# The ANALYST

The Journal of the Society for Analytical Chemistry: a monthly publication dealing with all branches of analytical chemistry

Published for the Society by
W. HEFFER & SONS LTD., CAMBRIDGE

Volume 87

No. 1038, Pages 689-768

September 1962

# THE ANALYST

THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY



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Volume 87, No. 1038 September, 1962

No. 110 September, 1962

# THE SOCIETY FOR ANALYTICAL CHEMISTRY

# BULLETIN

## FORTHCOMING MEETINGS

### Ordinary Meeting of the Society, October 10th, 1962

AN Ordinary Meeting of the Society will be held at 7 p.m. on Wednesday, October 10th, 1962, in the Meeting Room of the Chemical Society, Burlington House, Piccadilly, London, W.1.

The subject of the meeting will be **"Recent Developments in Polarography"** and the following papers will be presented and discussed:

"Pulse Polarography," by H. M. Davis, B.Sc., A.Inst.P.

"Differential Cathode Ray Polarography," by H. I. Shalgosky, B.Sc., A.R.I.C.

"Radio Frequency Polarography," by Dr. H. W. Nürnberg.

### Ordinary Meeting of the North of England Section, October 5th, 1962

AN Ordinary Meeting of the Section will be held at 6 p.m. on Friday, October 5th, 1962, in the Lecture Theatre, Research Laboratories, Pilkington Brothers Ltd., **Lathom.**

A lecture on "The Analytical Laboratory in the Glass Industry," will be given by F. Hartley, F.S.G.I., F.R.I.C.

The meeting will be preceded at 3 p.m. by a tour of the Research Laboratories, Pilkington Brothers Ltd.

### Ordinary Meeting of the Scottish Section, October 26th, 1962

AN Ordinary Meeting of the Section will be held at 7.15 p.m. on Friday, October 26th, 1962, in Room 24, Royal College of Science and Technology, **Glasgow.**

The following paper will be presented and discussed:

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

### Joint Meeting of the Western Section with the Mid-Southern Counties Section of the Royal Institute of Chemistry, October 12th, 1962

A JOINT Meeting of the Western Section with the Mid-Southern Counties Section of the Royal Institute of Chemistry will be held at 7.45 p.m. on Friday, October 12th, 1962, at the Training College, The Close, **Salisbury.**

The following paper will be presented and discussed:

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

The meeting will be preceded at 2.30 p.m. by a visit to the Microbiological Research Establishment, Porton.

### Ordinary Meeting of the Midlands Section, October 9th, 1962

AN Ordinary Meeting of the Section will be held at 6.30 p.m. on Tuesday, October 9th, 1962, at Regent House, **Birmingham, 3.**

The meeting will be for the reading of the Elwell Award Papers.

### Ordinary Meeting of the Midlands Section, October 25th, 1962

AN Ordinary Meeting of the Section will be held at 7 p.m. on Thursday, October 25th, 1962, at the Technical College, **Nottingham.**

The following papers will be presented and discussed:

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

### London Discussion Meeting of the Microchemistry Group, October 24th, 1962

THE thirty-sixth London Discussion Meeting of the Group will be held at 6.30 p.m. on Wednesday, October 24th, 1962, in "The Feathers," Tudor Street, off Bouverie Street, Fleet Street, London, E.C.4.

The subject for discussion will be "Differences Between Continental and British Practice in the Determination of Elements in Organic Compounds" to be opened by Dr. W. Schöniger.

### Ordinary Meeting of the Physical Methods Group, October 30th, 1962

AN Ordinary Meeting of the Group will be held at 6.30 p.m. on Tuesday, October 30th, 1962, in the Meeting Room of the Chemical Society, Burlington House, Piccadilly, London, W.1.

