 per cent.

Standard error of a single determination on a given sample = $\pm \sqrt{\sigma_0^2 + \sigma_1^2} = \pm 0{\cdot}5712$; coefficient of variation = 1·53 per cent.

*** Significant at the 0·1 per cent. level.

CONCLUSIONS

The proposed method shows that milligram amounts of rubber hydrocarbon soluble in benzene can be rapidly determined by iodimetric titrations, after preliminary bromination of the rubber molecule. Various experimental conditions necessary to attain satisfactory accuracy and precision are specified. They include exclusion of light during a definite bromination period, correction for different brominating temperatures, the use of an inorganic brominating reagent in order to ensure quantitative addition of bromine, and careful control of the procedure used for the iodimetric determination. The determination of rubber hydrocarbon by the proposed method is also shown to be closely correlated with the determination, by a standard method, of the dry rubber content of field latex.

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REFERENCES

1. Lewis, W. K., and McAdams, W. H., *Ind. Eng. Chem.*, 1920, **12**, 673.
2. Fisher, H. L., Gray, H., and Merling, R., *Ibid.*, 1921, **13**, 1031.
3. Willits, C. O., Swain, M. L., and Ogg, C. L., *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 439.
4. Baker, T. I., Jayko, L. G., Stubblefield, R. D., and Anderson, R. F., *Anal. Biochem.*, 1961, **2**, 287.
5. Meeks, J. W., Crook, R. V., Pardo, C. E., and Clark, F. E., *Anal. Chem.*, 1953, **25**, 1535.
6. Burger, V. L., Donaldson, W. E., Baty, J. A., *Rubb. Chem. & Tech.*, 1943, **16**, 660.
7. Bloomfield, G. F., *J. Chem. Soc.*, 1944, 114.
8. ——, *J. Soc. Chem. Ind.*, 1945, **64**, 274.
9. Kemp, A. R., and Mueller, G. S., *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 52.
10. Kolthoff, I. M., and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," Third Edition, The Macmillan Company, New York, 1952.
11. Spence, D., and Caldwell, M. L., *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 371.
12. Gibbons, W. A., and Brass, P. D., "Properties of Latex," *in* Davis, C. C., and Blake, J. T., *Editors*, "Chemistry and Technology of Rubber," Reinhold Publishing Corporation, New York, 1937.
13. "ASTM Standards 1961," Part 11, American Society for Testing Materials, Philadelphia, p. 490.
14. Stavely, F. W., and co-workers, *Ind. Eng. Chem.*, 1956, **48**, 778.
15. Sekhar, B. C., "Abnormal Groups in Rubber and Microgel," Paper presented at the Fourth Rubber Technology Conference, London, 1962.

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Determination of Arsenic in Copper and Copper-base Alloys

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Existing procedures for determining arsenic in copper and its alloys have known limitations and disadvantages, especially when less than about 100 p.p.m. of arsenic are present and a 5-g sample is not available.

A procedure has been developed, involving not more than 1 g of sample, and successfully applied to the analysis of typical samples, including copper-base alloys containing up to 0·2 per cent. of arsenic. Limited tests have shown the method to have a potential application in ferrous analysis.

The sample is dissolved in a hydrochloric acid - hydrogen peroxide mixture; quinquivalent arsenic is reduced with hypophosphorous acid, and an empirical extraction of the arsenious chloride is made into chloroform. The recovered arsenic is oxidised to the quinquivalent state and then determined absorptiometrically after reduction of arsenomolybdate to molybdenum blue.

The recommended procedure is suitable for determining arsenic down to at least 5 p.p.m. in copper and 20 p.p.m. in brass, bronze or cupro-nickel; it is not subject to interference from alloying elements and impurities normally present in these materials. A single determination takes about 2 hours, but at least 8 determinations can be completed by one analyst in a normal working day.

Several methods are available for determining arsenic in non-ferrous materials, but none is entirely suitable for amounts of less than 100 p.p.m. when the sample weight is restricted to 1 g or less. Although such amounts of arsenic would normally be determined spectrographically, there is still a need for an accurate and sensitive method for analysing standard samples.

Two procedures are given in B.S. 1800,[1] one based on a preliminary distillation of arsenious chloride, the other on an initial precipitation, with hypophosphorous acid, of elemental arsenic, together with selenium and tellurium, and then by separation of interfering elements; both procedures are completed by titration with a standard iodine solution. These two methods have known limitations and disadvantages; *e.g.*, in both procedures, when the amount of arsenic present is small, the volume of standard iodine solution is also small, and a minimum sample weight of 5 g is therefore necessary when the arsenic content is less than about 100 p.p.m.

Other methods are available for determining arsenic in non-ferrous materials,[2,3,4,5,6] but phosphorus, selenium, tellurium and silicon, which are present in some grades of copper and its alloys, interfere in one or other of these methods.

The separation of arsenic by precipitation with hypophosphorous acid is only 90 to 95 per cent. complete[7]; selenium and tellurium are also precipitated. This separation has been used by Case[8] in the preliminary stages of a method for determining arsenic at levels above 0·1 mg in copper-base alloys before determining the arsenic as molybdenum blue. Experiments in these laboratories have shown that, when the amount of arsenic separated in this way is less than 0·1 mg, the efficiency of separation is variable—frequently less than 90 per cent.—and that selenium suppresses development of the molybdenum-blue colour. Variable recoveries of arsenic after precipitation with hypophosphorous acid seem to be associated with conditions for precipitation and subsequent washing of the elemental arsenic. Opinions on optimum conditions for these operations are conflicting, and the authors' work has failed to improve the reproducibility of the procedure for determining arsenic below 100 p.p.m.

Tervalent arsenic can be extracted from a hydrochloric acid solution into certain organic solvents; *e.g.*, from 11 M hydrochloric acid, recoveries of 94 per cent. with benzene[9] and about 75 per cent. with carbon tetrachloride[10] have been reported. These observations were made the basis of subsequent experimental work designed to provide a satisfactory method

for determining small amounts of arsenic when the weight of sample was restricted to about 1 g. It was proposed to complete the determination absorptiometrically by the method described by Case.[8]

Experimental

Absorptiometric determination of arsenic—

A calibration graph was prepared, without involving an extraction, by using the colour development conditions recommended by Case.[8]

A standard solution of tervalent arsenic was prepared by dissolving arsenious oxide in sodium hydroxide solution. Volumes of this solution, containing from 0·01 to 0·1 mg of arsenic, were placed in separate 50-ml calibrated flasks. To the contents of each flask were added 5 drops of 0·1 N iodine, to oxidise tervalent arsenic, 5·0 ml of a 1 per cent. w/v solution of ammonium molybdate in dilute sulphuric acid (1 + 6) and 2·0 ml of 0·15 per cent. w/v hydrazine sulphate solution. Each flask was immersed in a boiling-water bath for 10 minutes, cooled, and diluted to the mark; the optical densities were then measured at 8400 Å in 2-cm cells.

The relation between optical density and concentration of arsenic was linear, 0·05 mg of arsenic corresponding to an optical density of 0·69.

Formation and extraction of tervalent arsenic—

Tests in which tervalent arsenic was extracted from 11 M hydrochloric acid into benzene, chloroform or carbon tetrachloride showed that the efficiency of extraction decreased in this order and, although benzene was over 20 per cent. more efficient than chloroform, separation of the organic phase was less defined than when chloroform was used. From 50 ml of 11 M hydrochloric acid containing 0·05 mg of tervalent arsenic, 71 per cent. of the arsenic was extracted by 25 ml of chloroform, and this amount decreased with decrease in the concentration of acid.

Based on these observations, conditions for extracting arsenious chloride were standardised, and a series of standards was prepared and examined. Volumes of a standard solution of tervalent arsenic, containing 0·01 to 0·1 mg of arsenic were placed in separate 100-ml separating funnels, each containing 50 ml of concentrated hydrochloric acid. To the contents of each funnel were then added 25 ml of chloroform, the mixture was shaken vigorously for 3 minutes, and the aqueous layer was discarded. The chloroform was then shaken for 1 minute with 20 ml of water, and discarded. The aqueous layer was run into a 50-ml calibrated flask, 5 drops of 0·1 N iodine were added, and the molybdenum-blue complex was developed as described earlier. Recoveries were plotted, and the resulting graph was linear (0·05 mg of arsenic corresponding to an optical density of 0·48), indicating that extraction of arsenious chloride into chloroform could provide a suitable method for determining arsenic.

Because the sample must be dissolved under oxidising conditions, to prevent loss of arsenic, arsenic is maintained in the quinquivalent state during solution of the sample, and, as such, less than 5 per cent. is extracted into chloroform. Attempts to reduce quinquivalent arsenic to the tervalent state in solutions of cupric chloride in concentrated hydrochloric acid with hydroxyammonium chloride or hydrazine hydrochloride were unsuccessful; both reagents were unsuitable, and subsequent recoveries of arsenic were low. Improved, although variable, recoveries were obtained when stannous chloride was used as a reducing agent.

At temperatures below about 50° C, quinquivalent arsenic in 6 M hydrochloric acid is reduced by hypophosphorous acid[11] to tervalent arsenic, and not, as might be expected, to elemental arsenic. It was also found that, when quinquivalent arsenic was reduced with hypophosphorous acid, provided copper was completely reduced to the cuprous state, nearly 70 per cent. of the arsenic present in a cupric chloride - 11 M hydrochloric acid solution was recovered by a single extraction into 25 ml of chloroform at 20° C.

When this reduction procedure was applied to a sample of vacuum-cast copper, arsenic values, obtained by the molybdenum-blue method, were high and variable, but if the chloroform extract was washed with 11 M hydrochloric acid before the arsenious chloride was extracted, which presumably had the effect of removing entrained phosphorus-containing salts, the values were low (as expected) and consistent.

A graph obtained under these conditions was linear, although of lower slope than the earlier graphs, 0·05 mg of arsenic corresponding to an optical density of 0·44. The values obtained agreed with the values calculated from the known distribution of tervalent arsenic between chloroform and hydrochloric acid, indicating that complete reduction of tervalent arsenic had been achieved. It was also found that equilibrium between the chloroform and the 11 M acid phase was established within 1 minute of shaking.

To extend the range of application of the procedure to determining arsenic in excess of 100 p.p.m., the effect of extracting 0·06 mg of arsenic from solutions containing from 0·1 to 1 g of copper was examined. Results showed that the amount of tervalent arsenic extracted increased progressively with increase in copper concentration, but became constant when 0·4 g or more of copper was present (see Table I). This observation was not altogether surprising, because it is known that a relatively large amount of copper must be present in order to achieve quantitative reduction of quinquivalent arsenic with hypophosphorous acid. To make the calibration graph independent of sample weight, therefore, the amount of copper present should be greater than 0·4 g, and, in subsequent experiments, pure copper was added to the weighed sample, when necessary, so that the total weight of copper present was 1 g.

TABLE I

EFFECT OF COPPER ON EXTRACTION OF 60 p.p.m. OF ARSENIC

Copper present, g	Optical density (2-cm cells; 8400 Å)	Copper present, g	Optical density (2-cm cells; 8400 Å)
0·1	0·445	0·5	0·556
0·2	0·480	0·7	0·558
0·3	0·540	0·8	0·558
0·4	0·558	1·0	0·562

EFFECT OF REAGENTS—

The extraction of tervalent arsenic into chloroform is governed by a distribution law, and therefore the effect of altering the amounts of the various reagents had to be considered. The amounts of hydrochloric acid and chloroform for the first extraction were fixed at 60 and 25 ml, respectively; these volumes were convenient for manipulation purposes. A 1-ml variation in the volume of the hydrochloric acid did not significantly affect the recovery of arsenic, and this reagent was added from a measuring cylinder. A similar variation in volume of chloroform was significant, and addition was made from a pipette. Salts entrained in the chloroform extract were reduced to an insignificant level by washing with 10 ml of concentrated hydrochloric acid, and, although the volume of water necessary to remove arsenic from the chloroform extract could be as low as 5 ml, 20 ml was used to dilute any residual hydrochloric acid in the separating funnel, and also to allow the aqueous extract to be conveniently washed into a 50-ml calibrated flask. The hydrochloric acid and water were both added from measuring cylinders.

TABLE II

RECOVERY OF ARSENIC FROM HIGH-CONDUCTIVITY COPPER

Sample No.	Element added	Amount of element added, %	Amount of arsenic added, p.p.m.	Amount of arsenic found, p.p.m.
V.C. A	Germanium	0·1	60	58
	Selenium	0·1	60	57
	Tellurium	1	60	61
V.C. A	—	—	50	50·7, 49·3, 49·6, 49·8, 50·5, 50·6, 51·2, 50·1
C.C.	—	—	Nil	4
			5	7
L.V. 6	—	—	Nil	4
			5	8
W.P.	—	—	Nil	7
			5	14
B. 19	—	—	Nil	60
			5	65

The concentration of hypophosphorous acid was shown to be unimportant, provided it was sufficient to reduce copper completely to the cuprous state. However, to maintain a constant acidity the volume of this reagent added was fixed at 3·0 ml.

Provided the acid ammonium molybdate and hydrazine sulphate solutions were freshly prepared, the calibration graph was reproducible. Because the molybdenum-blue reaction is dependent on pH, these reagents were added from a pipette.

EFFECT OF OTHER ELEMENTS—

Samples of vacuum-cast copper (1 g), to which had been added a standard solution equivalent to 60 p.p.m. of arsenic and solutions of germanium, selenium or tellurium, were examined by the recommended procedure. No interference was observed from the presence of 0·1 per cent. of either germanium or selenium. Selenium and tellurium were both precipitated by hypophosphorous acid, but, whereas selenium accumulated on top of the chloroform interface and remained in the separating funnel when the chloroform was removed, the presence of 1 per cent. of tellurium obscured the phase boundary and made a clear separation of the phases difficult. This difficulty was overcome by filtering the reduced solution through a Whatman No. 542 filter-paper before extraction into chloroform (see Table II).

The information contained in Table III indicates that the alloying constituents and impurities present in these samples do not interfere in the proposed procedure.

TABLE III

ANALYSIS OF MISCELLANEOUS SAMPLES

Sample		Arsenic found by— proposed procedure, p.p.m.	alternative procedure, p.p.m.	Certificate value, p.p.m.
Brass (70/30)	No. 7	36, 36	39	—
	No. 11	21, 23	17	—
	No. 15	35, 35	33	—
	No. 17	1860, 1870	1930	—
Brass (85/15)	No. 8	48, 46	45	—
	No. 9	71, 70	70	—
	No. 10	53, 53	49	—
	No. 21	30, 32	31	—
	No. 22	130, 129	140	—
Everdur S185 (96 Cu/3 Si/1 Mn)		100, 100	90	—
Arsenic de-oxidised copper, S186		3400, 3400	3500	—
Chrome copper S187 (99 Cu/0·5 Cr/0·3 Zn/0·2 Ni)		59, 62	63	—
Alumbro M5363 (78 Cu/20 Zn/2 Al)		410	420	—
B.C.S. 183 Bronze A (85 Cu/10 Sn/2 Zn/2 Pb/0·25 P)		620	—	500 to 600*
B.C.S. 179 Manganese brass B (59 Cu/34 Zn/1 Mn/1 Fe/2 Sn/1·5 Al/2 Pb/1 Ni)		190	—	200 to 400*
B.C.S. 207 Bronze C (86 Cu/10 Sn/2·5 Zn/0·1 Ni/0·5 Pb)		620	—	500
B.C.S. 183/1 Bronze (85 Cu/5 Sn/5 Zn/4 Pb/0·5 P/0·5 Ni)		1380	—	1400
B.C.S. 180/1 Cupro-nickel (67 Cu/31 Ni/0·8 Fe/0·8 Mn)		120, 119, 118	—	50 to 80*
B.C.S. 239/1 Carbon steel		370, 360	—	330

* These certificate values are not standardised. Comparisons are given to indicate that the values obtained by the proposed procedure are likely to be correct and that the procedure is applicable to these materials.

APPLICATION OF THE PROCEDURE—

Several samples of brass (85 per cent. of copper, 15 per cent. of zinc and 70 per cent. of copper, 30 per cent. of zinc) were examined by the proposed procedure. They were also analysed by a method in which arsenic was determined absorptiometrically as described in the proposed procedure, but after a preliminary distillation of arsenic; good agreement was obtained in all these tests (see Table III).

The precision of the proposed procedure was established by examining a 10-g sample of pure copper to which had been added, as a standard solution of arsenic, the equivalent of 50 p.p.m. of arsenic. The sample was dissolved in a hydrochloric acid - hydrogen peroxide

mixture, and arsenic was determined in eight aliquots each containing the equivalent of 1 g of copper. The standard deviation obtained was 0·6 p.p.m., and the maximum deviation was 0·9 p.p.m. (see Table II).

