See Notices on p. 150

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

THE Annual General Meeting of the Society was held at 3.15 p.m. on Friday, March 9th, 1945, at The Chemical Society's Rooms, Burlington House, London, W.1. The chair was taken by the President, Mr. S. Ernest Melling, F.R.I.C. The Financial Statement for 1944 was presented by the Hon. Treasurer and approved and the Auditors for 1945 were appointed. The Report of the Council for the year ending March, 1945, was presented by the Hon. Secretary and adopted. The following were elected Officers and Council for the coming year:

President—G. W. Monier-Williams, O.B.E., M.C., M.A., Ph.D., F.R.I.C.

Past Presidents serving on the Council—F. W. F. Arnaud, Bernard Dyer, John Evans, Edward Hinks, E. B. Hughes, G. Roche Lynch, S. Ernest Melling, W. H. Roberts.

Vice-Presidents—B. G. McLellan, J. R. Nicholls, E. Voelcker and, *ex officio*, H. M. Mason (Chairman, North of England Section) and J. B. McKean (Chairman, Scottish Section).

Hon. Treasurer—George Taylor.

Hon. Secretary—Lewis Eynon.

Other Members of Council—A. L. Bacharach, C. A. Bassett, H. Childs, R. C. Chirnside, A. A. D. Comrie, S. Dixon, W. F. Elvidge, J. H. Hamence, D. W. Kent-Jones, (Mrs.) J. W. Matthews, A. More, G. H. Walker and, *ex officio*, Arnold Lees (Hon. Secretary, North of England Section) and R. S. Watson (Hon. Secretary, Scottish Section).

Finally, the retiring President, Mr. S. Ernest Melling, delivered his Presidential Address, in the course of which he pointed out that this was the Seventieth Anniversary of the Society. The Address included some observations on Water and Water Supplies and will be published in a later issue of THE ANALYST.

NEW MEMBERS OF THE SOCIETY

Arthur Bennett, A.R.I.C.; William Herbert Bennett, M.Sc. (Lond.), F.R.I.C.; Philip Bilham, M.Sc. (Lond.), F.R.I.C.; Miss Dorothy Joan Simpson Bishop, B.Sc. (Lond.), A.R.I.C.; Colin Campbell, B.Sc. (Manc.), A.R.I.C.*; Frederick Jacob Elliott, M.Sc., Ph.D. (Dunelm.), F.R.I.C.†; Alan Ffoulkes Evans, B.Sc. (Manc.)*; Thomas Sydney Harrison, B.Sc. (Lond.), B.Met. (Sheff.), F.R.I.C.*; Alfred Arnold Maddy, B.Sc. (Lond.), A.R.I.C.; Miss Flora Hester Jean McLaren; Hector Murray McLean, A.H–W.C., A.R.I.C.; John Thomas Minster, B.Sc. (Lond.), F.R.I.C.*; Alan Percy Platt, B.Sc., Ph.D. (Liv.), A.R.I.C.; John Hammond Sibley, B.Sc. (Lond.), A.R.C.S., A.R.I.C.; Miss Dorothy Elsie Stillwell, B.Sc. (Lond.), A.R.I.C.; Maurice Bernard Thompson, A.R.S.M., B.Sc., Ph.D. (Lond.)*; John Townend, B.Sc. (Lond.), A.R.I.C.*; Roland C. Voss, B.Sc. (Lond.)*; Leonard George Lewis Wright.*

SCOTTISH SECTION

THE following office bearers for 1945 were elected at the Tenth Annual General Meeting of the Section held on January 17th:

Chairman: J. B. McKean. *Vice-Chairman:* H. Dryerre. *Committee:* A. Scott Dodd, J. Sword, M. J. Robb, A. Dargie, A. N. Harrow, A. M. Smith. *Hon. Secretary and Treasurer:* R. S. Watson. *Hon. Auditors:* A. R. Campbell, W. M. Cameron.

Analytical Methods Committee

DETERMINATION OF TOTAL SOLIDS IN FRESH LIQUID MILK

THE Society of Public Analysts and Other Analytical Chemists has been requested to give "specific instructions about the technique of the generally accepted method of determining total solids in milk known as the Society of Public Analysts' method." Although the method has, on several occasions, been described in general terms, no precise details of technique, such as are desirable in a standard process, have been given.

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* Through the North of England Section. † Through the Scottish Section.

The method was originally published by the Society in the Report of its Milk Committee in THE ANALYST in 1885[1] and was approved for use in 1886.[2] It was again described in the Report of the Departmental Committee appointed by the Board of Agriculture in 1900 to inquire into and report upon the desirability of Regulations for milk and cream.[3] On the results of analysis produced in evidence before that Committee, all determined by the Society of Public Analysts' methods, the Board of Agriculture made the Sale of Milk Regulations, 1901,[4] which specified presumptive standards of milk fat and of milk solids other than milk fat in "milk (not being milk sold as skimmed, separated or condensed milk)."

A Sub-Committee was appointed by the Standing Committee on Uniformity of Analytical Methods to investigate the methods of analysis of condensed milk when the Public Health (Condensed Milk) Regulations, 1923,[5] were made. Report No. 1 of the Sub-Committee[6] dealt with the determination of total solids in condensed milks, but, in view of the requirement in the Regulations to correlate condensed milk with the quantity of fresh milk to which it was equivalent, much work was done on fresh milk also. The Sub-Committee found that the technique, and directions about dishes, ovens and desiccators, given in that Report were equally necessary in the analysis of fresh milk, with the exception that the use of sand as a support was unnecessary if the milk after drying was in a uniform and sufficiently thin film. The method, adapted for fresh milk, is given below and ascertains the weight of the residue of milk solids when milk is dried (in equilibrium with air) at 98° to 100° C., taking precautions to avoid, as far as possible, either re-absorption of moisture during cooling and weighing, or weighing before the milk solids have cooled to room temperature.

METHOD—Weigh about 5 g of the thoroughly mixed sample of fresh milk (Note *a*) in a dry (*b*) round flat-bottomed metal dish (*c*), about 7 to 8 cm in diameter and 2 cm in depth, and provided with a readily removable but closely fitting lid, which is weighed with the dish. Place the dish, uncovered, on a rapidly boiling water-bath (*d*) for 30 minutes. Wipe the bottom of the dish and transfer the dish and lid to a well-ventilated oven at 98° to 100° C. (*e*), as recorded by a thermometer in the air immediately above the dish. After 3 hours in the oven (*f*), cover the dish before removal from the oven and transfer it to a desiccator with an effective desiccant, using a separate desiccator for each dish. Cool for 30 minutes (*f*) and weigh dish with lid. Return dish and lid to the oven and heat for one hour, with the dish uncovered. Remove to desiccator, cool and weigh as before. Repeat the re-heating, etc., if necessary, until the loss of weight between successive weighings does not exceed 0·5 mg.

NOTES—(*a*) The foregoing method applies to milk in a *fresh* condition, *i.e.*, milk which has not undergone appreciable change. When the acidity, phenolphthalein being used as indicator, exceeds 0·20% expressed as lactic acid, a slight loss of acid may occur on drying, and the quantity of strontium hydroxide solution necessary to neutralise the sample should be added before heating, a deduction being made for the added strontia (1 ml of $N/10$ $Sr(OH)_2$ ≡ 0·00428 g).

(*b*) The empty dishes and lids should be dried immediately before use by heating in the oven for not less than 30 minutes and cooling in the desiccator for 30 minutes.

(*c*) Dishes made of aluminium, platinum, nickel or stainless steel are suitable; blank determinations with water should be made to establish that the dishes are not altered in weight by the treatment.

(*d*) Dishes should not come in contact with the metal of the water-bath, and they should be in a horizontal position, so that the milk solids will form a thin uniform film.

(*e*) In electric ovens the temperature may be low near the bottom and front, and much over 100° C. near the walls, especially at back corners; also, by conduction of heat through the metal of the dish and shelf, the milk solids adhering to the dish may be overheated. Dishes should not be placed near the walls of the oven, and should be insulated from the shelf, *e.g.*, by a silica or glass triangle. The shelf used should be near the middle of the oven.

(*f*) The oven and desiccator should not be opened during the periods of heating and cooling respectively.

REFERENCES

1. ANALYST, 1885, **10**, 216.
2. *Id.*, 1886, **11**, 2 and 62.
3. Report of Departmental Committee on Milk and Cream, 1901. Cd. 484, par. 3741.
4. Statutory Rules and Orders, 1901, No. 657.
5. —— 1923, No. 509.
6. ANALYST, 1927, **52**, 402.

APPOINTMENT OF A STANDARD METHODS SUB-COMMITTEE

The Council has authorised the Analytical Methods Committee to proceed with a survey of current analytical methods, with particular reference to standard methods lacking or insufficiently described, to collate the information so obtained, and to report and act thereon. The Committee will take steps to make approach to other bodies in order to co-operate in devising approved methods, and later, possibly, to sponsor them.

To assist in the collection of information the Analytical Methods Committee has appointed a sub-committee, to be called the STANDARD METHODS SUB-COMMITTEE, consisting of Messrs. G. Taylor, F.R.I.C. (*Chairman*), N. L. Allport, F.R.I.C., R. C. Chirnside, F.R.I.C., D. C. Garratt, B.Sc., Ph.D., F.R.I.C., D. W. Kent-Jones, B.Sc., Ph.D., F.R.I.C. (*Hon. Secretary*), J. R. Nicholls, D.Sc., F.R.I.C., and K. A. Williams, B.Sc., F.R.I.C.

All correspondence on the Sub-Committee's business should be addressed to its Hon. Secretary, Dr. D. W. Kent-Jones, 88, Madeley Road, Ealing, London, W.5.

Annual Report of Council: March, 1945

THE roll of the Society numbers 1197, an increase of 117 over the membership a year ago.

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

G. W. Clough	S. Emsley	L. S. Fraser	E. J. Parry
F. A. Dawson	J. S. Ford	H. Hunter	E. V. Suckling
G. D. Elsdon	Sir J. J. Fox	S. G. Liversedge	T. Swinden

Elsdon, who died at the age of 56, had been a member of the Society for 34 years and served on the Council for two periods, 1919–20 and 1932–33. He was at one time Chief County Analyst for Lancashire and subsequently Chief Inspector to the Lancashire Rivers Board.

Emsley, who died in his 56th year, became a member of the Society in 1934. He graduated with honours in chemistry at Manchester in 1911. After filling a number of appointments, he became in 1922 Borough Analyst and Agricultural Analyst for Southampton and also, in 1930, Public Analyst for the Isle of Wight and Winchester. (Obituary, ANALYST, 1945, **70**, 37.)

Ford, who died at the age of 77, was elected a member of the Society in 1899. He studied at Edinburgh University and in 1889 was appointed chemist to Messrs. William Younger & Co., Brewers, Edinburgh. He contributed numerous papers on brewing and allied subjects to scientific journals and in 1940 was awarded the Horace Brown Medal by the Institute of Brewing.

Sir John Fox, who died in his 71st year, had been a member of the Society for 19 years. The whole of his professional life was spent in the Government Service and, since 1896, in the Department of the Government Chemist of which he became the Head in 1936. He was elected F.R.S. in 1943 and received the honour of Knighthood in 1944. (Obituary, ANALYST, 1945, **70**, 1.)

Fraser, who died in his 49th year, had been a member of the Society since 1927. He was trained at the Imperial College of Science and Technology obtaining the diplomas and B.Sc. degree. He served in the Royal Engineers during the war of 1914–18, and was subsequently employed by Messrs. J. & S. Fry & Sons, Bristol, and then by Messrs. Scribbans & Co., Smethwick.

Hunter, who died at the age of 47, had only recently become a member of the Society. He served in the Special Brigade, R.E. during the war of 1914–18. Shortly after that war he obtained the B.Sc. (Lond.) degree, and the D.Sc. degree in 1925. After some experience in teaching and research, he was, in 1928, appointed Head of the Rayon Department at the Shirley Institute.

Liversedge, who died in his 60th year, had been a member of the Society since 1940. He studied at the Yorkshire College, Leeds, was assistant successively to A. H. Allen and Sir Charles Cameron, and served in the war of 1914–18, first in the infantry and then in the Special Brigade, R.E. In 1920 he joined the staff of Howard & Sons, Ilford, where he remained until his death.

Parry, who died at the age of 72, had been a member of the Society since 1909. He obtained the B.Sc. (Lond.) degree with honours in chemistry in 1891 and was awarded the

D.Sc. degree in 1935. He also qualified as a barrister. He was in practice as a Consulting and Analytical Chemist for many years.

Suckling, who died in his 52nd year, began his professional career as assistant to Dr. J. C. Thresh. He served in the R.A.M.C. during the war of 1914–18 and, after qualifying in medicine, he entered into partnership with Messrs. Thresh & Beale, becoming sole Director of the firm in 1938. He was an eminent authority on Water Supplies, Sewage and Trade Effluents and was an Examiner in this Branch to the Royal Institute of Chemistry. (Obituary, ANALYST, 1945, 70, 37.)

Swinden, who died at the age of 58, had only recently become a member of the Society. His career was devoted almost entirely to the metallurgy of iron and steel, a field of work to which he contributed much original research and in which he was awarded numerous distinctions.

ORDINARY MEETINGS—Five meetings were held during the year and the following papers were communicated:

"The Determination of Residual Carbon Dioxide in Aerating Powders." By C. K. Boundy, A.R.I.C., and R. W. Morris, B.Sc., A.C.G.F.C., F.R.I.C.

"The Volumetric Determination of Tin in Brasses and Bronzes." By F. H. Edwards, B.Sc., and J. W. Gailer, B.Sc.

"The Determination of Lead as Molybdate." By H. Holness, M.Sc., A.R.I.C.

"The Detection and Determination of Auxins in Organic Manures. Part 2. Extraction of Auxins from Manures and Applications of the Perchloric Acid Test for Indolylacetic Acid and of the Went Pea Test. With a Short Introduction on Auxins." By J. H. Hamence, M.Sc., Ph.D., F.R.I.C.

"The Rapid Photometric Determination of Tellurium in Tellurium-Copper Alloys." By P. B. Crossley, F.R.I.C.

"The Micro-Determination of Carbon by Wet Combustion." By A. A. Houghton, B.Sc., Ph.D., D.I.C., F.R.I.C.

"Some Experiences of Micro-Biological Assays of Riboflavin." By D. W. Kent-Jones, B.Sc., Ph.D., F.R.I.C., and M. Meiklejohn.

"A New Method for the Estimation of Micro-quantities of Cyanide and Thiocyanate." By W. N. Aldridge.

"Some Examples of the Use of the X-Ray Powder Diffraction Method in Quantitative Analysis: The Determination of Small Amounts of (*a*) Calcium Oxide in Magnesium Oxide, (*b*) Zinc Oxide in Zinc Sulphide." By H. P. Rooksby, B.Sc., F.Inst.P.

The December Meeting was a Joint Meeting with the Food Group of the Society of Chemical Industry. The subject was "Methods of Sampling Foodstuffs for Analysis," and the following papers were read and discussed:

"Some Experiences in the Sampling of Foodstuffs in Bulk." By J. King, O.B.E., F.R.I.C.

"Sampling of Cooked Meals for Nutritional Analysis." By C. A. Mawson, Ph.D.

"Sampling for Metabolism Studies." By E. M. Widdowson, Ph.D.

GROUPS FOR SPECIAL SUBJECTS—The year has been made notable in the history of the Society by the formation of two Groups dealing with special subjects—The Microchemistry Group and The Physical Methods Group.

MICROCHEMISTRY GROUP—The Microchemistry Group (Chairman, Professor H. V. A. Briscoe), which now numbers 143 members, held its Inaugural Meeting on October 4th, when Dr. J. W. Matthews, Chairman of the late Microchemical Club, gave an Address entitled "The Development of Micro Methods in Analytical Chemistry."

At its second meeting, on January 23rd, the following papers were read and discussed:

"A Scheme for the Photometric Determination of Minute Amounts of Arsenic, Copper, Lead, Zinc, Iron and Certain Other Metals in Organic Compounds, *e.g.*, Medicinals." By N. Strafford, M.Sc., F.R.I.C., P. F. Wyatt, B.Sc., and F. C. Kershaw.

"Microchemistry and its Forensic Applications." By C. G. Daubney, M.Sc., F.R.I.C.

"Recent Advances in the Application of Micro-Analysis to Medical Chemistry." By Dr. E. J. King.

PHYSICAL METHODS GROUP—The Physical Methods Group (Chairman, Mr. R. C. Chirnside), which now numbers 115 members, held its Inaugural Meeting on February 7th, when Mr. R. C. Chirnside gave an address entitled: "Physics and the Analyst."

THE ANALYST—The restrictions of the Paper Controller have remained the same as last

year and THE ANALYST has therefore contained the same number of pages (388) as in 1943. In the autumn a permit was issued for the use of an additional 5 per cent. of paper to increase the circulation, not the size of the journal, but this concession is illusory, since the extra paper must be supplied from printer's stock which is now exhausted. By suitable adjustments of the weight of paper used, the printers will be able to increase the numbers published by at least 150 more than in December. The number of papers published in THE ANALYST was 40, as against 42 in 1943, and there were 39 notes as compared with 38 in the previous year. The subject matter was fairly distributed between Food and Drugs and Inorganic Chemistry (13 papers and 8 notes on each branch respectively). Other branches of analytical chemistry were also well covered. Owing to lack of space, the Publication Committee decided to restrict notes from the Reports of Public Analysts to items of exceptional interest. The summaries of the Statutory Rules and Orders of the Ministry of Food have been continued.

HON. TREASURER'S REPORT—The Hon. Treasurer reports that the financial state of the Society continues to be satisfactory, the increasing expenditure being offset by increase of income due to the considerable influx of new members.

ANALYTICAL METHODS COMMITTEE—The Committee has published one report during the year on "The Determination of Small Amounts of Fluorine in Foods." (ANALYST, 1944, **69**, 243.)

In response to a request from a Committee of the British Standards Institution for specific instructions regarding the technique of the generally accepted method of determining total solids in milk, a new sub-committee has been appointed to draw up a detailed method of procedure; there is also under consideration the question of a method for determining soya bean in sausages.

At the request of the Council, the Committee has considered a proposal that the Society should make itself responsible more generally for the publication of standard methods of analysis, and last autumn it conveyed to the Council its views that the possibilities of the proposal should be fully explored and recommended that a sub-committee should be appointed for this purpose. The Council accepted the Committee's report and a sub-committee has now been appointed.

Owing to war conditions, most of the sub-committees still remain inactive.

SEVENTIETH ANNIVERSARY OF THE SOCIETY—The seventieth anniversary of the Society was marked in the most appropriate manner by sending, on behalf of the Society and in the name of the President, hearty congratulations to Dr. Bernard Dyer (the sole surviving member, elected at the first General Meeting on February 5th, 1875), assuring him of its lasting gratitude and admiration for his eminent services and sustained devotion to its welfare during this long period and wishing him continued good health and an abiding content for many years to come.

NORTH OF ENGLAND SECTION—Three meetings have been held during the year and the following papers have been read:

"Barley Sugar." By H. M. Mason, M.Sc., F.R.I.C.

"The National Milk Testing Scheme." By C. A. Scarlett, B.Sc., A.K.C., F.R.I.C.

"The Analysis of Diethylamine." By H. N. Wilson, F.R.I.C., and A. E. Heron, A.R.I.C.

"A Note on the Determination of Ephedrine." By N. A. Hurt, A.M.C.T., F.R.I.C.

There have been good attendances at the meetings considering the increasing difficulties of travel.

The Section now numbers 187, an increase of 27 on the previous year.

The Hon. Secretary wishes to express his appreciation of the loyal support and assistance accorded to him by the Chairman and members of the Committee during the year.

SCOTTISH SECTION—Three meetings were held in the course of the year, at which the following papers were read and discussed:—

"The Defence (Sale of Food) Regulations, 1943."

"The Labelling and Advertising of Foods."

Discussion led by A. Scott Dodd, B.Sc., Ph.D., F.R.I.C.

"Notes on Whiskey." By M. J. Robb, F.R.I.C.

"The Significance of Chemical Tests on Cereals." By C. H. Herd, Ph.D., B.Sc., F.R.I.C.

"Notes on Oxygen Absorbed Tests." By W. N. Cameron, F.R.I.C.

The Committee records with regret the death of one of the members of the Section, Mr. J. S. Ford, F.R.I.C.

There has been an increase of seven in the membership of the Section during the year, the total membership now being sixty-three.

BRITISH STANDARDS INSTITUTION—Mr. K. A. Williams was appointed as representative of the Society on the Technical Tallows and Technical Greases Committee of the British Standards Institution.

BRITISH DISINFECTANT MANUFACTURERS' ASSOCIATION—Mr. A. Sciver was appointed as representative of the Society at a meeting of the Co-ordinating Committee of the British Disinfectant Manufacturers' Association.

The high standard of attendance at Council and Committee meetings has been maintained during the year and the Council again desires to express its thanks to organisations and to members of the Society for accommodation and hospitality to the Committees.

S. E. MELLING, *President*
LEWIS EYNON, *Hon. Secretary*

Inaugural Address to the Physical Methods Group of the Society of Public Analysts and Other Analytical Chemists

(*February* 7, 1945)

Physics and the Analyst

BY R. C. CHIRNSIDE*

I was struck by a remark made by Sir Jack Drummond in this room a month or two ago during the discussion following a paper on the use of micro-biological methods for the assay of vitamin B. He confessed to an innate distrust or suspicion of methods other than what might properly be called chemical methods of analysis, and he attributed this to his training as a chemist. It occurred to me at the time how unsuitable a choice I was for this inaugural address to the Group dealing with physical methods of analysis, for I have to admit to a similar latent prejudice. It goes further than that, for I was brought up in the school whose faith was firmly grounded in gravimetric analysis, and even volumetric methods were suspect for anything important. There were exceptions, of course, but that was the broad division. Not that we can afford to let go of classical gravimetric methods with the formation of this Group, particularly when we are up against samples, such as some of the special glasses used in lamp and valve manufacture shown in the table below in which all the ingredients of the students' nightmare appear, Group 3 (and Group 4 also) in the presence of phosphate, with a few more elements thrown in.

GLASSES USED IN LAMP AND VALVE MANUFACTURE

L. L.		H. D.	
SiO_2 ..	58·80%	SiO_2	50·80%
PbO ..	19·90	Al_2O_3 and Fe_2O_3	19·00
Al_2O_3 and Fe_2O_3	0·74	CaO	12·20
BaO ..	2·88	MgO	2·10
SrO	2·52	BaO	0·97
MgO ..	1·23	ZnO	7·80
B_2O_3.. ..	1·00	B_2O_3	6·30
Na_2O ..	5·86	P_2O_5	0·80
K_2O ..	7·19		
	100·12		99·97

But though I have to confess to a classical analytical bias, I have also to acknowledge my debt—I had almost said my conversion—to the physicist. Conversion would not have been correct, for I have not quite thrown over old gods for new but rather have extended and enriched my faith.

Now it has been extremely difficult to know just what aspect of analytical chemistry to talk about this afternoon. There is obviously not time to discuss any particular physical

* Research Laboratories of The General Electric Company, Limited, England.

method of analysis in detail, and it occurred to me therefore that I might more usefully enumerate briefly some of the more elaborate as well as some of the simpler methods and their applications and conclude by some reference to their possible social implications, social, that is, as they affect the chemical and analytical community.

The foundations of classical analytical chemistry were laid in the earlier half of the 19th century, and many of our methods and much of our apparatus date from that period. Although analysis has since made great and essential contributions to all branches of chemistry, there has been a long interval in which it has remained a neglected branch of the science. But there are welcome signs of a renewed interest in analytical chemistry, and in the analyst himself. This Society, whose main object as laid down in the Memorandum of Association is "to encourage, assist and extend the knowledge and study of analytical chemistry . . . ," in forming Groups to deal, first with Microchemistry, and to-day with Physical Methods of analysis has, Mr. President, in my view, given impetus to some sort of movement towards a renaissance in analytical chemistry. It may be that not the least service you have done this Society, and the larger chemical community, during your Presidency will have been the carrying through of these measures. Only lack of euphony, I imagine, has prevented this Society being known since 1905 by its proper name—The Society of Public Analysts and Other Analytical Chemists—but I am sure that the Other Analytical Chemists are conscious of their earlier debts to the Public Analysts—for the formation of this Society—for its Journal, THE ANALYST—and, not least, for providing the training schools for analysts. It will be for the members of this, or any other group that may be formed, to show that they can enrich the life of the Society; that while much may be added, nothing will be taken away from the unique atmosphere of its gatherings.

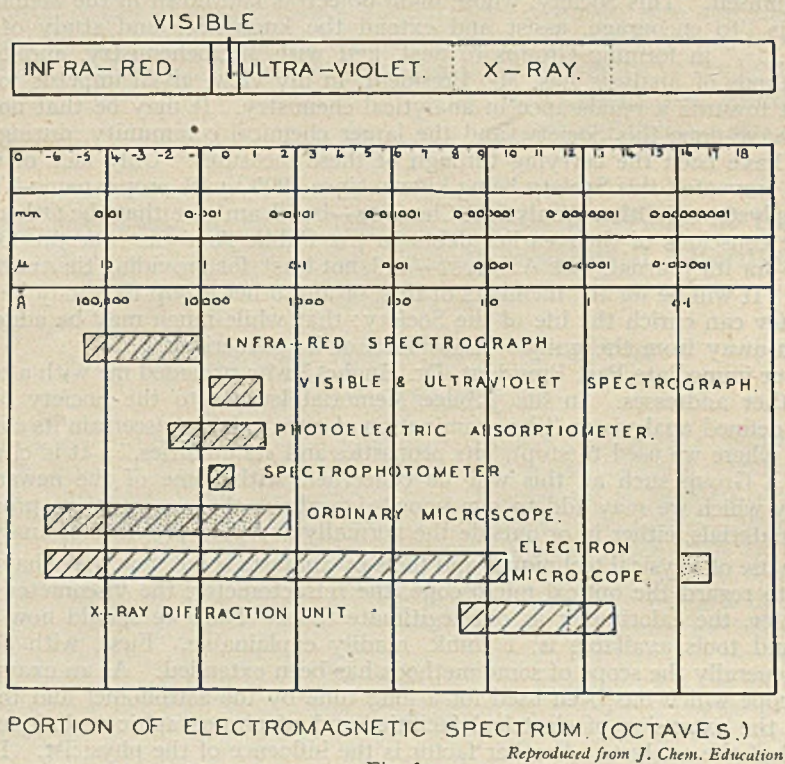
It was our immediate Past President, Dr. Hughes,[1] who provided me with a text for this and some other addresses. In his Jubilee Memorial lecture to the Society of Chemical Industry he defined analysis as "the examination of a material to ascertain its composition" (and that is where we used to stop), "its properties and its qualities." It is clear that the activities of a Group such as this will be concerned with some of the newer tools and techniques by which we may add to our knowledge about the composition, properties and qualities of materials, either in or outside the normally accepted province of analysis.