The subject of the meeting will be **"Recent Work in Radiochemical Methods of Analysis"** and the speakers will be T. B. Pierce, B.Sc., M.A., D.Phil., T. T. Gorsuch, B.Sc., Ph.D., A.R.I.C., and J. K. Whitehead, M.Sc., A.R.C.S., D.I.C., A.R.I.C.

## BRITISH STANDARDS INSTITUTION

### DRAFT SPECIFICATIONS

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

Draft Specification prepared by Panel TLE/5/3/1—Methods of Analysis for Cathode Nickels.

D 62/2635—Draft B.S. Methods for the Analysis of Nickels for Use in Electronic Tubes and Valves. Part 7: Determination of Iron (Photometric Method).

Draft Specification prepared by Sub-Committee NFE/-/3—Sampling and Analysis of Aluminium and Aluminium Alloys.

D 62/3368—Draft B.S. Methods for the Analysis of Aluminium and Aluminium Alloys. Part 13: Titanium (Absorptiometric - Chromotropic Acid Method).

Draft Specification prepared by Technical Committee SFE/17—Sampling and Analysis of Gases.

D 62/4463—Draft B.S. Glossary of Terms Relating to Gas Chromatography.

Draft Specification prepared by Technical Committee CHE/43—Test Sieves.

D 62/4857—Draft B.S. Specification for Test Sieves (Revision of B.S. 410).

Draft Specifications prepared by Sub-Committee WPC/10/2—Insect Tests on Wood Preservatives.

D 62/5101—Draft B.S. Method of Test for Toxicity of Wood Preservatives to Wood-boring Insects by Larval Transfer.

D 62/5102—Draft B.S. Method of Test for Toxicity of Wood Preservatives to Wood-boring Insects by Egg-laying and Larval Survival.

D 62/5103—Draft B.S. Method of Test for Toxicity of Wood Preservatives to Lyctus Beetles.

D 62/5104—Draft B.S. Methods for Sampling Coal Tar and its Products (Revision of B.S. 616).

Draft Specification prepared by Technical Committee SFE/45—Coal and Coke.

D 62/5808—Draft B.S. Methods for the Analysis and Testing of Coal and Coke. B.S. 1016, Part 14: Analysis of Coal Ash and Coke Ash.

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# Notices

## ROYAL INSTITUTE OF CHEMISTRY

### Meldola Medal for 1962

THE Meldola Medal is the gift of the Society of Maccabaeans and is normally awarded annually. The next award will be made early in 1963 to the chemist who, being a British subject and *under* 30 *years of age at December* 31*st*, 1962, shows the most promise as indicated by his or her published chemical work brought to the notice of the Council of the Royal Institute of Chemistry before December 31st, 1962.

No restrictions are placed upon the kind of chemical work or the place in which it is conducted. The merits of the work may be brought to the notice of the Council, either by persons who desire to recommend the candidate or by the candidate himself, by letter addressed to The President, The Royal Institute of Chemistry, 30 Russell Square, London, W.C.1, the envelope being marked "Meldola Medal."

The letter should be accompanied by *six copies* of a short statement on the candidate's career (date of birth, education and experience, degrees and other qualifications, special awards, etc., with dates) and of a list of titles, with references, of papers or other works published by the candidate, independently or jointly. Candidates are also advised to forward one reprint of each published paper of which copies are available.

## THE PITTSBURGH CONFERENCE ON ANALYTICAL CHEMISTRY AND APPLIED SPECTROSCOPY

THE fourteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Penn-Sheraton Hotel, Pittsburgh, Pennsylvania, U.S.A., from March 4th to 8th, 1963. About 190 papers on all phases of analytical chemistry and spectroscopy will be presented. A symposium entitled "Solution Techniques in X-Ray and Emission Spectroscopy" will be arranged jointly with the Society for Applied Spectroscopy, and a symposium on "Techniques Related to Infrared Spectroscopy" is being co-arranged with the Coblentz Society. Symposia will also be held on "Nuclear Magnetic Resonance—Nuclei other than Hydrogen," "Gas Chromatographic Analysis of Metallo-Organics and Related Compounds," "Use of Reaction Rates in Analytical Chemistry" and "The Analysis of Refractory Metals."