The procedure was also applied to British Chemical Standard samples of leaded tin-bronze, manganese-brass and cupro-nickel, and the arsenic values found were in agreement with those reported in the Certificates; most of the arsenic values are quoted in the Certificates over a relatively wide range. When the method was applied to copper-base alloys containing alloying amounts of silicon, aluminium or chromium, the arsenic values found were in good agreement with those obtained by alternative procedures. In the examination of chromium-bearing samples it was necessary to dissolve the sample with the aid of perchloric acid, to ensure complete solution of chromium.

Limited tests on a sample of carbon steel to which 1 g of copper had been added indicated that the procedure could be extended to ferrous materials.

These values are summarised in Table III.

Method

Reagents—

Standard arsenic solution—Dissolve 0·132 g of arsenious oxide, previously dried at 105° C, in 5 ml of warm 5 per cent. w/v sodium hydroxide solution. Dilute to 100 ml, add diluted sulphuric acid (1 + 1) until the solution is just acid to litmus paper, and then dilute to 1 litre. Dilute 50 ml of this solution to 250 ml.

1 ml ≡ 0·02 mg of arsenic.

Ammonium molybdate solution, 1 per cent. w/v—Add, slowly, 14 ml of concentrated sulphuric acid to 60 ml of water, and then dissolve 1 g of ammonium molybdate in the warm solution. Cool, and dilute to 100 ml.

This reagent must be freshly prepared.

Preparation of calibration graph—

Place, separately, 1·0, 2·0, 3·0, 4·0 and 5·0 ml of the standard arsenic solution (1 ml ≡ 0·02 mg of arsenic) in each of five 100-ml beakers containing 1·0 g of pure copper; use a sixth beaker containing 1·0 g of copper for a blank determination.

Continue with each beaker as described below.

Add 5 ml of concentrated hydrochloric acid, and then place in a cold-water bath. Add 3 ml of 100-volume hydrogen peroxide, allow the initial reaction to subside, and then add a further 7 ml of the hydrogen peroxide. When solution of the sample is complete, remove the beaker from the water bath, and allow the solution to simmer at the side of a hot-plate to decompose the excess of hydrogen peroxide; finally, evaporate the solution to dryness.

To the residue add 50 ml of concentrated hydrochloric acid, stir to dissolve soluble salts, adjust the temperature to 20° C, add 3·0 ml of 50 per cent. w/w hypophosphorous acid, and then set the solution aside for 5 minutes. Transfer the solution to a dry separating funnel, with the aid of 10 ml of concentrated hydrochloric acid, add 25·0 ml of chloroform, and then shake vigorously for 1 minute. Allow the two layers to separate, and run the lower (chloroform) layer into a dry separating funnel; discard the aqueous layer. Shake the chloroform extracts with 10 ml of concentrated hydrochloric acid for 30 seconds. Allow the two layers to separate, and run the lower (chloroform) layer into a dry separating funnel; discard the aqueous layer. Add 20 ml of water, and shake vigorously for 1 minute; allow the two layers to separate, discard the lower (chloroform) layer, and transfer the aqueous layer to a dry 50-ml calibrated flask with about 5 ml of water.

Add the reagents listed below in the order stated; wash down the neck of the flask, and mix well after each addition—

5 drops of 0·1 N iodine solution;
5·0 ml of 1 per cent. w/v ammonium molybdate solution;
2·0 ml of freshly prepared 0·15 per cent. w/v hydrazine sulphate solution.

Stand the flask in a boiling-water bath for 10 minutes, then cool to 20° C, and dilute to the mark.

Measure the optical density at 8400 Å in 2-cm cells.

PROCEDURE—

Dissolve 1 g of the sample (see Notes 1 and 2), and continue as described under "Preparation of Calibration Graph" (see Note 3).

With each batch of samples, simultaneously determine a reagent blank value on 1 g of pure copper.

NOTES—

1. Applicable to samples containing up to 100 p.p.m. of arsenic. For arsenic contents above this range, use a proportionally smaller weight of sample, and add sufficient pure copper to bring the weight of copper to 1 g.

2. In the examination of alloys containing chromium, *e.g.*, Kumium, dissolve the sample in 5 ml of perchloric acid, sp.gr. 1·54, and 1 ml of concentrated nitric acid, and then evaporate to dryness. Dissolve the residue in 50 ml of concentrated hydrochloric acid, and continue as described under "Preparation of Calibration Graph."

3. In the examination of alloys containing tellurium, above about 0·1 per cent., redissolve the residue, after evaporation, in 30 ml of concentrated hydrochloric acid. Adjust the temperature to 20° C, add 3·0 ml of the hypophosphorous acid, and set aside for 5 minutes. Filter the solution through a Whatman No. 542 filter-paper into a dry separating funnel, and wash the filter-paper with three 10-ml portions of concentrated hydrochloric acid. Continue as described under "Preparation of Calibration Graph."

CONCLUSIONS

The proposed procedure is suitable for determining arsenic down to at least 5 p.p.m. in copper and 20 p.p.m. in copper-base alloys containing common alloying constituents. Selenium and tellurium up to at least 0·1 and 1 per cent., respectively, do not interfere. A single determination takes about 2 hours, but at least 8 determinations can be completed by one analyst in a normal working day; the precision of the method is within 1 p.p.m. at the 50 p.p.m. of arsenic level.

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REFERENCES

1. "Methods for the Analysis of Raw Copper," British Standard 1800 : Parts 2 and 8 : 1951.
2. "A.S.T.M. Methods for Chemical Analysis of Metals," American Society for Testing Materials, Philadelphia, 1956, p. 487.
3. Gullstrom, D. K., and Mellon, M. G., *Anal. Chem.*, 1953, **25**, 1809.
4. Steel, M. C., and England, L. J., *Analyst*, 1957, **82**, 595.
5. Boltz, D. F., and Mellon, M. G., *Anal. Chem.*, 1947, **19**, 873.
6. Sandell, E. B., "Colorimetric Determination of Traces of Metals," Third Edition, Interscience Publishers Inc., New York, 1959, p. 282.
7. Smales, A. A., and Pate, B. D., *Anal. Chem.*, 1952, **24**, 717.
8. Case, D. P., *Ibid.*, 1948, **20**, 902.
9. Green, M., and Kafalas, J. A., *J. Chem. Phys.*, 1954, **22**, 760.
10. Fischer, W., Hurre, W., Freese, W., and Hackstein, K. G., *Angew. Chem.*, 1954, **66**, 165.
11. Challis, H. J. G., *Analyst*, 1941, **66**, 58.

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The Determination of Arsenic in Germanium Dioxide

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A method is described in which tervalent arsenic is separated from germanium in oxalic acid solution by extraction with diethylammonium diethyldithiocarbamate in chloroform. The extracts are scrubbed with dilute oxalic acid, evaporated successively with nitric - perchloric acid, hydrochloric acid and, finally, evaporated to fumes with sulphuric acid. After addition of zinc to the diluted sulphuric acid, arsine is absorbed in a pyridine solution of silver diethyldithiocarbamate to form a red compound, the optical density of which is measured spectrophotometrically. A radioisotope of arsenic was used to find the best conditions for extraction. Variables in the evolution procedure are discussed.

The method can be used for determining down to 0·1 μg of arsenic with an error of $\pm$0·05 μg; this corresponds to 0·02 p.p.m. of arsenic in the germanium dioxide sample.

Arsenic is an extremely undesirable impurity in germanium used in the manufacture of transistors. It is consequently necessary to examine samples of germanium dioxide, which is used as a raw material, to determine their arsenic content. The maximum acceptable limit for arsenic in germanium dioxide is 0·1 p.p.m.; hence a suitable method of analysis is one that can determine arsenic within the range 0·02 to 0·1 p.p.m.

The literature was studied, and the methods of Payne[1] and Luke and Campbell[2] were used as starting points for the subsequent work. Payne dissolved the sample in a mixture of oxalic acid and ammonium oxalate, reduced the arsenic to the tervalent state, and extracted it with diethylammonium diethyldithiocarbamate in chloroform. After wet oxidation of the extract and heating until fumes of sulphuric acid were evolved, the solution was diluted and the arsenic evolved electrolytically as arsine. This was passed over a cotton thread impregnated with mercuric chloride, and the length of the black stain produced after treatment with silver nitrate was a measure of the arsenic present. Similar methods of dissolution and separation were used by Luke and Campbell, but, after wet oxidation of the organic complex in the chloroform layer, evaporation with hydrochloric acid was carried out to remove any entrained germanium. The solution was then heated until fumes of sulphuric acid were evolved, diluted, and the arsenic determined by a molybdenum-blue procedure.

Little modification was needed to the dissolution and extraction steps in these methods, but the electrolytic Gutzeit determination of the traces of arsenic occasionally gave non-reproducible stains and also involved setting the solution aside overnight. The final molybdenum-blue procedure was subject to interferences, presumably from silica derived from the Pyrex glassware. The blank values of the acid, ammonium molybdate and hydrazine sulphate were equivalent to between 0·5 and 0·7 μg of arsenic, and the difference between replicates as well as the blank values were considered unsatisfactory for the determination of traces of arsenic. For determining more than a few micrograms up to several hundred micrograms of arsenic, however, the molybdenum-blue method is excellent.

Silver diethyldithiocarbamate was first described as a reagent for arsenic by Vašák and Šedivec[3]; it has since been used in the analysis of iron products,[4] naphthas,[5,6] petroleum products and catalysts.[7] The method involves evolution of arsine and its absorption in a solution of the reagent in pyridine. Work in this laboratory has shown that microgram amounts of germanium interfere with this procedure, so that quantitative separation of germanium from the arsenic is essential.

Experimental

Separation—

Five grams of germanium dioxide and 18 g of oxalic acid were weighed into a 500-ml conical flask; 170 ml of water were added, and the contents of the flask were boiled gently, with occasional swirling, until the sample had dissolved. The addition of ammonia, recommended by previous workers,[1,2] was found to be unnecessary. After the solution had been

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cooled to about 50° C, 50 ml of concentrated hydrochloric acid, 1 ml of potassium metabisulphite solution and 1 ml of potassium iodide solution were added, and the whole was set aside for 15 minutes. The solution was transferred to a 500-ml separating funnel, saturated with chloroform, extracted twice with a solution of diethylammonium diethyldithiocarbamate in chloroform and finally shaken with chloroform. The combined organic layers were scrubbed with a solution of oxalic and hydrochloric acids in a 100-ml separating funnel, transferred to a 100-ml conical flask and oxidised with nitric and perchloric acids. Evaporation with hydrochloric acid removed any last traces of germanium, and finally the volatile acids were removed by heating the solution until fumes of sulphuric acid were evolved.

The probable sources of error in the separation described above include loss of arsenic on dissolution of the sample, incomplete extraction of the arsenic, loss of arsenic on scrubbing the chloroform extract, loss of arsenic during the final stages of fuming and introduction of arsenic from the reagents, especially the oxalic and hydrochloric acids.

To study the efficiency of the separation, a series of experiments was carried out on a radioisotope of arsenic. The initial activity of the isotope was such that 0·25 μg of arsenic-76 in 10 ml of solution gave about 35,000 counts per minute. Measurements were made with a M6H liquid counter (20th Century Electronics Ltd.) and a Panax Ratemeter type 5054. To determine the activity of a solution, its volume was measured, and 10 ml were transferred by means of a measuring cylinder to the liquid counter; 2 minutes were allowed for the ratemeter to stabilise, and nine readings were taken at 15-second intervals. The product of the volume of the solution and the average count rate (corrected for lost counts) was taken as a measure of the arsenic in the solution. No correction was applied for variations in density or composition of the solutions being measured.

The initial experiments, performed by adding quinquivalent arsenic-76 as sodium arsenate, before dissolution of the germanium dioxide in oxalic acid, confirmed that no loss of arsenic occurred when the germanium dioxide was dissolved and that about 99 per cent. of the tervalent arsenic was extracted into the chloroform. Quinquivalent arsenic was not extracted, and reduction to the tervalent state by sulphite and iodide did not take place in the absence of hydrochloric acid under the conditions described above. When the chloroform extract was scrubbed with hydrochloric and oxalic acids to reduce its germanium content, about 12 per cent. of the arsenic returned to the aqueous phase. If hydrochloric acid was omitted from the scrubbing solution the loss of arsenic was reduced to 3 per cent. This was considered satisfactory.

Determination of arsenic—

Of the methods available for determining submicrogram amounts of arsenic, that described by Liederman, Bowen and Milner[7] appeared the best for further study. In this method the arsenic in dilute sulphuric acid is reduced to the tervalent state with stannous chloride and potassium iodide; 5 g of zinc are added, and the evolved hydrogen, containing all of the arsenic as arsine, is bubbled through a solution of silver diethyldithiocarbamate in pyridine. After hydrogen has been bubbled through the solution for 45 minutes, the optical density is measured at 540 mμ, and the red colour of the complex formed is proportional to the arsenic content of the solution in the range 0 to 5 μg of arsenic.[6] Antimony, which accompanies arsenic through the whole procedure, forms a colour with an absorption peak at 510 mμ. The optical density of antimony at 540 mμ is 8 per cent. of that of arsenic under these conditions, but the traces of antimony present in the sample of germanium dioxide are too small to contribute measurably to the final colour.

The apparatus used for the evolution and absorption of arsine is described by Crawford, Palmer and Wood.[8] It consists of a 50-ml conical flask with a B19 neck, an inverted U connecting tube with a B19 cone at one end and a B7 cone at the other, a narrow gas-delivery tube, with a B7 socket at one end, and a glass helix about 3 inches long fitting outside the delivery tube and inside a flat-bottomed glass cylinder. Before use, the bulb below the B7 socket of the bubbler tube is plugged with cotton-wool impregnated with lead acetate. By pipette, 3 ml of silver diethyldithiocarbamate solution in pyridine are put into the absorber cylinder, the gas-delivery tube and the helix are inserted, and the apparatus is assembled. When the apparatus was new no lubricant was used on the ground-glass surfaces; after several months it was necessary to moisten the joints with a small amount of glycerol.

INTERFERENCE BY GERMANIUM—

There is no reference in the literature to the effect of germanium on the determination of arsenic. If any germanium is present in the evolution solution some will be evolved as germane, which forms an unstable red complex with the silver compound. The position of the optical-density peak around 490 mμ changes slowly, and the colour intensity is reduced by 90 per cent. in about 5 hours. Germanium also interferes by preventing complete evolution of arsenic as arsine. This inhibition is not reproducible, and the addition of oxalic acid to the evolution solution (to complex the germanium) does not completely suppress the interference.[1] It is therefore essential to reduce the germanium content to the submicrogram level before the evolution of arsenic is carried out. If significant amounts of germanium are present in the solution, the optical density of the pyridine solution at 490 mμ will be greater than that at 540 mμ; should this be so, the determination must be repeated.

PURIFICATION OF OXALIC ACID—

Payne[1] recommended one re-crystallisation from hydrochloric acid and then two from water to purify the oxalic acid. This was tried, but it was found that traces of hydrochloric acid in the oxalic acid gave rise to loss of arsenic during dissolution of the sample. Radioactive arsenic-76 was used to compare this mode of purification with triple re-crystallisation from water. Measurement of the activity of the mother liquor after each re-crystallisation step, whether from acid or water, showed that about 85 per cent. of the arsenic present was removed with each operation, so re-crystallisation from water was adopted as the method of purification.

EVOLUTION CONDITIONS—

The largest source of arsenic from the reagents was the zinc metal used in the evolution step. It was observed that the arsenic blank values rose with an increase in the amount of zinc dissolved, and this in its turn increased with the time allowed for evolution. An experiment was carried out to determine the time after which an acceptable proportion of the arsenic had been evolved as arsine and absorbed in the pyridine solution. Optical-density measurements were made at 15-minute intervals on absorption solutions from standards containing 0·5 and 2·5 μg of arsenic. For the former, about 98 per cent. of the arsenic was evolved within 30 minutes. The latter sample took 45 minutes for 98 per cent. to be evolved, though 95 per cent. was liberated after half an hour. As, in the proposed determination, less than 0·5 μg of arsenic is to be evolved, the evolution time was fixed at 30 minutes. The weight of zinc used for the evolution was reduced to 2 g with no change in the optical density produced by 0·5 μg of arsenic. This had the dual effect of diminishing the blank value and conserving the selected batch of low-arsenic zinc.

METHOD

APPARATUS—

As well as normal laboratory glassware, three sets of apparatus for the evolution and absorption of arsine are required. The apparatus is described by Crawford, Palmer and Wood.[8]

The glassware must be cleaned with chromic acid cleaning solution. Ensure that the taps and stoppers of the separating funnels fit well and that the stems and taps are dry. Dry them with acetone and a current of air if necessary. Reserve the flasks and funnels for determinations of trace amounts of arsenic.