Now the use of physical techniques and tools by analysts is not new. We have long been accustomed to regard the optical microscope, the refractometer, the viscometer (so-called), the polarimeter, the calorimeter as our legitimate tools. That we should now have more techniques and tools available is, I think, readily explainable. First, with advances in technology generally the scope of some methods has been extended. As an example of this, the spectroscope which has been used for a long time by the astronomer and the physicist has through the extension of electrical facilities and of photographic technique become a valuable tool of the analyst. Another factor is the influence of the physicist. I have been fortunate enough to have physicists as colleagues, and I would formally acknowledge the debt I owe to them and would put on record the salutary influence chemists and physicists have on each other when they rub shoulders every day on the same problem. There is no doubt that the analytical chemist has benefited much from contact with this later comer to industry, the physicist. Physicists have an increasingly valuable contribution to make to all branches of industry, and the value of that contribution will be enhanced in proportion to the amount of co-operation that can be achieved between the two professions.

Physical instruments and techniques are available in increasing variety; the list of those available to the analyst who is fortunately enough placed is an impressive one. It must comprise the spectrograph, both for emission and absorption spectrophotometry, X-ray diffraction, electron diffraction, the electron microscope, the polarograph and amperometric titration, electrolytic and electrographic analysis, chromatography, thermo-analytical methods, the mass spectrometer, physical methods of gas analysis, electrometric methods generally, absorptiometric and fluorimetric methods and fluorescence analysis, molecular distillation, the use of vacuum-jacketed columns and of azeotropic methods, the use of the ultra-centrifuge. This is a formidable list, and I have no doubt that there are important omissions.

It will not do to object that these instruments are expensive, that only the best equipped laboratories will be able to afford them, or that they require full-time experienced men for their proper use. If only a few organisations are able to employ these new resources the outcome of their pioneer work cannot but influence knowledge and activity in other branches of science and, not least, in analytical chemistry.

Now in considering what methods are available for obtaining information about a substance which could not be obtained by ordinary chemical methods, or methods which will give information similar to that from chemical methods but with other advantages such as saving of time, it may be useful for a moment to think of the electromagnetic spectrum. A substance may be exposed to radiation and the response of its atoms or molecules may be recorded. Alternatively, the atoms and molecules may be made to emit radiation, and information can be obtained from the determination of the section of the electromagnetic spectrum in which that radiation falls. Fig. 1 shows the spectrum arranged at the top in octaves, like the piano keyboard, starting with the visible as the middle octave. The next



PORTION OF ELECTROMAGNETIC SPECTRUM. (OCTAVES.)

Reproduced from J. Chem. Education

Fig. 1

scale marked mm gives wavelengths and distances in millimetres, that marked μ in microns and below are Angstroms. The diagonally shaded regions show the maximum working range of the instruments mentioned; the dotted regions give the wavelength range of the radiation employed in the particular technique. With the electron microscope the equivalent wavelength of the electron beam used falls outside the theoretical range of distances explorable with the instrument (Fig. 1).

With this general picture we may consider how some of these instruments have been applied as analytical tools. First of all, the emission spectrograph; this has found extensive use, particularly in the metallurgical industry, for rapid control, an application in which it has displaced chemical methods. I might single out the work of Barker of the Admiralty Bragg Laboratory and D. M. Smith of the British Non-ferrous Metals Research Association for their work in the ferrous and non-ferrous worlds respectively. But the spectrograph has less specialised but equally useful applications where it gives information complementary to that of the chemical methods. I would summarise its use in the general inorganic field as follows: First—for rapid qualitative analysis of the whole of the metallic constituents of a substance, particularly as a basis for planning the quantitative analysis. In my view this is probably its greatest use to the analyst. Secondly—for approximate analyses by sight, *i.e.*, without quantitative measurement of the intensity of the spectral lines. Thirdly—for the examination of precipitates for freedom from contaminants. Fourthly—for the detection

of traces of metallic impurities or of unexpected elements. Fifthly—for the examination of substances of which only a small amount is available.

To elaborate for a moment the point about qualitative analysis—with certain types of material, *e.g.*, glasses or silicates, a qualitative analysis frequently takes as long as a quantitative examination. Indeed, it may not be possible to satisfy oneself that all the constituents of a substance have been discovered unless a quantitative summation is obtained. Moreover, in the absence of complete qualitative knowledge such as the spectrograph can give, the analysis may be incorrectly planned. This preliminary examination, although incomplete, will usually be more than merely qualitative, and the elements may be classified as (*a*) major constituents, (*b*) impurities of sufficient importance to figure in a chemical analysis, (*c*) traces of other materials. A unique advantage of the spectrograph is that it does not discriminate between that which is looked for and that which is wholly out of mind.

Turning from emission spectroscopy to absorption spectrophotometry we shall find that, quite apart from its use in the advancement of our knowledge of molecular structure, infra-red spectroscopy has made great progress as a straight analytical tool. The radiation absorbed (in this case of wavelength 1–25 μ) excites molecular vibrations and the characteristic molecular frequencies are determined by the masses of the atomic nuclei and the forces which hold them together. In principle, no two molecules other than a pair of optical isomers can have an exactly similar set of frequencies and, although compounds which are closely related may have several absorption bands at identical wavelengths, there will be some spectral regions in which differences may be found. The infra-red spectrum may well be one of the most characteristic physical properties of the molecule.

Infra-red absorption spectroscopy is being used increasingly in the field of industrial organic chemistry. One of its great merits is speed and, apart from the simpler applications of qualitative recognition of substances and classification according to structural type, quantitative analysis of multi-component mixtures of chemically similar substances can be made rapid and reliable. For automatic plant control sturdy spectrometers are now used on a by-pass in the production line of materials such as the components of synthetic rubber. A continuous record of the concentration of one component is made, with automatic control through suitable relays. An obvious application of this method is in following the rate of reactions such as polymerisation.

Analogous methods, using an ultra-violet spectrophotometer, have also been employed. As an example, some American workers have detected conjugated di-, tri- or tetra-ethenoid C_{18} acids by the position of the absorption bands and estimated them to within 5%.[2] It has been found, for example, that linseed oil blown with air at 105° C. has bands at 232 $m\mu$ and 270 $m\mu$, indicating the presence of both di- and tri- ethenoid acids, but that oil when heat-polymerised at 300° C. shows only the 232 $m\mu$ band. Methods have been outlined for the determination of linoleic and linolenic acids, and in a paper in the *J. Optical Soc. of America* for 1941[3] there are given quantitative absorption spectra data for a number of conjugated and non-conjugated fatty acids, esters and alcohols, and some indication is given of their application to the determination of these compounds in mixtures such as natural or dried fats.

Chromatography is too well established to require more than a passing reference and, in making it, I would instance its application also to the analysis of linseed oil. F. T. Walker has very fully resolved linseed oil on a suitable alumina and his work is described in the *J. Soc. Chem. Ind.* for 1942.[4]

Norman Strafford, who has been an enthusiast for the use of physical methods, has combined chromatography and ultra-violet absorption spectrophotometry in a method for the determination of small amounts of anthracene in tar and tar oil fractions.[5]

Those of you who have read that very entertaining biography of Harry Brearley, "*Knotted String*," will remember his remarks about the analyst in the steel industry. "He was esteemed," said Brearley, "beyond merit so long as it was confidently believed that his determinations measured the properties of steel that matter. He lived at one time amongst admirers able to believe that figures representing the chemical composition of steels could be transmuted by mathematical skill into a satisfying statement of mechanical properties." "This alluring belief," he added, "is not quite dead, but no amount of juggling with pierced cards and mechanical shufflers can restore it." I have quoted this because Brearley went on to show that the elements that were thought to matter in steel were in fact those that could be determined analytically—C, Mn, S, Si and P. Oxygen, hydrogen, nitrogen, gases in general, were ignored, for in any case they could not be determined. But the fashion has

changed, methods are now available, physical methods, for the determination of these elements and, whether or not for the reason Brearley suggested, they are now thought to be important. In the industry with which I am connected the metals used in vacuum devices have to be examined for gas content and the quantity of gas available for analysis may amount only to 0·001 ml. It is obvious that ordinary chemical procedure cannot be used. I do not wish to offend the susceptibilities of the Microchemistry Group on this occasion, but even their methods do not meet the situation, although several ingenious techniques have been employed to analyse as little as 0·1 ml. Generally speaking, these micro methods employ capillary burettes and solid absorbents in the form of beads. The analysis by physical methods of these very small samples is carried out at low pressure. A technique which my colleague Dr. Ransley[6] has used in studying the diffusion of gases in metals conveniently divides the sample into two fractions, which are analysed separately, (*a*) the condensable gases or vapours, such as carbon dioxide, sulphur dioxide and water (which are determined by means of differential evaporation or by the use of suitable freezing agents), and (*b*) the permanent gases hydrogen, oxygen, carbon monoxide, nitrogen, argon. The whole apparatus (shown in Fig. 2) can be evacuated to a pressure of less than 10^{-5} mm and can be isolated from the pump at the mercury cut-off B. At A there are two McLeod gauges; the fine one reads from 10^{-5} mm up to 0·1 mm, the coarse one up to 5 mm. The Pirani gauge at C reads up to 0·03 mm, and these readings serve as a cross check. D is a palladium thimble which can be heated so as to allow hydrogen to diffuse through it; E is a silver tube which at 700° C. will allow oxygen to pass. F is a platinum filament for burning the carbon monoxide and in the separate bulb I there is a tantalum strip filament which when heated absorbs nitrogen. Two freezing-out bulbs at G and H complete the system.

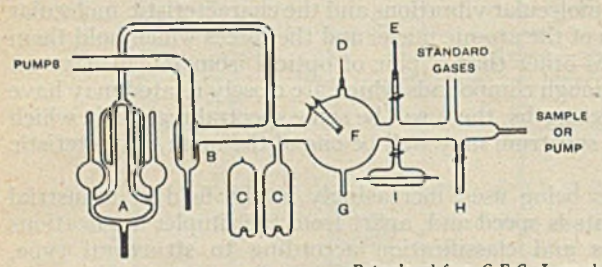


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Fig. 2

The experimental procedure for the analysis of a mixture presumed to contain hydrogen, oxygen, carbon monoxide and dioxide, nitrogen and argon is briefly this:

(1) After pumping out the system and degassing the various metal filaments, etc., the sample is admitted and freezing trichloroethylene (—86° C.) is placed round H. The water is frozen out in a few seconds, and a pressure reading is taken after this and each of the following operations. (2) Liquid air (—183° C.) on H and then the tap closed, thus isolating the condensable gases carbon dioxide, sulphur dioxide, etc. (3) Liquid air on G and platinum filament glowed for 2 minutes to remove free oxygen. (4) Palladium tube heated to diffuse out hydrogen. (5) Excess of oxygen admitted through silver tube E. (6) Platinum filament glowed for the combustion of carbon monoxide, methane, etc. (7) Residual oxygen removed by admitting excess hydrogen, burning on platinum and finally removing excess of hydrogen through palladium. (8) Tantalum filament heated to 1200° C. to remove nitrogen. (9) System pumped out and carbon dioxide condensed during combustion released by replacing liquid air with freezing T.C.E. and then measured. (10) System pumped out again and the condensable gas isolated in H at the second operation investigated by means of a vapour-pressure time curve.

A typical tabulated result on an actual determination is given below.

Methods of analysis	Vol. of sample taken	Composition, %				
		CO_2	O_2	H_2	CO	N_2
Macro-analysis. Hahn's modified Orsat apparatus	51·4 ml	5·6	nil	14·1	9·25	remainder
Low-pressure method	0·0159 ml	5·5	,,	13·5	10·9	,,
	0·0157 ,,	5·3	,,	14·6	9·5	,,

Similar techniques for the determination of carbon in metals have been employed.[7] Iron and iron alloys containing 0·005 to 0·01% of carbon are heated in an all-glass apparatus by high frequency current. The carbon dioxide from the combustion is condensed in a liquid nitrogen trap and finally determined by a pressure measurement.

The mass spectrometer has been described as a device for sorting molecules. Its use has been associated in most of our minds with the name of Aston and his classic work on isotopes, but it has lately been developed in the U.S.A. as an analytical tool. In Fig. 3 there is a diagram of one type, used for the analysis of hydrocarbon gases. The gas mixture to be analysed enters through the inlet to chamber *a*. The molecules are given an electric charge so that they can be moved by the combined action of electric and magnetic fields. The charge is imparted by bombarding the molecules with a stream of electrons in an ionisation chamber shown at *a*. The ions are pulled out of chamber *a* by means of the field existing between the electrodes *d*, *e*, *f*. The ions enter the analyser tube at high velocity and are sorted out according to their mass by means of the magnetic field. The heavier ions follow a circular path of greater radius than that of the lighter ions. The radius may be made larger or smaller by varying the field strength. Each ionic mass can therefore be made to fall on the collector *c*, where their quantity is measured by amplifying and recording equipment. The technique has been applied with some success to C_1 to C_6 paraffin mixtures. I might just quote two sentences from a recent American paper on the technique. "A large amount of work has been directed to the development of short-cut methods for analysing more complicated mixtures. The computing manual which explains these methods is over 100 pages in length." The unconscious humour of that sentence and a photograph of the apparatus[8] will perhaps convince you that the mass spectrometer is not yet everyone's tool.

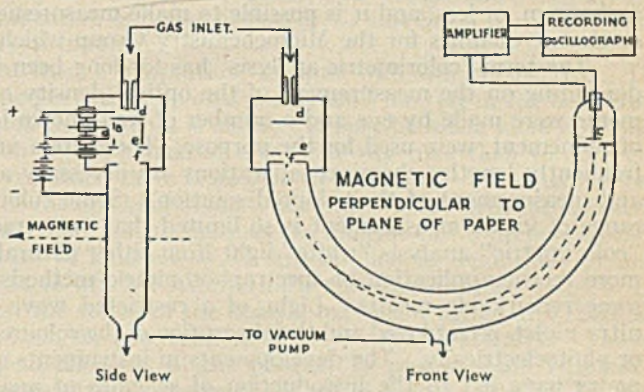

Fig. 3 *Reproduced from Ind. Eng. Chem.*

The powdered crystal method of X-ray analysis, in my experience, surpasses in general value any other physical method. I have described elsewhere how, in our own Laboratories, we make use of the combined power of spectrographic, X-ray and chemical methods of analysis. As my colleague Mr. Rooksby is to describe some specific applications of this technique later this afternoon I will say no more now (see next issue of THE ANALYST).

The study of surface films is becoming increasingly important, *e.g.*, in the working of photo-cells, thermionic valves, photographic emulsions, surface coatings, studies on wear and corrosion. There is no time this afternoon to do more than mention the techniques and tools of electron diffraction and electron microscopy. Suffice it to say that electron diffraction, by analysing the surface of a material, gives information complementary to that obtained from the examination of the main body of the material by X-ray diffraction methods, while the electron microscope, by means of which magnifications of 50,000 and more are readily available, opens new worlds. In bacteriology the implications are obvious, and in the inorganic sphere the size, shape and structure of colloidal particles such as dusts, fumes, pigments, emulsions can be examined.

In essence, the polarograph is a simple electrolytic cell. A solution of the sample is the electrolyte, the anode is a pool of mercury and the cathode is formed of fine droplets of mercury from a capillary jet. If a gradually increasing voltage is applied to the cell the current increases too, not regularly but in a series of steps, each step corresponding to a particular ion. The voltage at which the step occurs is characteristic of the ion, while the height of the step or the magnitude of the current is a measure of the concentration of the ion in solution. The effect depends on the ion being reducible at the cathode and substances which can be determined include most metals, some anions, *e.g.*, nitrate, nitrite and bromate, and many organic substances.

But the polarograph is not the analytical slot machine it may at first appear to be; though it is simple and elegant in conception, there are serious limitations to its operation. The reduction potentials of many substances are too close together for identification. Usually an interval of at least 0·2 volt is desirable and a preliminary chemical separation may therefore be necessary. Some workers are prepared to go to any length to use the polarograph. One

man separates molybdenum from a sample of steel by precipitation as MoS_2, roasts this to MoO_3 (and I daresay loses a good deal of it in the process), dissolves the MoO_3 in sulphuric acid and then, and only then, polarographs the solution. There are many chemists, and possibly more physicists, who have failed to realise that in applied analysis those operations which make the determination possible are often more important than those that attend the determination itself.

The polarograph may also usefully be employed in the determination of "trace" impurities in "pure" metals. The polarograph is capable of detecting very small concentrations, down to 1 p.p.m. or less, and it is possible to make measurements on as little as 0·1 ml of solution, so that it qualifies for the Microchemistry Group whichever way you look at it!

The term "colorimetric analysis" has for long been incorrectly applied to those methods depending on the measurement of the optical density of coloured solutions. The measurements were made by eye and a number of well-known instruments, differing in their degree of refinement, were used for the purpose. There are a number of limitations to this method; frequently lengthy chemical separations are necessary as a preliminary to the development and measurement of the coloured solution. Some colour reactions are so sensitive and the range of visual measurement is so limited that only trace elements can be determined. In "colorimetric" analysis "white" light from either natural or artificial sources is used, but the more recent application of spectrophotometric methods to chemical analysis has produced some remarkable results. Light of a restricted wave band, which may extend into the ultra-violet, is employed and the absorption of the coloured solution is measured either visually or photoelectrically. The developments in instruments using this technique of spectrophotometry have led to the introduction of schemes of analysis based on the measurement of absorption of coloured solutions and having an accuracy equal to, and sometimes exceeding, that of the best classical methods. Nowhere has this been more striking than in metallurgical analysis, largely owing to the pioneer work of E. J. Vaughan of the Admiralty Bragg Laboratory,[9] using a British instrument, the Hilger Spekker Photoelectric Absorptiometer. Barker[10] of the same Laboratory had already worked out schemes for the analysis of steels by quantitative spectrographic methods and had made a very great contribution in that field. But the necessity for obtaining samples of special shape and dimensions was a serious limitation to the spectrographic technique, and Vaughan's work provided an answer to the problem, so acute in war time, of how to deal rapidly with thousands and thousands of steel analyses.

These absorptiometric methods eliminate the time-consuming operations such as filtration, precipitation, drying, evaporation. Composite schemes of analysis have been worked out,[11] for example, for the determination of Mn, Cr, V, Cu, Co, Ni and Mo on one small sample of steel, while Si and Ti may be determined on two further small separate samples. Composite schemes have been worked out similarly for copper alloys, aluminium alloys and magnesium alloys. It should be realised that with these photoelectric methods the so-called colorimetric analysis is no longer confined to trace elements. Major constituents may be determined, say, chromium in steel or silicon in silicon-aluminium, copper in a copper alloy or aluminium in a magnesium alloy. This has worked something of a revolution in some laboratories engaged in routine analytical control, but it may not be quite so obvious that these methods have many applications in laboratories engaged on much more general and miscellaneous work. In my own laboratory we have used the Spekker instrument for such diverse analyses as the determination of iron in glass, tellurium in copper, molybdenum in tungsten, silicon in aluminium, to mention a few that come to mind. In every instance one of the greatest advantages is the extended range of the method. There are limitations of course; for example, it may not always be chemically permissible to dilute a too optically dense solution, but there is no doubt that this is a revolutionary technique. The accuracy of the method is said to be of the order of $\pm 1\%$ of the concentration of the element present.

Finally, what of the social implications of this application of physics to analytical methods? How does it affect the analyst himself? Shall we need a new type of analyst, with a different kind of training? There can be no simple answer to any of these questions, and if I am rash enough to put forward a few ideas that suggest themselves I hope I shall not prove to be too wide of the mark.

First of all, it is clear that it will no longer be possible for analysis, in the widest sense of the word, to be anything but a co-operative effort of a number of experts, each having some considerable knowledge of the work of the other members of the team. Sooner or later this

must affect the consultant, who is unlikely to have available some of the more expensive tools I have mentioned. The individual, in analysis as in other things, will have to be a many-more sided man than his predecessor. Besides his chemical knowledge he will need to have a knowledge of the various branches of physics—optics, electricity, etc.—together with all that other knowledge which the complete analyst must have of metallurgy, geology, bacteriology, engineering practice, to mention only a few side lines. You may feel that I have been making too great a demand on the new generation of analysts, but I must say there is hope, for the knowledge of electrical circuits, to say nothing of that of aircraft design and recognition, of the average student of to-day (to mention only one or two of *his* side lines) is, to one even so little older as I am, nothing short of inhuman.

But there is a danger here, or at least a temptation, to those who lack perspective. It will be fatally easy to lose sight of the purpose of an analysis in one's interest in the beautiful and complicated instruments by which the analysis is made. It may be much more exciting to watch the end-point of a titration on the screen of a cathode ray tube than to observe the colour change of an indicator, even when there is no gain in precision. We must not be led into the use of power hammers for the cracking of analytical nuts. But with the rational employment of these magnificent new tools and techniques the analyst can contemplate the broader possibilities and potentialities of analysis which are implied in definitions of his functions, such as that by Dr. Hughes to which I referred earlier in this address.

Another possible outcome is that the status of the analyst may grow again, and there is room for growth; for too long he has been the poor relation of the chemical fraternity. Those industries in which constant chemical checking of the product or processes are required, *e.g.*, the steel industry, have been responsible for the employment of a class of people known as routine-analysts, and, let me hasten to add, worthy people many of them are. They have produced accurate results in circumstances where no delay was possible and often under difficult working conditions. The amount of chemical knowledge demanded of them varies with circumstances, but I think the trend of events will be such that there will be a gradual decrease in their numbers and the amount of chemical knowledge required of them may be further reduced. Testing may cease to be called analysis and this term reserved for the more exacting part of chemical examination. The gradual shortening of the time allowable for much of this control analysis has stimulated the search for more rapid methods. Gravimetric methods have given way to volumetric methods, and these in their turn are now giving way to physical methods of one kind or another. While the methods will have to be worked out and the general control exercised by skilled chemists or physicists or both, many routine determinations will be carried out by people not so highly skilled or knowledgeable about classical wet methods of analysis as was the older type of control analyst. Much of this sort of work is already being done very well indeed by intelligent girls.

It can be said with some truth, that the use of physical methods is coming to the rescue of routine chemical analysis and will save it from being completely overwhelmed by the demands of our present industrial system. It may be that the chemist, if he is artful enough, will be able to bequeath to the physicist and the physical chemist the drudgery of the routine determinations of to-day and thus enable himself to get back to his own heritage and to make his contribution in the equally important fields of analysis and synthesis.

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Micro-Determination of Carbon by Wet Combustion

By A. A. HOUGHTON

(*Read at the Meeting, October* 3, 1944)

Introduction—The Liebig combustion method for the determination of carbon requires considerable skill and continual practice. This applies even more to the Pregl micro method. Dry combustion methods cannot be used directly on solutions, which must first be evaporated to dryness; this is not always practicable with biological fluids, which may contain volatile components. For these reasons chemists have long sought a wet combustion method. Names first associated with such a method are, according to Fresenius,[1] Rogers, Brunner Ullgrens and Classen. Sulphuric acid and chromic acid mixtures were used to oxidise carbon to the dioxide, which was swept over in a stream of air. Low results were sometimes obtained and variously attributed to formation of carbon monoxide, acetaldehyde and acetic acid. To overcome this difficulty, Messinger[2] introduced an auxiliary furnace. Grey,[3] working with aliphatic compounds, some in solution, showed that excess of oxidising agent prevented carbon monoxide formation but that acetic acid was difficult to oxidise. He devised a mixture which oxidised methyl groups to acetic acid and the remaining carbon to the dioxide. These were then independently determined. In the same year Ames and Gaither[4] described a mixture which oxidised all the carbon in soils to carbon dioxide. Schollenberger[5] improved on this mixture. Meanwhile, to catalyse the oxidation and reduce interference by halogens and sulphur, lead[6,7] and silver[8] chromates and a number of mercury salts[9] were being introduced. Other oxidising mixtures, *e.g.*, permanganate,[10] iodate[11,12] and persulphate[13] have also been recommended.

In 1927 Nicloux[14] devised a micro-method whereby the oxidation was carried out with silver chromate and sulphuric acid while caustic alkali absorbed carbon dioxide, all *in vacuo*. Boivin[15] in 1929 published his classical researches on the micro-determination of carbon, using Nicloux's apparatus, which he later improved by introducing an electrically heated platinum wire to oxidise carbon monoxide to dioxide. Using a eudiometer, he measured the formation of carbon monoxide as well as of dioxide. He re-checked all the published work and showed that raising the temperature and the use of silver chromate accelerate the oxidation of carbon. He also showed that silver chromate was not indispensable and that an even more efficient mixture could be formed by replacing part of the silver chromate by potassium dichromate. Unlike Messinger, Nicloux had not found a copper oxide furnace necessary. Boivin was able to explain this by showing that the not readily oxidisable substances with which Nicloux had tested his apparatus were not those that tend to produce carbon monoxide. He showed that, whilst acetic acid, carbazole, anthracite, charcoal, graphite, etc., are difficult to oxidise, the compounds which give rise to carbon monoxide are simple and complex cyanides and glucose, fructose, lactose and sucrose in the dry state. Using another monoxide producer, dixanthyl urea, Boivin showed that the use of a silver catalyst increased the proportion of monoxide formed, and this despite Florentin's statement that in some instances, in presence of copper sulphate or silver chromate, carbon monoxide formation was reduced and, with mercuric sulphate, was completely suppressed. Returning to carbohydrates, Boivin showed that in solution they give solely carbon dioxide by Nicloux's method, and proceeded to investigate the oxidation of the dry materials. By adding water to the sample, followed by anhydrous sodium sulphate to extend the surface area of the sugar, he obtained greatly improved results. Investigating the effect of acid concn. on various compounds, Boivin next showed that materials which dissolve slowly in hot oxidising mixture are no more readily oxidised if the sulphuric acid is anhydrous than if it is 50%. Some substances are sensitive to the presence of water, urea for instance. He also showed that

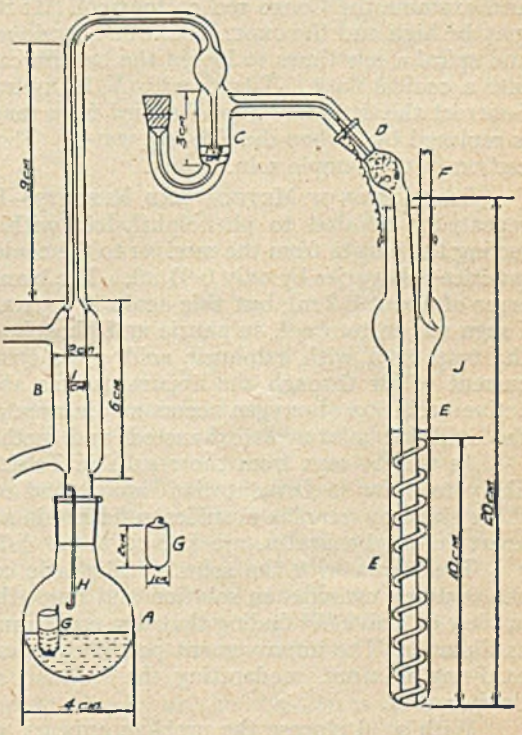
the concn. of chromic acid is of much less importance. Kuhn and L'Orsa[16] found that compounds containing the structure $-CH_2.C(CH_3)=CH-$ yield acetic acid on oxidation with chromic acid and sulphuric acid.