Original paper on all aspects of analytical chemistry and spectroscopy are invited. Three copies of a brief abstract (150 words), with a letter listing the names of the authors, the laboratory in which the work was done and the current addresses of the authors should be addressed to Dr. William A. Straub, Program Chairman, The Fourteenth Pittsburgh Conference, Applied Research Laboratory, United States Steel Corporation, Monroeville, Pennsylvania, U.S.A. The final date for receipt of abstracts is October 15th, 1962. One copy of the complete paper must be submitted by January 1st, 1963.

An exhibition of the newest analytical instrumentation will also be held; more than 130 companies will display instruments, chemicals and equipment.

The fourth OCEANS (Omnibus Conference on Experimental Aspects of N.M.R. Spectroscopy) will be held at the Mellon Institute, Pittsburgh, from Thursday, February 28th, to Saturday, March 2nd, the week before the Pittsburgh Conference. For the convenience of those wishing to attend both meetings, the N.M.R. sessions of this Conference will be held on Monday, March 4th.

## ANALYTICAL METHODS FOR FRUIT JUICES

A VALUABLE compilation on this subject has recently been produced in Paris by the International Federation of the Producers of Fruit Juices. It consists of methods of analysis acceptable to members from all countries affiliated to the Federation. The project has been the responsibility of the Scientific and Technical Commission of the Federation, and the collaborative work has been organised by the Sub-Committee on Unification of Analytical Methods, of which Professor Diemair of Frankfurt University is the Chairman.

The Brochure just published contains seven methods of analysis accompanied by drawings of all apparatus, graphs and tables necessary for the determination of specific gravity, alcohol, titratable acidity, sugar (before and after inversion), volatile acidity and total sulphur dioxide.

The methods are presented in French, German and English.

The complete compilation can be obtained, postage paid, for NF 15—from Federation Internationale des Producteurs de jus de fruits, 16 rue de la Chaussee d'Antin, Paris ($9^{0}$).

THE ANALYST

# The Determination of Low Concentrations of Organic Carbon in Water

By H. A. C. MONTGOMERY and N. S. THOM
(*Water Pollution Research Laboratory, Stevenage, Herts.*)

An accurate method is described for determining low concentrations of organic carbon in fresh and saline water. The sample is evaporated to dryness and the residue is burned in oxygen. The gases evolved, including water vapour, are passed over cupric oxide at 900° C to complete the oxidation; an infrared gas analyser is used for determining the resulting carbon dioxide. The method is particularly suitable for sewage effluents and river waters; less than 0·1 p.p.m. of organic carbon can be detected, except in samples of high salinity for which the sensitivity is less. The efficiency of the method has been confirmed by the combustion of standard substances, and the blank value obtained for a 50-ml sample is less than 0·2 p.p.m., compared with 6 to 12 p.p.m. by the official chromic acid method.

The determination of organic carbon in water is useful as a measure of pollution. Its value as a research tool has hitherto been limited by the lack of a reliable method of determination, particularly at lower concentrations. Most existing methods depend either on evaporation to dryness and then ignition, or on wet combustion. Both approaches can give low recoveries of organic carbon, since volatile materials may be lost by evaporation, and some organic substances are not completely converted to carbon dioxide by wet oxidation in dilute aqueous solution or suspension. The chromic acid method,[1] which is perhaps the most widely used, often gives low results (see below) and has the further disadvantage that the blank value of 6 to 12 p.p.m. of carbon is too high to permit precise measurements to be made at low concentrations.