Exelo piston pipettes can conveniently be used to transfer the organic solutions.

REAGENTS—

All reagents must be of recognised analytical grade unless otherwise stated.

Water once distilled from a Pyrex-glass still is satisfactory.

Standard arsenic solution—Dissolve 0·132 g of arsenic trioxide in 2 ml of N sodium hydroxide in a covered beaker. Add 10 ml of water and 2 ml of 100-volume hydrogen peroxide, and set aside until effervescence ceases. Dilute the solution to 1000 ml. From this stock solution (0·100 mg arsenic per ml), prepare daily a fresh working solution containing 0·25 μg of arsenic per ml.

Oxalic acid—Batches having an extremely low arsenic content have been obtained. If the arsenic level exceeds 0·0025 p.p.m. (0·05 μg of arsenic in 20 g) re-crystallise twice or three times from water.

Hydrochloric acid—Examine all available samples for arsenic content, and reserve the best batch for this determination.

Potassium iodide solution, 10 per cent. w/v, aqueous—Discard after 2 weeks.

Potassium metabisulphite solution, 5 per cent. w/v, aqueous—Discard after 2 weeks.

Diethylammonium diethyldithiocarbamate solution, 0·25 per cent. w/v in chloroform.

Oxalic acid solution, 5 per cent. w/v, aqueous.

Nitric - perchloric acid (3 + 1) *v/v*—Mix 3 volumes of concentrated nitric acid with one volume of 72 per cent. perchloric acid.

Diluted hydrochloric acid—Dilute the concentrated acid with an equal volume of water, and add 1 per cent. v/v of concentrated nitric acid.

Mixed acid—Add 2 volumes of concentrated sulphuric acid (low in arsenic) and 1 volume of 72 per cent. perchloric acid to 1 volume of concentrated nitric acid.

Stannous chloride solution, 10 per cent. w/v—Dissolve stannous chloride, $SnCl_2.2H_2O$, in diluted hydrochloric acid (1 + 2). Discard after 2 weeks.

Silver diethyldithiocarbamate[7]—This can be purchased from the Fisher Scientific Co., or prepared as described below. Prepare two solutions, one containing 1·7 g of silver nitrate in 100 ml of water and the other containing 2·3 g of sodium diethyldithiocarbamate in 100 ml of water. Cool to below 20° C, and mix slowly, with stirring. Filter off the lemon-yellow product, and wash thoroughly with distilled water. Dry in a vacuum desiccator below 30° C. The dry salt is stable for at least 6 months.

Silver diethyldithiocarbamate solution, 0·5 per cent. w/v in pyridine.

Zinc—Select a batch of granulated zinc with an arsenic content below 0·05 p.p.m.

Cotton-wool—Impregnated with lead acetate (obtained from British Drug Houses Ltd.)

PROCEDURE—

Carry out one determination of arsenic in the reagents with each sample or group of samples.

Heat 5 g of germanium dioxide, 20 g of oxalic acid and 150 ml of water in a 500-ml conical flask, with occasional swirling, until the solution is clear. Set aside to cool, add 30 ml of concentrated hydrochloric acid, and adjust the temperature to between 60° and 65° C. Add 2 ml of potassium iodide solution and 1 ml of potassium metabisulphite solution to the contents of the flask, and set aside for 15 minutes to permit the reduction of quinquivalent arsenic to the tervalent state.

Transfer the contents of the flask to a 500-ml separating funnel containing 5 ml of diethylammonium diethyldithiocarbamate solution and 5 ml of chloroform. Swirl the funnel carefully, and loosen the stopper (not the tap) to release the pressure; repeat this operation until the whole of the funnel is at the same temperature, and then shake the funnel vigorously for 40 seconds. Allow the layers to separate, and then run the lower layer slowly into a 100-ml separating funnel, great care being taken that no aqueous phase enters the tap. Add 5 ml of carbamate solution to the contents of the 500-ml separating funnel, and repeat the pressure releasing operation, the extraction and separation. Finally, shake the germanium oxalate solution with 5 ml of chloroform, separate, and combine with the other extracts.

Shake the combined chloroform phases with 10 ml of 5 per cent. oxalic acid solution for 40 seconds to remove any entrained germanium. Allow the layers to separate completely, and run the lower layer into a 100-ml conical flask. Add 2 ml of nitric - perchloric acid to the contents of the conical flask, evaporate the chloroform carefully, and then heat the flask until fumes of perchloric acid appear. Set aside to cool, add 2 ml of diluted hydrochloric acid, and repeat the evaporation to fumes. This treatment removes the last traces of germanium. Finally, add 4 ml of mixed acid to the contents of the conical flask, and heat to fumes of sulphuric acid. During the heating with mixed acid the nitric acid is evaporated first; fumes of perchloric acid are evolved and the solution turns yellow, and after the perchloric acid has been removed the solution is almost colourless. Continue the heating until sulphuric acid is condensing 1 cm above the bottom of the flask. Remove the flask, and set it aside to cool to room temperature; add 2 ml of diluted sulphuric acid (1 + 1) and 12 ml of water, and transfer the solution to the 50-ml conical flask of the arsine-evolution apparatus. Add 1 ml of potassium iodide and 1 ml of stannous chloride solution to the contents of this

flask, and set it aside for 15 minutes. Fit the bubbler tube with lead acetate impregnated cotton-wool, and with the aid of a piston pipette transfer 3·0 ml of silver diethyldithiocarbamate solution to the bubbler. After 15 minutes add between 2 and 2·3 g of zinc to the contents of the conical flask, and connect the flask to the apparatus. Allow hydrogen to be evolved for 30 minutes, disconnect the apparatus, and transfer the pyridine solution to a 1-cm cell. Measure the optical density spectrophotometrically against the pure silver diethyldithiocarbamate solution at 540 mμ with a slit width of 0·1 mm. Subtract the optical density produced by the reagents alone from the figure so obtained, and determine the arsenic content of the sample by comparing it with a standard solution taken through the same procedure. Prepare the standard solution by adding 0·5 μg of quinquivalent arsenic, as sodium arsenate, to 5 g of germanium dioxide, and calculate the optical density due to the recovered arsenic. If the standard arsenic is in a hydrochloric acid solution, the acid must be added after the dissolution of sample in oxalic acid, or loss of arsenic will result.

NOTES—

1. Obtain the cell blank value by measuring each cell in turn against the reference cell with silver diethyldithiocarbamate solution in each. Subtract the cell blank value from the measured optical density of the sample. Empty the cells with a piston pipette. If the faces of the cells are wetted or touched repeat the cell blank measurement.

2. If the results are higher than expected and the presence of germanium in the evolution flask is suspected, measure the optical density of the coloured solution at 490 mμ. If this figure exceeds the optical density at 540 mμ, repeat the determination.

3. Depending on the thermal history of the sample, complete dissolution in oxalic acid may not be attained within 50 minutes. All of the samples examined so far have either dissolved completely within 30 minutes, or have had about 5 per cent. (estimated) remain undissolved after 50 minutes. The undissolved sample can be ignored in the determination by permitting it to settle during the 15-minute reduction period and decanting the supernatant solution into the 500-ml separating funnel.

Most of the remaining germanium dioxide collects at the liquid interface, and if the chloroform phase is run through the tap slowly (say over a period of 1 minute) no solid passes through the tap. It is not essential to plug the stem of the tap funnel with glass-wool.

4. During the 15-minute reduction period the temperature of the solution drops from about 60° to 45° C. If the solution cools below about 35° C, crystallisation of oxalic acid from the reagent blank solution will begin with consequent blocking of the stem above the tap of the funnel. For convenience, therefore, the extraction should be effected within 15 minutes of completion of reduction.

5. Some batches of silver diethyldithiocarbamate have been prepared that showed a variable reaction to small amounts of arsenic. Amounts up to 1 μg of arsenic give no reaction with these batches, although above this "threshold" the optical density per microgram of arsenic compares favourably with the good batches of reagent. The

TABLE I

RESULTS OF THE ANALYSIS OF 3 SAMPLES OF GERMANIUM DIOXIDE

Sample No.	Solution	Optical density at 540 mμ of— 1-cm cell blank value	solution: uncorrected	solution: corrected	Optical density ratio of As in sample to As recovered from 0·5 μg	Arsenic content, p.p.m.
1	Reagent blank solution ..	−0·013	−0·009	0·004	0·0 to 0·042	<0·01
	5 g of germanium dioxide ..	−0·016	−0·013	0·003		
	5 g of germanium dioxide + 0·5 μg of arsenic ..	−0·015	0·030	0·045		
2	Reagent blank solution ..	0·005	0·018	0·013	0·007 to 0·037	0·02
	5 g of germanium dioxide ..	−0·007	0·013	0·020		
	5 g of germanium dioxide + 0·5 μg of arsenic ..	0·0	0·057	0·057		
3	Reagent blank solution ..	−0·001	0·013	0·014	0·011 to 0·039	0·03
	5 g of germanium dioxide ..	−0·011	0·014	0·025		
	5 g of germanium dioxide + 0·5 μg of arsenic ..	−0·003	0·061	0·064		

only variables in the preparation procedure that appeared to be significant were that there should be an excess of silver after the precipitation, and that the product should be dried thoroughly. Variations in the purity of the sodium diethyldithiocarbamate may also be important.

6. Arsine is slightly soluble in water. If the inside of the inverted U connecting tube has drops of water adhering to it (above the B19 cone) poor recoveries of arsenic frequently result. It has been found necessary to clean the connecting tube with cleaning solution, and to dry the tube so as to leave a hydrophilic surface. Drops of dilute acid spray are then able to drain back into the evolution flask.

A plug of cotton-wool impregnated with lead acetate is omitted from the B19 cone for the same reason, *i.e.*, spray from the hydrogen evolution wets the cotton-wool and often causes low results. The small plug in the B7 cone of the bubbler is sufficient to retain any traces of sulphide.

Three samples of germanium dioxide were analysed during one day; the method was exactly as described, except that 50 ml of concentrated hydrochloric acid were used in the reduction step before extraction. The results are shown in Table I.

Two further samples were analysed some months later exactly as described in the proposed procedure, *i.e.*, 30 ml of concentrated hydrochloric acid being used in the reduction step; the results are shown in Table II.

TABLE II

RESULTS OF THE ANALYSIS OF 2 SAMPLES OF GERMANIUM DIOXIDE

Sample No.	Solution	Optical density at 540 mμ of— 1-cm cell blank value	solution: uncorrected	solution: corrected	Optical density ratio of As in sample to As recovered from 0·5 μg	Arsenic content, p.p.m.
4	Blank solution	−0·010	−0·003	0·007	0·009 to 0·051	0·02
	5 g of germanium dioxide	−0·014	0·002	0·016		
	5 g of germanium dioxide + 0·5 μg of arsenic	−0·021	0·046	0·067		
5	Blank solution	0·006	0·009*	0·003*	<0·007 to 0·043	<0·015
	5 g of germanium dioxide	0·012	0·022	0·010		
	5 g of germanium dioxide + 0·5 μg of arsenic	0·001	0·054	0·053		

* Represents that part of the total blank value contributed by the reagents added for oxidising the chloroform extracts and by the reagents added subsequently.

DISCUSSION OF THE METHOD

The sample dissolution and arsenic extraction described are extremely satisfactory. One possible improvement would be to find a method of reducing quinquivalent arsenic involving reagents that could be easily purified. However, the batches of reagents used in this work have contributed extremely little arsenic to the total blank value.

The spread in the values of the reagent blank solution (0·004 to 0·014 units) in samples 1 to 4 may be caused partly by non-reproducibility in the optical-density readings (about 0·002 units), but may also be caused by inhomogeneous distribution of arsenic in the zinc. There is also a considerable variation in the amount of granulated zinc left undissolved at the end of the 30-minute evolution period. If zinc chippings or borings of more uniform thickness were easily obtainable it would be possible to reduce the spread of the blank value. Strictly, an average reagent blank value (in this instance about 0·009) should be subtracted from the optical-density readings for the sample. The difference between the average reagent blank value and the extreme blank values is a measure of the error in the determination, which for this batch of zinc is about ±0·005 optical-density units, *i.e.*, ±0·05 μg of arsenic.

The agreement between the optical densities of the 0·5 μg of reserved arsenic (0·041, 0·037, 0·039, 0·051, 0·043) is satisfactory considering the grade of zinc used. Sample 4 inadvertently had a 40-minute evolution period, which may partly account for its high value.

It is difficult to pin-point the reasons for the wide variations in the cell blank values. The cells were cleaned with cleaning mixture before samples 1 and 4 were measured, and were never handled during measurements on samples 1 to 3 or 4 and 5. The changes in optical density of the cells during each of the 2 days were probably caused by the formation of salts

of pyridine (*e.g.*, the hydrochloride) by sublimation on the outer faces of the cell. The magnitude of the cell blank values shows the need for the extra set of measurements before each group of sample optical-density measurements.

The variables that must be reconciled to obtain the conditions for the most accurate results from the evolution step are the arsenic content, the weight and the surface area of the zinc, the amount and concentration of the dilute sulphuric acid used, the evolution time and the percentage of arsenic converted to arsine, the volume of absorption solution and the optical path length. As granulated zinc was used, the differences in the thickness of the granules was considerable and difficult to take into consideration. The batch of zinc with the lowest arsenic content was selected from those available. As a result of the experiment described above the evolution time was fixed at 30 minutes.

Most of the published work suggests the use of 5 g of zinc; to diminish the blank value this amount was reduced first to 3 g and later to 2 g, with a corresponding lowering in the amount of sulphuric acid used. This reduction involves a decrease in the range over which Beer's law is obeyed. With 3 g of zinc the optical density per microgram of arsenic stayed constant up to 5 μg, but with 2 g of zinc the value dropped above 1 μg. The amount of sulphuric acid used is sufficient to react with all the zinc and provide a 50 per cent. excess; its dilution permits a satisfactory rate of hydrogen evolution. Three millilitres of pyridine solution used in the gas absorber are sufficient to cover the helix and so provide a long gas-to-liquid contact time. That the absorption reaction is rapid is shown by the frequent appearance of an intensely coloured red compound inside the inner bubbler tube where the glass had been wetted by the absorbent. This substance must be dissolved in the absorption solution before optical-density measurements are taken. The bubbler was designed for the absorption of arsine in iodine solution[8]; it is possible that a smaller volume of absorbent will suffice for silver diethyldithiocarbamate in pyridine. A cell of longer path length per unit volume would decrease the lower detectable limit of arsenic, although a good grade of zinc is necessary for any large improvement in sensitivity.

FURTHER APPLICATIONS—

To extend the method to the analysis of other materials the factors detailed below must be considered. Milligram amounts of copper, nickel and cobalt interfere with the evolution of arsine,[11] and traces of germanium and antimony are reduced to germane and stibine, which form coloured complexes with silver diethyldithiocarbamate. Arsenic, together with antimony and tin, can be separated from milligram amounts of the elements mentioned above, and many more, by Wyatt's procedure.[10] In this procedure an oxidised solution containing quinquivalent arsenic and antimony and quadrivalent tin is extracted with diethylammonium diethyldithiocarbamate; the extracted solution, adjusted to 2 N in hydrochloric acid, is reduced with potassium iodide and potassium metabisulphite, and is re-extracted. Traces of iron may accompany the arsenic, antimony and tin, but these will be insufficient to interfere with the evolution of arsine.

Antimony thus remains the only interfering element. Work in this laboratory has shown that the separation of antimony from arsenic can be effected by reduction of the antimony with hydrazine sulphate and heating to fumes of sulphuric acid, and then extraction of the antimony with cupferron.

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REFERENCES

1. Payne, S. T., *Analyst*, 1952, **77**, 278.
2. Luke, C. L., and Campbell, M. E., *Anal. Chem.*, 1953, **25**, 1588.
3. Vašák, V., and Šedivec, V., *Chem. Listy*, 1952, **46**, 341.
4. Večeřa, Z., and Bieber, B., *Giessereitechnik*, 1957, 61.
5. Powers, G. W., jun., Martin, R. L., Piehl, F. J., and Griffin, J. M., *Anal. Chem.*, 1959, **31**, 1589.
6. Albert, D. K., and Granatelli, L., *Ibid.*, 1959, **31**, 1593.
7. Liederman, D., Bowen, J. E., and Milner, O. I., *Ibid.*, 1959, **31**, 2052.
8. Crawford, A., Palmer, J. G., and Wood, J. H., *Mikrochim. Acta*, 1958, 277.
9. Strafford, N., Wyatt, P. F., and Kershaw, F. G., *Analyst*, 1945, **70**, 232.
10. Wyatt, P. F., *Ibid.*, 1955, **80**, 368.
11. Sandell, E. B., "Colorimetric Determination of Traces of Metals," Second Edition, Interscience Publishers Inc., New York and London, 1950, p. 176.