In 1929 Friedemann and Kendall[17] showed that low results were due to the oxidising mixture being too dilute and described a mixture containing phosphoric acid, which, on the macro scale, gave almost theoretical results with a large number of pure substances and solns. including acetic acid and the sugars. Lieb and Krainick,[18] apparently unaware of Friedemann and Kendall's work, re-introduced the auxiliary furnace in their micro apparatus and obtained accurate results on a large number of pure compounds. It is unfortunate that they record no results on sugars or the cyanides. Schadendorff and Zackerl[19] published in the same year details for handling pure liquids in Lieb and Krainick's apparatus.

In 1932 Kirk and Williams[20] improved on Boivin's apparatus, but, although they suggest their modifications as suitable for biological fluids, they quote only analyses of pure substances. Adams[21] in 1934, working on soils, brought forward an apparatus, and Pollard and Forsee[22] in 1935 modified it for the analysis of pure substances. In the same year Robertson and Shewan[23] re-introduced the auxiliary furnace in the analysis of pure substances. Since then, attention has been directed towards the determination of carbon and nitrogen[24] or carbon and hydrogen[25,26,27] in the same samples. Most recently Van Slyke and Folch[28] have devised a method giving accurate results with as little as 0·5 mg of the sample, including sugars. The oxidation is of the usual type and the carbon dioxide formed is measured in the usual Van Slyke manometric apparatus after rather elaborate precautions have been taken. This method, however, is only applicable to pure compounds or solns. of non-volatile compounds which can be evaporated to dryness.

I became interested in the general question of carbon determination by wet combustion when it was desired to determine carbon in mould and bacterial fermentation liquors. Birkenshaw and Raistrick's[29] modification of Messinger's method for this purpose was tried and was found to be somewhat unwieldy.

As there appeared to be no reliable micro method for use with dil. solutions, it was decided to devise one that would be relatively simple. When the analysis of solutions was proved satisfactory it was hoped to analyse dry materials of recorded difficulty. The tabulated details of published work were drawn up to assist in this task. The details are necessarily abbreviated and in some instances given approximately. The figures in the error column are the largest errors the authors appear to accept as satisfactory. An apparatus, constructed in Pyrex glass and shown in the scale drawing, is a slight modification of the micro-alkoxyl apparatus of Houghton and Wilson,[30] which was used satisfactorily for many preliminary experiments.



Apparatus—A is the reaction flask joined by a ground-glass stopper to the condenser B and with capillary tubing to trap C, which is conveniently constructed at right angles to the plane of the diagram and is only necessary if compounds or mixtures containing halogens are to be analysed. The receiver E is connected to the rest of the apparatus by the ground-joint D, both before and after which is a bend of 45°. Thus, by rotating the receiver about its joint, it can be inclined at any desired angle to retard the ascent of gas bubbles. The receiver E is made with ground centre tube and slit exactly as described by Houghton and Wilson,[30] only on a larger scale. It contains 10 ml to the top of the spiral, which conveniently has 8 turns in 10 cm. The top of the receiver is just wide enough for the insertion of a pipette

F, the tip of which is bent to facilitate drainage. The sample is weighed in a specially constructed boat G, which is *ca.* 2 cm high and 1 cm diam., so that it will pass easily through the neck of flask A. On one side, at the top, G has a hook for hanging it on the balance and for lowering it into A. The lowering may be done either by a hooked rod H permanently attached to B or by means of a hooked platinum wire. G is weighted at the bottom with a stout piece of platinum, so that when filled it floats upright in the reaction mixture in A.

REAGENTS—*Oxidising mixture*—Mix 600 ml of carbon-free conc. sulphuric acid with 400 ml of carbon-free 90% phosphoric acid and 100 ml of water. Dissolve 150 g of twice recrystallied potassium dichromate in the mixture by heating to 140° C. If chromic anhydride crystallises out on cooling, shake before use.

Congo red cottonwool—Introduce 25 g of cottonwool into a boiling soln. of 1 g of Congo red in 2 litres of water and heat for 30 min. Squeeze the cottonwool and wash a few times in water. Dry at 100° C. in presence of a very small dish of ammonia and tease out until fluffy.

Baryta soln.—Saturate water containing 0·5% of butyl alcohol with baryta (33 g per litre) and allow the carbonate to settle. Pour off the supernatant liquor and dilute with CO_2-free water to approx. *N*/10. The butyl alcohol is present to reduce the surface tension of the soln.

N/10 *Hydrochloric acid*—Standardise accurately. *Carbon-dioxide-free water*—Boil distilled water for 15 min. *Phenolphthalein soln.*—0·05% Phenolphthalein in 50% alcohol.

Hydrazine soln.—Adjust a conc. hydrazine hydrate soln. to *p*H 6 with conc. hydrochloric acid.

RECOMMENDED PROCEDURE—Put 10 ml of oxidising mixture into the flask. Weigh *ca.* 0·75–1·0 g of the sample soln. of suitable concn. in the weighing boat. Dry the centre tube of the receiver and pack just inside the joint with a little Congo red cottonwool followed by ordinary cottonwool. Assemble the apparatus and fill the receiver with the carefully pipetted baryta soln. Lower the weighing boat into the flask and replace the condenser. Shake the apparatus to sink the boat and mix its contents with the oxidising mixture. Heat with a small micro Bunsen flame so that oxygen is evolved steadily for about 30 min., and then increase the flame so that oxygen is again evolved for 5 or 10 min. Remove the receiver and examine the Congo red cottonwool. If it is altered in colour right through, the result may be high and the expt. should be abandoned. Otherwise raise and lower the centre tube and spiral a few times to loosen the barium carbonate and rinse the contents of the receiver into a conical flask. Titrate with *N*/10 hydrochloric acid, using phenolphthalein indicator. Subtract the titration figure obtained from that obtained in a blank expt. in which the sample is replaced by carbon-dioxide-free water. The difference (in ml) multiplied by 0·6 gives the carbon in the sample soln. in mg.

DISCUSSION OF METHOD AND RESULTS—Experiment showed that *N*/10 baryta can be repeatedly titrated to phenolphthalein with a variation of only about 0·01 ml. Transferring the baryta from the receiver to the conical flask introduces an error of 0·1 ml, and with practice this varies by only 0·01 ml. The blank in the oxidising mixture represents a further error of about 0·2 ml, but this again is constant within 0·02 ml. Before the introduction of Congo red cottonwool, sulphuric and phosphoric acid mist, which could not be removed by the trap even with sulphuric acid, gave errors sometimes as high as 1·0 ml. The usual current of air through the apparatus was abandoned as the result of experience. When active evolution of oxygen occurs no air stream is necessary. When oxygen evolution ceases, the oxidising mixture is exhausted, and further oxidation does not occur.

As will be seen from the results in Table I, the analyses of dilute solns. of substances likely to occur in fermentation liquors and other biological fluids were satisfactory. Also those given by complex cyanides, solid and in solution, are shown, and a few pure solids which, apart from phenacetin, are known to be difficult to analyse.

The errors with the solns. of aliphatic compounds are of tolerable magnitude. With the complex cyanides in solution and pure, the close approximation to theory is surprising in view of Boivin's[15] finding that dry potassium ferrocyanide gave only *ca.* 50% of its carbon as dioxide. The improvement possibly represents the advantage of phosphoric acid in the oxidising mixture, moderating the reaction so that oxidation is carried out at a higher temperature.

With solid glucose the problem appears to be difficult. Boivin records recovering 75% of glucose carbon as dioxide. Friedemann and Kendall obtained theoretical results which, using the former's oxidising conditions on a micro-scale, I have been unable to repeat.

Besides Van Slyke, who obtained theoretical results, other workers appear to have neglected the carbohydrates. It is suggested that carbohydrates are first dehydrated to carbon and that this is slowly oxidised to carbon dioxide. When the oxidising mixture is becoming exhausted carbon monoxide may be evolved. It also seems possible that unoxidised carbon may remain. The present work was carried out on glucose crystals *ca.* ½–1 mm in diam. Friedemann and Kendall may have used finely powdered samples, thus getting a larger area for oxidation. Van Slyke used a much more vigorous oxidising mixture.

TABLE I

RESULTS OF CARBON DETERMINATIONS ON VARIOUS SUBSTANCES

Substance	Carbon taken mg	Carbon found mg	Error %
N Sodium carbonate solution	3·85	3·87	+0·5
	4·62	4·61	−0·2
	3·21	3·19	−0·6
Glucose 1·5% solution	3·85	3·82	−0·8
	3·98	4·00	+0·5
	4·10	4·08	−0·5
	4·53	4·53	0
Ethyl alcohol 0·8% solution	3·69	3·65	−1·1
	3·79	3·77	−0·5
	3·77	3·76	−0·3
	3·24	3·23	−0·3
Acetic acid 1% solution	3·45	3·46	+0·3
	2·78	2·75	−1·1
	2·82	2·77	−1·8
	3·51	3·49	−0·6
Urea 3% solution	3·86	3·86	0
	3·44	3·50	+1·7
Oxalic acid 3% solution..	3·47	3·42	−1·4
	4·14	4·13	−0·2
Potassium ferrocyanide 3% solution ..	3·27	3·28	+0·3
	3·31	3·29	−0·6
	3·44	3·44	0
Potassium ferricyanide 2·5% solution..	3·64	3·62	−0·6
	3·83	3·83	0
Potassium ferrocyanide	3·95	3·98	+0·8
	3·62	3·61	−0·3
Phenacetin	3·20	3·21	+0·3
Glucose	1·92	1·75	−8·9
	3·55	3·33	−6·2
Tyrosine	4·08	3·84	−5·9
	3·93	3·79	−3·6

INTERFERENCE BY VOLATILE ACIDS—It was anticipated that, besides sulphuric and phosphoric acid mists which have already been dealt with, interference might occur from sulphide, sulphite, nitrite, nitrate and chloride, all of which might occur in biological fluids. Sufficient of a salt of each to be equivalent to about 7 ml of *N*/10 was introduced into the apparatus. Only chloride caused any interference, which was at once indicated by the Congo red cottonwool as well as by titration. A small proportion of chromyl-chloride is probably formed, but most of the chlorine appears as the element and as hydrochloric acid. The latter is removed by water in the trap, while the former is indicated by the Congo red changing to a brownish-purple. The hydrazine soln. described among the reagents effectively stops both chlorine and hydrochloric acid without interfering with carbon dioxide; it is placed in the trap C.

SUMMARY—The literature on carbon determination by wet combustion is reviewed and some essential details are tabulated.

An apparatus and method needing no special technique or micro-analytical experience are described for the determination of 3–5 mg of carbon as water-soluble compound in aqueous

soln. For the oxidation, a mixture of potassium dichromate, phosphoric and sulphuric acids and water is used. Acid mist is stopped with Congo red wool. No air stream is needed to carry over the carbon dioxide, which is determined by absorption in baryta and back titration. Results are quoted showing that the usual standard of accuracy for this type of analysis can be attained. Attempts to extend the method to all carbon compounds have not fully succeeded, but some advances have been made. Radicles likely to interfere in the determination have been investigated; only halogens give trouble. Halogens and halogen acids can be removed by a trap containing hydrazine solution.

I wish to acknowledge my indebtedness to Miss I. Wyllie for assistance in surveying the literature and in preparing the tabulated literature summary and also for her patience in carrying out the many repeat analyses needed to trace the sources of error. I also wish to thank Imperial Chemical Industries, in whose Explosives Group Research Laboratories this work was carried out, for permission to publish.

TABULATED DETAILS OF LITERATURE

Authors	Oxidising materials per 1/100 part of carbon	Furnace if used	Method of determining CO_2	Type of material analysed	Difficult material	Scale	Time (hrs.)	% Error
Messinger (1890)	0·6 CrO_3 9 H_2SO_4	Yes	Absorbed by soda lime and weighed	Pure substances	—	M	2½	1
Grey (1914)	6·8 H_3PO_4 3·6 $K_2Cr_2O_7$	No	Gasometric then acetic acid titrated	Dilute solutions	Succinic acid(2), Urea(2)	m	½	1
Ames and Gaither (1914)	10 H_2O 3·3 CrO_3 9 H_2SO_4	No	Absorbed by NaOH and titrated	Soils and soil extracts	Soils(2)	M	½	5
Schollenberger (1916)	1 H_2O 0·8 CrO_3 1·2 H_3PO_4	No	Absorbed by $Ba(OH)_2$ and titrated	Soils	Soils(2)	M	½	3
Florentin (1914)	5 H_2O 5 CrO_3 22·5 H_2SO_4	Yes	Absorbed by KOH and weighed	Pure substances	—	m	¾	0·5
Nicloux (1927)	9 H_2SO_4 0·15 Ag_2CrO_4	No	Absorbed by $KOH.BaCO_3$, ppt. dissolved in HCl and CO_2 weighed in KOH	Solutions	Quinoline sulphonic acid(1)	m	½–¾	2
Lescoeur[31] and Turobinski (1928)	189 H_2SO_4 8·0 $K_2Cr_2O_7$ 2·0 Ag_2CrO_4	No	Absorbed by $Ba(OH)_2$ and titrated	Solutions	—	m	½	0·8
Friedemann and Kendall (1929)	0·8 H_2O 0·7 CrO_3 10·2 H_3PO_4 9·0 H_2SO_4 + 2 ml per ml H_2O	No	Absorbed by NaOH. Titrated in presence of $BaCl_2$	Pure substances and solutions	Acetic acid(1) Stearic acid(1)	M	½–1	1
Boivin (1929)	30 H_2SO_4 0·8 $K_2Cr_2O_7$ 0·2 Ag_2CrO_4	E.F.	Absorbed by NaOH. $BaCO_3$ pptd. dissolved and titrated	Solids and solutions	Acetic acid(1) Aromatics(1) Cyanides(2) Dry Sugars(2)	m	1/12 12	2
Lieb and Krainick (1931)	62 H_2SO_4 2·0 $K_2Cr_2O_7$ 4·0 Ag_2CrO_4	Yes	Absorbed by $Ba(OH)_2$ and weighed as $BaCO_3$	Pure substances	—	m	1	0·5
Kirk and Williams (1932)	54·0 H_2SO_4 6 Ag_2CrO_4 1·0 Na_2SO_4	E.F.	Absorbed by NaOH. $BaCO_3$ precipitated and removed. Liquid titrated	Solids and solutions	—	m	—	2·0
Adams (1934)	10·8 H_2SO_4 0·3 $K_2Cr_2O_7$	No	Absorbed by NaOH and titrated	Soils	—	M	½–¾	1·5

TABULATED DETAILS OF LITERATURE—*continued*

Authors	Oxidising materials per 1/100 part of carbon	Furnace if used	Method of determining CO_2	Type of material analysed	Difficult material	Scale	Time (hrs.)	% Error
Robertson and Shewan (1935)	1·5 H_2SO_4 0·2 $K_2Cr_2O_7$	Yes	Absorbed by KOH and weighed	Soils. Pure substances	8-Hydroxy quinoline(1)	M	½	2–1
Pollard and Forsee (1935)	10·8 H_2SO_4 0·3 $K_2Cr_2O_7$	No	Absorbed by ascarite and weighed	Pure substances	—	M	1–2	0·2
Acharya (1936)	0·4 H_2O 0·2 CrO_3 2·0 H_2SO_4	No	Absorbed by Sofnolite and weighed	Pure substances and soils	Pyridine(1) and Quinoline	M	½	3
Williams, Rohrman and Christensen (1937)	1·0 H_2O 45·0 H_2SO_4 0·5 or 100% excess KIO_3	No	Iodine formed, titrated and carbon calculated	Pure substances	Acetanilide(1)	m	½	4
Christensen and Facer (1939)	7·2 H_2SO_4 0·12 KIO_3	No	Absorbed by $Ba(OH)_2$ and titrated	Liquids and solids	Succinic acid	m	1½	0·5
Van Slyke and Folch (1940)	0·5 CrO_3 10·0 Oleum 5·5 H_3PO_4 1·0 KIO_3	No	Van Slyke manometric apparatus	All types of substance	Solutions of volatile substances impossible	m	¼	0·2
Christensen and Wong (1941)	90 H_2SO_4 0·25 KIO_3	No	Absorbed by $Ba(OH)_2$ and titrated	Pure substances	Aromatic compounds(1)	m	½	2·4

(1) Slow oxidation. (2) Carbon monoxide formation. M=Macro. m=Micro. E.F.=Electric Filament.

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"ROWANHURST," GROVE ROAD
BEACONSFIELD, BUCKS.

August, 1944

Discussion

The President, in inviting a full discussion, regarded it as very appropriate that, following inauguration of the Microchemical Group, Dr. Houghton should bring to the notice of the general body of members a readily available, semi-micro technique for the determination of carbon, requiring no elaborate equipment, and the precision of the method would warrant its application to many biological fluids. He presumed that in respect of the organic carbon content of water, sewage effluent, etc., the method, when correlated with the result of one or other arbitrary moist combustion (oxygen absorption) process, might have considerable significance. In recording warm thanks to the author one could not pass over, without a word of appreciation, the painstaking analytical work of his assistant in the preparation of the tabular records.

Mr. W. C. Wake asked whether the author had had any experience of the wet combustion of substances containing methyl side chains, *e.g.*, methyl cyclohexenes or terpenes. In the Kuhn–Roth method of determining methyl groups an identical oxidising mixture was used and acetic acid was formed and removed by steam distillation. The yield varied and results were interpreted by reference to the yield obtained from some analogous compound of known structure. The author's method was of interest to analysts both here and in America, for the estimation of natural rubber in compounds which might contain other rubbers was largely done by oxidation in this chromic-sulphuric acid mixture to acetic acid. The yield was 75% and a correction factor of 4/3 was employed. The present paper might throw light on this unsatisfactory yield. What was required was to avoid the complete combustion of rubber to carbon dioxide and to stop at the acetic acid stage. Most rubber compounds contained carbon black.

Dr. G. G. A. Griffiths asked whether the blank due to carbonaceous matter in the reagents would be largely eliminated by a short preliminary heat treatment of the mixed reagents in the reaction flask before addition of the material in which the carbon was to be determined.

Miss Hadfield asked if the author had tried titrating directly into the absorption tube while the oxygen was still being evolved, in the manner suggested by Niederl for the determination of carbon dioxide formed during a dry combustion of carbon compounds.

Mr. G. H. Chamberlain asked if a carbon dioxide-acetone cold trap had been tried to remove sulphur trioxide vapour from the gases evolved during the determination.

Dr. Houghton, replying to Mr. Wake, said that he had had no experience with substances containing methyl side chains, but suggested reference to some work published in the *Journal of the Chemical Society*, 1914, 105, and in *J. Biol. Chem.*, 1929, 8, 245. The complete combustion of acetic acid to carbon dioxide by his method was possible, as had been shown, and therefore it should be possible similarly to complete the combustion of rubber.

Studies in the Analytical Chemistry of Tungsten. III—The Precipitation of Tungsten with Tannin

By D. A. LAMBIE

Sections I and II of this series[1,2] dealt (*inter alia*) with the precipitation of tungstic acid from sulphate and phosphate solns. by the tannin-cinchonine method.[3,4] A re-examination of the pptn. of tungsten with tannin, recorded in this Section, has been undertaken chiefly with the object of finding a substitute for cinchonine which, owing to the War, is in short supply.

According to Schoeller and Jahn,[4] when an alkaline tungstate soln. containing tannin is acidified with hydrochloric acid, the bulk of the tungsten is pptd. as a tannin complex, the balance of which remains in colloidal suspension; this may be flocculated by adding tannin precipitants such as alkaloids. In the original method[1,4] cinchonine is so employed. Subsequently Moser and Blaustein[5] published a modification of the method in which they use phenazone (antipyrine) instead of cinchonine, without, however, acknowledging Schoeller and Jahn as the originators of the principle. My tests of Moser and Blaustein's method failed to give a quantitative recovery; this I ascribe to their use of too little tannin and phenazone. Further, they acidify the tungstate soln. *prior* to addition of the tannin which, in presence of certain elements, causes contamination of the ppt. due to the formation of heteropoly acids (see (*B*)).

When the work here described was in the final stages, the use of rhodamine B as a substitute for cinchonine was advocated by Box.[6] My check tests, described under (*D*), proved that complete recovery of the tungsten requires much more rhodamine B than is prescribed by Box, and the bulkiness of the ppt. limits the amount of tungsten that can be conveniently determined to half that adopted as a maximum for the tannin-cinchonine method. On the strength of the few tests given in his note, Box inclines to the opinion that "neither reagent is perfect," but I strongly disagree with him as far as cinchonine is concerned, and would point out that my own published work[1,2] has confirmed the reliability of the tannin-cinchonine method beyond reasonable doubt.

In searching for a cinchonine substitute I tried gelatin first (see *A*), but, after exhaustive tests described below under (*C*), abandoned it in favour of a new phenazone procedure. None of the substances tested is so efficient as cinchonine, but with phenazone its lower cost compensates for the use of a larger quantity.

Experimental

Two solns. of "AnalaR" sodium tungstate were prepared and standardised by means of the tannin-cinchonine method and by evaporation with perchloric acid.[7] Twenty-ml portions gave: Soln. I, 0·1002 g, 0·1003 g, 0·1006 g, 0·1003 g; adopted 0·1003 g/20 ml. Soln. II, 0·1005 g, 0·1004 g, 0·1005 g, 0·1005 g; adopted 0·1005 g/20 ml; all as WO_3.

(*A*) Gelatin as Flocculating Agent—In most of the test analyses (unless different conditions are specified), the solns. were prepared as follows: sodium tungstate soln., 20·00 ml; diluted ammonia (1 + 1), 5 ml; 20% ammonium chloride soln., 50 ml; total vol., 200 ml. In Expt. 1 the soln. was treated at 60° C. in succession with 1 g of tannin dissolved in a few ml of water, diluted hydrochloric acid (1 + 1) to slight acid reaction (litmus paper), filter pulp, and 25 ml of 1% gelatin soln. After standing overnight the ppt. was collected on a Whatman No. 41 paper, washed with cold 2% ammonium chloride soln., ignited and weighed. Error: 0·0098 g (see Table I).

In Expt. 2 the soln. was neutralised and then acidified with 5 ml of diluted hydrochloric acid (1 + 1) before addition of the pulp and gelatin; the filtrate was re-treated with a further 25 ml of gelatin soln., and the two ppts. were ignited and weighed separately. Found: 0·0958 g and 0·0049 g of WO_3. Total error, +0·0004 g. A third pptn. yielded 0·0002 g of a ferruginous precipitate.

Further expts. were carried out under varying precipitation conditions (see Table I). In Expts. 5–10 the filtrates from the tannin-gelatin ppts. were treated by the tannin-cinchonine method, and the ignited secondary ppts. were tested colorimetrically by Feigl and Krumholtz's method.[8]

Table I

(WO_3 taken, 0·1003 g)

Expt.	Tannin added g	Gelatin added g	WO_3 in tan.-gel.ppt. g	WO_3 in filtrate g	
1	1·0	0·25	0·0905	—	
2	1·0	0·25+0·25	0·0958	0·0049	
3	1·0	0·75	0·0994	—	
4	1·0	0·75	0·0970	—	Pptd. entirely in the cold.
5	1·0	0·75	0·0999	0·0010	Tannin added to hot soln. cooled prior to adding gelatin.
6	1·0	1·0	0·1000	0·0004	
7	0·5	0·5	0·1003	0·0004	
8	0·5	0·6	0·1004	0·0010	
10	1·0	1·1	0·0999	0·0001	

These tests prove that a fairly satisfactory tungsten recovery was effected when sufficient gelatin was added to precipitate substantially all the tannin, but larger proportions of gelatin were found to impede filtration.

(*B*) Phenazone as Flocculating Agent—In their modification of the tannin-cinchonine method Moser and Blaustein[5] add tannin to the acidified tungstate soln. and complete the flocculation of the tannin complex with phenazone. In Expts. 11 and 12, 20 ml of soln. I were pptd. according to their directions, and 0·0987 g and 0·0984 g were recovered. An additional 0·0023 g of tungstic oxide was obtained from the filtrate in Expt. 12 by the tannin-cinchonine method. In a further expt. 20 ml of soln. I, to which was added 0·01 g of P_2O_5 as sodium phosphate, was treated by their method. No perceptible ppt. was caused by addition of the tannin, but a small quantity of dense white crystals, undoubtedly ammonium phosphotungstate, separated. The ignited ppt. (0·1020 g) was blue-green and contained 0·0022 g of P_2O_5 as determined by my magnesia method.[2]

These three expts. demonstate that Moser and Blaustein's procedure neither achieves a quantitative pptn. of tungsten nor provides a separation from oxides which form heteropoly acids with tungstic oxide.

(*C*) Author's Phenazone Method—A number of expts. similar to those with gelatin (*supra*) were carried out with varying amounts of tannin and phenazone; the results, at first

complicated by losses due to the use of an unsuitable wash liquid, are summarised in Table II. As a result of these expts. the procedure given below was adopted.