Gorbach and Ehrenberger[2] have recently described a quantitative method for determining relatively high concentrations of organic carbon (approximately 0·1 per cent.) in which the sample is distilled over cupric oxide at 900° C. The non-volatile residue is then ignited in oxygen and the resulting carbon dioxide is purified and absorbed in an alkaline solution maintained at constant pH by an automatic-titration unit. Apart from the use of infrared gas analysis for determining the carbon dioxide, our method follows similar principles; much lower concentrations of carbon can, however, be determined.

## Experimental

Since there is no known method for directly determining small amounts of carbon in a mixture of unknown substances, the usual approach of conversion to carbon dioxide was retained in this work. Attempts were first made to develop an improved wet-combustion procedure, and the action of ammonium persulphate, silver permanganate and ceric sulphate on organic substances in boiling dilute sulphuric acid in the presence of various catalysts was investigated; recoveries of carbon dioxide were sometimes low. Electrolytic oxidation with a lead anode in the presence of oxygen carriers, such as salts of nickel, cobalt, praseodymium or silver, was also ineffective. It was concluded that the complete oxidation of dissolved, suspended and volatile matter could be ensured only by a combination of dry combustion and vapour-phase oxidation.

In the proposed method, the sample is acidified with potassium hydrogen sulphate and oxygen is passed through the solution to remove carbon dioxide. The solution is then distilled over cupric oxide at 900° C in the presence of approximately 1·5 per cent. of free oxygen in the vapour phase. At the end of the distillation, the residue is heated to above 950° C in an atmosphere of moist oxygen. The gaseous products are collected in an evacuated receiver and the carbon dioxide content is determined in an infrared analyser.

### Removal of inorganic carbon from samples—

In studies of the decomposition of inorganic carbonates in soils, Watkinson[3] observed interference due to the decarboxylation of organic matter in the presence of mineral acid. Decarboxylation was less noticeable, however, at pH 4·5. The use of strong acids for the preliminary acidification of water samples must therefore be regarded as undesirable. In fact, they are unnecessary as it was found that carbon dioxide was evolved at a satisfactory rate from carbonate solutions acidified to pH 5·5 and calculation showed that only 12 per cent. was present as bicarbonate ion. Potassium hydrogen sulphate was the best of several weakly acidic substances examined; recovery of organic carbon was not always complete when aluminium sulphate was used, and chromium trioxide gave insoluble residues in the combustion flask. With the last-named there is the further disadvantage that partial oxidation of sensitive organic substances may occur while inorganic carbon is being removed.

It was confirmed that ethanol, phenol and formic and acetic acids are not evolved at a significant rate when oxygen is passed through their aqueous solutions. Hydrogen cyanide, however, is removed fairly rapidly at 20° C at pH 4·8. This can be prevented by treating the sample with a small excess of silver sulphate solution before acidification; the cyanide is then determined quantitatively as organic carbon.

### The combustion—

After evaporation of the sample to dryness, the residue is heated by a bunsen burner to bright redness in a stream of oxygen. The condensation of volatile substances is prevented by wrapping the exposed parts of the combustion flask and tube with electrical heating tape. Quantitative recovery of organic carbon from hard waters is obtained only in the presence of excess of potassium hydrogen sulphate (compare the use of the sodium salt in dry combustion by La Force, Ketchum and Ballard[4]). By using the amount of potassium hydrogen sulphate specified below, complete combustion of α-alanine was achieved in the presence of 20 mg of calcium (added as calcium hydroxide). The hydrogen sulphate forms a melt that assists combustion by retaining the organic matter in the position of greatest heat.

At first, low recoveries were obtained from a detergent solution containing approximately 250 μg of surface-active material in 20 ml. This loss, which was presumably due to the transfer of surface-active material to the upper part of the flask before combustion took place, was prevented by working at greater dilution and by warming the solution during the preliminary sweeping-out to prevent foaming. Quantitative recovery was obtained from approximately 120 μg of surface-active material in 40 ml.