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The Detection and Determination of Glycerol in Tobacco

The Use of Paper and Cellulose-column Chromatography for determining Glycerol in the Presence of Sugars

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A simple method of extraction and a sensitive paper-chromatographic procedure for the identification of glycerol, and of propylene glycol, which occasionally accompanies it in tobacco samples, are described.

For quantitative determination of glycerol, a method has been developed in which the glycerol is effectively separated from sugars on a column of cellulose; a layer of activated charcoal at the top of the column removes other tobacco materials, which would interfere with the subsequent determination of the glycerol by oxidation with periodate.

Customs Regulations in this country prohibit the sale of cigarettes containing added glycerol, although its addition is permitted in some other countries.

The method for determining glycerol in tobacco proposed by Chapman[1] some years ago has been considered to be the only method capable of providing accurate results, but it has the disadvantage of being extremely time-consuming and inconvenient for routine control purposes; the method outlined in the "Tobacco" monograph of Thorpe's Chemical Dictionary[2] has been in use for some years in the Laboratory of the Government Chemist. In this procedure, which is known to yield incomplete recovery of the glycerol present, the glycerol is separated by passing steam into the tobacco heated to 130° C under low pressure.

The qualitative paper-chromatographic procedure described in this paper serves as a preliminary sorting test; when the presence of added glycerol is indicated, the amount present can be determined quantitatively by the column procedure. When propylene glycol is present, it emerges from the column in the same eluate as the glycerol, and further investigatory work is continuing in order to provide an extension to the method so that both glycerol and propylene glycol can be determined accurately in tobacco.

Qualitative paper-chromatographic test for glycerol in tobacco—

As a running solution for use in the paper chromatography of glycols and other polyhydric alcohols, solutions containing n-butanol have been recommended, *e.g.*,[3,4,5]; we prefer water-saturated n-butanol for separations by both ascending- and descending-solvent chromatography. Ammoniacal silver nitrate is used for developing the spots, the most satisfactory definition being obtained when the papers are impregnated with silver nitrate before the chromatograms are run and exposed to an atmosphere of ammonia immediately on removal from the tank.

Simple extraction of tobacco with water, and then, possibly, with solvent, is attractive as a means of obtaining a suitably concentrated solution for spotting on a chromatographic paper; however, when such a procedure is employed, interference from other materials extracted from some types of tobacco masks appreciable amounts of glycerol, as shown in Fig. 1 (No. 1). By mixing the tobacco with carbon during the extraction, some of the interfering materials were removed and a clearer solution was obtained for overspotting, but the interference from salts was not effectively removed (see Fig. 1, No. 2). By mixing the tobacco with diethylaminoethylcellulose powder the glycerol spots were satisfactorily isolated; this treatment was effective even when only traces of glycerol were present (see Fig. 1, Nos. 3 and 6). Acetone is the most convenient solvent for use in this procedure.

As a final washing solution after development of the chromatogram, it is considered that the use of 10 per cent. v/v ammonium hydroxide in the proportion recommended yields slightly more distinct spots than does sodium thiosulphate solution.

Fig. 1 shows the spots from a standard solution (No. 5) and also from a tobacco containing 1 per cent. of added glycerol (No. 4).

PAPER-CHROMATOGRAPHIC METHOD FOR DETECTING GLYCEROL AND PROPYLENE GLYCOL IN TOBACCO

REAGENTS—

Charcoal powder—For decolourising purposes, activated, washed with acid (obtainable from the British Drug Houses Ltd.).

Diethylaminoethylcellulose powder—Whatman D.E.50.

Dilute standard solution of glycerol and propylene glycol—0·1 per cent. w/v glycerol and 0·2 per cent. w/v propylene glycol in acetone containing approximately 25 per cent. of water. This solution should be freshly prepared, and is conveniently obtained from a stronger aqueous stock solution of glycerol and propylene glycol diluted with acetone.

Silver nitrate solution in acetone—Dissolve 1 g of silver nitrate in 6 ml of water, and dilute to 50 ml with acetone. The solution must be freshly prepared immediately before use.

Ammonium hydroxide solution—A 10 per cent. v/v solution of ammonium hydroxide, sp.gr. 0·880, in water.

PROCEDURE—

Add 3 ml of distilled water to 1 g of the tobacco contained in a small beaker, and stir for 5 minutes with a pointed glass rod; use a pressing action to ensure that the water penetrates into the tobacco. Add 10 ml of acetone, and mix thoroughly. Add 1·5 g of the activated charcoal and 1·5 g of diethylaminoethylcellulose powder, stir well for about 1 minute to ensure homogeneity, and then with a flat spatula press out a small amount of solution, approximately 3 ml, into a small specimen tube. Insert the stopper in the tube, and set aside for a short time until some clear supernatant liquid separates; meanwhile, prepare the chromatography paper.

Overspot the extract from the tobacco five times on to Whatman No. 1 chromatography paper, and allow a short time for drying (at room temperature) after each spot has been applied. Each spot should contain approximately 5 μl of solution, and the outside spots should be at least 1½ inches from the edges of the paper.

A spot of dilute standard solution of glycerol and propylene glycol should be included every time a paper is prepared.

When the spots have dried, impregnate the paper with silver nitrate by rapidly dipping it in silver nitrate solution in acetone. Allow the acetone to evaporate at room temperature in subdued light, and run the chromatogram, with ascending or descending solvent according to preference, in a tank protected from daylight, overnight in water-saturated n-butanol. Satisfactory separations can also be obtained with a short 3 to 4 hour descending-solvent run. (See Note 2.)

After the chromatogram has been run, rapidly transfer the wet paper to a tank containing ammonia. Close the tank, keep the paper in it for 3 minutes, and then dry the paper in still air at room temperature, preferably in subdued light, for not more than 30 minutes; reverse its position after 10 to 15 minutes. Then heat the paper in an oven at 95° to 100° C for approximately 15 minutes, and wash with 200 ml of 10 per cent. ammonium hydroxide and then under running tap-water for 5 minutes.

A spot in the glycerol position from tobacco containing no added glycerol will be visible on the chromatograms. Calculated from the concentration of the tobacco extract, *i.e.*, 1 g of tobacco in 13 ml of solution overspotted 5 times, the standard comparison spot of 0·1 per cent. glycerol spotted once corresponds to the maximum "natural" glycerol spot likely to be encountered. Any spot from the tobacco of less intensity than the standard should be ignored; a heavier spot is indicative of added glycerol, and quantitative column analysis should be carried out.

There should be no spot from tobacco in the propylene glycol position.

NOTES—

1. Glycols slowly evaporate from the paper in draughts and at elevated temperatures; the papers must therefore be dried at all stages at room temperature, and draughts in fume cupboards must be avoided.

2. The water saturated n-butanol running solution slowly becomes contaminated with silver. It should be renewed and the container cleaned out when it has been used for approximately four runs.

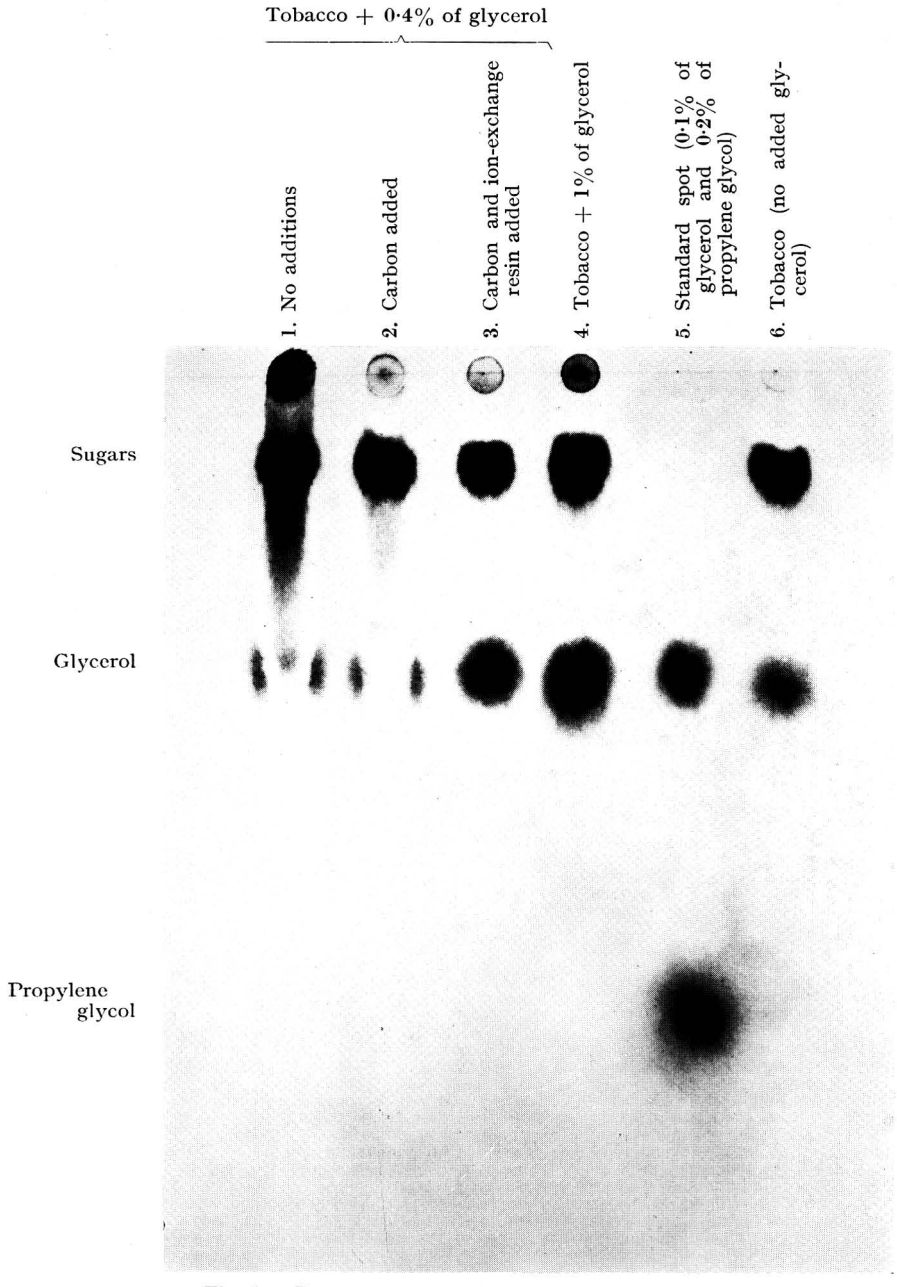

Fig. 1. Chromatograms of tobacco and standards on Whatman No. 1 paper, run in the machine direction, with ascending solvent for 17 hours at approximately 18° C

[To face p. 388

QUANTITATIVE DETERMINATION OF GLYCEROL BY CELLULOSE-COLUMN CHROMATOGRAPHY

Sporek and Williams[6] have described the determination of glycerol in its mixtures with sugars and the constituents of molasses, with alumina as adsorbent and acetone containing 5 per cent. of water and 0·05 per cent. of acetic acid as solvent. Sodium sulphite and sodium acetate are added to the sample solution to assist in the retention of sugars by the adsorbent. The solvent is later removed by evaporation from the eluate, and the glycerol is determined by oxidation with sodium metaperiodate and titration of the formic acid produced, thereby avoiding interference from other glycols present.

This method is most successful when the glycerol is present in materials less complex than tobacco. With tobacco we found that so much interfering material came through the column, even when it was modified by the addition of carbon, that the method was not considered suitable for our purpose. Moreover, traces of acetone are oxidised by periodate, and evaporation to ensure complete removal of acetone results in loss of propylene glycol.

Neish[7] separated glycerol from other materials present in fermentation solutions by elution with a mixture of benzene and n-butanol from a column of specially prepared Celite. The solvent was removed, and the formaldehyde formed from glycerol by oxidation with periodate was determined colorimetrically.

Our problem was somewhat different. We required a rapid accurate method for separating glycerol from appreciable amounts of sugars and from other tobacco materials, and a solvent for isolating glycerol that would allow oxidation with periodate to be carried out without the need for removing the solvent by evaporation. The special difficulties inherent in tobacco analysis were solved by using a two-layer column of cellulose powder and activated carbon. The preliminary extraction of glycerol was effected, without heating or evaporation, by stirring the sample first with a small volume of cold water and then with the solvent mixture. From experiments carried out with several solvents, we concluded that the most satisfactory and least obnoxious for our purpose was a mixture of two volumes of diethyl ether with one volume of ethanol.

In early experiments, excessive disturbance of the column was observed during elution. This disturbance was reduced as the width of the column was increased, but too wide a column gave insufficient separation of glycerol from sugars; the width recommended is the optimum for satisfactory separation. Occasionally, a column has shown some tendency to leave the sides of the tube, but no interference with the chromatographic separation was observed. The 5 g of carbon recommended is the amount we have found the most satisfactory for removing significant amounts of interfering materials from 1 g of tobacco and allowing solvent to run through the column at a suitable rate without the application of pressure or suction. The presence of the layer of carbon at the top also assists in maintaining the stability of the column.

Several variations of the method for determining glycerol by oxidation with periodate have been published since the oxidising action of periodates was first described by Malaprade.[8] Hartman's study of the procedure[9] contains a brief description of much of this work, and the accurate determination of glycerol by titration of the formic acid produced on oxidation with sodium metaperiodate is described in considerable detail by Erskine *et al.*[10] For our purpose we found that the simple procedure described below, based on total reduction of periodate, gives accurate results; removal of the solvent before oxidation is unnecessary provided sufficient water is added to the reaction mixture, and the addition of further water before the titration ensures that no preferential solution of iodine in the ether takes place. During the experimental work, we obtained duplicate titres agreeing to within 0·02 ml of 0·05 N sodium thiosulphate, although it is considered that titrating to the nearest 0·05 ml is sufficiently accurate for routine determinations.

SPECIAL APPARATUS—

Glass tubes for chromatography, 50 cm long and 2·5 cm internal diameter, widening out to approximately 4 cm diameter for the top 5 cm of length. A short length of 7-mm glass tubing is fused on to the bottom.

REAGENTS—

Ashless cellulose powder—Whatman standard grade.

Charcoal powder—For decolourising purposes, activated, washed with acid (obtainable from the British Drug Houses Ltd.).

Solvent mixture—Two parts by volume of diethyl ether mixed with 1 part by volume of 95 per cent. ethanol.

Potassium periodate solution—Dissolve 1·15 g of analytical-reagent grade potassium periodate in about 600 ml of distilled water containing 50 ml of 0·1 N sulphuric acid, warming if necessary, and dilute to 1 litre with distilled water.

Sodium thiosulphate, approximately 0·05 N.

Potassium iodide solution, approximately 10 *per cent. w/v., aqueous.*

Sulphuric acid, approximately 6 N.

Starch solution, approximately 1 *per cent., aqueous.*

PROCEDURE FOR SEPARATING THE GLYCEROL—

By pipette add 3 ml of distilled water to 1 g of the tobacco contained in a small beaker, and stir for 5 minutes with a small pointed glass rod; use a pressing action to ensure that the water penetrates into the tobacco. Add 10 ml of the solvent mixture, stir well, and set aside for about 20 minutes while preparing the column.

Place a small plug of absorbent cotton-wool inside the column, press well down, and moisten it with a little of the solvent mixture. Stir 30 g of the cellulose powder in a beaker with 200 ml of the solvent, and pour the mixture into the column as completely as possible in one operation. Any powder remaining in the beaker should be mixed with a small amount of solvent and added as rapidly as possible to the column before it has settled. When a layer of about 1 inch of solvent remains above the cellulose on the column, stir a mixture of 5 g of activated charcoal and 5 g of cellulose with 100 ml of solvent, and pour it into the column.

Allow the column to settle again, and in the meantime add 3·5 g of cellulose powder to the tobacco mixture in the beaker, and mix well. Occasionally, when dealing with fine cut tobacco, it may be necessary to add a little more cellulose in order to absorb all surplus liquid in the beaker. When a layer of about 2 inches of solvent mixture remains on the column, stopper the outlet with a short length of silicone rubber tubing closed by a short glass rod. Transfer the tobacco mixture quantitatively to the column, keeping sufficient solvent above the solid in the column to receive it, then unstopper the outlet, and place a 100-ml graduated flask underneath to receive the eluate. Allow the column to run until the head of liquid is reduced to about 2 mm above the tobacco, rinse the beaker with approximately 5 ml of the solvent, and transfer to the column; allow to drain down to a 2-mm head again, and repeat this procedure a further three times to ensure that all the material has entered the column. Reject the first 100 ml of eluate, and collect the glycerol into a further 500 ml of eluate in a graduated flask. At this stage it is permissible to keep a good "head" of solvent on the column, so that the flow is somewhat more rapid, and the 500 ml of eluate is collected in about 2 to 2½ hours.