TABLE II

(WO_3 taken, 0·1003 g)

Expt.	Tannin added	Phenazone added	WO_3 found	WO_3 in filtrate*	
	g	g	g	g	
14	0·5	0·5	0·0993	0·0010	Unsuitable wash liquid.
15	0·5	1·0	0·1003	0·00015	
16	0·5	0·5	0·0997	0·0007	
17	0·5	1·0	0·0999	0·00026	
18	1·0	1·0	0·1001	0·00028	
19	1·0	2·0	0·1000	nil	
20	1·0	2·5	0·1003	nil	

* In each expt. the WO_3 was determined as in Expts. 5–10.

PROCEDURE—To the alkaline tungstate soln., containing not more than 0·2 g of tungstic oxide, add 50 ml of 20% ammonium chloride soln. (unless sufficient is already present), dilute to about 200 ml and heat to 60–70° C. Add a freshly prepared soln. of tannin (1 g for each 0·1 g of tungstic oxide presumed to be present but in any event not less than 0·5 g) followed by diluted hydrochloric acid (1+1) added dropwise during continuous stirring until the soln. is acid to methyl orange and then 5 ml excess. Stir in creamed filter pulp (equivalent to half a 9-cm Whatman No. 41 filter-paper) followed by 10% soln. of phenazone in water added dropwise, 20 ml for each 1 g of tannin used. Cool in running water and leave until the supernatant liquid is clear, preferably overnight. Collect the ppt. on a close-textured paper (Whatman No. 44) and wash three times with a soln. containing 50 g of ammonium chloride, 25 ml of diluted hydrochloric acid (1+1) and 10 ml of 10% phenazone soln. per litre. Return the ppt. to the beaker by means of a jet of wash liquid directed into the inverted funnel, stir up the ppt. with the wash liquid, and re-filter. Clean beaker and stirring rod with the aid of filter-pulp and a rubber-tipped glass rod and complete the washing. Ignite wet in a tared porcelain crucible and weigh as WO_3.

Two series of tests of this method were made. In the first (Expts. 21–26), aliquots of soln. I were treated with 5 ml of diluted ammonia (1+1) and then pptd. as above. For the second series (Expts. 27–31) tungstic oxide was fused with sodium carbonate in platinum, the melt was leached with water, and the pptn. was carried out as before. As can be seen from Table III, satisfactory results were obtained.

Recovery of traces of tungstic oxide—Attempts made to ppt. amounts of tungstic oxide of the order of 0·1 mg from 200 ml of soln. by the above method resulted at first in recoveries of only about 70%, but by doubling the amount of phenazone used (20 ml) satisfactory results were obtained (Expts. 36–38, Table III). The ignited oxides were dissolved in sodium hydroxide soln., and the tungsten was determined colorimetrically.

Precipitation in presence of sulphates—As shown in Section I, the tannin-cinchonine method may be used to recover tungsten from solns. containing a large excess of sulphuric acid and sulphates.[1] Expts. were therefore made to confirm that the above procedure was equally satisfactory. Varying weights of tungstic oxide were fused with 2 g of potassium bisulphate in silica crucibles. In each test the melt was re-heated with 10 ml of conc. sulphuric acid and transferred to a beaker with water, the soln. was rendered alkaline with ammonia, and the tungsten was pptd. Expts. 32–35, Table III, show the recoveries to be quantitative.

TABLE III

Expt.	WO_3 taken, g	WO_3 found, g	Error g	Expt.	WO_3 taken, g	WO_3 found, g	Error g
21	0·2006	0·2007	+0·0001	30	0·0226	0·0226	nil
22	0·1003	0·1005	+0·0002	31	0·0111	0·0113	+0·0002
23	0·0502	0·0502	nil	32	0·2012	0·2015	+0·0003
24	0·0250	0·0249	−0·0001	33	0·1028	0·1032	+0·0004
25	0·0100	0·0099	−0·0001	34	0·0521	0·0523	+0·0002
26	0·0010	0·0009	−0·0001	35	0·0131	0·0136	+0·0005
27	0·2009	0·2010	+0·0001	36	0·0001	0·000095	−0·000005
28	0·1018	0·1020	+0·0002	37	0·0010	0·00093	−0·00007
29	0·0523	0·0527	+0·0004	38	0·0005	0·00050	nil

Precipitation in presence of phosphates—Expts. 39–46, Table IV, confirmed my expectation that the new phenazone method would afford a quantitative separation of tungstic and

phosphoric acids, as in the tannin-cinchonine method.[2] To provide as stringent a test as possible, varying amounts of sodium tungstate and phosphate solns. were mixed and acidified with hydrochloric acid to ensure formation of phosphotungstic acid, then rendered alkaline with diluted ammonia (1+1) (5 ml excess) and pptd. as above. The weighed ppts. were fused with sodium carbonate, etc., for the determination of phosphorus pentoxide[2]; although traces were found, the tungsten results are well within the limits of experimental error.

TABLE IV

Expt.	WO_3 taken, g	P_2O_5 taken, g	WO_3 found, g	WO_3 error, g	P_2O_5 in ppt., g
39	0·0502	0·20	0·0500	−0·0002	0·00006
40	0·1005	0·20	0·1001	−0·0004	0·00012
41	0·1005	0·10	0·1007	+0·0002	0·00009
42	0·0502	0·10	0·0502	nil	0·00005
43	0·0502	0·05	0·0503	+0·0001	nil
44	0·0502	0·02	0·0500	−0·0002	0·00004
45	0·0251	0·20	0·0253	+0·0002	0·00003
46	0·0005	0·20	0·0005*	nil	—

* Determined colorimetrically.

Precipitation in the presence of molybdates—Owing to the similarity between the reactions of tungsten and molybdenum and as a result of qualitative tests it has always been assumed that molybdic acid would be co-pptd. with tungstic acid by means of tannin. The following expt. confirms this view. Molybdic oxide (0·05 g) was dissolved in ammonia and pptd. with tannin and phenazone, and the ppt. was collected and washed as usual. The filtrate was tested for molybdenum after destruction of the organic matter by wet combustion, and a trace only was found.

When molybdenum is known to be present in smaller amount than tungsten the tannin pptn. may be performed as usual, the ignited ppt. weighed, and the molybdic oxide determined and subtracted. If molybdenum preponderates it should be separated as sulphide first and the tungstic oxide determined in the filtrate.

Precipitation in the presence of organic acids—In the following series of expts. 20-ml portions of soln. II were treated with an organic acid (tartaric, citric, or oxalic) to provide 1, 10 and 100 mols. of acid per mol. of tungstic acid, and the soln. was rendered alkaline with ammonia and treated with tannin and phenazone. The results recorded in Table V show that small quantities of organic acid are almost without effect, and even with the largest amount used the pptn. was not completely inhibited, especially in presence of oxalic acid.

TABLE V

(WO_3 taken, 0·1005 g)

Expt.	WO_3 found, g	Acid added, g	Nature of acid
48	0·1005	0·325	tartaric
49	0·0977	3·25	,,
50	0·0018	32·5	,,
51	0·1004	0·091	citric
52	0·0932	0·91	,,
53	0·0043	9·1	,,
54	0·0999	0·054	oxalic
55	0·0889	0·54	,,
56	0·0495	5·4	,,

TABLE VI

(0·1003 g of WO_3 taken in Expt. 62; 0·0502 g in all others)

Expt.	WO_3 found, g	Error g	Strong HCl added, ml	*p*H	Remarks
57	0·0459	−0·0043	—	7·65	0·5 ml of ammonia (1 + 1)
58	0·0419	−0·0083	—	4·25	No ammonia or acid added
59	0·0485	−0·0017	—	3·90	Rendered just acid to litmus
60	0·0501	−0·0001	—	3·05	One drop acid to methyl orange
61	0·0498	−0·0004	10	0·35	
62	0·1007	+0·0004	10	0·35	
63	0·0489	−0·0013	20	—	(0·89 *N*)
64	0·0476	−0·0026	30	—	(1·33 *N*)

Effect of pH on the precipitation—In Section I[1] the tannin-cinchonine pptn. was shown to be quantitative over a wide range of acidity. To determine if the substitution of phenazone caused any change, pptns. were carried out in which the final acidity was varied, the ppts being collected and the *p*H of the filtrate, exclusive of washings, determined by means of a Coleman *p*H meter (glass electrode), except in Expts. 63 and 64, in which the acid was titrated with standard alkali. The results (Table VI) show pptn. to be quantitative between *p*H 3 and 0·35.

(*D*) Rhodamine B as Flocculating Agent—In Expt. 65 (*cf.* Table VII) the test soln., prepared as for Expt. 1, was treated as in the tannin-cinchonine method, except that 5 ml of 1% rhodamine B soln. was used instead of cinchonine soln. There was a large negative error, and the missing fraction —0·0109 g— was quantitatively recovered from the filtrate by application of my phenazone procedure. Increased quantities of rhodamine B improved the recovery; 0·1 g of tungstic oxide was found to require 2 g of the dye (Expt. 68). The ppt. was, however, much more voluminous than the corresponding tannin-phenazone ppt., and filtration and washing were slower.

In Expts. 69 and 70 I endeavoured to duplicate Box's results[6] by decreasing the amount of tungstic oxide and following his directions (*i.e.*, use of Schoeller and Jahn's tannin-cinchonine procedure, but substituting 5 ml of 1% rhodamine B soln. for the cinchonine soln.; in Expt. 70 only, addition of 15 g of sodium sulphate, 10 g of sodium chloride, and 5 g of potassium sulphate). These three tests gave a large negative error.

Table VII

Expt.	Tannin added, g	Rhodamine B added, g	WO_3 taken, g	WO_3 found, g	Error g
65	1·0	0·05	0·1003	0·0894	—0·0109
66	1·0	0·5	0·1003	0·0932	—0·0071
67	1·0	1·0	0·1003	0·0982	—0·0021
68	1·0	2·0	0·1003	0·1002	—0·0001
69	0·5	0·05	0·0250	0·0214	—0·0036
70	0·5	0·05	0·0250	0·0196	—0·0054

The conclusion I draw from these tests is, that for small amounts of tungsten (well below 0·1 g) rhodamine B may be used as a substitute for cinchonine, provided that a much larger addition of the dye is made than proposed by Box, while for speed in manipulation the cinchonine and phenazone ppts. are definitely superior. In addition, rhodamine B is more expensive than phenazone.

Summary—Phenazone (antipyrine) has been shown to be a satisfactory substitute for cinchonine in Schoeller and Jahn's tannin-cinchonine method, quantitative recoveries of tungsten from solns. containing ammonium salts, sulphuric acid, and alkali sulphates and phosphates being achieved. Organic acids, except in small amount, and molybdic acid should be absent. Moser and Blaustein's phenazone method has been shown to be unreliable. Box's rhodamine B modification can hardly be recommended as a general method.

In conclusion I desire to express my thanks to the Directors of Messrs. Cooper, McDougall and Robertson for permission to publish this paper and to Dr. W. R. Schoeller for his continued interest in the work.

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The Determination and Separation of Bismuth and Magnesium, using 8-Hydroxyquinoline

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According to Goto[1] bismuth is quantitatively precipitated by oxine within the *p*H range 4·8–10·5, whilst precipitation of magnesium normally occurs upwards of *p*H 7·5. The possible *p*H range for separation therefore appears to be 4·8 to 7·5, but zinc is pptd. by oxine in a similar range to bismuth (*viz.*, 4·4 upwards) and Moyer and Remington[2] showed that magnesium is pptd. with zinc down to *p*H 5·5. Assuming an analogy, then, between the two, separation of bismuth from magnesium should be possible within the range 4·8 to 5·5. Preliminary work indicated that the lower *p*H limit given for the complete pptn. of bismuth, *viz.*, 4·8, was too low, and this was confirmed as follows.

Bismuth solution: prepared from B.D.H. pure bismuth in dilute nitric acid; strength checked by oxyiodide method indicated 100·1% purity.

Procedure—Add to 25 ml of bismuth soln. (0·07 g of Bi) *ca.* 40 ml of water, 10 ml of 50% tartaric acid soln. and a few drops of B.D.H. "678" indicator, and neutralise the soln. to *p*H 7 (green colour) with ammonia. Add 30 ml of buffer solution (10/3 *N* sodium acetate and 10/3 *N* acetic acid in required proportions), heat to 60–70° C., add 15 ml of 2% alcoholic oxine soln., heat the soln. just to boiling and then cool in cold water for 20 min. Filter off the pptd. complex, using a No. 40 Whatman paper, wash well with hot water and re-dissolve in 50 ml of hot 4·5 *N* HCl. (The *p*H of pptn. is determined electrometrically on the filtrate, using a glass electrode). Titrate the cool soln. with *N*/10 bromate-bromide and thiosulphate solutions in the standard manner (without addition of carbon disulphide), keeping the concn. of hydrochloric acid above 3 *N*.

Table I

NaAc : Acet. acid Buffer ratio	*p*H	0·07045 g of Bi Wt. of Bi oxinate, g	Recovery, %
18·0 : 12·0	4·80	0·1849	85·5
19·5 : 10·5	4·90	0·2024	93·6
21·0 : 9·0	5·00	0·2147	99·3
22·5 : 7·5	5·16	0·2158	99·8
24·0 : 6·0	5·24	0·2162	100·0

Precipitation is, therefore, only complete above *p*H 5·2.

Magnesium Determination—Current methods for the precipitation of magnesium with oxine fall under three general headings, from which the following four detailed procedures are derived; apparent non-essentials have been made uniform.

A. To 75 ml of soln. add 2 g of ammonium chloride, neutralise with ammonia (0·88) to *o*-cresolphthalein, adding a small excess (3 ml), heat to 80° C., add dropwise an excess of 2% soln. of oxine in 0·8 *N* acetic acid and digest for 10 min. (Miller and McLennan[3]).

B. To 75 ml of soln. add 2 g of ammonium acetate, heat to boiling, add a small excess of 2% oxine in 0·8 *N* acetic acid, and then ammonia dropwise until the liquid is alkaline to phenolphthalein. Boil for 1 to 2 min. and allow to settle (Vogel[4]).

C. As in B, but with 10 min. digestion replacing the boiling.

D. To 75 ml of soln. add 5 g of sodium tartrate, neutralise to litmus with dilute sodium hydroxide soln., and add 10 ml of 2 *N* sodium hydroxide and an excess of 2% soln. of oxine in 0·8 *N* acetic acid. Heat to 60° C., and allow to settle (Berg[5]).

For this investigation a standard soln. of magnesium was prepared in diluted nitric acid from metal of 99·99% purity, the strength of the soln. being checked gravimetrically.

For each determination an aliquot corresponding to 0·014304 g of Mg was taken; the oxinate ppt. was filtered off on a No. 41 Whatman paper; the flask and then the filter were washed four times each with hot water, the ppt. was dissolved in 2 *N* hydrochloric acid and the soln. was titrated with 0·1 *N* bromate-bromide and thiosulphate in the standard manner.

Results determined by these methods are summarised in Table II.

TABLE II

Excess of oxine, %	Recovery, %				
	Method A		B	C	D
10	100·0	104·6*a*	101·1	101·1	104·8
	102·1*c*	100·3*e*			102·2*b*
33	101·0	103·7*a*	—	—	—
66	103·4	104·1*d*	102·7	104·7	105·5
					103·1*b*

(*a*) Ten g ammonium acetate used. (*b*) Solution boiled for 2 min. after pptn., then digested for 10 min. (*c*) Ten g of ammonium chloride used. (*d*) Washed 10 times. (*e*) Ten ml excess of conc. ammonia added; oxine deposited in the filtrate.

The following conclusions emerge, largely in agreement with those of Miller and McLennan.[3]

(1) Method A gives results accurate at least to within 0·5%, provided that not more than 10% excess of oxine is used.

And with this method: (*a*) excess of ammonium acetate or chloride causes high results; (*b*) excess of ammonia has no effect, provided hot water is used for washing; (*c*) 33 to 66% excess of oxine causes results approx. 1 to 4% high, which cannot be avoided by prolonged washing. Where the amount of magnesium is unknown, a fair excess of oxine is inevitably added in the first instance, but results accurate to within about 1% can be obtained by re-precipitation, adding a further 0·5 ml or less of oxine soln., and then following procedure B.

(2) Sodium hydroxide is not suitable as a precipitating agent for accurate work.

SEPARATION OF BISMUTH FROM MAGNESIUM—Bismuth was determined by the procedure already given and the magnesium on an aliquot of the filtrate, using method A with an approx. 10% excess of oxine, including that derived from the excess of alcoholic oxine (the alcohol was first removed by boiling). Results are shown in Tables III and IV.

TABLE III

NaAc : Acet. acid Buffer ratio	*p*H	0·07045 g of Bi Recovery, %	0·1430 g of Mg Recovery, %
24·0 : 6·0	5·24	100·2	—
24·7 : 5·3	5·31	100·4	100·5
25·5 : 4·5	5·40	100·5	—
26·5 : 3·5	5·54	100·7	—
27·5 : 2·5	5·80	100·8	99·9
29·0 : 1·0	6·17	101·0	100·2
29·8 : 0·2	6·90	103·3	Mg deposited in the filtrate

The following figures were obtained with other proportions of bismuth and magnesium.

TABLE IV

Bi, g	*p*H	Bi found, g	Recovery, %	Mg, g	Recovery, %	Mg: Bi ratio
0·07045	5·30	0·07072	100·4	0·4290	100·4	6 : 1
0·01408	5·30	0·01425	101·1	0·1430	99·9	10 : 1

Evidently, under these conditions, bismuth can be determined with a maximum positive error of 0·3 mg only within the *p*H range of 5·2 to 5·4. Addition of 25 ml of a buffer solution (136 g of sodium acetate dihydrate plus 14·5 ml of glacial acetic acid made up to 300 ml) to a neutral solution as prepared above, gives a consistent *p*H of 5·3.

A positive error of 0·3 mg of bismuth would be equivalent to the co-precipitation of 0·05 mg of magnesium. An attempt was made to detect this magnesium as follows. The bismuth ppt., obtained at *p*H 5·3 from 0·07 g of bismuth in presence of 0·14 g of magnesium was dissolved in hydrochloric acid, the organic matter was destroyed with sulphuric and nitric acids, and the bismuth was pptd. as sulphide and filtered off. The filtrate was evaporated to 5 ml to give a detectable concn. of magnesium and the Magneson II test was applied, but no reaction for magnesium was obtained. It seems certain, therefore, that co-precipitation of magnesium with the bismuth is negligible for practical purposes.

Despite the narrowness of the *p*H range permissible, I have found, during the course of some 100 analyses of mixtures of commercial bismuth carbonate and magnesium carbonate,

that this procedure gives accurate and consistent results within 0·5% for both the bismuth content and the magnesium content, determined on the filtrate.

SUMMARY—The lower *p*H limit for the quantitative precipitation of bismuth with oxine is 5·2, and bismuth can be determined in presence of magnesium within the *p*H range 5·2–5·4, using a strong acetate buffer. Various procedures for the determination of magnesium with oxine have been quantitatively investigated, the one recommended by Miller and McLennan[3] being found the best; this procedure was then successfully applied in the determination of magnesium on the filtrate from bismuth determinations on bismuth-magnesium mixtures.

I wish to thank the International Chemical Company, Ltd., in whose laboratory this work was carried out, for permission to publish it.

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Notes

A RAPID DETERMINATION OF ALKALIS IN PORTLAND CEMENT

THE recent discovery by Stanton[1] of the important part played by alkalis in the deterioration of concrete makes a rapid yet accurate method for the determination of alkalis in Portland cement urgently needed. A special application of my method of determining alkali by the sulphate-decomposition method[2] is suitable for the purpose. If soda and potash in Portland cement are determined by the general procedure for this modification of the Berzelius method, so much calcium sulphate is formed that there is danger of spattering during the early stages of the decomposition. Fortunately, however, Portland cement lends itself to special treatment, as it is readily decomposed by sulphuric acid alone, enabling quite four-fifths of the calcium sulphate to be removed, by filtration, at the very outset. This special precaution not only lessens danger of spirting during "fuming," but also facilitates the subsequent thermal decomposition of the sulphates of iron, aluminium and titanium.

PROCEDURE—Take separate 1-g samples for soda and potash determinations, each in a squat 100-ml Pyrex beaker, and proceed as follows. Add to each, while stirring, first *ca.* 20 ml of cold water, and then from a pipette slowly, while stirring, 2-ml of diluted sulphuric acid (1+1). Leave covered, with occasional stirring, on the water-bath for 1 hr. Filter through a 9-cm medium-open paper into a second similar 100-ml beaker, washing with hot water until this beaker is nearly two-thirds full. Transfer the filtrate to a 100-ml platinum basin (3 in. diam.) on the water-bath, to evaporate. Meanwhile rinse the residue on the filter back into the original beaker, using *ca.* 30 ml of hot water, add a further 2 ml of sulphuric acid (1+1), and again leave covered, with occasional stirring, on the water-bath for 1 hour. Filter through the same paper, and again wash until the second beaker is nearly two-thirds full. Empty this filtrate also into the platinum basin and evaporate to a small volume. Add 8 ml of hydrofluoric acid, swirl the contents of the basin, and with a platinum spatula scrape down the loosened deposit from its sides. Transfer to a uralite plate or asbestos hot-air bath. Heat with a low flame and carefully (especially in this first "fuming") as the acid approaches the fuming stage. When fuming ceases, run a further 2 ml of diluted sulphuric acid (1+1) from a pipette around the inside of the basin, and again "fume" carefully to complete dryness. Next cover the platinum basin with a porcelain crucible-lid (that of crucible No. 4, 81 mm diam.) or with a Vitreosil lid (of the 150-ml crucible, 3⅛ in. diam.) or with the flat form (F_2, 25 ml, 2⅞ in. inside diam.) Vitreosil dish fitting inside the basin rim. Place on a triangle above the small naked flame of a Bunsen burner, raise the flame gradually,[2] and then heat with full flame for at least 10 min. Remove the lid, cool, and add about 20 ml of hot water.

Determination of Soda as Uranyl Acetate—With a short rubber-tipped "policeman" loosen and stir one of the powdery red residues, and decant the fine suspension of oxides through a 7-cm medium-open paper (Green's 802 or Whatman's 41) into a 30-ml Pyrex beaker. Return this small filtrate to the basin and re-filter, catching the filtrate, now crystal-clear, in a 150-ml beaker marked at 60-ml and 100-ml levels. Leach the residue in the basin with successive small vols. of hot water, until the filtrate fills the beaker to the 60-ml mark; all the oxides have meanwhile been gradually transferred to the filter. For a second extraction, return the filter-paper and contents to the platinum basin, burn off the paper, "fume" again with 2 ml of sulphuric acid (1+1) to dryness, cover and ignite the basin cautiously and then strongly as before, and again leach the residue with hot water through a 7-cm medium paper, up to the 100-ml mark on the beaker. Then remove the sulphate[2] with 5 ml of a barium chloride soln. containing 5 g of barium chloride ($2H_2O$) per 100 ml, catch the filtrate in a 150-ml flat-bottomed Pyrex evaporating basin, evaporate to dryness on the water-bath, and determine the soda as sodium magnesium uranyl acetate by Kahane's method[2]; factor for Na_2O, 0·0202.

Determination of Potash as Cobaltinitrite—Similarly make a double extraction of the alkali sulphates from the second of the oxide residues, but without removing sulphate catch the two filtrates directly in a 150-ml flat-bottomed Pyrex evaporating-basin, evaporate to dryness on the water-bath, and determine

potash by Piper's method and with his factors,[2] but titrating with ceric sulphate rather than permanganate. Using Table I herewith (which is intended rather for the general sulphate-decomposition procedure) take half the value given against the titration.

TABLE I

% K_2O ON 0·5 g, FOR 0·05 *N* CERIC SULPHATE

Add.	Ttn.	% K_2O	Add.	Ttn.	% K_2O	Add.	Ttn.	% K_2O	Add.	Ttn.	% K_2O	Add.	Ttn.	% K_2O
·0071	0·0	0·000	·0072	10·0	0·715	·0074	20·0	1·443	·0075	30·0	2·185	·0076	40·0	2·941
	1·0	0·071		11·0	0·787		21·0	1·517		31·0	2·260		41·0	3·017
	2·0	0·142		12·0	0·859		22·0	1·591		32·0	2·335		42·0	3·093
	3·0	0·213	·0073	13·0	0·932		23·0	1·665		33·0	2·410	·0077	43·0	3·170
	4·0	0·284		14·0	1·005		24·0	1·739		34·0	2·485		44·0	3·247
	5·0	0·355		15·0	1·078		25·0	1·813		35·0	2·561		45·0	3·324
·0072	6·0	0·427		16·0	1·151		26·0	1·887		36·0	2·637		46·0	3·401
	7·0	0·499		17·0	1·224		27·0	1·961	·0076	37·0	2·713		47·0	3·478
	8·0	0·571		18·0	1·297	·0075	28·0	2·035		38·0	2·789		48·0	3·555
	9·0	0·643		19·0	1·370		29·0	2·110		39·0	2·865		49·0	3·632
	10·0	0·715		20·0	1·443		30·0	2·185		40·0	2·941		50·0	3·709

Note—"Add." = proportional part addition for tenth-ml. increase of titration "Ttn."

A comparison of determinations of soda and potash by the method with those obtained by the Lawrence Smith method is given in Table II. The accuracy is satisfactory.

TABLE II

Sample	Na_2O, %		K_2O, %	
	Sulphate-decomp.	L. Smith	Sulphate-decomp.	L. Smith
Portland cement No. 1 ..	0·63, 0·65	0·66*	0·49, 0·50	0·46*
	0·64, 0·65		0·49, 0·49	
,, ,, No. 2 ..	0·29	0·31	0·41	0·39
,, ,, No. 3 ..	0·29	0·29	0·38	0·36

* Determined by F. T. Seelye, Chief Chemist, Dominion Laboratory, Wellington.

The time taken (using two 100-ml platinum basins) is longer than for the general sulphate-decomposition method (8 hr.) only by the extra 2–3 hr. needed for solution in acid, and for the longer evaporation resulting from the initial filtering-off of calcium sulphate. This compares very favourably with the three days required for the A.S.T.M. standard method,[3] or with the two days for the tentative-revision method.[3] Moreover, most of the time is taken up by evaporations and "fumings" requiring little personal attention, while all filtrations are rapid. Apparently the only interference would come from high phosphate, retaining alkali on ignition.