### Combustion catalysts—

At the high flow rates involved (when a sample is distilled at 0·5 ml per minute the water vapour travels through the combustion tube at several centimetres per second) a careful choice of filling for the combustion tube is important. Empty-tube combustion methods were considered to be impracticable under these conditions. Of the catalysts tested, platinised

asbestos and thermally decomposed silver permanganate on asbestos[5] caused inconveniently high back-pressures to develop in the apparatus. Good results were initially obtained when cobalto-cobaltic oxide supported on pumice[6] was used at 700° C in the presence of moist oxygen (when water vapour was not present throughout the combustion recoveries were slightly low). However, difficulty was experienced in preparing material that combined high catalytic activity with a suitable physical form. Also, some apparently good batches lost their activity after three or four determinations. Possible explanations of these difficulties are changes in the structure of the catalyst in an atmosphere of water vapour and the effect of alkaline impurities.[7] Attempts to re-activate the catalyst failed.

Cupric oxide, though less active than cobalto-cobaltic oxide, was free from these defects. It is also available commercially and requires much less conditioning than the other catalysts. When cupric oxide in wire form was used at 900° C consistently good results were still being obtained from a single charge after 6 months' use. A slow bleed of oxygen during the distillation keeps the partial pressure of oxygen high enough to prevent decomposition of the catalyst. As with cobalto-cobaltic oxide, combustion is complete only when moist oxygen is used.

### Determination of the carbon dioxide formed by combustion—

Conventional procedures for determining small amounts of carbon dioxide are difficult to apply in the proposed method for several reasons. An unusually large volume of oxygen is passed at a rate of flow varying between wide limits, and the time required for a determination also varies widely according to the concentration of the sample. A precise method was devised, in which the distillate was collected in a spiral absorber initially containing 0·1 N sodium hydroxide. Sodium chloride was added and the carbon dioxide absorbed was determined by potentiometric titration between pH 8·0 and 5·2. The procedure is unfortunately tedious because of the slow response of the pH meter at the concentrations involved. The effect of interfering substances was not investigated fully. Visual titration by McKinney's method[8] was unsatisfactory because the colour changes of the mixed indicator were too subtle and uncertain.

The use of an infrared gas analyser* capable of determining 0 to 200 p.p.m. of carbon dioxide offered a convenient solution of the problem. The oxygen is collected in an evacuated brass gasholder having two outlets. This is then connected to a closed-circuit pumping system in which the gas circulates through the measuring cell of the analyser at 1 litre per minute. Equilibrium is reached rapidly and a direct reading can be made of the carbon dioxide present. Water vapour and sulphur dioxide, which both give a slight response, are previously removed. The instrument is calibrated with a mixture of carbon dioxide and nitrogen originally standardised by comparison with a mixture prepared by diluting a known amount of carbon dioxide, evolved from pure sodium carbonate, with nitrogen in a flask of accurately known volume.

Wilson[10] has recently described the use of an infrared analyser for determining the carbon dioxide produced by heating sea water with potassium persulphate.

### Blank values—

High blank values were obtained early in the investigation. Several blank combustions were carried out, and analysis of the curves obtained by plotting the concentration of carbon dioxide in the oxygen leaving the apparatus against time showed that carbon dioxide was coming from many different sources. In particular, it was evolved rapidly from fresh batches of catalyst in the presence of water vapour. With platinised asbestos and cobalto-cobaltic oxide on pumice the evolution ceased only after prolonged conditioning. With cupric oxide, however, a single distillation removed interfering carbonaceous matter.

Water distilled from alkaline permanganate contained approximately 0·5 p.p.m. of organic carbon. Further distillation of this water from chromium trioxide through a short fractionating column, however, brought the organic-carbon content below the limit of detection.

It was found essential to use combustion flasks made of high-purity silica. Ordinary commercial silica devitrified after several determinations and became porous to carbon dioxide.