PROCEDURE FOR OXIDISING THE GLYCEROL WITH PERIODATE—

By pipette transfer 50 ml of the eluate to a 500-ml conical flask having a ground-glass socket, add 100 ml of distilled water and then 25 ml of the potassium periodate solution from a pipette, mix, close the flask with a glass stopper, and set aside at room temperature in the dark for 40 minutes. Add 200 ml of distilled water, 10 ml of 20 per cent. potassium iodide solution and then 10 ml of 6 N sulphuric acid, mix, and titrate immediately with 0·05 N sodium thiosulphate from a 25-ml burette. Titrate as rapidly as possible, mixing well after each 1-ml addition of sodium thiosulphate solution. Add 1 ml of freshly prepared starch solution when about 1 ml from the end-point, stopper the flask, shake thoroughly, and complete the titration with frequent shaking until one drop discharges the colour. Carry out a blank titration at the same time on 50 ml of the solvent mixture. Duplicate titrations should agree to within 0·05 ml. If the titration difference between blank and sample exceeds 4·0 ml

of 0·05 N sodium thiosulphate under the conditions recommended, the oxidation should be repeated on a smaller portion of the eluate.

1 ml of N sodium thiosulphate ≡ 0·023 g of glycerol.

Added glycerol = total glycerol (per cent.) — x (see Table II)

where x is the blank value determined on unadulterated tobacco of similar origin.

Recovery of glycerol from the column

The volume of eluate collected adequately allows for the satisfactory recovery of glycerol unaccompanied by sugars over a temperature range of 15° to 30° C, *e.g.*, in the experiment illustrated by the histogram (Fig. 2), a mixture of 50 mg of glycerol with 100 mg each of sucrose, dextrose and laevulose was applied to the column, and the eluate was collected in fractions that were separately analysed for glycerol.

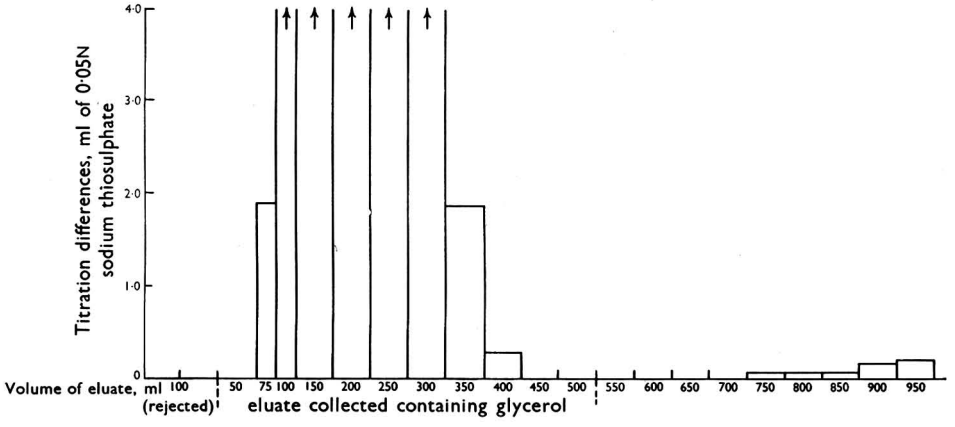

Fig. 2. Histogram for the recovery of glycerol from a mixture of glycerol, sucrose, dextrose and laevulose (column temperature 17° C)

Table I

Recovery of glycerol from tobacco

Experiment No.	Glycerol added	Glycerol content of the solution, %	Glycerol recovered from the column: Cellulose, %	Glycerol recovered from the column: Tobacco, %	Blank test on tobacco, %
1	1 ml of glycerol solution mixed with cellulose powder	3·0	3·0	—	—
2	1 ml of glycerol solution + 100 mg each of dextrose and laevulose mixed with cellulose powder ..	1·9	1·9	—	—
3	1 ml of glycerol solution + 200 mg of sucrose mixed with cellulose powder	3·9	3·9	—	—
4	1 ml of glycerol solution mixed with 1 g of tobacco	1·9	—	1·9	0·1
5		2·0	—	2·1	0·1
6		2·9	—	2·9	0·1
7		3·0	—	3·0	0·1
8		3·0	—	3·0	0·1
9		3·9	—	4·0	0·2
10		4·9	—	5·0	0·2
11	1 ml of glycerol solution dried into 1 g of tobacco	1·9	—	2·0	0·1
12		2·1	—	2·1	0·1
13	Blank solvent elution of column ..	—	No glycerol recovered		—

The results of various recovery experiments, including a blank experiment on the column, are shown in Table I. In each experiment glycerol was added to the sample as an accurately measured volume of an aqueous solution; at the same time an equal volume of the glycerol solution was diluted to 500 ml with solvent mixture, and the glycerol content of this control solution was determined by oxidation with periodate alongside the column eluate. Experiments 11 and 12 show the recovery of glycerol added to tobacco under conditions more severe then a manufacturer might be expected to employ: a measured volume of glycerol solution was mixed with 1 g of tobacco and heated in an oven at approximately 100° C for 1½ hours; the glycerol was then eluted from the column and determined alongside a control solution as in the other recovery experiments. In the recovery experiments from tobacco a determination of glycerol was carried out on the tobacco used without any added glycerol (see column 5).

Glycerol content of tobacco

The first samples of imported cigarettes containing glycerol examined by this method gave results unexpectedly higher than those obtained by the vacuum steam-distillation procedure. In one experiment a recovery of over three times as much was obtained, and it was considered advisable to establish that no appreciable interference might be encountered when dealing with a tobacco from a foreign source. Samples of imported unmanufactured tobacco leaf and cigarettes containing no added glycerol originating from several different sources were examined, and the results (see Table II) range from 0·4 per cent. of apparent glycerol down to a negligible amount, but are mostly about 0·2 per cent.

Comparative figures obtained by the qualitative paper-chromatographic procedure, in which the density of spots appearing in the glycerol position were compared with glycerol standards, are shown in column 4 of Table II. A typical spot, equivalent to 0·2 per cent. of glycerol, is shown in Fig. 1 (No. 6).

Table II

Results by column and paper chromatography for tobacco containing no added glycerol

Sample No.	Country of origin	Apparent glycerol content by— column procedure, %	Apparent glycerol content by— paper procedure, % (approx.)
Unmanufactured tobacco—			
1	U.S.A.	0·2	<0·1
2	U.S.A.	0·2	<0·1
3	U.S.A.	0·2	<0·1
4	U.S.A.	0·2	0·1
5	U.S.A.	0·2	0·1
6	U.S.A.	0·3	0·1
7	U.S.A.	0·2	0·1
8	U.S.A.	0·2	0·1
9	India	0·3	0·1
10	India	0·2	0·1
11	India	0·2	0·1
12	India	0·3	0·1
13	India	0·2	0·1
14	India	0·2	0·1
15	India	0·2	0·1
16	India	0·2	<0·1
17	Rhodesia	0·2	<0·1
18	Rhodesia	0·2	0·1
19	Rhodesia	0·1	0·1
20	Rhodesia	0·2	0·1
21	Rhodesia	0·2	0·1
22	Rhodesia	0·2	<0·1
23	Rhodesia	0·1	<0·1
24	Rhodesia	0·1	<0·1

Sample No.	Country of manufacture	Apparent glycerol content by— column procedure, %	Apparent glycerol content by— paper procedure, % (approx.)
Cigarettes—			
1	U.S.A.	0·2	0·1
2	U.S.A.	0·2	0·1
3	India	0·2	<0·1
4	United Kingdom	0·1	0·1
5	United Kingdom	0·2	0·1
6	United Kingdom	0·1	0·1
7	United Kingdom	0·2	<0·1
8	United Kingdom	0·1	<0·1
9	France	<0·1	<0·1
10	Cuba	0·1	<0·1
11	Cuba	0·1	<0·1
12	Italy	0·2	0·1
13	Turkey	0·4	
14	Russia	0·3	0·2
15	Greece	0·2	0·1
16	Egypt	0·4	0·2

It can be seen from Table II that there is usually a slight discrepancy between the results by the column and by the paper-chromatographic procedures, and, as diethylaminoethylcellulose has been successfully used for removing salts before paper chromatography, experiments were carried out in which various amounts of the ion-exchange resin were incorporated in the cellulose - carbon column. Some reduction of the figures shown (less than **0·1** per cent.) was obtained, but the inclusion of ion-exchange resin in the column is considered unnecessary, since the extremely small differences involved would not be detected within the limits of accuracy of titration considered to be the most suitable for routine work. Reductions of the same order were obtained when the initial aqueous extracting solution was rendered alkaline with sodium hydroxide.

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References

1. Chapman, A. C., *Analyst*, 1926, **51**, 382.
2. Thorpe's Dictionary of Applied Chemistry, Fourth Edition, 1954, Volume II, Tobacco Monograph, p. 650.
3. Smullin, C. F., Hartmann, L., and Stetzler, R. S., *J. Amer. Oil Chem. Soc.*, 1958, **35**, 179.
4. Buchanan, J. G., Dekker, C. A., and Long, A. G., *J. Chem. Soc.*, 1950, 3162.
5. Hough, L., *Nature*, 1950, **165**, 400.
6. Sporek, K., and Williams, A. F., *Analyst*, 1954, **79**, 63.
7. Neish, A. C., *Canad. J. Res., B.*, 1950, **28**, 535.
8. Malaprade, L., *Bull. Soc. Chim. France*, 1928, **43**, 683.
9. Hartman, L., *J. Appl. Chem.*, 1953, **3**, 308.
10. Erskine, J. W. B., Strouts, C. R. N., Walley, G., and Lazarus, W., *Analyst*, 1953, **78**, 630.

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The Determination of Free Sulphur Dioxide in Soft Drinks by a Desorption and Trapping Method

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Experiments have shown that, under specified conditions, the desorption of free sulphur dioxide in soft drinks is much faster than the dissociation of combined sulphur dioxide. This principle has been used in developing a method for determining free sulphur dioxide as an alternative to methods involving direct titration of the sample with iodine. The proposed method does not suffer from drifting end-points or high blank values, which are often encountered in direct titration methods. Free sulphur dioxide is desorbed at room temperature and at pH 1 to 2 by a rapid stream of oxygen-free nitrogen. For 50 p.p.m. or more of free sulphur dioxide, it is trapped in in alkaline glycerol and the determination completed iodimetrically. Lower concentrations are trapped in sodium tetrachloromercurate reagent, and the determination is completed colorimetrically. With slight modification the method has been applied to samples having high and low concentrations of sulphur dioxide, samples having high and low contents of solids and to coloured and colourless samples. When the proposed method was applied to various soft drinks the results agreed satisfactorily with those obtained by a direct titration method.

The classical method for determining free sulphur dioxide in fruit juices and soft drinks consists of direct titration of the sample with iodine, and then titration of a second portion with iodine in the presence of a carbonyl compound, the difference in titres being due to free sulphur dioxide. The chief disadvantages of this type of method are drifting end-points in one or both titrations, a relatively high second or blank titre compared with the titre difference (particularly if the ascorbic acid content of the sample is high) and difficulty in assessing the end-point with coloured samples. To overcome two of these disadvantages, Vas[1] showed that, at pH values of less than 2, the greater stability of glucose bisulphite leads to sharper end-points, and these can be further improved by an electrometric method described by Ingram,[2] which also permits determination in coloured samples.

Nevertheless, results from this type of method, which depends on the difference between the two iodine titrations, both of which are carried out in the presence of a large amount of reducing or potentially reducing organic material, are bound to depend to some extent on the personal judgment of the analyst. This could be avoided if it were possible to remove free sulphur dioxide from the sample in a similar way to the removal of total sulphur dioxide in the Monier-Williams method.[3]

Previous experience in desorbing dissolved oxygen from soft drinks had indicated that the desorption of sulphur dioxide from small volumes, though not as fast as that of oxygen, was still fairly rapid. Further, examination of the dissociation constants of glucose bisulphite showed that, at pH 1 to 2 and under conditions likely to be found in soft drinks, the extent of dissociation in 30 minutes would be extremely small; if this was also true for other sulphur dioxide complexes found in drinks, then it should be possible to complete the desorption of free sulphur dioxide before any effective dissociation of combined sulphur dioxide occurred.

Experimental

Preliminary experiments—

The first experiment was carried out in a pear-shaped polarographic cell described by Lloyd and Parkinson,[4] which can be used to follow the rate of desorption of certain dissolved gases. It was found that approximately 40 p.p.m. of free sulphur dioxide could be desorbed at room temperature from a dextrose solution in acetate buffer, acidified to a pH value of 1 to 2, by a rapid stream of oxygen-free nitrogen at room temperature in about 5 minutes. Subsequent dissociation of combined sulphur dioxide was found to be negligible, and blank titres were extremely small.

These results were so promising, even when the near-ideal desorption conditions in the pear-shaped cell were taken into account, that an apparatus of the type shown in Fig. 1 was made. With this apparatus, a similar experiment to that in the pear-shaped polarographic cell was carried out, but the desorbed sulphur dioxide was trapped and determined. The choice of trapping reagent and subsequent method of determination was made at this stage. The use of neutral hydrogen peroxide in the traps and then titration with standard sodium hydroxide solution did not give sufficiently sharp end-points, even when screened methyl orange was used as indicator. By trapping in alkaline glycerol, however, the subsequent determination could satisfactorily be made by Aulenback and Balmat's[5] polarographic method or alternatively by acidification and iodimetry. A colorimetric method, in which were used the reagents described by Beetch and Oetzel,[6] was found to be particularly suitable for small amounts of trapped sulphur dioxide. In our experiments, to avoid the use of a comparatively expensive polarograph, the iodimetric method was adopted for high concentrations and the colorimetric method for low concentrations of free sulphur dioxide.

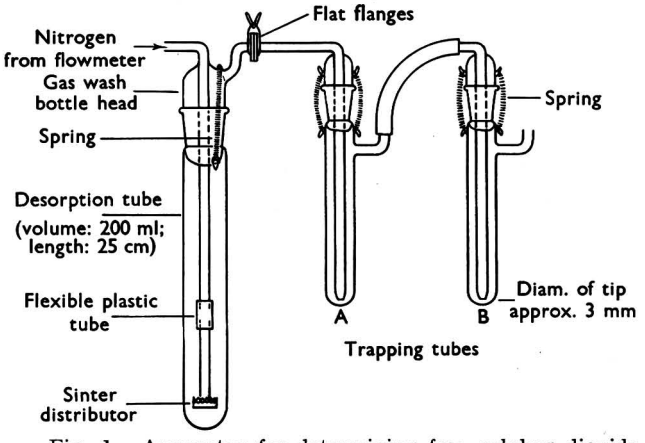

Fig. 1. Apparatus for determining free sulphur dioxide by a desorption and trapping method

Further preliminary experiments were carried out to study the application of the method to various sugar solutions and a sucrose - ascorbic acid solution, all of which had been sulphited and stored at pH 3 until equilibrium between free and combined sulphur dioxide was attained. Free sulphur dioxide was simultaneously determined by direct iodimetry of an acidified sample, formaldehyde being used as the binding agent in the blank determination as described by Ponting and Johnson[7]; for the sucrose - ascorbic acid mixture, this method gave poor end-points and Downer's method[8] was used. The results are shown in Table I.

TABLE I

COMPARISON OF RESULTS BY THE DESORPTION AND TRAPPING METHOD AND DIRECT IODIMETRY

Sugar solution	Total sulphur dioxide content, p.p.m.	Desorption and trapping method			Free sulphur dioxide found by direct iodimetry, p.p.m.
		Free sulphur dioxide found, p.p.m.	Desorption flow rate, ml per minute	Time required for desorption, minutes	
Dextrose, 10 per cent. w/v in acetate buffer	240	128	250	30	132
Liquid glucose, 10 per cent. w/v in acetate buffer	245	191	300	20	180
Fructose, 10 per cent. w/v in acetate buffer	258	254	300	20	245
Sucrose, 10 per cent. w/v in acetate buffer	251	258	300	20	245
Sucrose, 10 per cent. w/v in acetate buffer containing 100 mg of ascorbic acid per 100 ml ..	213	213	1500	15	224

During these experiments it was observed that a small amount of sulphur dioxide dissolved in droplets of moisture on the side of the desorption tube, but losses were avoided by washing back once during the desorption period. The size of desorption tube and the desorption flow-rate were also considerably increased at this stage. Recoveries of sulphur dioxide from standard solutions of sodium metabisulphite prepared in aqueous glycerol (to prevent oxidation) were carried out by the refined method. Results are shown in Tables II, III and IV.