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THE USE OF ANTIPYRINE FOR THE MICRO-ANALYSIS OF TANNINS

CROUZIL[1] was the first to suggest the use of antipyrine as a quantitative tannin precipitant, but his method was discredited by Cornimboeuf,[2] with the result that it disappeared from the literature until revived by Ware and Smith[3] as a qualitative test for tannin. I have attempted to use it as a check on the micro method that I recently described,[4] but with disappointing results. Whereas my method can be used to estimate with certainty as little as 0·25 mg of tannin, the antipyrine method, as elaborated by Ware and Smith, gives doubtful results with 1 mg and entirely fails with 0·75 mg.

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NOTE ON ERGOTOXINE ETHANESULPHONATE

SINCE the publication of the British Pharmacopoeia in 1932, ergotoxine ethanesulphonate has been widely used as a standard in the colorimetric and biological assays of ergot and its preparations. The continued use of this ergot standard has been rendered uncertain, however, by the recent work of Stoll and Hofmann[1] on the isolation of ergocristine ($C_{35}H_{39}O_5N_5$), ergokryptine ($C_{32}H_{41}O_5N_5$) and ergocornine ($C_{31}H_{39}O_5N_5$) from ergotoxine by fractionation of the di-(*p*-toluyl)-*l*-tartrates. These authors reported that of two samples

of commercial ergotoxine ethanesulphonate examined, the purer contained 90% of ergocornine and 10% of ergocristine ethanesulphonate.

When commercial ergotoxine, purified in our laboratories by the process of Stoll and Hofmann, was converted into ethanesulphonate a salt was obtained which gave the following figures upon analysis. (Found: C, 58·96; H, 6·71; N, 10·18.; calc. for $C_{31}H_{39}O_5N_5,C_2H_5SO_3H$: C, 58·99; H, 6·75; N, 10·42%. $[\alpha]_D^{20}$ + 124·1; $(\alpha)_{5461}^{20}$ + 157·8°; *c*, 4·0 in 2 vols. of acetone + 1 vol. of water.) On comparing this material colorimetrically with ordinary ergotoxine ethanesulphonate, using the B.P. solution of dimethylaminobenzaldehyde as reagent, no difference could be detected with a Klett visual colorimeter. The Spekker absorptiometer indicated that the purified salt gave a slightly stronger colour.

This result, together with the observation of White[2] who found no great difference in biological activity between ergocristine and ergotoxine, as we have known it heretofore, indicates that the adoption of the purified salt as a standard would raise no serious difficulty. Moreover, much confusion would be avoided if this product continued to be known as ergotoxine ethanesulphonate.

I am indebted to Dr. E. Walton for the di-(*p*-toluyl)-*l*-tartaric acid which enabled this work to be done, to Mr. A. Bennett, A.R.I.C., for the micro-analyses, and to the Directors of the Wellcome Foundation for permission to publish this note.

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1. Stoll, A., and Hofmann, A., *Helv. Chim. Acta*, 1943, **26**, 1570.
2. White, A. C., *Quart. J. Pharm.*, 1944, **17**, 100.

WELLCOME CHEMICAL WORKS
DARTFORD

G. E. FOSTER

March, 1945

Order in Council

STATUTORY RULES AND ORDERS*

1944—No. 1311. Order adding Regulation 60CAA to the Defence (General) Regulations, 1939, November 23, 1944. Price 2d.

It shall not be an offence against the Public Health (Preservatives, etc. in Food) Regulations, 1925, *to sell or import into the United Kingdom citrus fruit containing diphenyl owing to its having been wrapped outside the United Kingdom in wrappers treated with diphenyl, provided that the Minister of Food has authorised the importation and that the wrappers contain only the authorised quantity of diphenyl.*

By authority of the Minister and in accordance with the terms of his licence any of the following articles of food may be manufactured for sale:—(a) meat containing sulphur dioxide; (b) margarine containing borax; (c) bacon containing borax; (d) dehydrated vegetables containing SO_2*; (e) jam containing sulphur dioxide. It shall not be a contravention of Art. 4 of the said Regulations for the articles mentioned to contain the respective preservatives, or in the case of jam for the proportion of sulphur dioxide to exceed that specified in Part I of the First Schedule to the said Regulations.*

It shall not be a contravention of Art. 11 of the said Regulations to import, with the authority of the Minister, into the United Kingdom bacon in the manufacture of which borax has been used in quantity not exceeding the authorised quantity, or any article of food in the manufacture of which borax has been necessarily introduced by the use of bacon containing borax not exceeding the authorised quantity.

It shall not be a contravention of Art. 11 of the said Regulations to import into the United Kingdom, under authority of the Minister, dehydrated vegetables or any article of food for the manufacture of which the use of dehydrated vegetables has been authorised, by reason only that they contain sulphur dioxide necessarily introduced by the use of such dehydrated vegetables which contained sulphur dioxide not exceeding the authorised quantity.

It shall not be a contravention of Art. 4 of the said Regulations to manufacture for sale or to sell any article of food which contains sulphur dioxide or borax necessarily introduced respectively by the use in its manufacture of (a) meat, margarine, bacon, dehydrated vegetables or jam the sale of which is made lawful by the present Regulations; (b) any meat, margarine, bacon, dehydrated vegetables or jam manufactured by the Minister of Food; (c) any bacon the importation of which is made lawful by this Regulation; (d) any dehydrated vegetables the importation of which is made lawful by this Regulation.

It shall not be a contravention of Art. 4 of the said Regulations to sell any article of food, the importation of which is made lawful by this Regulation.

Art. 4 of the Public Health (Condensed Milk) Regulations, 1923 *(which imposes certain requirements as to the labelling of containers and the quality of the contents), shall not apply to the sale, or the dispatch or delivery of any full cream unsweetened condensed milk intended for human consumption which (a) is sold, dispatched or delivered under the terms of a licence of the Minister of Food; or (b) being imported milk, contains not less than 7·8% by weight of milk fat and not less than 25·5% by weight of all milk solids including fat.*

Art. 9 of the said Regulations shall not apply to the importation of any full cream unsweetened condensed milk intended for human consumption, which is imported in accordance with the terms of a licence of the Minister of Food granted for the purpose of this Regulation.

In this Regulation, "bacon" includes hams and any other part of the carcase of a pig (except the offals, the feet and the head without the chaps) which—(*a*) has been subjected to a dry-curing process, or to a process of pickling for a period not exceeding 48 hours, or has matured after removal from pickle for a period not exceeding 48 hours; (*b*) has been cured in any other way but is not pickled pork.

* Obtainable from H.M. Stationery Office. Italics signify changed wording.

Ministry of Food

CIRCULAR FSL/2/45. FLS/2S/45 (SCOTLAND)

THE following circular has been sent by the Ministry to the Clerks of Councils.

REGULATION 60 CAA OF THE DEFENCE (GENERAL) REGULATIONS, 1939

1. I am directed by the Minister of Food to ask you to bring to the notice of your Authority the above mentioned Regulation, which has the effect of modifying in certain respects the statutory restrictions as to the nature and quantity of preservative which may be contained in meat, margarine, bacon, oranges and dehydrated vegetables. As regards meat, margarine and bacon the Regulation merely re-enacts the provisions of the Meat (Addition of Preservative) Order, 1941, the Margarine (Addition of Borax) Order, 1940, and the Bacon (Addition of Borax) Order, 1940. The relaxation under the Regulation has effect in the same manner as under these Orders by virtue of Ministry of Food authorisations or licences permitting the importation or manufacture of the food in question and if necessary imposing quantity limits. The following notes set out the extent of the relaxation and the quantity limits in force or to be put into force. Subject to such relaxations the relevant statutory regulations continue to have effect.

2. *Meat*—Preservative is applied in a limited number of cases under the control of Ministry of Food Officers in Government slaughterhouses. The process consists in rubbing down the surface of the meat with a solution containing 2% of SO_2. Owing to the nature of the process it is not practicable to specify any limits to the amount contained in the meat, but in view of the solution strength the quantities absorbed are very slight.

3. *Margarine*—The maximum addition permitted by licence under the Margarine (Addition of Borax) Order, 1940, was 0·25% of borax including boric acid and other borates (expressed as boric acid). It is intended to continue this limit under the Regulation. This may involve an amendment of the Regulation to make it clear that boric acid and borates may be used in addition to borax itself.

4. *Bacon*—The addition of borax is permitted only for imported produce. As in the case of meat it is not practicable to prescribe any maximum quantity and the controlling factor lies in the nature of the permitted process, namely, the external dusting of the bacon with powdered borax. When the borax on the surface of the meat is washed off in the usual way only negligible traces of the preservative should remain.

5. *Jam*—The maximum quantity now permitted by Ministry of Food licence is 100 parts per million instead of the 40 parts per million which has hitherto been lawful.

6. *Oranges*—In those cases where Ministry purchasing arrangements make provision for oranges in diphenyl treated wrappers and their importation is authorised accordingly, the maximum content of diphenyl which will be permitted in the orange wrappers will be 40 mg per 100 square inches.

7. *Dehydrated Vegetables*—The following are the quantity limits which have been prescribed by licence.

Description of Dehydrated Vegetables. Maximum permitted quantity of sulphur dioxide — Parts per million

Cabbage	3,000
Potatoes (including mashed potato powder)	500
Beans	2,000
Turnips	2,000
Spinach	2,000
Swedes	2,000

8. The authorities to whom this circular is being sent will be notified of any changes in the above-mentioned limits.

9. Copies of this Circular are being sent to the Medical Officers of Health and Public Analysts of all Food and Drugs Authorities, to the corresponding authorities in Scotland and Northern Ireland, to Port Health Authorities and Officers of Customs and Excise concerned with imports affected by the Regulations. Copies of the Regulation (S.R. & O., 1944, No. 1311) may be obtained from H.M. Stationery Office.

10. A second copy of this Circular is enclosed and it would be appreciated if you would be good enough to pass it on to your sanitary inspector.

February 12, 1945

STATUTORY RULES AND ORDERS*

1945—No. 244. Order, dated March 3, 1945, amending the Soft Drinks Order, 1943. Price 1d. This Order amends the Soft Drinks Order, 1943, by increasing the sugar content (*to* 24 *oz.*) and reducing the saccharin content (*to* 79 *grains per* 10 *galls.*) of standard unconcentrated soft drinks. The amendment takes effect on April 1, 1945, but stocks of soft drinks complying with the former standard (18 *oz. of sugar and* 82 *grains of saccharin*) may be sold by the manufacturers up to May 1, and by other persons up to July 1, 1945.

Geological Survey and Museum

WAR-TIME PAMPHLET, No. 35—DETERMINATION OF TIN, WITH SPECIAL REFERENCE TO TIN ORES†

THIS pamphlet, which is in leaflet form, summarises critically work that has been published during the last four years on the determination of tin and gives references to the original papers. It includes the

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* Italics signify change of words.

† By C. O. Harvey, B.Sc., F.R.I.C. 2nd Edition. November, 1945.

method for the volumetric determination of tin as dioxalatothiometastannate (Willard and Toribara, *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 716; ANALYST, 1943, **68**, 93), the determination of tin with mercuric chloride (Fairchild, *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 625; ANALYST, 1944, **69**, 63), the colorimetric determination of tin with silicomolybdate (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 269; ANALYST, 1944, **69**, 284), and two contributions by B. S. Evans and D. G. Higgs (ANALYST, 1944, **69**, 201 and 291). Clark's "dithiol" method has been adapted by Schwaibold, Borcher and Nagel (*Biochem. Z.*, 1940, **306**, 113) to the determination of tin in biological material, the tin being first distilled as halide.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Starch in Sweet Potato Products and other Plant Materials. E. T. Steiner and J. D. Guthrie (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 736–739)—The method entails treatment of the sample at b.p. with dil. ammonium carbonate soln., pptn. of the starch with iodine, decomposition of the starch iodide with repetition of the pptn. and decomposition, pptn. of the starch with alcohol, dispersion in calcium chloride soln., pptn. of any remaining protein with uranyl acetate and determination of the optical rotation. It is recommended for samples containing 10% or more of starch on a moisture-free basis. To 0·9–1·0 g of the finely ground sample (80 mesh) in a 100-ml heavy unlipped Pyrex centrifuge tube add 2 g of Celite and 50 ml of 0·3% ammonium carbonate soln. and stir with a strong glass rod until the material is thoroughly wetted. Boil the mixture in an oil-bath maintained at 117°–120° C., stirring the suspension frequently and adding a drop of octyl alcohol to reduce frothing but maintaining vigorous boiling after frothing has subsided. To the cooled soln. add 20 ml of 20% sodium chloride soln. and 2·5 ml of an aq. soln. containing 30 g of iodine and 50 g of potassium iodide in 250 ml. Almost fill the tube with water, stopper tightly, invert and shake gently until all the starch has reacted with the iodine and leave for at least 5 min. after pptn. begins. Rinse any starch iodide adhering to the stopper into the tube and centrifuge for 10 min. Remove and discard the supernatant liquid, suspend the starch iodide in 20 ml of the sodium chloride soln., and add sodium thiosulphate soln. (125 g of sodium thiosulphate pentahydrate per litre) until the starch iodide is all decomposed. Approx. 2·5 ml will be required and excess should be avoided. Add 10 ml of *N* hydrochloric acid, 2·5 ml of the iodine soln. and enough water to fill the tube. Centrifuge the liquid and discard the supernatant layer as before. Add *ca.* 50 ml of 95% alcohol, completely suspend the starch iodide, and decolorise the suspension with sodium thiosulphate soln., avoiding excess. Add enough water to reduce the alcohol to 70%, stopper the tube, shake thoroughly and, after 15 min., centrifuge for 10 min. Wash the pptd. starch once with 50 ml of 70% alcohol. Add 60 ml of calcium chloride soln. (2 parts of the hexahydrate and 1 part of water adjusted to a density of 1·3, made very faintly pink to phenolphthalein and filtered) in small amounts at a time and stir until the material is free from lumps. Add 3 ml of 0·8% acetic acid and boil in the oil-bath for 18 min. To the hot liquid add 5 ml of 5% aq. uranyl acetate soln. and stir well. Rinse the liquid into a 100-ml flask with water, cool and dilute to vol., adding 1 ml of water to correct for the vol. of Celite and, if necessary, making a correction for the vol. of tissue residue. Centrifuge for 10 min. in a dry tube and filter the supernatant liquid through coarse paper. Determine the optical rotation of the filtrate at 25° C., using the sodium D line and taking 10 readings, approaching the match point alternately from each side. If α is the observed rotation, l the tube length in dm, and w the wt. of sample in g, the % of starch is given by

$$\frac{\alpha \times 100 \times 100}{l \times 200{\cdot}9 \times w}.$$

Cloudiness in the final soln., which may occur with maize starch, wheat starch and waxy maize starch can be removed by shaking the soln. with carbon tetrachloride and centrifuging. Chloroform may be used, but correction must then be made for the solubility of chloroform in the starch dispersion. With materials relatively free from pectin and protein the second pptn. of starch iodide may be omitted. The specific rotation of starch (200·9) was ascertained first by determination of the major impurities in the starch sample under investigation and assuming the remainder to be starch, then by assuming that the malt diastase method gives correct results when the factor 0·93 is used to convert glucose to starch, and finally by separation of the starch from the calcium chloride dispersion by dialysis and determining its moisture and ash contents before determining its optical rotation after re-dispersion in calcium chloride soln. The method gives results agreeing satisfactorily with those obtained by other methods. Of a number of constituents of biological material which were added to starch samples, white potato dextrin showed slight interference, and results with samples containing higher dextrins and glycogen are of doubtful validity. A. O. J.

Report on Sulphur Dioxide in Beer. L. V. Taylor (*J. Assoc. Off. Agr. Chem.*, 1944, **27**, 386–389)—Previous work (*J. Assoc. Off. Agr. Chem.*, 1933, **20**, 610; 1936, **23**, 189) showed that the method of Monier-Williams (Ministry of Health Rept., No. 43; ANALYST, 1927, **52**, 343, 415) gave reliable results in the determination of sulphur dioxide in beer, wine and malt beverages and led to its adoption as the official method (first action). Before its recommendation for final acceptance, the method was compared with other methods appearing in recent literature, *viz.*, (*a*) the direct titration method adapted from work by Bennett and Donovan on citrus juices (ANALYST, 1943, **68**, 140) with suggestions from Mapson's work on ascorbic acid in presence of sulphur dioxide (*Biochem. J.*, 1942, **36**, 196; ANALYST, 1942, **67**, 305); (*b*) a steam distillation procedure adapted from a method used by Kirkpatrick (*J. Soc. Chem. Ind.*, 1941, **60**, 226; ANALYST, 1942, **67**, 172); and (*c*) the Nissen-Petersen modification of the Monier-Williams procedure (*Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 129). Direct titration methods would entail, first, the titration of total reducing substances including sulphur dioxide and then titration of the natural reducing substances after sulphur dioxide had been removed either by evolution as gas or by formation

of a compound not reacting with iodine. Of several variations of this method, including one in which attempts were made to remove sulphur dioxide from the sphere of action by formation of the addition compound with acetone, none proved successful, the starch-iodine end-points being indefinite and the iodine consumed by the natural reducing substances being disproportionately great in comparison with that used by the sulphur dioxide. In the modification of the steam-distillation method of Kirkpatrick a 300-ml sample was used and the 100-ml Kjeldahl flask of the original method was replaced by a 750-ml flask. Results were variable and were less than 25% of those found by the A.O.A.C. procedure. In the Nissen-Petersen modification of the method of Monier-Williams the hydrogen peroxide is adjusted to *p*H 4·0 by potentiometric titration with sodium hydroxide soln. and, after absorption of sulphur dioxide, is again titrated to *p*H 4·0 electrometrically with 0·01 *N* sodium hydroxide. In the A.O.A.C. method the hydrogen peroxide is neutralised to the bromophenol blue end-point with barium hydroxide soln. and the sulphate originally present is removed by filtration. Six samples of beer, representing six brands, were examined for sulphur dioxide content both volumetrically and gravimetrically by the two procedures. The data presented show that the two methods agree very well. As Nissen and Petersen pointed out, when the hydrogen peroxide is neutralised with barium hydroxide, the volumetric results tend to be slightly lower than the gravimetric results owing to presence of excess of barium ion. In these expts. the error was no greater than the variation between duplicate samples. In the more reliable gravimetric method, determination of sulphur dioxide is not affected by the modification, except that presence of original sulphuric acid in the hydrogen peroxide causes a more variable and higher blank result than when the A.O.A.C. procedure is used. The gravimetric blank determinations in the Nissen-Petersen procedure were equiv. to 1·1–4·2 mg of sulphur dioxide per litre, whereas those for the A.O.A.C. procedure were constant and equiv. to 0·7 mg per litre. Although the modification has the possible advantage of time saving and greater precision in the volumetric estimation, the accuracy of the more reliable gravimetric check is not improved and may be endangered. The accuracy of the present A.O.A.C. method has thus been demonstrated, and it is recommended that the procedure as it appears in "*Methods of Analysis of the A.O.A.C.*," 1940, 154, be made official (final action) and that further work on the method be discontinued. A. O. J.

Histology of Belladonna Root. C. Melville. I. *Atropa Belladonna* Linn. II. Indian Belladonna (*Quart. J. Pharm.*, 1944, **17**, 201–213; 213–220)—The histology of the root, rootstock, stem base and stolon of *Atropa Belladonna* Linn. and of Indian belladonna, *Atropa acuminata* Royle ex Lindley, is described in detail and a number of diagrams are given. It is stated that examination has revealed no significant anatomical differences between the two drugs, any differences being of degree only. The root of *A. acuminata* may be distinguished from that of *A. Belladonna* by the following characters: the cork cells are longer and the number per unit area is less, a mean value of less than 344 cells per sq. mm., calculated from 10 fields of *ca.* 0·1 sq. mm., indicating *A. acuminata*, while over 347 cells per sq. mm. indicates *A. Belladonna*; fibres and fibrous cells occur in the secondary phloem; the vessel elements are longer; the xylem fibres are longer and more numerous; starch grains of more than three components are absent. For further details reference should be made to the original papers. J. A.

Biochemical

Citric Acid Determination. A. S. Goldberg and A. R. Bernheim (*J. Biol. Chem.*, 1944, **156**, 33–46)—Citric acid has previously been determined by conversion into pentabromoacetone followed by a colour reaction with sodium sulphide. A new modification of the pentabromoacetone reaction has now been developed which gives satisfactory results with samples containing only 1 to 40 mg of citric acid. In this method the citric acid is oxidized with manganese dioxide in presence of bromine to acetone dicarboxylic acid, which is rapidly converted into pentabromoacetone. After reduction of the excess of manganese dioxide and bromine with hydrazine, the pentabromoacetone is isolated by extraction with light petroleum. Treatment with a sulphite soln. liberates all five bromine atoms as bromide ions and these are determined by titration with silver nitrate soln. Collect a 24-hr. specimen of urine and add 25 ml of 27 *N* sulphuric acid as preservative. Put 25 or 30 ml of the urine into a 50-ml volumetric flask, and add 10 ml of 27 *N* sulphuric acid and 2 ml of bromide-bromate soln. (85·7 g of sodium bromide and 28 g of sodium bromate in 500 ml of water). Leave the flask in the dark for 10 min. at room temp., add 2 ml of 2 *N* silver nitrate, and shake well. Discharge the residual bromine by adding the minimum of solid sodium metabisulphite and make up to volume, adding a drop of octyl alcohol if necessary. Shake vigorously, filter, and extract the filtrate with 10 ml of light petroleum. Transfer 25 ml of the aqueous soln. to a separating funnel, add 1 ml of 2 *M* manganese sulphate (111·5 g of $MnSO_4 4H_2O$ in 250 ml) and 1 ml of bromide-bromate mixture. Add 0·2 *N* potassium permanganate dropwise from a pipette with a drawn-out tube, with constant swirling to avoid local excess, until the orange colour of the bromine is replaced by a brown colour (1 to 3 ml). If the colour deepens and a slight ppt. of manganese dioxide appears, or if the colour becomes lighter, add more permanganate. Leave for 20 min., and add 10 *N* hydrazine soln. (32·5 g of hydrazine sulphate in 49 ml of 20% sodium hydroxide soln. diluted to 100 ml) dropwise to reduce the manganese dioxide and bromine (about 6 drops). Shake the colourless soln. for 3 min. with 10 ml of light petroleum, and discard the aqueous phase. Add 20 ml of water, shake for 20 sec., and discard the water without first swirling the funnel. (This allows suspended matter to collect on the walls in a film and not at the apex, where it is more difficult to deal with.) Allow 1 or 2 ml of 0·01% methylene blue soln. to flow down the walls of the funnel to permit easy observation of the interface and, after 1–2 min., wash the stem of the funnel with water, and draw off the methylene blue layer until the light petroleum enters and just fills the bore of the stopcock. Remove the water in the stem of the funnel with 1-ml portions of light petroleum, and add the washings to the tube. Evaporate the extract to about 0·5 ml, and then remove the rest of the solvent by evaporation at room temp. to avoid loss of pentabromoacetone, which is slightly volatile. Rinse the wall of the tube with 2 ml of alcohol and add 4 ml of sulphite reagent. (Dissolve 26·0 g of halogen-free sodium bisulphite in

water, add slightly less than 40 ml of 20% sodium hydroxide soln. and 50 ml of alcohol, adjust the *p*H, if necessary, to 7·4 to 7·8 and dilute to 500 ml; store in the refrigerator in small, completely filled bottles). Immerse the tube in a boiling water-bath and, after 3 min., cautiously add 1 ml of 18 *N* sulphuric acid. Boil the contents of the tube over a free flame for a few sec. to expel sulphur dioxide, add 0·5 ml of 25% ferric alum soln. (50 g dissolved in 7 ml of 27 *N* sulphuric acid and diluted to 200 ml), boil for a few more sec. and cool. Add 1 ml of 0·002 *N* potassium thiocyanate and titrate with 0·4 *N* silver nitrate. This procedure is only applicable to normal human urines or to pure citrate solns.; with the latter the preliminary bromination or clarification is unnecessary. Urines containing protein should be treated with solid trichloroacetic acid, and the filtrate used instead of the original urine. Urines containing iodine give a light petroleum extract which shows a violet tinge. This is removed by washing with dilute sodium arsenite soln. In presence of glucose, low results are obtained, and the following procedure should then be used. Dilute a sample containing 1 to 2 mg of citric acid to 15 ml, and add 4·3 ml of 27 *N* sulphuric acid. Add 2 ml of bromide-bromate soln. and 1 ml of manganese sulphate soln., and immerse the funnel in ice-water. Add sufficient of a manganese dioxide suspension (prepared by adding 4 ml of 27 *N* sulphuric acid to 7·5 ml of 2 *M* manganese sulphate cooled in a freezing mixture, and then adding, with stirring, 7·5 ml of cold 26·1% $NaMnO_4 3H_2O$ soln.) and leave the mixture for at least 3 hr. at 0° C., inspecting it occasionally to ensure that excess of manganese dioxide is present. Leave for a further 1 hr. at room temp., then add hydrazine and complete the analysis as described above. Acetoacetic acid, if present, is removed by the preliminary bromination, and hydroxybutyric acid is removed in the form of bromination products on extraction with light petroleum before the second bromination. The average deviation from the mean in a group of samples containing 40 to 45 mg of citric acid was less than 0·2%. With 2- and 1-mg samples, the deviation was less than 0·4%. The recovery of citric acid added to human urine was 99·0 to 99·4% of the theoretical. F. A. R.