* The analyser used in this work was type L/SCR (Infra-Red Development Co., London, N.W.1) based on the designs of Luft.[9]

Electrolytic oxygen was shown to contain less organic impurity than ordinary commercial oxygen. Even with electrolytic oxygen, however, it was found advisable to pass the gas first through a preheater containing platinised asbestos at 950° C and then an absorber for carbon dioxide.

After sources of organic impurity had been eliminated as far as possible, the blank value remained at the equivalent of 25 to 30 $\mu$g of carbon. It was discovered that this was largely due to sulphur dioxide formed by the decomposition of potassium hydrogen sulphate. Manganese dioxide,[11] surprisingly, proved unsatisfactory as an absorbent, since the carbon dioxide was delayed by reversible adsorption on the solid. A short column (1 cm) of manganese dioxide was inefficient. However, the sulphur dioxide was efficiently removed when acidified potassium dichromate solution was added to the distillation receiver, and the blank value fell to the equivalent of 7 to 10 $\mu$g of carbon.

SUSPENDED MATTER AND THE SAMPLING PROBLEM—

The question of taking representative samples is complicated by the presence of suspended matter. The larger particles of vegetable matter are likely to be concentrated near the surface and the finer material often has a tendency to flocculate. Inspection of water from the Thames, for example, reveals a considerable amount of fibrous material in filaments and flocs that will just pass through a 10-mesh sieve. This material settles rapidly after sampling.

For these reasons samples should be collected at positions of good mixing. It is also desirable that fairly large samples be taken and homogenised in some way before a sub-sample is taken for analysis. Good replicate analyses were obtained in this work when samples (50 to 80 ml) were processed in a "MSE" bench homogeniser, in which a sharp stainless-steel cutter rotates rapidly inside a fluted-glass container.

SALINE WATERS—

Quantitative recoveries with a coefficient of variation of $\pm 2{\cdot}6$ per cent. were obtained when known amounts of sucrose, $\alpha$-alanine and quinoline were added to 10-ml samples of sea water in which 2·6 p.p.m. of organic carbon had previously been found. When solids equivalent to more than 10 ml of sea water were present efficient combustion was prevented by the mass of salts. The amount of potassium hydrogen sulphate was kept to a minimum to reduce volatilisation of the catalyst in the gases evolved. The use of the method for routine determinations in saline water has not been studied.

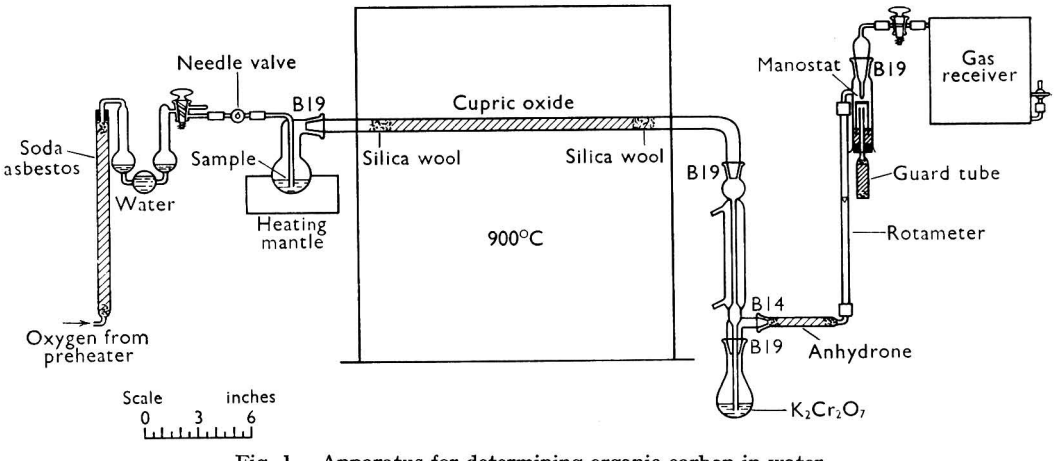


Fig. 1. Apparatus for determining organic carbon in water

## METHOD

APPARATUS—

A scale diagram of the apparatus is shown in Fig. 1. Oxygen is obtained from a cylinder fitted with a reducing valve. The preheater tube and combustion tube are of clear silica and have internal diameters of 16 mm. The preheater tube is loosely packed with platinised