TABLE II

PROPORTION OF TRAPPED SULPHUR DIOXIDE IN FIRST TRAPPING TUBE

Total sulphur dioxide trapped, mg ..	3·53	4·42	5·25	6·09	7·58	8·31
Percentage in first tube	100	100	100	99	99	99

TABLE III

RECOVERY OF SULPHUR DIOXIDE FROM STANDARD SOLUTIONS (IODIMETRIC METHOD)

Sulphur dioxide added, mg ..	0·47	0·94	1·40	1·88	2·81	3·75	4·69	5·63	7·50	8·44	9·38
Sulphur dioxide recovered, mg	0·49	0·93	1·38	1·88	2·77	3·73	4·72	5·61	7·41	8·47	9·28

Average recovery, 100 per cent. Range, 99 to 104 per cent.

TABLE IV

RECOVERY OF SULPHUR DIOXIDE FROM STANDARD SOLUTIONS (COLORIMETRIC METHOD)

Sulphur dioxide added, mg ..	0·31	0·62	0·94	1·25	1·56	1·87	2·18
Sulphur dioxide recovered, mg	0·32	0·61	1·02	1·20	1·56	1·86	2·13

Average recovery, 100 per cent. Range, 96 to 108 per cent.

In the colorimetric method only one tenth of the volume of liquid in the traps is normally taken for measurement, but for extremely low concentrations of sulphur dioxide a larger volume can be taken to make the method more sensitive.

METHOD

PREPARATION OF APPARATUS—

Set up the apparatus as shown in Fig. 1. More than one assembly may be used by one operator. The flow-rate required is approximately 1½ litres per minute of oxygen-free nitrogen for each assembly. This is conveniently controlled by use of a gas regulator with built-in flowmeter (British Oxygen Gases Ltd., Medical Division, Oxygen Regulator No. 330018).

Lightly grease the interchangeable joints of the apparatus. Into each of the two trapping tubes place 10 ml of 10 per cent. v/v glycerol in 0·1 N potassium hydroxide (alkaline glycerol reagent) if the iodimetric method is to be used or 10 ml of sodium tetrachloromercurate reagent[6] if the colorimetric method is to be used. The iodimetric method is preferred for 1 to 10 mg and the colorimetric method for smaller amounts up to 2 mg of trapped sulphur dioxide. Place 25 ml of water or 10 per cent. v/v glycerol in water (as specified for the type of sample to be examined) in the desorption tube. Pass a stream of air-free nitrogen through the assembly at 1½ litres per minute for approximately 5 minutes, and check that the joints are gas-tight.

PREPARATION OF SAMPLE—

Samples containing not more than 50 *per cent. of solids or* 400 *p.p.m. of sulphur dioxide*— Use distilled water in the desorption tube when preparing the apparatus. After passing nitrogen for 2 to 3 minutes, fairly quickly carry out the sequence of operations described below. Weigh 25 ± 0·02 g of sample into a second desorption tube. Add a few drops of water-soluble thymol blue and sufficient 5 N sulphuric acid to change the colour of the indicator from orange-yellow to red, and add 1 drop in excess. (If the colour of the sample interferes, determine the amount of 5 N sulphuric acid required on a separate equivalent portion with thymol blue as an external indicator or by using a pH meter, and then add the same amount of acid to the portion under test.) Turn off the flow of nitrogen. Replace the desorption tube containing water with the one containing the acidified sample, and ensure that the joint is gas-tight. If the samples show a marked tendency to froth, place a smear of Midland Silicones Ltd. anti-foam paste A on the side of the desorption tube.

Samples containing more than 50 *per cent. of solids or* 400 *p.p.m. of sulphur dioxide*—Use 10 per cent. glycerol in the desorption tube when preparing the apparatus and, after passing nitrogen for approximately 5 minutes, fairly quickly carry out the sequence of operations described below. Remove the desorption tube, but do not empty it. Weigh by difference a suitable portion of sample, and add it to the desorbed 10 per cent. glycerol in the desorption tube, ensuring that none of the sample adheres to the side of the tube. (For samples containing up to 400 p.p.m. of free sulphur dioxide, 25 g is a suitable amount of sample to use; decrease the amount of sample taken as the expected content of free sulphur dioxide increases.) Stir to dissolve, and acidify in exactly the same way as described in the previous paragraph. Replace the desorption tube containing the dilute acidified sample, and ensure that the joint is gas tight.

DESORPTION OF FREE SULPHUR DIOXIDE—

Turn on the supply of nitrogen, adjust the rate of flow to approximately $1\frac{1}{2}$ litres per minute, and desorb at room temperature for 10 minutes. Turn off the nitrogen, disconnect the assembly between the desorption tube and the first trapping tube, and wash down the outlet tube of the wash bottle head and the walls of the desorption tube with a jet of distilled water. Reconnect the apparatus, and desorb for a further 5 minutes. Turn off the nitrogen flow, and combine the contents of the trapping tubes, washing out the tubes with distilled water. Recharge the trapping tubes, desorb for a further 5 minutes, and combine the contents separately. (For most samples it will be possible to omit the second desorption period if the conditions during the first period are rigidly observed; the full procedure, however, must be carried out for the first few determinations in each product to ascertain if this is possible.)

MEASUREMENT OF SULPHUR DIOXIDE IN THE TRAPPED LIQUIDS—

Iodimetric method—To the combined alkaline glycerol solutions in a 150-ml conical flask add a few drops of thymol blue and sufficient 5 N sulphuric acid just to give a red colour. Titrate with 0·02 N iodine to the first permanent blue colour, with starch or starch substitute as indicator. Simultaneously carry out a reagent blank determination by acidifying and titrating 20 ml of alkaline glycerol in the same way.

$$\text{Free sulphur dioxide content, p.p.m. w/w} = \frac{32{,}000\ (t - b)\ \text{N}}{w}$$

where t and b are the titres (in millilitres) for the sample and blank solutions, respectively, N is the exact normality of the iodine solution and w is the weight of sample taken (in grams).

Colorimetric method—Combine the trapped sodium tetrachloromercurate solutions in a 50-ml calibrated flask, wash in quantitatively, dilute to the mark with distilled water, and mix. Complete the determination on a suitable portion (usually 5 ml) by using the colour developing procedure described by Beetch and Oetzel.[6]

RESULTS

The method was applied to some soft drinks and a concentrate. Results compared with those obtained by Downer's method of direct iodimetry (with electrometric titration when the colour of the sample interfered) are shown in Table V.

It is considered that there is satisfactory agreement between the results for free sulphur dioxide obtained by the two different methods. Difficulty was found in obtaining reliable results by direct iodimetry for the glucose beverage because of its low sulphur dioxide content and for the compounded blackcurrant juice because of its colour and complex nature. This probably accounts for the apparent disparity between the results for these samples.

In all the desorption and trapping determinations complete desorption occurred generally within 15 minutes and always within 20 minutes. No subsequent dissociation of free sulphur dioxide of any significance was observed. The method has since been applied to carbonated lemon drinks containing free sulphur dioxide in the range 3 to 40 p.p.m. and has given precise results after 15 minutes desorption; further desorption did not yield any more free sulphur dioxide.

TABLE V

COMPARISON OF RESULTS BY DIFFERENT METHODS

Sample	Total sulphur dioxide, p.p.m.	Free sulphur dioxide found by— desorption and trapping method, p.p.m.	Free sulphur dioxide found by— direct iodimetry, p.p.m.
Lemon squash	300	169, 161 (I)	167, 166
Orange squash	269	156, 156 (I)	152, 154
Lemon barley A	345	232, 240 (I)	232, 236
Lemon barley B	237	83, 83 (I)	62, 62
Lemon barley C	225	70, 73 (I)	66, 62
Blackcurrant cordial	311	178, 180 (I)	179, 177
Lemon juice	317	132, 135 (I)	132, 122
Liquid glucose beverage	30	11, 11 (C)	5
Lime juice cordial A	295	193, 191 (I)	196, 197
Lime juice cordial B	237	116, 116, 112 (I)	116, 114
Lime juice cordial B with added dehydroascorbic acid	225	48, 49 (I)	47, 43
Syrup of blackcurrant	301	99, 112 (I)	97, 120
Concentrated blackcurrant juice compound	1000 to 1200	160 (I)	203

I = Iodimetric method. C = Colorimetric method.

CONCLUSIONS

The work described has shown that, for a variety of soft drinks and raw materials, desorption and trapping provides a valid method of determining free sulphur dioxide.

The desorption and trapping method takes rather longer than do the iodimetric methods, but, by using two or more assemblies, one operator can complete at least four determinations in an hour. The apparatus required is relatively simple.

Advantages of the proposed method over direct iodimetric methods are: low or negligible blank values; elimination of drifting end-points and hence factors of personal judgement; application to samples of high and low solids content, high and low free sulphur dioxide content and to coloured and colourless samples.

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REFERENCES

1. Vas, K., *J. Soc. Chem. Ind.*, **1949**, **68**, 340.
2. Ingram, M., *Ibid.*, 1947, **66**, 50.
3. Monier-Williams, G. W., Ministry of Health Reports on Public Health and Medical Subjects, No. **43**, H.M. Stationery Office, 1927.
4. Lloyd, W. J. W., and Parkinson, T. L., "Food Science and Technology," Volume III, Gordon and Breach, New York, in the press.
5. Aulenback, D. B., and Balmat, J. L., *Anal. Chem.*, 1955, **27**, 562.
6. Beetch, E. B., and Oetzel, L. I., *J. Agric. Food Chem.*, 1957, **5**, 951.
7. Ponting, J. D., and Johnson, G., *Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 682.
8. Downer, A. W. E., *J. Soc. Chem. Ind.*, 1954, **62**, 124.

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The Flame Photometric Determination of Sodium, Potassium and Calcium in Nickel-Alumina Catalysts

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A method is described for determining sodium, potassium and calcium in the range 0·05 to 4 per cent. in the presence of a large excess of nickel and alumina. The nickel and alumina are removed, as oxinates, by solvent extraction; the sodium, potassium and calcium are then determined with an E.E.L. flame photometer.

THE determination of sodium, potassium and calcium in nickel - alumina catalysts is of interest as sodium and potassium may be added as promoters and sodium and calcium may be introduced into the catalyst during its manufacture, *e.g.*, during washing. The composition of the catalysts vary, but they may contain up to 50 per cent. of nickel and up to 75 per cent. of alumina. Sodium, potassium and calcium in low concentrations are usually determined by flame photometry, the method being rapid and accurate provided interfering elements are removed. Nickel and alumina are present in large excess in the catalysts being considered; Pinta and Bove,[1] Ettre and Ádám,[2] Schuhknecht and Schinkel[3] and others have shown that they interfere with the flame emission produced by sodium, potassium and calcium. They must therefore be removed if flame photometry is to be used to determine these elements.

It seemed feasible to remove nickel and aluminium as oxinates because they both form complexes soluble in chloroform. Calcium oxinate is insoluble in chloroform, and there is no evidence that sodium and potassium form oxinates. Extraction of an aqueous digest should therefore separate the elements in the manner required. It has been shown that the extraction of nickel is facilitated by adding tartrate,[4] but this has been found to affect the determination of calcium and potassium because of their precipitation as tartrates. Moeller[5] has shown that, if pH is controlled, nickel can be removed from the solution by successive extraction without the use of tartrate.

Experimental

Flame emissions produced by nickel and aluminium—

The flame emissions of nickel and aluminium were determined with an E.E.L. flame photometer (Evans Electroselenium Ltd.) on solutions prepared from analytical-reagent grade nickel nitrate and laboratory-reagent grade aluminium nitrate, the appropriate filters for sodium, potassium and calcium being used. The solutions contained nickel and aluminium in the same concentrations as would be present in typical acid digests of catalysts. Hydrochloric acid was added in an amount sufficient to give an acid concentration the same as that used to dissolve catalysts. The reagents tested were typical of those used in the

Table I

Flame emissions produced by synthetic catalyst solutions

Composition of catalyst in the solid state	Sodium		Potassium		Calcium	
	Flame photometer reading	Oxide concentration, p.p.m.	Flame photometer reading	Oxide concentration, p.p.m.	Flame photometer reading	Oxide concentration, p.p.m.
Nickel, 10 per cent. Alumina, 75 per cent.	6½	0·6	3	0·3	9½	9·2
Nickel, 25 per cent. Alumina, 50 per cent.	20	1·8	18½	1·8	49	25
Nickel, 50 per cent. Alumina, 25 per cent.	29½	2·7	53	5·2	>100	>50

preparation of catalysts. The flame photometer was set so that full-scale deflection (100 divisions on the galvanometer) was equivalent to 10 p.p.m. of sodium oxide, 10 p.p.m. of potassium oxide and 50 p.p.m. of calcium oxide. The galvanometer deflections and metal-oxide equivalents for three synthetic catalyst digests are shown in Table I.

The results show either that the reagents used already contain sodium, potassium and calcium, the latter in relatively high concentration, or that the nickel and aluminium have a natural flame emission at the wavelengths normally used for determining sodium, potassium and calcium. In the latter instance, the emission masks the traces of sodium, potassium and calcium, which must be assumed to be present, and makes it impossible to determine sodium, potassium and calcium by flame photometry. It has been shown that the emission was due to nickel and aluminium and not to relatively high concentrations of sodium, potassium and calcium by determining in a true blank solution the traces of sodium, potassium and calcium remaining after the nickel and aluminium had been extracted from portions of the same solutions.

Determination of true blank values—

The synthetic catalyst digests used for determining the flame emissions produced by nickel and aluminium were extracted by the technique described below. Ten-millilitre portions of the solutions were extracted with 25 ml of 5 per cent. w/v 8-hydroxyquinoline (oxine) solution in chloroform; it was observed that very little nickel was extracted. When ammonium hydroxide was added and the solution was shaken, the nickel readily passed into the organic phase as the dark-green nickel oxinate. Addition of more ammonium hydroxide caused aluminium oxinate to be formed as a yellow precipitate that could only be re-dissolved with difficulty when the sample was extracted with pure chlorofom. Alternate extraction with a 5 per cent. solution of oxine in chloroform and then with pure chloroform, together with a gradual increase in pH (by adding ammonium hydroxide, sp.gr. 0·88) to 8 to 9, gave a satisfactory extraction procedure. The metals were found to be completely removed, and the gradual change in pH minimised separation difficulties due to the production of a flocculent aluminium oxinate precipitate. The aqueous solution after extraction was no longer green, but had a brown tint, presumably due to a small amount of dissolved oxine. A final washing with ethyl acetate made the aqueous phase the lower layer, which facilitated a quantitative transfer from the separating funnel. The aqueous solution was boiled to remove all dissolved organic solvents, as these could cause enhanced results[6,7] in the subsequent flame photometry. The solution was made up to 50 ml in a calibrated flask, and used directly in the E.E.L. flame photometer, which was set so that a full-scale deflection was equivalent to 10 p.p.m. of sodium oxide, 10 p.p.m. of potassium oxide and 50 p.p.m. of calcium oxide. A blank determination was made on 25 ml of distilled water by taking it through the same extraction procedure. The results are shown in Table II.

Table II

Flame photometer readings for distilled water and synthetic catalyst solutions after extraction with oxine

A flame photometer reading of 100 is equivalent to 10 p.p.m. of sodium oxide 10 p.p.m. of potassium oxide and 50 p.p.m. of calcium oxide

Element	Distilled water	Digest from synthetic catalyst— A*	B†	C‡
Sodium	7, 9	15	16	15
	9, 8	15·5	15	15·5
	9, 9	15	15	15·5
Potassium	2, 2·5	3	2·5	3
	2, 2	3	3	3
	2·5, 2·5	2	2·5	2·5
Calcium	<0·5	<0·5	<0·5	<0·5

* Contains 10 per cent. of nickel and 75 per cent. of alumina.
† Contains 25 per cent. of nickel and 50 per cent. of alumina.
‡ Contains 50 per cent. of nickel and 25 per cent. of alumina.

The results in Table II show that the nickel - aluminium concentration has been reduced to a level that did not cause interference in the determination of sodium, potassium and calcium, and also that very little sodium, potassium and calcium are introduced by the reagents used in the extraction procedure. The concentrations of potassium and calcium in both the distilled water and the synthetic catalyst solutions are virtually identical, indicating complete removal of the interference due to nickel and aluminium. The slightly increased level of sodium in the synthetic catalyst solutions is well within the maximum permissible level of impurities in the reagents used for the preparation of the solution.