Colorimetric Estimation of Phenylalanine in some Biological Products. A. A. Albanese (*J. Biol. Chem.*, 1944, **155**, 291–298)—Difficulties were encountered in obtaining satisfactory results with the Kapeller–Adler method of estimating phenylalanine, and the modifications of Block *et al.* were found to be unsatisfactory. Contrary to the view expressed by Block *et al.*, it appears that the yellow colour due to tyrosine and histidine introduces an error roughly proportional to the amount of these amino acids present. A new method has now been devised in which tyrosine is destroyed by permanganate, and histidine is removed by adsorption on Permutit. Other modifications have been introduced, including the use of 20% sodium hydroxide soln. in place of ammonia for developing the colour; this reduces the risks to the operator. Heat the protein under reflux with 5 ml of 20% hydrochloric acid per g for 22 to 24 hr., and remove the excess of hydrochloric acid *in vacuo* by three successive concentrations and additions of water. Transfer to a volumetric flask, dilute to the mark, and remove aliquots for nitrogen determination by the micro-Kjeldahl method. Transfer a sample of the hydrolysate, containing 25 to 50 mg of protein-nitrogen, to a 50-ml volumetric flask, dilute to about 25 ml, adjust to *p*H 4 with 10% sodium hydroxide soln., and then dilute to the mark. Run the soln. at the rate of 1 drop per sec. through a column of 10 g of Permutit properly activated. The filtrate should give a negative reaction to Knoop's histidine test. Transfer duplicate 3- and 5-ml samples of the soln. to 30-ml porcelain evaporating dishes, and destroy the tyrosine by the dropwise addition of excess of acid permanganate soln. (5 g of potassium permanganate in 100 ml of 10% sulphuric acid). Transfer duplicate 1- and 2-ml samples of *dl*-phenylalanine standards (100 mg in 100 ml) to similar dishes, and evaporate all the solns. to dryness in an oven at 120° C. Remove the dishes as soon as the contents become dry, add to each 2 ml of nitrating mixture (10 g of potassium nitrate in 100 ml of conc. sulphuric acid), and heat the samples on a hot air-bath for 30 min. Transfer the solns. to 50-ml volumetric flasks with a minimum of water (5 to 10 ml), add 5 ml of hydroxylamine reagent (15 g of hydroxylamine hydrochloride and 20 g of ammonium sulphate in 100 ml of water) and, after 5 min., 20 ml of 20% sodium hydroxide soln. Dilute each soln. to the mark, cool in an ice-bath for 10 min., and measure the colours in a photoelectric colorimeter with a 540*mμ* filter. The colour remains stable for 1 hr. after the initial period of development. The method is not only more rapid than the original Kapeller–Adler procedure, but is also more accurate, duplicates generally agreeing within 1%. F. A. R.

Estimation of Phenylalanine in Proteins. W. L. Brown (*J. Biol. Chem.*, 1944, **155**, 277–282)—Tryptophan interferes with the estimation of phenylalanine by the modification of the Kapeller-Adler method described by Block and co-workers (*J. Biol. Chem.*, 1940, **134**, 567). An improved modification is described, in which the tryptophan is removed from the protein hydrolysate by means of mercuric sulphate before the phenylalanine is nitrated. Hydrolyse 1 g of protein by heating under reflux in an oil-bath at 125° C. with 16 ml of 5 *N* sodium hydroxide for 24 hr. Then add slowly 24 ml of 7 *N* sulphuric acid to the hot soln., with stirring, and transfer the mixture to a 100-ml volumetric flask. Cool, dilute to 100 ml, and add 400 mg of kaolin. Shake vigorously, centrifuge and filter through a dry filter-paper, covering the filter with a watch-glass to prevent evaporation. Pipette 4 equal aliquots of the filtrate, containing 1·5 to 2 mg of phenylalanine, into 40-ml graduated centrifuge tubes and add water to the 20-ml mark. Add 6 ml of 15% mercuric sulphate soln. (prepared by adding 80 to 90 ml of 7 *N* sulphuric acid to 30 g of mercuric sulphate, diluting with 30 ml of water, shaking until the solid has dissolved, and then diluting to 200 ml with 7 *N* sulphuric acid), and immerse the tubes in a boiling water-bath for 10 min. Cool, add 4 ml of 7 *N* sulphuric acid, dilute to the 40-ml mark with water, add 20 mg of Celite filter-aid, mix and centrifuge for 5 min. Decant the supernatant soln. into a 50-ml centrifuge tube, drain and rinse the lip with a few drops of water. Remove the mercury from the supernatant soln. with hydrogen sulphide, centrifuge and filter Add 1 drop of 7 *N* sulphuric acid in 12 ml of water to the suspended ppt. of mercury sulphide, and again pass hydrogen sulphide. Centrifuge and decant the washings through the same filter. Remove the excess of sulphuric acid from the combined filtrate by adding, with stirring, 8 g of barium hydroxide (octahydrate) dissolved in 10 ml of hot

water. The soln. should remain acid to Congo red paper. Transfer the soln. and ppt. to a 100-ml centrifuge tube, centrifuge and decant the supernatant soln. through a filter. Mix the barium sulphate ppt. with 50 ml of hot water containing a drop of sulphuric acid and a drop of capryl alcohol, centrifuge and decant the supernatant soln. through the filter. Repeat the washing and centrifuging with 40 ml of hot water and a drop of 7 *N* sulphuric acid. Evaporate the filtrate and washings of each aliquot to dryness in porcelain dishes, cool, add 4 ml of nitrating mixture (20 g of potassium nitrate in 100 ml of conc. sulphuric acid) to each dish, and warm on the steam-bath for 20 min. Transfer the solns. while still hot to 50 ml stoppered graduated Pyrex cylinders. Cool to 0° C., and add 5 ml of 30% hydroxylamine hydrochloride soln. to three of the cylinders. The fourth cylinder contains the soln. to be used as a blank. Again cool in ice-water for 1 min., and then dilute all the solns. to the 50-ml mark with ice-cold conc. ammonium hydroxide. Mix and allow the colour to develop at room temp. for 45 min., re-adjusting to volume before the end of this period. If a ppt. forms, filter the soln through a fast dry paper. Measure the colour in a spectrophotometer, using a 560$m\mu$ filter, with the soln. containing no hydroxylamine as the blank. It is better to calculate the results from freshly prepared standard phenylalanine solns. containing approx. the quantity expected in the test solns. than to use a calibration curve. When mixtures of known composition were analysed, satisfactory results were obtained by this method, whereas the results obtained when tryptophan was not removed were considerably higher. The method was applied to the estimation of phenylalanine in a number of proteins. F. A. R.

Use of Spectrophotometer in the Determination of Cystine by Sullivan's Reaction. R. J. Evans (*J. Biol. Chem.*, 1944, **156**, 373–378)—Adjust the *p*H of the soln. to 1·0 and make up to vol. with 0·1 *N* hydrochloric acid. To 5 ml of the soln., containing 25–150 p.p.m. of cystine, add 2 ml of freshly prepared 10% sodium cyanide soln., shake and leave for exactly 10 mins. Add 1 ml of freshly prepared 0·5% sodium 1 : 2-naphthaquinone-4-sulphonate soln., shake and leave for 20–30 sec. Add 5 ml of a freshly prepared 10% soln. of sodium sulphite in 0·5 *N* sodium hydroxide, shake and leave for exactly 30 min. Add 1 ml of freshly prepared 2% sodium hydrosulphite soln. in 0·5 *N* sodium hydroxide, shake and leave for 10–40 min. Measure the % transmission in a spectrophotometer at 500 $m\mu$, and calculate the cystine content from a standard curve prepared with pure solns. of cystine. F. A. R.

Inhibition of Utilisation of Aneurine and Aneurine Diphosphate for Growth of Microorganisms. H. P. Sarett and V. H. Cheldelin (*J. Biol. Chem.*, 1944, **156**, 91–100)—Woolley and White (*J. Exp. Med.*, 1943, **78**, 489) recently showed that pyrithiamine (1-[(4-amino-2-methyl)-5-pyrimidylmethyl]-2-methyl-3-(β-hydroxyethyl)-pyridinium bromide hydrobromide) competitively inhibits the growth of microorganisms requiring aneurine. It has now been shown that less pyrithiamine is required to inhibit the growth of *Lactobacillus fermentum* and *Penicillium digitatum* when aneurine diphosphate (co-carboxylase) was supplied as growth factor than with aneurine itself. This observation is difficult to reconcile with the hypothesis that aneurine utilisation involves preliminary phosphorylation to co-carboxylase. The problem was therefore investigated further. It was found that both organisms grow faster in presence of co-carboxylase than with aneurine and that concentrations of pyrithiamine sufficient to suppress growth with co-carboxylase are insufficient with equimolecular amounts of aneurine. The ratios of pyrithiamine to aneurine necessary to inhibit growth of *L. fermentum* to the extent of 50% were 50 and 10 when the organism was grown in presence of aneurine or co-carboxylase respectively. The corresponding figures for *P. digitatum*, which requires only the thiazole moiety for growth, were 150 and 40 respectively. Addition of iodoacetate, fluoride, malonate, cyanide or dinitrophenol inhibited the growth or acid production of *L. fermentum*, the effects being similar in presence of aneurine, aneurine monophosphate or aneurine diphosphate. It seems unlikely therefore that aneurine follows a different metabolic route from its phosphoric esters. It is suggested that aneurine must be attached to the carboxylase protein *before* it is phosphorylated, this resulting in a different carboxylase from that obtained when aneurine diphosphate is supplied. F. A. R.

Simple Modification of the Colorimetric Method for Routine Aneurine Clearance Tests. M. Hochberg and D. Melnick (*J. Biol. Chem.*, 1944, **156**, 53–59)—In the modification of the method of Melnick and Field (*J. Biol. Chem.*, 1939, **130**, 97; ANALYST, 1940, **65**, 56) now proposed, the benzyl alcohol extraction step of the original method is avoided by testing a 1-hr. urine aliquot; this contains insufficient salt and other materials to interfere with the adsorption of aneurine on the zeolite column. The use of an inert atmosphere is also unnecessary, so that the apparatus and technique are simpler than in the original method. By the new method, 12 to 15 samples of urine may be analysed in the course of a day. The zeolite used for adsorption is stirred with four 10-vol. portions of 3% acetic acid for 10 min. Between the second and third washes, a 15-min. treatment with 5 vols. of 25% potassium chloride soln. is given. The zeolite is washed with water, alcohol and ether, and dried in air. Adjust a 1-hr. aliquot of the urine to *p*H 4·5 and pass it through a zeolite column at room temp. with the aid of mild suction at a rate of 3–4 drops per sec. Pass steam through the jacket of a condenser attached to the top of the zeolite column, pour 30 ml of water down the inner tube of the condenser and, after ½-min., draw it rapidly through the zeolite with maximum suction. Elute the aneurine immediately, by passing 10 ml of a 25% soln. of potassium chloride in 0·1 *N* hydrochloric acid down the wall of the hot condenser, and collect the eluate at the rate of 1 drop per 2 sec., drawing off the last few drops by suction. This eluate is used for the subsequent determination of aneurine. Wash the zeolite with 200 ml of water under full suction with steam passing through the jacket, and finally wash with 50 ml of water with the steam turned off. The apparatus is then ready for the next sample. At the beginning of each series of tests, run a standard aneurine soln., containing 25 μg in 50 ml of acidulated water (*p*H 4·5), through the column, transfer the eluate to a 100-ml centrifuge tube, and add 10 ml of phenol-alcohol soln. (15·6 g of phenol in 2 litres of 95% alcohol) and 2 drops of 1% alcoholic thymol blue indicator. Treat the eluates from all the samples in this way, so that all are ready for colour development at the

same time. Add 2 *N* sodium hydroxide dropwise until the first distinct blue colour is produced, and then immediately add 25 ml of aneurine reagent. This is prepared as follows: To 274 ml of buffer soln. (prepared by dissolving 40 g of sodium hydroxide in 1·5 litres of water, adding 57·6 g of sodium bicarbonate and then diluting to 2 litres), add rapidly, with stirring, 20 ml of diazotised *p*-aminoacetophenone soln. (dissolve 6·35 g of *p*-aminoacetophenone in 90 ml of conc. hydrochloric acid diluted to 1 litre. To 5 ml of this soln. cooled in ice, slowly add 5 ml of 4·5% sodium nitrite soln. and stir for 10 min.; add a further 20 ml and stir for an additional 30 min. Use the soln., which should be kept below 5° C., within 24 hr.). The reagent is ready for use when the initial faint purple colour is replaced by pale yellow (5–20 min.). After addition of the reagent, mix the soln. and leave in the dark at room temp. for at least 2 hr. Add 5 or 10 ml of xylene, shake vigorously for 3 min. to extract the red pigment and centrifuge. Measure the colour of the xylene layer by any convenient method, preferably by means of a photoelectric colorimeter with a 520 *mμ* filter, and calculate the results from the value obtained with the standard soln. The simplified method gave results on the average about 10% higher than those obtained by the original Melnick–Field method.

F. A. R.

Use of *Lactobacillus fermentum* 36 for Aneurine Assay. H. P. Sarett and V. H. Cheldelin (*J. Biol. Chem.*, 1944, **155**, 153–160)—A new microbiological method, offering several advantages over existing methods, has been devised, using *Lactobacillus fermentum* 36, the growth response of which is measured turbidimetrically after 16 to 18 hr. Under the conditions of the test the pyrimidine and thiazole components of aneurine are inactive alone, together or in presence of aneurine. The organism shows a quantitative response in presence of 0·005 to 0·04 μg of aneurine per 10 ml. Maintain the organisms by making stab-cultures on a soln. of 1% of glucose, 1% of Difco yeast extract and 2% of agar, incubating at 37° C. until heavy growth occurs (24–36 hrs.), and then storing in the refrigerator until required. Make fresh stab-cultures every month. Always prepare the inoculum from the stab-culture, never by sub-culturing. Transfer the organisms to the basal medium containing 0·1 μg of aneurine and 5 mg of Difço yeast extract, and incubate at 37° C. for 16 to 24 hr., but not longer. The basal medium has the following composition: alkali-treated peptone (+ sodium acetate) 20 g, acid-hydrolysed vitamin-free casein 5 g, glucose 40 g, anhydrous sodium acetate 12 g, cystine 200 mg, adenine sulphate 20 mg, guanine hydrochloride 20 mg, uracil 20 mg, salt solution A* 10 ml, salt solution B* 10 ml, riboflavin 200 μg, calcium pantothenate 200 μg, *p*-aminobenzoic acid 200 μg, nicotinic acid 200 μg, pyridoxine hydrochloride 200 μg, biotin 0·8 μg, folic acid (potency 40,000) 0·5 μg, distilled water to 1 litre, *p*H 6·5. To prepare the casein hydrolysate, autoclave for 16 hr. with 25% sulphuric acid, remove the sulphate with barium hydroxide, treat at *p*H 3 with 10 g of Norit per 100 g of casein, and then neutralise. Put 5 ml of the basal medium (*p*H 6·5) into a series of Pyrex test tubes, and to 1 set of tubes add 1 to 4 ml of the test sample, containing 0·005 to 0·01 μg of aneurine per ml, and to another set solns. containing 0·005, 0·01, 0·015, 0·02, 0·03, 0·04 and 0·05 μg of aneurine. Dilute all the solns. to 10 ml with distilled water, plug with cottonwool and steam at 100° C. for 15 min. Cool, and inoculate with one drop of a suspension prepared by adding 0·05 ml of the 24-hr. inoculum to 10 ml of sterile saline. Incubate at 37° C. for 16 to 18 hr., cool in a refrigerator for 15 min., and measure the turbidity in a photoelectric colorimeter with a 540 *mμ* filter and an uninoculated tube as blank. The aneurine content of the sample is calculated from a calibration curve prepared from the series of standard tubes. In assaying foodstuffs or tissues, digest 1 g of the finely minced sample for 16 to 24 hr. with 20 mg each of papain and taka-diastase in 40 ml of 0·5% acetate buffer, *p*H 4·5. Steam the digest, dilute to 50 ml, filter with the aid of Celite filter-aid, and adjust the *p*H to 6·5 to 6·6. Dilute an aliquot for the microbiological test, as described above, so that 1 ml contains 0·005 to 0·01 μg of aneurine. The recovery of aneurine added to white flour, dehydrated pork or urine ranged from 90 to 110% of the theoretical. The results were shown to agree well with those obtained by the thiochrome method.

F. A. R.

* Solution A: KH_2PO_4, 25 g; K_2HPO_4, 25 g; water to 250 ml. Solution B: $MgSO_4 7H_2O$, 10 g; NaCl, 0·5 g; $FeSO_4.7H_2O$, 0·5 g; $MnSO_4.4H_2O$, 0·5 g; water to 250 ml.

Use of *Lactobacillus arabinosus* in the Microbiological Estimation of Pantothenic Acid. H. R. Skeggs and L. D. Wright (*J. Biol. Chem.*, 1944, **156**, 21–26)—The organism used, *Lactobacillus arabinosus* 17–5, is carried by monthly transfer on to a medium containing 1% of yeast extract, 1%e of glucose and 1·5% of agar. Prepare inoculum tubes either by direct transfer from stock culture or by daily transfer on to a medium containing 1% of yeast extract and 1% of glucose broth. After incubation for 24 hr. at 33° C., centrifuge and re-suspend in physiological saline. From this dense suspension, prepare a second very light suspension for inoculation of the samples. The basal medium is as follows, the values being per 100 ml medium (double strength): casein (hydrochloric acid-hydrolysed, Norit-treated, vitamin-free) 1·0 g, cystine 20·0 mg, tryptophan 20·0 mg, sodium acetate (anhydrous) 1·2 g, adenine 1·0 mg, guanine 1·0 mg, uracil 1·0 mg, xanthine 1·0 mg, inorganic salts A* 1·0 ml, inorganic salts B* 1·0 ml, glucose 4·0 g, aneurine chloride 200 μg, riboflavin 200 μg, nicotinic acid 200 μg, pyridoxine hydrochloride 400 μg, *p*-aminobenzoic acid 20 μg, biotin 0·5 μg, *p*H adjusted to 6·6–6·8. Pipette quantities of a soln. of calcium pantothenate (100 μg per ml), containing 0·02 to 0·20 μg, into a series of tubes, and quantities of the material to be assayed, containing 0·01 to 0·20 μg of pantothenic acid, into another series. Dilute the contents of each tube to 5 ml with distilled water and add 5 ml of the double strength basal medium. Plug each tube with cottonwool and autoclave at 15 lb. for 15 min. Add one drop of the inoculum to each tube, incubate for 72 hr. at 33° C., and titrate the resulting acid with 0·1 *N* sodium hydroxide, using bromothymol blue as indicator. The results obtained by this method agreed well with those obtained by microbiological methods involving the use of *L. casei*, and recoveries of pantothenic acid ranging from 92 to 106% were obtained. Instead of estimating growth by titration of the acid, equally good results were obtained by turbidimetric methods after only 18 hr. incubation. Like *L. casei*, *L. arabinosus* gave

* See preceding abstract.

increased growth in presence of oleic acid. This source of error could be eliminated by adding approx. 500 μg of oleic acid to all the tubes. *L. arabinosus* has certain advantages over *L. casei* for microbiological assays: the latter does not give consistent results when its growth is measured turbidimetrically after 18 hr., and it frequently gives high blanks, being more sensitive than *L. arabinosus* to impurities. F. A. R.

Studies on the Distribution, Properties and Isolation of a Naturally Occurring Precursor of Nicotinic Acid. W. A. Krehl and F. M. Strong (*J. Biol. Chem.*, 1944, **156**, 1–12)—When wheat bran and certain other natural materials are treated with alkali, the apparent nicotinic acid content, as measured by the microbiological method, increases. This apparent increase was due not to stimulation of the test organism, *Lactobacillus arabinosus* by fatty acids, but presumably to the presence of a compound readily convertible into nicotinic acid. Attempts to extract this precursor by means of hot or cold water, alcohol, aqueous alcohol, or dilute acid or alkali, were unsuccessful, as were attempts to isolate it by pptn. with heavy metals. The precursor was destroyed by autoclaving with *N* sulphuric acid or by boiling with 2 *N* hydrochloric acid. The precursor was adsorbed from aqueous soln. by Norit A, and was eluted from the adsorbate with greater difficulty than nicotinic acid. Nicotinic acid could be estimated microbiologically while still adsorbed on charcoal, but adsorbates carrying both the precursor and nicotinic acid, after treatment with a 3 : 2 mixture of pyridine and methanol to elute the free nicotinic acid, showed little or no activity when assayed directly. On subsequent treatment with alkali, however, they yielded additional nicotinic acid. In this way the amounts of precursor and free acid could be estimated microbiologically. A concentrate of the precursor was prepared by treating an acid extract of wheat bran (*p*H 4) with charcoal and eluting the nicotinic acid with pyridine-methanol. The product contained 13·5 times as much precursor as nicotinic acid. It is believed that the precursor consists of the nicotinyl radicle attached to a component containing groups which render the molecule acidic and water-soluble. F. A. R.

Biological Activity of a Precursor of Nicotinic Acid in Cereal Products. W. A. Krehl, C. A. Elvehjem and F. M. Strong (*J. Biol. Chem.*, 1944, **156**, 13–19)—Several known compounds related to nicotinic acid, together with several preparations of the precursor, were assayed microbiologically and with dogs and chicks, with the object of throwing light on the constitution of the precursor. In the microbiological assays, ethyl, propyl and butyl nicotinates behaved in the same way as the precursor towards alkali, whereas quaternary compounds were somewhat less active after alkali treatment than before. The charcoal adsorbate (*cf.* preceding abstract), containing 0·12 and 1·65 mg of nicotinic acid and precursor respectively per g, was eluted with 5% ethanolic potassium hydroxide soln., and the eluate was concentrated and neutralised. The concentrate by microbiological assay showed 49·6 mg of nicotinic acid, whereas not more than 3·6 mg could have come from the free nicotinic acid of the original adsorbate. This preparation rapidly alleviated the symptoms of black tongue in dogs deficient in nicotinic acid and, from the magnitude of the response, it was concluded that the eluate had as much nicotinic acid activity toward the dog as toward *Lactobacillus arabinosus*. The adsorbate itself was fed to a nicotinic-acid deficient dog, and gave a response far in excess of that expected from the free nicotinic acid present. Moreover, control expts. indicated that the dog is unable to utilise free nicotinic acid adsorbed on charcoal. Ethyl nicotinate was as effective on dogs as an equimolecular amount of the free acid. Ethyl, propyl and *n*-butyl nicotinates were not utilised as efficiently as equimolecular amounts of nicotinic acid by chicks, and charcoal adsorbates of the precursor and of free nicotinic acid were both inactive for the chick. Alkali-treated precursor, on the other hand, was more active than could be accounted for by the amount of free nicotinic acid originally present. It is concluded, therefore, that the dog, though not the chick, can utilise the precursor as a source of nicotinic acid. F. A. R.

Bacteriological

Avian Salmonellosis. Types of Salmonella Isolated and their Relation to Public Health. W. R. Hinshaw, E. McNeil and T. J. Taylor (*Amer. J. Hyg.*, 1944, **40**, 264–278)—The data summarised and discussed were obtained from 291 outbreaks of salmonellosis in turkeys; 43 in chickens; 7 in pigeons; 3 in ducks and partridges; 2 in geese, and one each in pheasants, peafowl, rheas and secretary birds. Salmonellosis in birds is primarily a disease of the young, occurring most frequently during the first month after hatching, and often it is egg-transmitted and hatchery-disseminated. There is danger of attendants becoming infected on ranches and in poultry killing and dressing establishments. A total of 47 Salmonella types other than *S. pullorum* and *S. gallinarum* have been isolated, and 41 of these have also been isolated from man. The report deals with 561 cultures from 353 avian outbreaks caused by 23 different antigenic types, 21 of which have also been isolated from man. *Salmonella typhimurium* accounted for 60% of the 291 outbreaks in turkeys and for 35% of 43 outbreaks in chickens. Multiple infection may exist on the same ranch; on each of two ranches 6 different types accounted for losses in the period covered. Each type of the Salmonella isolated is briefly discussed in relation to its importance to mortality in birds and also in relation to public health. D. R. W.

Organic

Determination of Hydrocyanic Acid, especially in Coke-Oven Gas. J. A. Shaw, R. H. Hartigan and A. M. Coleman (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 550–553)—Pass the gas at a rate not exceeding 2 cu. ft. per hr. through 2 Shaw sulphur flasks in series, each containing 20 ml of 20% potassium hydroxide soln., with a meter at the end of the train. Have the flasks as close to the main as possible. Do not use more than 2·5 cu.ft. (1 cu.ft. suffices for contents of 10 grains per 100 cu.ft.). Read the meter, disconnect, and combine the 2 solns. in one flask, using a minimum of water. Add 10–15 drops of ammonium polysulphide soln. (prepared from strong ammonia freshly saturated with hydrogen sulphide and excess of micro sulphur; bottled off after 15 min. contact). Mix and set aside for 2 min., unstopper, and slowly add strong hydrochloric acid, while

shaking, until the yellow colour is bleached, and then enough acid to ensure *N* acidity when the iodide is added later (about 8 ml per 100). Avoid local concn. of acid. Cool to room temperature and cautiously evacuate the flask (carbon dioxide is evolved), finally at full suction, and disconnect. Add small portions of bromide-bromate soln. (12·5 g KBr + 25 g $KBrO_3$ per 1000 ml) through the adjustable vent in the funnel top. An excess of *ca.* 2 ml of the reagent, estimated by the depth of the bromine colour, is required. Set aside for 5 min., rinse the funnel top with a little water, allowing a few drops to pass into the flask; mix and set aside for 2–3 min.; add 1 ml of 5% phenol soln. and mix, eliminating the yellow colour. Add 4 ml of iodide soln. (50 g KI per 100 ml), and after 2 min. admit the air and remove the stopper after placing a little water in the funnel. Titrate with 0·1 *N* thiosulphate, adding starch near the end: $CNBr + 2HI = HCN + HBr + I_2$. *Gas containing less than 5 grains per 100 cu.ft.*—Two trains connected by a T-tube are required to avoid the use of caustic potash: (1) Compressed air source, meter, and 3 test tubes (6 in. × 1 in.) in series, each containing 25 ml of strong ammonia; (2) two sulphur flasks as before and a test tube in series, each containing 25 ml of water, a sulphuric acid trap for ammonia, and a meter. The air from (1) is admitted through the T-tube in front of the first sulphur flask at a rate of *ca.* 10% of the gas to be tested, 10 cu.ft. of which are taken. The air meter reading is subtracted from that of the other meter. The contents of the 2 sulphur flasks, if titrated separately, indicate the scrubbing efficiency: flask (1) should contain about 4 times as much as (2). This ensures more than 97·5% recovery. *Pure cyanogen bromide*—Weigh 0·1–0·2 g in a small glass-stoppered bottle and immerse this in 100 ml of *N* hydrochloric acid containing 4 ml of iodide soln. Titrate as before after 30 sec. For solns. of cyanogen bromide, deliver an aliquot under the surface of the acid iodide soln.; stopper quickly, and titrate as before. Bromine converts both hydrocyanic and thiocyanic acids into the bromide.