DETERMINATION OF RECOVERY LEVELS—

Five-millilitre portions of a solution containing 100 p.p.m. of potassium oxide and 100 p.p.m. of sodium oxide were transferred by pipette to 100-ml beakers together with 5 ml of a solution containing 500 p.p.m. of calcium oxide; 10 ml of 10 per cent. v/v hydrochloric acid were added, and the solutions were boiled for 10 minutes, which was the average time normally required for a sample of catalyst to dissolve. The solutions were set aside to cool, and then transferred to 100-ml separating funnels and taken through the extraction procedure described. Subsequently, the solutions were made up to 50 ml in calibrated flasks and used directly for determining potassium and calcium. Sodium was determined on a portion diluted with an equal volume of water. The results obtained were corrected for blank values, and the percentage recoveries were calculated. The results are shown in Table III.

TABLE III

RECOVERY VALUES FOR SODIUM, POTASSIUM AND CALCIUM

Sodium (5 p.p.m. present)			Potassium (10 p.p.m. present)			Calcium (50 p.p.m. present)		
Flame photometer reading	Sodium oxide equivalent to reading, p.p.m.	Average corrected for blank value, p.p.m.	Flame photometer reading	Potassium oxide equivalent to reading, p.p.m.	Average corrected for blank value, p.p.m.	Flame photometer reading	Calcium oxide equivalent to reading, p.p.m.	Average corrected for blank value, p.p.m.
60	5·34	5·10* (Recovery, 102%)	86	8·42	8·45 (Recovery, 84·5%)	98·5	49·2	49·2 (Recovery, 98·4%)
61	5·43		85	8·27		98·0	49·0	
61	5·43		86	8·42		98·5	49·3	
62	5·55		87	8·51		99·0	49·5	
60	5·34		86	8·42		98·0	49·0	
61	5·43		88	8·65		98·5	49·2	
			86	8·42				
			85	8·27				
			86	8·42				

* The solution was diluted (1 + 1), therefore the blank value was equivalent to 0·33 p.p.m. of sodium oxide.

The results show that the recovery for calcium and sodium is effectively quantitative, when the number of operations involved in the method is taken into consideration. The slightly high recoveries for sodium may be due to some sodium being extracted from the beakers during the digestion with boiling hydrochloric acid. The recovery for potassium was not quantitative, but the percentage was sufficiently constant to make acceptable the use of a correction factor in subsequent determinations. The loss of potassium may be caused by its slight solubility in organic solvents.

These preliminary trials show that nickel and aluminium can be removed from the digests of catalysts to give a solution in which the sodium, potassium and calcium can be directly determined with a flame photometer. A factor is however required in the determination of potassium.

METHOD

REAGENTS—

Ammonium hydroxide, sp.gr. 0·88—Analytical-reagent grade.

Hydrochloric acid, 10 *per cent. v/v*—Analytical-reagent grade.

8-*Hydroxyquinoline* (*oxine*) *solution,* 5 *per cent. w/v*—Dissolve analytical-reagent grade oxine in chloroform.

Chloroform.

Ethyl acetate.

Standard sodium - potassium stock solution—Dissolve 0·1886 g of analytical-reagent grade sodium chloride in distilled water. Dissolve 0·1583 g of analytical-reagent grade potassium chloride in distilled water. Combine the solutions, dilute to 1 litre, and store in a plastic bottle. The solution contains 100 p.p.m. of sodium oxide and 100 p.p.m. of potassium oxide.

Standard sodium - potassium working solution—Dilute the stock solution 1 + 9. Prepare freshly each week, and store in a plastic bottle. The solution contains 10 p.p.m. of sodium oxide and 10 p.p.m. of potassium oxide.

Standard calcium stock solution—Dissolve 1·785 g of analytical-reagent grade calcium carbonate in 100 ml of 4 per cent. hydrochloric acid, boil the solution to expel carbon dioxide, cool, and dilute to 1 litre. The solution contains 1000 p.p.m. of calcium oxide.

Standard calcium working solution—Dilute the stock solution 1 + 19. The solution contains 50 p.p.m. of calcium oxide.

PROCEDURE—

Weigh accurately about 0·25 g of catalyst in a 100-ml Pyrex-glass beaker, add 10 ml of 10 per cent. hydrochloric acid, cover the beaker with a watch glass, gently boil until a clear solution is obtained, cool, and quantitatively transfer the solution to a 100-ml separating funnel. Add 25 ml of oxine solution, shake, add 10 drops of ammonium hydroxide, sp.gr. 0·88, shake for approximately 3 minutes, allow the phases to separate, and run off and discard the lower (chloroform) phase. Add 5 drops of ammonium hydroxide, sp.gr. 0·88, and 25 ml of chloroform, shake for approximately 3 minutes, allow the phases to separate, and discard the lower phase. Add 25 ml of oxine solution, shake, add 5 drops of ammonium hydroxide, sp.gr. 0·88, shake, adjust the pH of the aqueous phase to 8 to 9 (2 to 3 drops of ammonium hydroxide are usually required), shake for 3 minutes, allow the phases to separate, and discard the lower phase. Wash the aqueous phase twice with 25-ml portions of chloroform, and discard the lower layers. Add 25 ml of ethyl acetate, shake for approximately 3 minutes, allow the phases to separate, and run off the lower phase into a 100-ml Pyrex-glass beaker. Wash the ethyl acetate layer twice with 5-ml portions of distilled water, adding the washings to the aqueous extract in the 100-ml beaker. Boil the extract until it is free from chloroform, cool, and make up to 50 ml in a calibrated flask. Carry out a blank determination by taking 10 ml of 10 per cent. hydrochloric acid through the proposed procedure. Determine the percentage recovery on 5 ml each of the stock standard sodium - potassium and calcium solutions with 10 ml of 10 per cent. hydrochloric acid by the proposed procedure. Dilute the samples (see Note 1), and dilute a portion of the "recovery" solution (1 + 1) with distilled water. Determine the sodium, potassium and calcium with a flame photometer; use the undiluted "recovery" solution for potassium and the diluted solution for the sodium and calcium. Correct the results for recovery of standards and reagent blank values.

NOTES—

1. The dilution factors, when 0·25 g of catalyst and a final volume of 50 ml were used, were—

0 to 0·2 per cent. of sodium or potassium oxide—no dilution.
0·2 to 2·0 per cent. of sodium or potassium oxide—dilute 1 + 9.
2·0 to 4·0 per cent. of sodium or potassium oxide—dilute 1 + 19.

No dilution is usually required for calcium.

2. For the E.E.L. flame photometer with standard E.E.L. filters, the full-scale deflection is set to be equivalent to 10 p.p.m. of sodium oxide, 10 p.p.m. of potassium oxide and 50 p.p.m. of calcium oxide. A graph plotted of galvanometer deflection against concentration of sodium and potassium was curved and that for calcium was a straight line.

RESULTS

Four catalysts (50 per cent. of nickel, 25 per cent. of alumina) have been analysed in quadruplicate for sodium, potassium and calcium; the results are shown in Table IV.

TABLE IV

QUADRUPLICATE ANALYSES OF 4 NICKEL - ALUMINA CATALYSTS

Results corrected for the recovery of standards and reagent blank values

Catalyst No.*	Sodium oxide found, %	Potassium oxide found, %	Calcium oxide found, %
I	All <0·01	1·34, 1·34, 1·38, 1·35	0·06, 0·08, 0·07, 0·07
II	0·08, 0·08, 0·08, 0·08	1·35, 1·33, 1·33, 1·33	0·15, 0·07, 0·13, 0·06
III	2·63, 2·60, 2·63, 2·67	4·56, —, 4·56, 4·54	0·17, 0·15, 0·14, 0·15
IV	0·05, 0·05, 0·05, 0·06	All <0·01	0·04, 0·01, 0·01, 0·01

* Catalyst No. I contained 1·0 per cent. of potassium oxide and a trace of sodium and calcium oxides.

Catalyst No. II contained 1·0 per cent. of potassium oxide, 0·1 per cent. of sodium oxide and a trace of calcium oxide.

Catalyst No. III contained 2·0 per cent. of potassium oxide, 0·1 per cent. of sodium oxide and a trace of calcium oxide.

Catalyst No. IV contained 0·1 per cent. of sodium oxide and a trace of potassium and calcium oxides.

The results were reproducible for a given catalyst and, with the exception of catalyst No. III, they agreed with the known approximate composition.

As a check on (1) the validity of the results for catalyst No. III and (2) the quantitative nature of the method, a known amount of sodium, potassium and calcium was added to known weights of samples of catalyst Nos. III and IV; these samples were then extracted and determined by the proposed procedure. On the assumption that the results in Table IV are correct, the average recoveries were 95 per cent. of sodium, 98·5 per cent. of potassium and 94 per cent. of calcium. This confirmed that quantitative results were being obtained and that the analysis of catalyst No. III was correct. The wide spread of the relatively small amount of calcium in the sample of catalyst No. II may be due to inhomogeneity of the sample.

I thank the Gas Council for permission to publish this paper.

REFERENCES

1. Pinta, M., and Bove, C., *Mikrochim. Acta*, **1956**, 1788.
2. Ettre, K., and Ádám, J., *Z. anal. Chem.*, 1957, **155**, 105.
3. Schuhknecht, W., and Schinkel, H., *Ibid.*, 1958, **162**, 266.
4. Gentry, C. H. R., and Sherrington, L. G., *Analyst*, 1950, **75**, 17.
5. Moeller, T., *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 270.
6. Exley, R., and Sproat, D., *J. Sci. Instrum.*, 1958, **35**, 202.
7. Schachtschabel, P., and Schwertmann, U., *Z. PflErnähr. Düng.*, 1958, **82**, 38.

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SHORT PAPERS

Determination of Fluoride by Complexometric Titration

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THE direct titration of fluoride ions in aqueous solution with solutions of metal salts, such as thorium nitrate, suffers from lack of stoicheiometry and from adsorption of the indicator on the gelatinous precipitate. Precipitation of fluoride with excess of such reagents as calcium chloride or cerous nitrate, with titration of the excess of metal ion in the filtrate, frequently gives rise to precipitates of an intractable gelatinous nature or of dubious composition.

Lead chlorofluoride can, however, be precipitated quantitatively from a suitable solution in a coarse crystalline form of definite composition over a wide range of conditions. Also, in conjunction with this, lead ions are easily and accurately titrated with ethylenediaminetetra-acetic acid (EDTA).

In the proposed method fluoride is precipitated, in the presence of chloride and ethanol, with standard 0·05 M lead nitrate, a reagent now available in bulk in many routine laboratories.

Laszlovsky first introduced the general principle mentioned above, but titrated the lead content of the precipitate. Titration of the excess of precipitant in the filtrate is usually a simpler and more rapid procedure and only becomes impracticable when a great excess of precipitant is needed.

Vřešťál and co-workers[1] precipitated fluoride with 150-ml portions of a saturated solution of lead chloride. This did not appear to be a particularly suitable standard reagent for routine use. Their titration of lead in the filtrate with EDTA, with xylenol orange as indicator, is similar to the proposed method.

Sakharova and Shishkina[2] precipitated lead chlorofluoride from dilute acetic acid with standard lead acetate solution; I regard the presence of acetate ions as detrimental to such a precipitation (see Table I). They continued by titrating lead ions in the filtrate with EDTA at pH 10 to 11 and used tartrate as secondary complexing agent and Solochrome black T as indicator.

METHOD

PROCEDURE—

Dissolve 5 to 45 mg of dry AnalaR or "Extra Pure" sodium fluoride in 20 ml of water, and add 8·0 ml of 0·2 M sodium chloride and 13 ml of 95 per cent. ethanol. Heat almost to boiling, and add from a burette 25·00 ml of standard 0·05 M lead nitrate, dropwise at first, then more rapidly as the precipitate becomes established. Swirl the solution constantly. Maintain the mixture just at the boiling-point for 1 minute to coagulate the precipitate, cool to room temperature, filter, and wash the residue with four 15-ml portions of 20 per cent. v/v ethanol in aqueous 0·02 M sodium chloride. Titrate the filtrate and washings with standard 0·05 M EDTA with xylenol orange as indicator and solid hexamine to bring the pH to approximately 6.

1 ml of 0·0500 M lead nitrate ≡ 2·10 mg of sodium fluoride.

RESULTS AND DISCUSSION

Sixteen concurrent determinations carried out on 30- to 45-mg samples of pure sodium fluoride gave a mean recovery of 100·0 per cent. with a standard deviation of 0·19 per cent.

In the absence of fluoride, lead chloride does not precipitate unless the alcohol content exceeds 43 per cent. v/v. This does not rule out possible co-precipitation, though the relation between recovery and volume of solution at the precipitation stage indicates that there is little cancelling of errors due to co-precipitation and precipitate solubility. Some results showing the variation in recovery of 42 mg of sodium fluoride with the volume at precipitation, the concentrations of ethanol and sodium chloride being maintained at the levels indicated under "Method," were—

Total volume, ml	100	200	250
Recovery, %	100·0	100·0	99·7

The choice of wash liquid is important as lead chlorofluoride is appreciably soluble in cold water. A 20 per cent. v/v solution of ethanol was reasonably effective, but addition of sodium chloride to 0·02 M introduced a common-ion effect that completely overcame this difficulty.

The concentration of ethanol present at the precipitation stage is not critical, but for the best results it should lie between 10 and 20 per cent., as indicated by the results shown below—

Concentration of ethanol, % ..	0	10·0	14·3	18·6	28·6	51·5
Recovery, %	98·7	99·6	100·0	100·0	100·6	101·6

The quality of the precipitate is inversely proportional to the concentration of ethanol. Ethanol may be replaced by acetone or methanol.

The ratio of chloride to fluoride (tested up to 4 to 1) is not critical once the 1 to 1 ratio has been exceeded. In the absence of chloride, lead fluoride precipitates to give 87 per cent. recovery based on lead fluoride. This recovery rises to 99·3 per cent. when the ratio of $[Cl^-]$ to $[F^-]$ reaches 1·1 to 1.

The excess of lead nitrate is not critical provided that the weight of chloride present is kept constant. If 25 ml of 0·05 M lead nitrate are taken for a final volume of approximately 70 ml, as in the method, then good recoveries can be obtained on sample weights of sodium fluoride from 4 to 46 mg.

For a total volume at precipitation of 70 ml, the temperature at filtration is not critical and may rise to as high as 50° C with negligible loss in recovery. However, at greater volumes this influence becomes more important, and temperatures should not exceed 25° C.

The pH of the fluoride solution before precipitation may be from at least 4·5 to 10·1, as indicated by the results shown below (pH was adjusted with dilute nitric acid or sodium hydroxide solution)—

pH	2·48	2·96	3·91	4·50	5·13	6·95	7·90	9·14	10·1	11·0
Recovery, %	80·4	86·4	95·8	99·5	99·6	99·7	99·8	100·0	100·0	101·1

At low pH precipitation is slow and incomplete, but large crystals are formed. Co-precipitation of basic lead salts does not cause interference until pH 11 is reached.

In the absence of alcohol and additional acid or alkali—

pH before precipitation = 6·5
pH after precipitation = 4·0
(pH of 0·05 M lead nitrate = 4·3)

Thus if no buffering component is present the pH of the mixture after precipitation appears to be fixed by the acid nature of the lead nitrate. If buffering ions are present in similar concentration to the lead nitrate, the results shown above for the variation in recovery with pH would no longer be valid.

The possible introduction of a buffer at pH 4 to 6 cannot be recommended, since this must contain a weak acid radicle that will complex to a greater or lesser extent with lead. This statement is amply borne out for acetate. Different volumes of an acetic acid - sodium acetate solution 0·50 M in acetate and of pH 5·0 were introduced into the method and the recoveries noted (see Table I); the concentration of chloride was kept constant.

TABLE I

INFLUENCE OF ACETATE

Volume of 0·5 M acetate added, ml	Ratio $\frac{[CH_3COO^-]}{[Pb^{2+}]}$	Recovery, %
2·0	0·8	98·7
5·0	2·0	96·9
10·0	4·0	93·0

The stability constant for the equilibrium—

$$Pb^{2+} + 2CH_3COO^- = Pb(CH_3COO)_2$$

has a value[3] of log K = 4·2, which would well explain this interference from acetate.

From the foregoing considerations it is evident that an unknown fluoride solution, which may contain buffering components, should be brought to a pH of 5 to 6 by addition of dilute nitric acid or sodium hydroxide only.

Interference in the method is caused by ions that precipitate or complex lead or fluoride; *e.g.*, sulphate and phosphate can be titrated almost quantitatively as fluoride.

The method was applied to solutions resulting from oxygen flask combustion of fluorinated organic compounds, but carbonate ions seriously interfered, and the time involved in removing them rendered the method no more rapid than some conventional colorimetric procedures.