W. R. S.

Determination of Ethyl Acetate in Presence of Acetaldehyde. C. L. Lindeken, J. O. Clayton and D. A. Skoog (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 734–735)—Methods for estimating esters and aldehydes in mixtures are well known, the ester being determined by saponification and the aldehyde colorimetrically with sulphite-fuchsin soln. or volumetrically with sodium bisulphite. Although determination of ethyl acetate in presence of low concns. of aldehyde by saponification is satisfactory, erratic results were obtained with mixtures in which the ratio of aldehyde to ester was high, the error being ultimately traced to the tendency of acetaldehyde to consume alkali in a varying and irregular manner. Successful use of the saponification method thus depends upon quantitative removal of the acetaldehyde from soln. or quantitative conversion of the aldehyde to a form consuming alkali in a regular and reproducible manner. Removal of aldehyde by pptn. was found to be tedious and the oxidation of aldehyde to acetic acid by hydrogen peroxide was investigated. Since the oxidation occurs in presence of alkali it can be carried out simultaneously with the saponification. In the following method the sum of the two constituents is determined and a correction for the aldehyde present is determined from a sulphite pptn. value. Determine the density of the sample by means of a pycnometer with the usual precautions necessary with volatile liquids, and dilute 5 ml of the sample with water to 100 ml. Add 5 ml of the diluted sample to 50 ml of 0·1 *N* sodium bisulphite in a 250-ml iodine absorption bottle. The bisulphite soln. should contain 5 to 10% of alcohol and should be standardised daily. Shake the mixture intermittently for *ca.* 30 min., rinse the neck of the flask with water and add an amount of standard iodine soln. exactly equiv. to the sodium bisulphite. Titrate the excess of iodine with standard sodium thiosulphate soln. using starch indicator near the end-point. The amount of sodium thiosulphate soln. used is equiv. to the amount of acetaldehyde present. To determine the ethyl acetate, add 5 ml of the diluted sample to *ca.* 100 ml of water, 25 ml of 0·5 *N* sodium hydroxide and 5 ml of 30% hydrogen peroxide in an iodine absorption flask. Fasten the stopper firmly and heat the flask on a steam-plate for 15 min. The mixture attains a temp. of *ca.* 80° C. with a max. pressure inside the flask of 360 mm of mercury. Remove the flask from the plate and leave it for *ca.* 1 hr. Carefully remove the stopper, rinse down the neck of the flask with water, and titrate the excess of alkali with 0·5 *N* hydrochloric acid to phenolphthalein indicator. Make a blank determination simultaneously. The % of ethyl acetate in the original sample is given by

$$\frac{D \times 0{\cdot}088 \times 100}{0{\cdot}25 \times \text{density}},$$

where D is the number of mg-equivalents of alkali consumed less the number of mg-equivalents of acetaldehyde present. The average accuracy of the method is within 2%.

A. O. J.

Determination of *o*-Xylene in Recycle Styrene. R. P. Marquardt and E. N. Luce (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 751–753)—In the production of Buna S rubber the recovery of unpolymerised styrene monomer (b.p., 145°–146° C.) is important. Impurities such as 1,4-vinylcyclohexene, ethylbenzene, isopropylbenzene, *n*-propylbenzene, are easily removed by distillation, but none of the methods found in the literature seemed suitable for the determination of small amounts of *o*-xylene (b.p., 144° C.) and a new procedure was developed. The alkylbenzenes are separated from the styrene, 1,4-vinylcyclohexene and other olefinic compounds by treating the sample with aq. mercuric acetate soln. with subsequent steam distillation of the alkylbenzenes from the mixture, ethylbenzene being used as a carrier to aid in removing the *o*-xylene. The aq. mercuric acetate adds the groups –HgX and –OH to the olefinic double bond, the addition in general following Markownikoff's rule, mercury linking with the carbon atom having the most hydrogen atoms. In a few instances, particularly with the propenyl group, the mercuric salt oxidises the olefine to the glycol. Formation of an oily liquid sparingly sol. in water indicates organo-mercury compounds, whereas pptn. of mercurous acetate after prolonged steam distillation indicates formation of glycols. Both reactions may occur, but either brings about the desired result, *viz.*, the changing of olefines into compounds not volatile in steam. The separated alkylbenzenes are nitrated, and the dinitro compounds are treated with acetone and potassium hydroxide in accordance with the Bost–Nicholson colour reaction (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 190), in which the colour first formed by dinitromonoalkylbenzene is a deep blue and that formed by

dinitro-*o*-xylene a deep green. Since the blue colour gradually changes to a purplish red in presence of alkali, the unchanged green colour can be measured by means of a photoelectric colorimeter. Addition of monoethanolamine hastens the change of the blue colour and makes the red less intense. Connect a 300-ml, flat-bottomed, long-necked, vial-mouthed Florence flask fitted with a glass stand pipe with a 250-ml glass-stoppered Erlenmeyer flask connected in turn with a vertical condenser leading by means of an adapter to a Babcock milk-testing bottle graduated from 0 to 8%, each numbered graduation representing 0·2 ml. The glass connections should be narrow and short to avoid collection of a large vol. of water and rubber stoppers should be fitted. A shaker capable of holding the Erlenmeyer flask is needed; also a second shaker fitted with a small, internally-blackened box with a hinged cover containing a sponge-rubber mat with openings to take two 30-ml narrow-mouthed, French square type bottles with silver foil-lined screw caps. Another small internally-blackened box is also required. With samples containing more than 99% of styrene and less than 0·5% of *o*-xylene the procedure is as follows. To 60 ml of propylene glycol in the Erlenmeyer flask add 5 ml of the sample, determining its wt. by weighing an equal vol. Add 2 ml of xylene-free ethylbenzene and 75 ml of filtered mercuric acetate soln. (380 g of the anhydrous salt in 800 ml of cold water). Shake the securely stoppered flask in the shaking machine (*ca.* 280 times per min.) for 2 hr. Connect the flask with the distillation apparatus and steam-distil the ethylbenzene and *o*-xylene into the Babcock bottle, boiling the water in the steam generator before heating the contents of the Erlenmeyer flask and continuing distillation until the bottle is one-third full. Fill the bottle with water and centrifuge at 1500 r.p.m. for 5 min. Measure the vol. of the alkylbenzene layer, transfer it to a small vial for storage by means of a capillary tipped pipette, but complete the remainder of the analysis during the day, since the dinitro compounds are unstable. Pipette 0·05 ml into the neck of a dry 200-ml flask, rinse it immediately into the flask with 10 ml of a mixture of equal parts by vol. of nitric and sulphuric acids, shake the flask for a few sec., leave it for 1 hr. and finally allow it to cool in an ice-bath. Gradually add 25–30 ml of water and 10 ml of conc. nitric acid to dissolve or suspend the nitro compounds. Add a 5-ml aliquot of this soln. to 10 ml of water in a small separating funnel, and make the liquid alkaline with 1 ml of 50% potassium hydroxide soln., avoiding excess. Extract the liquid with 10 ml and then with 5 ml of ether, collecting the extracts in a dry 1-oz., narrow-mouthed, square bottle. Remove the ether by gentle evaporation leaving the nitro compounds and the water that was dissolved in the ether. Add 20 ml of acetone, 1 ml of monoethanolamine and 2 ml of 50% potassium hydroxide. Close the bottle tightly with a foil-lined screw cap and shake in the box on the shaker for 15 min. measured by a stop watch. Without stopping the watch place the bottle in the other box and allow it to stand so that the caustic soln. settles out of the coloured acetone soln. After 17 min. from the start of the shaking fill a 10 mm, 10 ml absorption cell with the soln. and immediately read the transmittance in the colorimeter, using a B660 and neutral grey filter with the transmittance of water at 100%. Ascertain the % of *o*-xylene from a standard curve prepared by subjecting known mixtures of *o*-xylene and ethylbenzene to the same procedure. Calculate the % of *o*-xylene in the original sample from the formula $\frac{A(B+C)DE}{\text{sample wt.}}$, where A is the vol. % of *o*-xylenes found colorimetrically, B is the vol. of alkylbenzenes measured in the Babcock bottle, C is a vol. increment correcting for mechanical loss and solubility of alkylbenzenes in water and determined empirically for the apparatus used, D is a correction factor necessary when impure *o*-xylene is used in preparing the standard curve and E is the sp.gr. (0·87) of *o*-xylene. In the investigation the *o*-xylene used in preparing the standard curve contained 6% of *m*-xylene and 2% of *p*-xylene, and the effect of factor D was negligible. A. O. J.

Identification of some Important Unsulphonated Azo-2-naphthol Dyes. L. Koch, R. F. Milligan and S. Zuckerman (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 755–756)—The simple semi-micro hydrogenation apparatus of Cheronis and Koeck (*J. Chem. Education*, 1943, **20**, 488), obtainable from the Wilkens–Anderson Co., Chicago, is adaptable to the reduction of azo dyes in peroxide-free dioxan. Subsequent isolation of the reduction products by means of immiscible solvents and their direct conversion into benzoyl derivatives avoids the separation of the unstable free amines. Purify the dye by crystallisation from dioxan, adding water to induce pptn. if necessary. Suspend 0·05 g of Adams–Vorhees platinum oxide in 25 ml of peroxide-free dioxan in the Cheronis hydrogenating unit and bubble hydrogen through the suspension for 2 to 5 min. to reduce the platinum oxide to colloidal platinum black. Add 1 g of the dye and 2·5 ml of conc. hydrochloric acid to the suspension, immerse the hydrogenating unit in water at 80°–90° C., and pass hydrogen through at a rate to maintain continuous agitation. When hydrogenation is nearly complete rinse down any dye particles adhering to the sides of the tube with 5 to 10 ml of dioxan. If a ppt. of the reduction products forms in the acidified dioxan soln., redissolve it by adding 5–10 ml of water and filter the soln. into a 500-ml Squibb separating funnel. Buffer the filtrate with 250 ml of 5% sodium acetate soln. and extract, with two successive 100-ml portions of ether, the amino-2-naphthol (indicated by a blue fluorescence) and any primary monoamine. Mix the aq. layer containing any water-sol. primary polyamine intimately with 5 ml of benzoyl chloride and wash the combined ethereal extracts with two 50-ml portions of water, running the washings into the benzoylated mixture. Make the aq. liquid alkaline with 10 g of solid sodium hydroxide and, after stirring the soln. frequently at room temp. during 30 min., expel dissolved ether on the steam-bath. Collect the benzoyl derivative of the diamine or triamine by filtration, wash it thoroughly with water and crystallise it from a suitable solvent. To separate amphoteric amino-2-naphthol from the primary monoamine, extract the ethereal soln. with four 50-ml portions of 2% sodium hydroxide soln. followed by two 50-ml portions of water, and run the alkaline extracts into 5 ml of benzoyl chloride with vigorous stirring. Remove dissolved ether on the water-bath, cool to room temp., collect the benzoyl derivative by filtration and, after washing with water, crystallise it from ethanol. Extract the ethereal soln. (containing the primary monoamine) with four 50-ml portions of *N* hydrochloric acid and 50 ml of water. Expel dissolved ether by heating, cool the acid soln., add 10 g of solid sodium hydroxide, and treat the mixture with 5 ml of benzoyl chloride. Leave the pasty mass of the benzoyl

derivative overnight, then collect it by filtration, wash it thoroughly with water and crystallise it from a suitable solvent. A table of the m.p. of 32 dyes and the benzoyl derivatives of the reduction products of their diazo components is given.
A. O. J.

Determination of Wax in Cotton Fibre. A New Alcohol Extraction Method. C. M. Conrad (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 745–748)—The following method is proposed for the determination of total wax in cotton fibre and similar materials. Extract 5 to 10 g of well-cleaned fibre in a coarse thimble in a large Soxhlet extractor (50 × 250 mm) with 250 ml of 95% alcohol for 6 hr., adjusting the source of heat so that the liquid siphons over at 3 to 4 min. intervals. Remove the sample and thimble and distil alcohol into the extraction compartment until only 75 to 85 ml of liquid remain in the flask. Transfer the warm alcoholic extract into a 500-ml separating funnel, rinsing the flask with several 5-ml portions of hot alcohol, and finally adding alcohol until the vol. is *ca.* 100 ml. Add 100 ml of chloroform to the alcoholic liquid and mix to form a homogeneous soln. Add 75 ml of water, agitate gently until the chloroform layer separates, and leave (overnight if necessary) until the layers become clear. Draw off the chloroform layer and re-extract the aq. layer with 50 ml of chloroform, again allowing the layers to stand until clear (*ca.* 2 hr.). Practically all the wax is now in the chloroform layers. Remove the aq. alcoholic residue from the separator and, without washing the separator, replace the chloroform extract in it, add 100 ml of water, shake gently, run the chloroform layer into the original flask and extract the aq. layer with two 5-ml portions of chloroform. Remove the solvent from the combined chloroform extracts in tared 100-ml beakers on the water-bath, keeping the beakers less than half full to avoid superheating. When the residue of wax is apparently dry, cool and weigh the beakers, reheating for 30-min. periods on the water-bath until the wt. is constant.
A. O. J.

Colorimetric Determination of Quaternary Ammonium Salts. M. E. Auerbach (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 739)—The method previously described (*Id.*, 1943, **15**, 492) has been modified by substituting benzene for ethylene dichloride. To 50 ml of water containing 50 to 75 μg of quaternary salt in a 125-ml separating funnel add 5 ml of 10% sodium carbonate soln., 1 ml of fresh 0·04% bromophenol blue soln., and exactly 10 ml of benzene. Shake steadily for 3 min., swirl after a short settling, and set aside for complete separation. Rinse a 15-ml centrifuge tube with part of the aqueous layer, discard this, and run the benzene layer into the tube. Cover with a clean rubber diaphragm stopper and centrifuge at 1000 r.p.m. Transfer the clear extract to a dry Klett–Summerson colorimeter tube and take the reading with a light-filter No. 60.
W. R. S.

Ground Starch as an Indicator. H. A. Conner and R. W. Bovik (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 772)—Suspend the starch in twice its weight of alcohol and grind it in a ball mill for at least 80 hr. Microscopic inspection should reveal almost total disintegration of the granules. Collect the ground starch, dry and re-grind, and keep it in an ordinary pepper shaker. It keeps indefinitely, and is added to the soln. towards the end-point of an iodimetric titration, the powder dissolving readily and almost completely in cold water.
W. R. S.

Inorganic

Salicylimines as Precipitants for certain Metals. F. R. Duke (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 750–751)—The salicylimine reagent is prepared by dissolving 1 g of salicylaldehyde in 100 ml of "10 to 90 ammonium hydroxide." The 5-nitro, 5-bromo, and 3,5-dibromo derivatives can be obtained in the same manner from substituted salicylaldehydes; 5-bromosalicylaldehyde requires 100 ml of strong ammonia per 0·25 g. The reagents are stable for 8 hr. Aqueous methylamine (25%) can be used in place of ammonia, giving stable solns. of N-methylimine. All tests are carried out in 5% sodium tartrate soln. to prevent pptn. of metallic hydroxides, the imine ppts. being soluble in acids and insoluble within the *p*H range 7–8 to 11–12. The following metals react: copper (green ppt.); nickel (orange or yellow); vanadium after reduction with zinc (red); palladium (yellow); cobalt (brown); iron (red). The pptn. of copper and nickel was found to be quantitative, the ppts. being collected in sintered-glass crucibles and dried at 100° C. The determination of copper in brass and bronze by salicylimine is described.
W. R. S.

Detection of Bismuth with Brucine Citrate. P. W. West and J. V. Tokos (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 761–762)—The reagent is prepared by dissolving 12 g of brucine in a soln. of 100 g of citric acid in 100 ml of water, and heating until the alkaloid is completely dissolved. Borate inhibitor soln. is made by mixing equal vols. of *M* solns. of boric acid and sodium hydroxide. Place a drop of the unknown soln. on a spot-plate, add 1 drop each of inhibitor, saturated sodium bisulphite soln., reagent, and 20% potassium iodide soln.; bismuth gives a brick-red ppt. at a limit concn. of 1 : 100,000. The test identifies 0·3 μg. No positive interferences were found, but 100 parts of cadmium, mercury, copper, silver, and lead to 1 of bismuth reduce the sensitivity and cause the bismuth ppt. to be deep orange instead of red. Brucine is considered the most satisfactory spot test without prior separation, and more selective than thiourea.
W. R. S.

Photometric Determination of Molybdenum in Metallurgical Products. H. Cox and A. A. Pollitt (*J. Soc. Chem. Ind.*, 1944, **63**, 375–378)—Vaughan's method for the macro determination of molybdenum, using the Spekker photoelectric absorptiometer (*Inst. Chem. Monograph*, 1941, p. 17) depends on the development of a molybdenum colour with sodium thiocyanate. In the standard procedure it is recommended that the coloured soln. be kept for 15 min. before the photometric measurements are made. The present investigation shows that when the standard method is applied to samples in the range 0·1 to 1·0% of molybdenum, the coloured soln. continues to fade during the first 2 hr. after preparation. The use of perchloric acid, however, has a stabilising effect on the thiocyanate colour, and the following procedure is found to be satisfactory. *Reagents*—Perchloric acid, 72% AnalaR; sulphuric acid, 50% by vol.; ammonium thiocyanate, AnalaR, 5% aq. soln.; stannous chloride, AnalaR, 10% in 5% hydrochloric acid. *Procedure*—For molybdenum in steels, dissolve 1 g of the sample in 20 ml of perchloric acid and 10 ml water in a 250-ml beaker, evaporate to fuming, cool, dilute with 50 ml of water to dissolve the salts, and make up to 100 ml in a graduated

flask. Pipette 10 ml of this soln. into a 50-ml graduated flask, add 10 ml of 50% sulphuric acid and then 10 ml of the ammonium thiocyanate soln. and 10 ml of the stannous chloride/hydrochloric acid soln. Cool and make up to volume with water. Prepare a blank, from a second 10-ml portion from the 100-ml flask, in the same manner but omitting the thiocyanate soln. Keep the coloured soln. and blank for 15 min. and then measure on the absorptiometer, using 1-cm cells and Ilford Spectrum Green filters No. 604. The molybdenum is then determined by reference to a calibration graph prepared from synthetic standard samples.

B. S. C.

Microchemical

Micro-determination of Chlorine and Bromine in Organic Compounds. R. Grangaud (*Bull. Soc. chim.*, 1943, **10**, 236–238)—The compound is decomposed by combustion and the chlorine or bromine is obtained as the sodium halide. The latter is estimated by Sendroy's method (*J. Biol. Chem.*, 1937, **120**, 335; ANALYST, 1937, **62**, 828), which consists in treatment with silver iodate, whereby silver chloride or bromide is pptd. and sodium iodate is formed. The latter is determined by titrating the iodine liberated on adding potassium iodide and acidifying. Thus 6 atoms of iodine are titrated for each atom of chlorine or bromine pptd. Weigh 3 to 5 mg of the compound in a platinum boat or in a sealed capillary. Carry out the combustion in a Pregl–Soltys spiral tube, absorbing the halogen in sodium carbonate soln.* containing sodium bisulphite in the usual manner ("*Quantitative Organic Microanalysis*," Pregl–Roth, trans. E. B. Daw, London, 1937, pp. 94–104). Into the test-tube which protects the tip of the spiral tube introduce 9 ml of water and 1 drop of sodium bisulphite soln. (prepared by treating satd. sodium carbonate soln. with sulphur dioxide). Draw this up into the combustion tube and allow it to flow slowly into a 50-ml platinum capsule. Repeat, using first 10 ml and then 11 ml of water without addition of bisulphite. Rinse the interior of the tube and the tip with 2 to 3 ml and a few drops respectively of water. To the combined washings add 11 drops of perhydrol and evaporate to 5 ml on the water-bath. Add 2 *N* nitric acid, drop by drop, until effervescence just ceases. Then add a further 11 drops of acid. Transfer the soln. to a graduated cylinder having a ground stopper, rinse the capsule with 4 1-ml portions of water, and add the rinsings to the contents of the cylinder. Dilute until the halide concn. is approx. 0·003 *N* (*i.e.*, 1·06 mg of Cl^- or 2·4 mg of Br^- in 10 ml). Add *ca.* 50 mg of silver iodate* weighed on the tip of a micro-spatula, stopper and shake vigorously for 2 min. Leave for a few sec., rinse the stopper and neck with 1 ml of diluted alcohol (2+1), swirling so that the alcohol does not float. Transfer by siphon to a Pregl filter-tube (Pregl–Roth, p. 98), the fritted plate of which is covered with a moderately compact 2-mm layer of asbestos fibre. Filter at the rate of 11 drops per sec., collecting the filtrate in a 100-ml Erlenmeyer flask, the stopper of which has a second hole to permit suction. The tip of the siphon should be kept at 2 to 3 mm below the surface of the liquid in the cylinder. Rinse with 1 ml of diluted alcohol, then twice with 95% alcohol, siphoning over successively. Detach the siphon and rinse the walls of the filtering tube with 1 ml of 95% alcohol. Add to the filtrate and washings 2 ml of freshly-prepared 10% potassium iodide soln. and 10 ml of *N* sulphuric acid. Leave for 1 min. and titrate the liberated iodine with 0·02 *N* sodium thiosulphate, adding 5 drops of 1% starch paste near the end-point and introducing the last drops of thiosulphate soln. at 10 to 15 sec. intervals. Prepare the thiosulphate soln. daily by diluting a 0·1 *N* soln. To check the titre, weigh 5 to 6 mg of potassium iodate, dissolve in 10 ml of water, add 2 ml of 10% potassium iodide soln., 10 ml of *N* sulphuric acid, and titrate with the dilute thiosulphate soln. The method is very sensitive and its precision is the same as that of the gravimetric process.

J. T. S.

* Dissolve 23 g of potassium iodate and 18 g of silver nitrate in 600 ml and 400 ml respectively of water. Add the latter soln., dropwise, to the former with constant stirring, filter, wash the ppt. twice by decantation and then on a Buchner filter with about twelve 100-ml portions of water until 10-ml portions of the filtrate on addition of 2 ml of 1 *N* sulphuric acid and a few crystals of potassium iodide liberate equal amounts of iodine. Dry *in vacuo* at room temp. in the dark, powder, and store in a brown bottle with a ground-glass stopper.

Micro-determination of Arsenic. A. Lespagnol, R. Merville and Mlle. Werquin (*Bull. Soc. chim.*, 1943, **10**, 378–80)—The method depends upon the reduction of arsenic to the elementary state by hypophosphorous acid. After separation, the arsenic is dissolved in iodine soln. containing hydrochloric acid, and the excess of iodine is titrated with sodium thiosulphate soln. A correction for the liberation of iodine by the action of air is obtained from a blank determination. Introduce 5 ml of the arsenical soln. into a conical centrifuge tube and add 5 ml of Bougault's reagent (dissolve 20 g of sodium hypophosphite in 20 ml of water and add 200 ml of hydrochloric acid (sp.gr. 1·17). Remove the pptd. sodium chloride by filtering through a pad of cotton.) Heat in boiling water for at least 30 min. and centrifuge. If a film of arsenic remains floating, sprinkle a little talc on the surface of the liquid and centrifuge again. Wash the residue several times with boiling water, separating each time by careful centrifuging. Add 1 ml of conc. hydrochloric acid and 10 ml of 0·1 *N* iodine containing 50 g of potassium iodide per litre. Triturate until the arsenic has dissolved completely and back-titrate with 0·1 *N* sodium thiosulphate in presence of starch paste. Make a blank determination by adding 10 ml of 0·1 *N* iodine to 1 ml of conc. hydrochloric acid. After 15 min. titrate with 0·1 *N* sodium thiosulphate. For quantities of 2 to 4 mg of arsenic the accuracy is 1 to 1·5%. With a few tenths of a mg separation of the ppt. is easier and addition of talc is often unnecessary. Five ml of 0·02 *N* iodine are added and the 0·005 *N* sodium thiosulphate is used for the titration. The accuracy is 5 to 10%, and the method is sensitive to *ca.* 0·01 mg of arsenic.

J. T. S.

Studies on the Micro-determination of Selenium in Toxicology. I. Preliminary Experiments on Selenium Sols. M. R. Dolique and S. Roca (*Bull. Soc. chim.*, 1943, **10**, 274–278)—In the colorimetric estimation of small quantities of selenium, sodium metabisulphite and glycerol are satisfactory reducing and stabilising agents respectively. In a medium which is 5 *N* with respect to hydrochloric acid, the colorimeter reading depends on both the temp. and time of heating. The optimum values are 70° C. and 7 min. respectively,

and are adhered to by use of a thermostat, followed by rapid chilling. Under these conditions the colorimeter reading is stable for 30 min. after removal of the sample from the thermostat. To the solution of selenious acid (or of a selenite) add successively 11 ml of 11 *N* hydrochloric acid, 1 ml of glycerin, and water to bring the vol. to 25 ml. Add 0·20 g of sodium metabisulphite, dissolve, and hold for exactly 7 min. in a thermostat operating at 70° C. Cool immediately under the tap. Examine in a photoelectric colorimeter, using a rose-coloured filter in front of one photocell with the liquid in a 5-mm cell in front of the other, and read the result from a calibration curve. As little as 0·01 mg of selenium may be estimated. The relative error for the range 1 to 0·1 mg of selenium is ±1–2%; while for the range 0·1 to 0·02 mg it is ±2–50%. Selenic acid (or a selenate) is not directly reduced by sulphurous acid, and must be converted into the selenious state. If the volume of the soln. exceeds 3 ml, neutralise and evaporate to 3 ml. Add 11 ml of 11 *N* hydrochloric acid and leave for 15 min. Add 1 ml of glycerin, dilute to 25 ml, and proceed as before. J. T. S.