REFERENCES

1. Vřešťál, J., Havíř, J., Brandštetr, J., and Kotrlý, S., *Chem. Listy*, 1957, **51**, 1677; *Anal. Abstr.*, 1958, **5**, 2199.
2. Sakharova, Ya. G., and Shishkina, N. I., *Zavod. Lab.*, 1959, **25**, 1442; *Anal. Abstr.*, 1960, **7**, 3239.
3. "Stability Constants of Metal-Ion Complexes, with Solubility Products of Inorganic Substances," Part I, Special Publication No. 6, The Chemical Society, London.

Received *October 24th*, 1962

Book Reviews

LES CYCLITOLS: CHIMIE, BIOCHIMIE, BIOLOGIE. By THÉODORE POSTERNAK. Pp. 491. Paris: Hermann. 1962. Price 48 NF.

This book is devoted to those isocyclic poly-alcohols in which the hydroxyl groups are directly attached to the cyclic carbon atoms. Such compounds include the cyclohexane hexols, pentols, tetrols and triols, their alkyl ethers and cyclohexanone analogues (cycloses) occurring in various forms in nature and in synthetic varieties.

The treatise is exhaustive and authoritative, the author having devoted the greater part of his career to the subject. There are some 1280 references, but from the point of view of the analyst and particularly the analytical biochemist, the interest lies almost entirely in some 18 pages dealing with the determination of meso-inositol and its naturally occurring phosphoric esters, the most generally known of this group of compounds. Details of six chemical methods are described, but since chemical methods lack specificity and entail laborious isolation and purification procedures, microbiological procedures are those most frequently used. Six such methods and three enzymatic methods are given in detail.

The book is well produced, and the spatial formulae necessitated in order to clarify the reactions where so many stereo-isomers exist are a feature. J. I. M. JONES

ROCK-FORMING MINERALS. VOLUME 2. CHAIN SILICATES. W. A. DEER, M.Sc., Ph.D., F.G.S., R. A. HOWIE, M.A., Ph.D., F.G.S., and J. ZUSSMAN, M.A., Ph.D., F.Inst.P. Pp. xii + 379. London: Longmans, Green and Co. Ltd. 1963. Price 95s.

Thirty-six important minerals of the pyroxene and amphibole groups, together with wollastonite, pectolite, rhodonite, bustamite and pyroxmangite, are dealt with in a manner similar to that for the minerals described in other volumes of this work (see *Analyst*, 1962, **87**, 607 and 914; 1963, **88**, 246). L. S. THEOBALD

QUANTITATIVE CHEMICAL ANALYSIS AND INORGANIC PREPARATIONS. By R. M. CAVEN, D.Sc., F.R.I.C. Second Edition. Revised by A. B. CRAWFORD, B.Sc., Ph.D., A.R.C.S.T., F.R.I.C., and W. A. ALEXANDER, B.Sc., F.R.I.C. Pp. viii + 428. London and Glasgow: Blackie & Son Ltd. 1962. Price 35s.

The first edition of this book appeared in 1923 and was reprinted 20 times—a tribute to its value as a text-book. This revised edition has been largely rewritten, and is praiseworthy for its attempt to give up-to-date explanations of many of the reactions used in analysis, and for its departure from the older style of presentation. One feels, however, that much duplication of material might have been avoided if the elementary parts had been omitted and the beginning student credited with enough intelligence and interest to be able to appreciate the fuller exposition given later in the text. The space so saved could have been used to enlarge on such topics as redox reaction mechanisms, which are left tantalisingly after a brief mention of their existence.

It is important for the future that analysis should be integrated with the rest of a teaching course. Analysis may be a tool for use by the other branches of chemistry, but it also is a branch in its own right and must make the utmost use of developments in physical, inorganic and organic chemistry.

An excellent feature of the book is its emphasis on the analysis of the compounds prepared by the student. This gives the student a determination of the purity of his product and a real sense of one of the main purposes of analysis—quality control. At the price, which is a modest one for text-books nowadays, the book is extremely good value.

R. A. CHALMERS

ANALYTICAL CHEMISTRY OF POLYMERS. Part II. ANALYSIS OF MOLECULAR STRUCTURE AND CHEMICAL GROUPS. Edited by GORDON M. KLINE. Pp. xvi + 619. New York and London: Interscience Publishers, a division of John Wiley & Sons. 1962. Price 132s.

ANALYTICAL CHEMISTRY OF POLYMERS. Part III. IDENTIFICATION PROCEDURES AND CHEMICAL ANALYSIS. Edited by GORDON M. KLINE. Pp. xii + 566. New York and London: Interscience Publishers, a division of John Wiley & Sons. 1962. Price 124s.

The ever-growing industrial importance of polymeric materials has stimulated intensive studies of their structure and their chemical and physical properties, and in consequence most of the analytical techniques of chemistry and physics, the term "analytical" being used in its widest sense, have been employed in this field.

These two books complete Volume 12 of a series of monographs on the chemistry, physics and technology of high polymers (Part 1 deals with the analysis of monomers and polymeric materials including plastics, resins, rubbers and fibres and was published in 1959).

Part 2 describes the analysis of molecular structure and chemical groups and contains 12 chapters, each of which deals with a particular analytical technique, *i.e.*, molecular weight and size (including discussions of fractionation, viscosity, light scattering, osmometry and ultracentrifugation), X-ray diffraction, optical methods (including refractive index, birefringence, dichroism, optical rotation and light transmission), differential thermal analysis, pyrolysis, mass spectrometry, ultraviolet and infrared spectrophotometry, fluorescence, chromatography, polarography and magnetic resonance spectroscopy (which includes NMR and ESR). In each chapter the basic principles, instrumentation and methods of using a technique are discussed with examples of typical applications to polymeric materials, and the whole text is supported with over 1600 references.

Part 3 deals with identification procedures and chemical analysis. The first chapter (100 pages) deals with systematic procedures for the qualitative analysis of a basic polymer present in a plastic formulation after removal of the other constituents, involving its burning characteristics, products of pyrolysis and various simple chemical and physical properties. The second chapter (119 pages) contains a comprehensive account of the simple chemical colour tests that can be used for the identification of polymers or their constituents. The remaining chapters deal with microscopy (89 pages), applications of radiochemical analysis (47 pages) and the determination of end-groups (15 pages). These chapters are supported by just under 1000 references, and in a separate section a further 145 references are given "to books and reviews of general interest and to articles which have been published recently." The latter are given in alphabetical order of authors and are not referred to in the index, so that one has to work hard to make use of them. The fact that around 100 of these references are dated 1959 to 1961 confirms one's impression that both volumes were probably drafted several years ago and little account of the most recent literature has been taken in the published version. This is a pity, since much interesting work has been missed. The last 146 pages are taken up with cumulative author and subject indexes covering Parts 1 to 3.

Where it has been necessary to discuss the basic principles of an analytical technique in these volumes, this has been done well and could be of considerable interest to analysts in other fields. It is not easy to judge from the text, however, the relative practical importance of the various techniques in use to-day, and a critical discussion of this would be welcome in the next edition; for example, no stress is laid on the value of ultraviolet or infrared spectrophotometry and the growing importance of gas chromatography (especially in conjunction with pyrolysis) compared with chemical identification procedures and the use of fluorescence and polarography, the latter particularly being given full discussion somewhat out of proportion to its practical value. However,

despite this and the absence of reference to the most recent developments, the three parts of Volume 12 now available do comprise a most valuable survey of the literature up to about 1959, which will repay careful study and be of great practical value to newcomers to the field of polymer analysis.

A. G. JONES

SYMBOLS, UNITS AND NOMENCLATURE IN PHYSICS. Document U.I.P. 9. (S.U.N. 61–44.) Recommendations composed by the Commission for Symbols, International Union of Pure and Applied Physics. Pp. 23. Obtainable in bulk from the Secretariat, I.U.P.A.P., 3 Boulevard Pasteur, Paris 15, France, Price P.B. 50 (approx. $15.00) 100 copies.

This document, which replaces earlier reports from the Symbols, Units and Nomenclature Commission of I.U.P.A.P., has been published with financial support from the UNESCO.

The scope of the recommendations is defined by the following list of sections included in the present edition—

1. Physical quantities—General recommendations.
2. Units—General recommendations.
3. Numbers and figures.
4. Symbols for chemical elements, nuclides and particles.
5. Quantum states.
6. Nomenclature.
7. Recommended systems for physical quantities.
8. Recommended mathematical symbols.
9. International symbols for units.

Appendix. Systems of quantities and units in electricity and magnetism.

The explanatory text is in English, but the names of the physical quantities, units and mathematical symbols in the classified lists are given in English and in French.

The recommendations in the report are in general agreement with recommendations of the following international organisations: International Organisation for Standardisation; General Conference on Weights and Measures; International Union of Pure and Applied Chemistry; International Electrochemical Commission; International Commission on Illumination.

Publications Received

COMPOUND SEMICONDUCTORS. Volume 1. PREPARATION OF III-V COMPOUNDS. Edited by ROBERT K. WILLARDSON and HARVEY L. GOERING. Pp. xxii + 553. New York: Reinhold Publishing Co.; London: Chapman & Hall Ltd. 1962. Price $25.

SOME GENERAL PROBLEMS OF PAPER CHROMATOGRAPHY: RELATIONS BETWEEN PAPER CHROMATOGRAPHIC BEHAVIOUR AND CHEMICAL STRUCTURE: ATTEMPTS AT SYSTEMATIC ANALYSIS. Edited by I. M. HAIS and K. MACEK. Pp. 220. Prague: Publishing House of the Czechoslovak Academy of Sciences. 1962. Price Kčs 22.50.

A Symposium organised by the Chromatography Group of the Czechoslovak Chemical Society at Liblice on 23rd June, 1961.

BIBLIOGRAPHY OF PAPER CHROMATOGRAPHY 1957–1960 AND SURVEY OF APPLICATIONS. By KAREL MACEK, IVO M. HAIS, JIŘÍ GASPARIČ, JAN KOPECKÝ and VLASTIMIL RÁBEK. Pp. 706. Prague: Publishing House of the Czechoslovak Academy of Sciences. 1962. Price Kčs 87.

TECHNICAL WRITING. By RICHARD W. SMITH. Pp. x + 181. New York: Barnes & Noble Inc. 1963. Price $1.25 (paper); $3.50 (cloth).

PRACTICAL METHODS FOR THE MICROBIOLOGICAL ASSAY OF THE VITAMIN B-COMPLEX AND AMINO ACIDS. By E. C. BARTON-WRIGHT, D.Sc., F.R.I.C., M.I.Biol. Pp. 52. London: United Trade Press Ltd. 1963. Price 10s. 6d.

Reprinted from Laboratory Practice.

THE CASE AGAINST THE NUCLEAR ATOM. By DEWEY B. LARSON. Pp. x + 139. Oregon: North Pacific Publishers. 1963. Price $4.50.

Notice to Authors

THE Society publishes papers on all aspects of the theory and practice of analytical chemistry, fundamental and applied, inorganic and organic, including chemical, physical and biological methods. Such papers may describe original work or may present in review form a critical evaluation of the existing state of knowledge on a particular facet of analytical chemistry. Papers may be submitted for publication by members of the Society or by non-members.

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Descriptions of new methods should be supported by experimental results showing accuracy, precision and selectivity.

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Tables, diagrams, etc.—The number of tables should be kept to a minimum. Column headings should be brief. Tables consisting of only two columns may often be arranged horizontally. No lines should be ruled in tables in the manuscript. Tables must be supplied with titles and be so set out as to be understandable without reference to the text.

* Rules for nomenclature in "Handbook for Chemical Society Authors 1961" (price 21s. from The Chemical Society, Burlington House, London, W.1) are followed. The Shorter Oxford English Dictionary is followed for spelling, but some words are given that Dictionary's secondary alternative spelling.

Tables or graphs may be used, but not both for the same set of results, unless important additional information is given by so doing.

In general, graphs should have a reasonable number of co-ordinate lines, and not only the two main axes. The information given by a straight-line calibration graph can usually be conveyed adequately as an equation in the text.

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Three sets of illustrations should be provided, two sets of which may be photographic or dyeline copies of the originals, or pencil sketches, for transmission to the referee; there is no need to prepare Indian-ink duplicates.

Photographs—Photographs should only be submitted if they convey essential information that cannot be shown in any other way. They should be submitted as glossy prints made to give the maximum detail. Colour photographs can only be accepted when a black-and-white photograph fails to show some vital feature.

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Percentage concentrations of solutions should be stated as "per cent. w/w" (alternatively "g per 100 g"), as "per cent. w/v" (alternatively "g per 100 ml") or as "per cent. v/v." Concentrations of solutions of the common acids, however, are often conveniently given as dilutions of the concentrated acids, such as "diluted hydrochloric acid (1 + 4)," which signifies 1 volume of the concentrated acid mixed with 4 volumes of water. This avoids the ambiguity of 1 : 4, which might be equivalent to *either* 1 + 4 *or* 1 + 3.

References—References should be numbered serially in the text by means of superscript figures, *e.g.*, Mackenzie and Mitchell[1] or Furman,[2] and collected in numerical order under "REFERENCES" at the end of paper. They should be listed, with the authors' initials, in the following form—

1. Mackenzie, R. C., and Mitchell, B. D., *Analyst*, 1962, **87**, 420.
2. Furman, N. H., *Editor*, "Standard Methods of Chemical Analysis," Sixth Edition, D. Van Nostrand Co. Inc., New York and London, 1962, Volume 1, p. 863.

For books, the edition (if not the first), the publisher and the place and date of publication should be given, followed by the volume or page number, or both if required.

The entry of "personal communications" in the reference list is not justified; full acknowledgment of such unpublished sources should be made in the text or in the acknowledgments at the end of the paper.

Authors must, in their own interest, check their lists of references against the original papers; second-hand references are a frequent source of error. The number of references must be kept to a minimum.

REPORTS OF THE ANALYTICAL METHODS COMMITTEE OBTAINABLE FROM THE SECRETARY

The Reports of the Analytical Methods Committee listed below may be obtained direct from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1 (not through Trade Agents), at the price of 1s. 6d. to members of the Society, and 2s. 6d. to non-members. Remittances must accompany orders and be made payable to "Society for Analytical Chemistry."

Sub-Committee on Dirt in Milk. Report. Determination of Dirt in Milk.

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Application of Gas - Liquid Chromatography to Essential-oil Analysis: Interim Report on the Determination of Citronellol in Admixture with Geraniol.

Metallic Impurities in Foodstuffs Sub-Committee:

Report No. 4. Determination of Zinc.
Determination of Lead in Foodstuffs: Tentative Method.

Metallic Impurities in Organic Matter Sub-Committee:

Methods for the Destruction of Organic Matter.
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Sub-Committee on the Determination of Unsaponifiable Matter in Oils and Fats and of Unsaponified Fat in Soaps:

Report No. 1. Determination of Unsaponifiable Matter in Oils and Fats.
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Report No. 4. Determination of Free Alkali and Silica in Silicated Soaps.
Report No. 5. Determination of Rosin in Soaps.
Report No. 6. Determination of Phenols in Soaps.

Poisons Sub-Committee appointed to investigate Methods of Assay for Various Substances appearing in the Poisons Schedules of the Poisons Regulations, 1935:

Report No. 1. Assay of Lobelia (*Lobelia Inflata*)
Report No. 2. Assay of Gelsemium.
Report No. 3. Assay of Aconite.
Report No. 4. Assay of Yohimba.
Report No. 5. Assay of Jaborandi.
Report No. 6. Assay of Ephedra and of Ephedrine in Nasal Sprays.

Sub-Committee on Vitamin Estimations:

Report on the Microbiological Assay of Riboflavine and Nicotinic Acid.
The Determination of Carotene in Green-Leaf Material. Part 1. Fresh Grass.
The Determination of Carotene in Green-Leaf Material. Part 2. Green-Leaf Materials other than Grass. (Gratis.)
The Chemical Assay of Aneurine [Thiamine] in Foodstuffs.
The Microbiological Determination of Thiamine.
The Estimation of Vitamin B_{12}.

Vitamin-E Panel:

The Determination of Tocopherols in Oils, Foods and Feeding Stuffs.

Tragacanth Sub-Committee:

Report No. 1. Evaluation of Powdered Tragacanth.
Report No. 2. Evaluation of Flake Tragacanth.

Soapless Detergents Sub-Committee:

Examination of Detergent Preparations.

Meat Products Sub-Committee (formerly Meat Extract Sub-Committee):

Analysis of Meat Extract.
Determination of Gelatin in Meat Extract and Meat Stocks: Interim Report.
Nitrogen Factors for Pork *and* Nitrogen Content of Rusk Filler (as one reprint).

Pesticides Residues in Foodstuffs Sub-Committee:

Determination of Small Amounts of Total Organic Chlorine in Solvent Extracts of Vegetable Material.

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