Microchemical Determination of Free and Combined Silica in Mine Dust. S. R. Rabson (*J. Chem. Met. and Min. Soc. of S. Africa*, 1944, 45, 43–49)—Available methods for the separate determination of free and combined silica in dusts are briefly discussed, and a microchemical method relying on the use of selective reagents is described. *Method*—Collect air-borne dust by drawing the air through a 5-cm filter-paper, previously dried and weighed. Dry again at 110° C. and weigh in a stoppered weighing bottle. Extract with benzene, dry and re-weigh; the loss of weight represents oil. Char the paper in a weighed 10-ml platinum crucible, remove the lid, and heat the crucible for several hours at 400° C.; the loss in weight, corrected for the weight of the filter-paper, gives the amount of carbonaceous matter. Heat the contents of the crucible with 5 ml of water, centrifuge, decant the liquid, dry the crucible, heat to 400° C. and re-weigh; the loss of weight represents soluble salts. At this stage the weight of the residue should preferably be 5 to 20 mg. Heat the contents of the crucible with 2 ml of conc. hydrochloric acid for 15 min. to dissolve all iron oxide. Dilute the acid, centrifuge, and transfer the liquid to a 25-ml standard flask. Wash the residue with hot 1% hydrochloric acid, centrifuge, and transfer the liquid to the flask. Neutralise the soln. with silica-free 10% sodium hydroxide soln., using a trace of phenolphthalein as indicator, acidify with 0·5 ml of 5 *N* hydrochloric acid and adjust to 25 ml. Use 10 ml for the colorimetric determination of the dissolved silica by the method described later and the remainder for the determination of iron by the thiocyanate method. Dry the crucible and heat at 950–1,000° C. for 30 min. to decrease the solubility of the quartz. Add 1 g of powdered potassium pyrosulphate (prepared by heating potassium bisulphate in a platinum basin until spattering ceases and sulphur trioxide is freely evolved) and heat the covered crucible in a muffle furnace at 550° C. for 1 hr. Cool, heat with 5 ml of 1% hydrochloric acid for 5 min., stirring frequently. Rinse down the rod (a stout platinum wire) and the sides of the crucible, centrifuge, and decant the soln. into a 100-ml standard flask. Add to the contents of the crucible 5·0 ml of silica-free 1% sodium hydroxide soln., heat nearly to boiling in 1 min., stirring continuously, and maintain the covered crucible at 90° C. for exactly 5 min., stirring at 1 min. intervals. Remove the crucible from the hot-plate, neutralise the alkali with 0·25 ml of 5 *N* hydrochloric acid and add a further 0·2 ml of the acid. Centrifuge, and decant the soln. into the 100-ml flask. Wash the residue with 5 ml of 1% hydrochloric acid, centrifuge, and transfer the liquid to the flask. Dilute the soln. to 100 ml and determine the silica colorimetrically, taking care that the acidity of the aliquot used is correctly adjusted. This value gives the combined silica in the sample plus some dissolved quartz. Treat the residue in the crucible with a further 5·0 ml of 1% sodium hydroxide soln., repeating the procedure given above except that the liquid is diluted only to 25 ml. Determine the silica dissolved by the second treatment, double the figure and subtract from the value for combined silica. The factor of 2 was determined by expts. on quartz. The quartz left in the crucible contains some undecomposed silicates. Add 0·5 ml of hydrofluoric acid and a micro-drop of sulphuric acid, evaporate to dryness, ignite and weigh. Separate the residue (the basic portion of the undecomposed silicates) from the crucible with hydrofluoric acid and ignite and weigh the crucible. To the weight of the residue thus found add half its weight of silica to approximate to the weight of the silicate. (The final weight of the crucible after cleaning must be taken as the tare because of the appreciable loss of weight during the pyrosulphate fusion.) The weight of the pure quartz (free silica) is obtained by subtracting from the weight of impure quartz the weight of undecomposed silicate and adding the weight of quartz dissolved in the two sodium hydroxide extractions. The amount of combined silica found by the first sodium hydroxide extraction must have subtracted from it the correction for dissolved quartz and added to it the silica in the undecomposed silicates and the silica dissolved during the removal of iron oxide. *Colorimetric method of silica determination*—To 10 ml of test soln. add 0·2 ml of 5 *N* hydrochloric acid and 0·5 ml of 10% ammonium molybdate soln. Mix, leave for 10 min., and compare in a colorimeter with a soln. containing 0·1350 g of potassium chromate and 5 g of borax per litre, which is equiv. to 0·025 mg of silica per ml of the original test soln. Interference by phosphate may be prevented by adding 0·2 ml of 15% oxalic acid soln. to the test soln. after developing the colour. Samples of rock do not require the preliminary treatment given to dusts. They are finely ground, weighed into the crucible, ignited, and fused with pyrosulphate. The method is satisfactory for rocks found in the Witwatersrand area, but it is known that some silicates, notably felspars, are only slightly decomposed by pyrosulphate fusion. L. A. D.

Micro-technique for the Size Grading of Mine Dust. S. R. Rabson (*J. Chem., Met. and Min. Soc. of S. Africa*, 1944, 45, 34–43)—Determination of the size grading of dust is of importance when studying silicosis, and methods giving the weights of the various fractions have some advantages over the particle counting method often used. The procedure described uses a small 325-mesh sieve and a fractional sedimentation apparatus. By the simpler modification a 5–20 mg sample is divided into 3 fractions, *viz.*, particles of diam. $>50\,\mu$, 5 to $50\,\mu$ and $<5\,\mu$; a more elaborate procedure allows division of a 50-mg sample into six fractions ranging in particle size from $>50\,\mu$ to $<2\,\mu$. The sedimentation apparatus consists of

a weighing bottle, 7·5 cm high and 2·5 cm diam., and a siphon to remove a predetermined depth of suspension without disturbing the sediment. Sedimentation is from distilled water containing 5% of abs. alcohol as dispersant. Settling times are calculated from Stokes's law,

$$V = \frac{(S-s)gd^2 \times 10^{-8}}{18\eta},$$

taking the mean sp.gr. of the dust (S) to be 2·8, the viscosity of the liquid to be 0·0128 poise at 20° C. and using a shape factor of 0·7 which was determined by observations on crushed quartz. With these constants $V = 0{\cdot}000054d^2$ and the times for dust particles to fall 2 cm are—

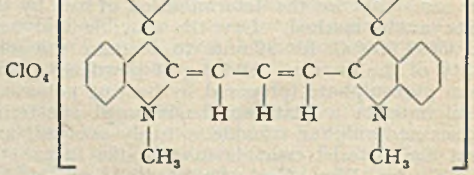
Size	Time	
μ	Hours	Min.
50	—	¼
20	—	1½
10	—	6
5	—	24
2	2	30
1	10	—
0·5	40	—

Method—Collect air-borne dust on a filter-paper and free it from oil and paper by ignition overnight at 400° C. Wash with hot distilled water to remove soluble salts and recover the dust by centrifuging. The determination must be completed without allowing the dust to dry, in order to avoid aggregation, and the weight of sample taken must be found by adding together the weights of the separate fractions. Mix the dust with a few ml of water-alcohol mixture and wash through the small sieve into the sedimentation bottle. Wash the oversize particles from the sieve into a 10 ml-beaker, centrifuge, decant the liquid, dry and weigh the solid, *i.e.*, the particles $>50\,\mu$. Dilute the suspension in the bottle with water-alcohol mixture to a mark 2 cm above the level to which the siphon drains the vessel. Stopper, shake vigorously and leave for 24 min. Insert the siphon carefully, start the flow by blowing gently and collect the liquid in a 10-ml beaker. Centrifuge and decant the liquid. Adding more water-alcohol mixture to the bottle, repeat the operation until the supernatant liquid is clear after 24 min. settling, collecting all the siphonates in the one beaker. Five to seven sedimentations are generally required. Dry and weigh the solid accumulated in the beaker, which comprises the particles $<5\,\mu$. The fraction of the sample between 5 and $50\,\mu$ in size remains in the bottle and should be rinsed into a beaker, centrifuged, dried and weighed. A 50-mg sample may be divided into 6 fractions by an extension of the method. Wash the sample through the sieve into a sedimentation bottle; the sieve retains the $>50\,\mu$ fraction. After 1½ min. siphon the liquid into a second bottle; after 6 min. in the second bottle siphon into a third; after 24 min. in the third siphon into a fourth, and after 2½ hr. in the fourth into a beaker. Repeat the whole sedimentation process until the supernatant liquids are quite clear after the correct settling period. Then the fractions are sized as follows: on the sieve, $>50\,\mu$; 1st bottle, $50–20\,\mu$; 2nd bottle, $20–10\,\mu$; 3rd bottle, $10–5\,\mu$; 4th bottle, $5–2\,\mu$; beaker, $<2\,\mu$. The method is shown to give useful quantitative results with air-borne mine dusts, but caution must be used when considering mineral residues from lung tissues, as both aggregation and loss of fine particles may result from the acid destruction of the organic matter and from ignition of the residue. L. A. D.

Physical Methods, Apparatus, etc.

Apparatus for Automatic Control of Electrodeposition with Graded Cathode Potential. C. W. Caldwell, R. C. Parker and H. Diehl (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 532–535)—Electrodeposition with graded cathode potential, introduced by Sand and developed by him and his co-workers (*cf.* "*Electrochemistry and Electrochemical Analysis*," Vol. II, London, 1940), permits very useful separations of metals. The automatic control apparatus described eliminates the need for continuous attention during the process and makes it more rapid, since an initial current larger than that which can be controlled by manual adjustment may be used. The apparatus, which is in the form of a compact assembly, maintains the cathode potential to within 10 millivolts of the desired value. It consists of 3 main portions, *viz.*, a rectifying unit operated from the A.C. mains supplying low voltage D.C. for the electrolysis, an amplifier-relay system to control the cathode potential, and a valve voltmeter to measure the latter. D.C. is obtained by using a selenium rectifier which is fed by a tapped-secondary step-down transformer. The rectified current is smoothed by an inductance-condenser system and passes to the electrodes through a shunted milliammeter. The primary of the transformer is supplied from the A.C. mains by means of a "Variac" (auto-transformer with variable output voltage), which may be operated either by hand or by an electric motor governed by the control system. The latter is a 2-stage amplifier which drives an A.C.-operated gas-filled tetrode valve. As the cathode potential increases, the critical "firing" potential of the tetrode is reached and it suddenly passes a current large enough to close a relay which causes the motor to operate the "Variac." When the cathode potential has been reduced to the pre-set value, the motor stops. Owing to stabilisation difficulties, the amplifier is battery-operated, but the batteries last 6 months in continuous operation. The valve voltmeter is the simple battery-operated design of Garman and Droz (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 398). Electrolysis is usually complete in 20 to 40 min. The application of the apparatus to the separation of copper from tin is described. J. T. S.

Standard Substance for Spectral Absorption Measurements. H. v. Halban and K. Wieland (*Helv. Chim. Acta*, 1944, **27**, 1032–1038)—A useful reference material for spectral absorption measurements in both the visible and ultra-violet regions is the perchlorate of the dyestuff Astrophloxin FF (*Ges. Chem. Ind., Basel*) (mol. wt. 456·7), which has the formula



The molecular extinction coefficient of this material in water solution has been determined and is tabulated throughout the wavelength range 2175A to 5750A at maximum intervals of 50A. B. S. C.

Techniques of Quantitative Spectrographic Analysis. J. R. Churchill (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 653–670)—This is the first of

a series of papers on modern analytical techniques. Stress is laid on the limitations, as well as the advantages, of the methods discussed. The various topics dealt with include: methods of exciting the spectrum; influence of characteristics of the sample on the resulting spectrum; the spectrograph; the photographic technique; photometry of the photographic plate; calibrations and calculations. The characteristic features of six makes of spectrograph are compared, and also of three types of microphotometer. Special emphasis is laid on the rigorous standardisation and care that are necessary in the use of the methods under discussion. See also **Equipment used in Quantitative Analysis. Proposed Minimum Requirements. C. L. Guettell** (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 670–675). B. S. C.

Determination of Members of the Brenthol or Naphtol AS Series by Ultra-violet Absorption. C. H. Giles (*J. Soc. Dyers and Col.*, 1945, **61**, 47–49)—A previous method (Giles *J. Soc. Dyers and Col.*, 1944, **60**, 279) for the determination of the Brenthol or Naphtol AS series (arylamides of 2-hydroxy-3-naphthoic acid and related compounds) involves the formation of azo solns. by coupling with diazo-sulphanilic acid in buffered 50% aqueous ethanol, and photometric measurements with visible light, using the Spekker photoelectric absorptiometer. A simpler and more accurate method has now been developed making use of the high absorption in the ultra-violet region of uncoupled Brenthol solns., which are of insufficient tinctorial value to be analysed photometrically by the use of visible light. The Spekker Absorptiometer was used with a mercury lamp and a filter to isolate radiation of wavelength 3650A. Cells of 1 cm thickness were employed throughout. As a precaution against any error introduced by the dispersing agent, the water control cell in the absorptiometer contained a soln. of alkali and dispersing agent in the same concns. as those in the diluted Brenthol soln. under test. The substantivity of Brenthol AT for cotton, linen and viscose rayon has been determined by the new method. B. S. C.

Polarographic Determination of Sodium in Aluminium and its Alloys. P. Urech and R. Sulzberger (*Helv. Chim. Acta*, 1944, **27**, 1074–1079)—The effect of small concns. of sodium on the grain size of aluminium and aluminium alloys is important. A spectrographic method has been developed (Rohner, *Helv. Chim. Acta*, 1944, **27**, 268) for estimating such small concns., and the polarographic technique appeared to offer the best alternative method of checking the values of sodium content in the range 0·001 to 0·01%. The procedure involves a treatment with hydrochloric acid in order to increase the sodium concn. of the sample, and the formation of a tetramethylammonium-aluminium complex to prevent interference by the aluminium. Starting with 1 g of the metal, the method gives a sodium concn. of 2×10^{-4} to 2×10^{-3} *N*, which is sufficiently high to render unnecessary the removal of oxygen from the soln. It is important to use the purest reagents available and to carry out blank tests. The sodium is estimated from the height of the polarogram step at 2·20 volts. The method gives results in quite reasonable agreement with the spectrographic method. B. S. C.

New Procedure for Evaluating the Opacifying Properties of Pigments. A. P. Adrian (*Paper Trade J.*, 1944, **119**, 12th Oct., *T.A.P.P.I. Sect.*, 149–155)—In existing methods used in the paper industry the pigment is incorporated into a sheet of paper, and the opacity of the sheet is measured by one of the usual optical methods. In the present method the pigment is formed into a film as follows. To 300 ml of distilled water in the bowl of a mechanical mixer add sufficient air-dry pigment to form a fairly conc. slurry (*e.g.*, 254 and 116 g of a water-dispersed and non-water dispersed titanium pigment, respectively). Mix at moderate speed for 1 hr., dilute with distilled water to a concn. of 0·15 g of oven-dry pigment per ml, and dilute sufficient of this to 1000 ml to produce a final concn. of 0·31 g per 150 ml. Stir for 10 min. in a high-speed malted-milk mixer, dilute 150 ml to 300 ml, and stir for 5 min. Place a film of sheet ethyl cellulose (Ethocel) around the inner wall of the bowl of a Sharples supercentrifuge, rotate at 16,000–17,000 r.p.m., and introduce the 300 ml of suspension into the bowl through the base, from a height of 7 ft., using a glass funnel and rubber tube attached to a 1/16-in. injection tube. Then rotate at 20,000 r.p.m. for 7–8 min. The pigment film is all deposited on the backing and may be removed from the bowl with it. Dry in air for *ca.* 2 min., replace the film in an inverted position, and repeat the deposition, using a further 300 ml of suspension. Dry in air for at least 1 hr. Use central horizontal strips (2·0 × 1·50 in.) for the opacity measurements. The pigment is now in such a form that there is an appreciable difference in its reflectance when it is backed by a white and by a black surface; this enables opacity measurements to be made in terms of contrast ratios. The use of the Kubelka and Munk equation for this purpose is described. The G.E.C. recording spectrophotometer (Hardy) was used for these measurements, with a magnesium carbonate block (absolute reflectance, 0·97) as standard. The method gives reproducible results for measurements of the specific scattering coeff. and specific absorption coeff. It is suitable for measurements of the influence of the compacting of pigment particles, of particle size, and of the presence of mixtures of pigments on the light scattering properties of pigment films. J. G.

Apparatus for Measuring Rate of Gas Penetration through Food-packaging Materials. F. R. Smith and M. Kleiber (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 586)—The partial pressure of oxygen in the surrounding gas is a major factor in the spoilage of many dehydrated foodstuffs. Previous methods for measuring the gas permeability of film materials (*cf.* Todd, *Paper Trade J.*, 1944, **118**, 32; ANALYST, 1944, **69**, 226) do so without regard to changes in partial pressure such as will occur with an undesirable material of high oxygen- and low nitrogen-permeability. The apparatus described consists of a vertical glass diffusion chamber (outside diam. 6 cm, length *ca.* 18 cm), to the upper open end of which the packaging material, in the form of sheet, pouch or sack, is secured by adhesive tape or rubber bands. The joint is sealed with mercury. A system of stopcocks and mercury vessels permits satisfactory replacement of the air within the apparatus by nitrogen under constant positive pressure, and also enables samples of the gas within the chamber to be withdrawn for analysis by a modified Haldane apparatus (Kleiber, *J. Biol. Chem.*, 1933, **101**, 583). A sample of gas is taken

initially and a second at the completion of the test. The increase in oxygen content is used to calculate the rate of penetration/unit area/unit time. J. T. S.

Determination of Air Resistance of Paper. Anon. (*Paper Trade J.*, 1944, **119**, 7th Dec., *T.A.P.P.I.Sect.*221–222)—The corrected T.A.P.P.I. Tentative Standard Method (T 460 m–43) described is intended for paper products which permit the passage of 100 ml of air in 2 sec. to 30 min., excepting those which cannot be securely clamped against surface and edge leakage (*e.g.*, corrugated papers). The conditioned sample is held between clamps so as to close the top of a hollow, vertical, open-ended, light metal cylinder, which can slide freely up and down inside an outer vertical cylinder containing a standard light spindle oil (viscosity, 60–70 sec. Saybolt Universal at 100° F.). The time taken by the inner cylinder to sink a marked distance in the oil in the outer cylinder, under standard conditions, is a measure of the air resistance of the paper, which is reported as the average no. of sec. for 100 ml of air to be displaced through 1 sq. in. of paper (reproducibility, 5% for 40 sec.; 10% for 300 sec.). The apparatus is tested for air leaks by using tin-foil in place of the sample; the leakage should not exceed 50 ml in 5 hr. J. G.

Surface Printing as an Aid in the Investigation of Faults in Textiles. K. Schwertassek (*Melliand Textilberichte*, 1943, **24**, 79–81)—Soak a strip of the sample in 1·0 *N* ferric chloride, remove excess of soln. by light pressure against damp blotting paper, and press the cloth firmly between glass photographic plates against a strip of writing paper which has been soaked completely and uniformly in 3% potassium thiocyanate soln. and dried slowly to avoid cockling. The resulting print on the paper may be photographed and it shows up fine structural differences on the web, and especially streaks on the surface of rayon textiles. With heavily dyed, thick fabrics 5% potassium ferrocyanide soln. is preferable to the thiocyanate soln., but the prints are less permanent and do not reproduce photographically so well. J. G.

Reviews

METALLURGICAL ANALYSIS BY MEANS OF THE "SPEKKER" ABSORPTIOMETER. By F. W. HAYWOOD, Ph.D., F.R.I.C., and A. A. R. WOOD. Pp. viii + 128. London: Adam Hilger, Ltd. 1944. Price 18s.

The appearance of E. J. Vaughan's two monographs on "The Use of the Spekker Photoelectric Absorptiometer in Metallurgical Analysis," published by the Institute of Chemistry in 1941 and 1942, gave a tremendous impetus to the application and further development of absorptiometric methods and numerous requests were made for a "standard" text-book on the subject. The present work is the result of this demand and the authors are to be congratulated on the general excellence of a compilation which will undoubtedly be welcomed and should enjoy a wide sale.

The book is divided into two parts. In the first part the authors deal with fundamental principles and the manipulation and operation of the absorptiometer. In this part they have perhaps erred on the side of over-elaboration, with some unnecessary repetition, but they certainly give the reader the essential information required for successful operation of the instrument without previous acquaintance with either its principles or operation. Very wisely they devote a section to the limitations of absorptiometric analysis and draw attention to the factors affecting the accuracy of the results.

The second part of the book deals with the methods of absorptiometric analysis developed during the last three or four years as applied to standard engineering alloys. From personal experience, I can state quite definitely that girls and youths after suitable training, and if in possession of a Higher School Certificate with Chemistry as the principal subject, experience no difficulty in reporting analytical results obtained by absorptiometric methods of a sufficiently high order of accuracy to be accepted, without question, for ordinary routine metallurgical analysis, so far as most steels and many non-ferrous alloys are concerned.

Readers of the book will certainly appreciate the Composite Schemes of Analysis interspersed throughout the book. A great advantage of these composite schemes is the very material saving in the costs of analytical reagents as compared with those involved when the more conventional chemical methods of analysis are used. For instance, the analysis of a steel containing chromium, cobalt, copper, manganese, molybdenum, nickel and vanadium can be carried out on an initial weight of 2 g of the material and, moreover, in a much shorter time than when purely chemical methods are employed in the determination of these elements.

At the same time, however, it must be appreciated that the accuracy of the results depends on the compositions of the reagents and alloys, which have been analysed by purely chemical means, employed in the construction of the calibration curves. For instance, in the analysis of, say, a modern high speed steel, it is most desirable, when one specific element is being determined, that the calibration graphs should be checked by using a "standard" steel of similar composition, in view of the influence of dissolved salts, coloured or uncoloured.

Since the manuscript was written further refinements have been made in the methods of analysis, but this is hardly surprising having in mind the fact that the application of the absorptiometer is relatively new. Some teething troubles still exist, particularly in regard to the influence of interfering elements, but there is little doubt that these will successfully be overcome.

The book can be confidently recommended to all interested in the subject, although the price seems rather high, even in war-time, for a work of 125 pages.

EDWIN GREGORY

REPORTS OF THE PROGRESS OF APPLIED CHEMISTRY. Vol. XXIII. 1943. Issued by the Society of Chemical Industry. Pp. 459 (excluding indexes). Price to members, 20s.; non-members, 11s. 6d.

Most of the contributors to the volume deplore the paucity of material to report upon, but the general chemical reader will still find much that is of interest. Despite the reduced output of original papers, due to war-time needs and restrictions on publication, much that has been published is of first-class quality and likely to be as useful in peace as in war. A few notes on general tendencies may be of interest. An ever-diminishing supply of coal has continued to direct the attention of producers and consumers to methods of economy, every aspect of which has received attention. The gas and allied industries have likewise been largely concerned with increasing their own efficiency and supplying the needs of others. A further investigation into methods for determining volatile matter in the proximate analysis of coal, resulting in a lower temperature specification, has provoked adverse criticism. The report on mineral oils deals mainly with records of work in America directed towards production of high octane petrol and the so-called synthetic rubbers; while real rubber, it is said, is submitted to destructive distillation and the hydrogenated and alkylated product used by the Japanese in Malaya to increase the octane value of motor spirit. Sodium nitrite is favourably reported upon as an inhibitor of corrosion in pipe-lines. Work on the synthetic fibres continues, and the use of the electron microscope is leading to interesting results. The pulp and paper trade has devoted itself mainly to the economics of its processes, in which the possibilities latent in waste sulphite liquor afford an interesting chemical study. It is noted that economy in chlorine for pulp bleaching is limited, for material to be used for packing products liable to infection, by its germicidal properties.

Some interesting summaries dealing with raw materials and glass melting have appeared. The low coefficient of expansion and low thermal conductivity of glass have been advantageously utilised in making engineering gauges, for which purpose it is stated to be superior to tool steel, In the ceramic industry, the main interest in refractories has been to keep the iron and steel industries supplied with essential needs. A report of fundamental work on the hydration of calcium aluminates is of interest in the cement section.

Foundry sands and ingot moulds have been subjects of research in the iron and steel trades. Reports from the electro-chemical and non-ferrous metal industries include an account of the use of nickel-plated wire to replace the pure metal in filament supports for electric light bulbs, and plating with hard chromium to reduce wear and replace metal lost by abrasion in machine parts. Electro-deposition has reduced the weight of tin per basis box of tinplate to $\frac{1}{2}$ lb. and makes it possible to plate mild steel strip at the rate of 1500 sq.ft. per minute. A new test for porosity and resistance to corrosion of this material also receives notice.

In the section dealing with oils, fats and detergents a mixture of ethyl alcohol and trichloroethylene is suggested as a means of extracting oil from soya. Methods for determining unsaponifiable matter have been the subject of an exhaustive investigation in America; the "S.P.A. method," although not the simplest or the most rapid of the four examined, received favourable comment and gave the highest results.

The section of the report dealing with plastics describes *inter alia* an interesting field of research that is being developed in the border-line between the thermo-plastic and thermo-setting regions. Extruded pipes for domestic plumbing, and leather substitutes are now among the possibilities.

In the leather section the opportunity has been taken to review recent advances in the interesting but difficult and complex chemistry of the amino acids of collagen, and in that of the tanning process.

Continued progress in the sugar and starch industries is described in a very readable article, in which attention is drawn to the publication of a U.S. Bureau of Standards circular on Polarimetry, Saccharimetry and the Sugars, which is likely to interest analytical chemists. Important events in the fermentation industry during 1943 were the partial substitution of unmalted oat flakes for malt in the mash tuns of English brewers, a contribution to the study of wild yeasts, and a demonstration that the brewing value of the hop cannot be judged by the amount of visible lupulin.

A comprehensive, well-balanced and ably written section (the longest in the volume) on food covers the year's progress in every aspect of human and animal nutrition, including analytical methods. In fine chemicals and medicinal substances much attention has been given to antibiotics and antimalarials, with methods for increasing production of penicillin and mepacrine as the principal object.

Water and sewage are continually offering new problems in treatment and purification, and at no time have such been more numerous or more pressing than in recent years. This has resulted in numerous investigations of permanent value.

In trying to form an estimate of this volume as a whole and to compare it with pre-war numbers in the series, one is impressed by the way in which the standard of excellence has been maintained. To all concerned in its production, from contributors to publishers, is due a tribute of praise and congratulation from the chemical profession. F. L. OKELL

PHYSICAL METHODS GROUP

A MEETING of the Physical Methods Group will be held at 3 p.m. on Thursday, May 3rd, at The Chemical Society's Rooms, Burlington House, London, W.1, at which Dr. H. W. Thompson will give a lecture on

"Infra-red Spectrography in Relation to Chemical Analysis."

The meeting is open to all members of the Society.

MICROCHEMISTRY GROUP

A JOINT Meeting of the Microchemistry Group with the Manchester and District Section of the Royal Institute of Chemistry will be held at Manchester on Friday, May 25th. The programme is as follows:

2.15–3.15 p.m. Visit to the Microchemical Laboratories at the Manchester College of Technology.

From 3.30 to about 6 p.m., with an interval for tea, meetings will be held at the Grand Hotel, Aytoun Street, *viz.*,

3.30–3.40 p.m. General Meeting of the Microchemistry Group.

3.40–6 p.m. Joint Meeting with the following programme:

(1) Opening address by Professor H. V. A. Briscoe.

(2) Physico-chemical Methods used in Micro-analysis; by Dr. Cecil L. Wilson.

(3) The Determination of Traces of Sulphur Dioxide—with special reference to the Determination of Sulphur in Ferro-alloys; by Mr. G. Ingram.

(4) Micro-methods used in the Analysis of Cotton; by Miss M. Corner.

The Joint Meeting will be open to all members of the Society.

The next meeting of the Group will be held in Newcastle in the autumn.

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