asbestos over its entire heated length, and a 35-cm portion of the combustion tube is closely packed with cupric oxide so as to lie centrally between the ends of the 18-inch tube furnace. The cupric oxide is retained by plugs of silica wool. Dimensions of the combustion flask, which is made of high-purity silica (known commercially as "high purity quartz"), are shown in Fig. 2 and the Cartesian manostat is shown in detail in Fig. 3. The gas receiver,

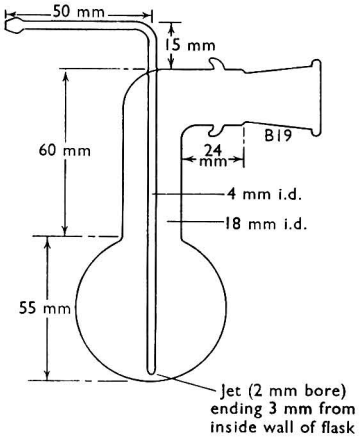


Fig. 2. Combustion flask

capacity 2·5 litres, is constructed of $\frac{1}{8}$-inch brass with silver-soldered joints and fitted with glass spring-loaded vacuum stopcocks as in Fig. 1. The flow of oxygen into the combustion flask is controlled by a stainless-steel needle valve.

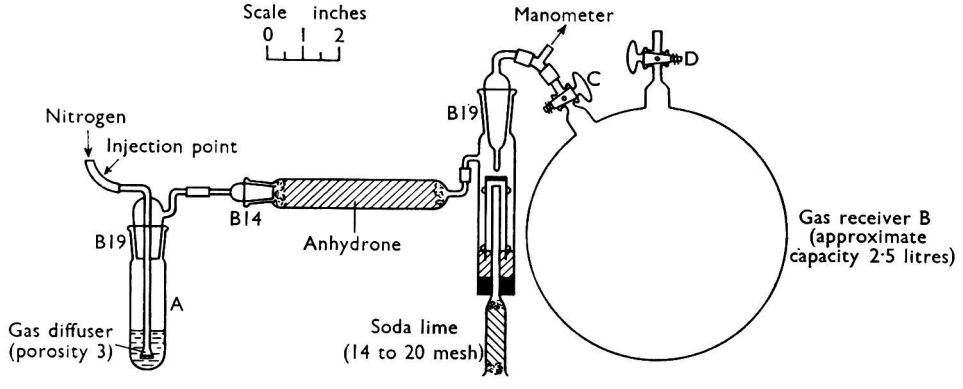


Fig. 3. Apparatus for standardising the reference gas. (The dimensions of the manostat float are 55 mm × 14 mm external diameter; it is kept vertical by 6 glass nodules. The centre tube has an external diameter of 5 mm and projects 35 to 40 mm above the mercury level. The manostat jet is a "pipette jet" accurately ground and flame-polished. The leakage rate of the manostat should not exceed 5 ml per minute. The mercury charge should be just sufficient to raise the float to the jet at atmospheric pressure)

All ground joints are fitted with hooks and springs (not shown in the diagrams); all are lubricated with silicone grease except that on the combustion flask, which is lubricated with sulphuric acid. Other connections, which are glass-to-glass, are made with thick-walled silicone rubber tubing. All glassware is borosilicate. Thermostatic control is necessary for the combustion furnace.

The apparatus for standardising the reference gas mixture is shown in Fig. 3. A sealed sampling pump (model E/45 obtained from Boughton Pumps Ltd., Effingham, Surrey) is used to circulate the gas in the closed-circuit gas-measuring system.

Other apparatus not shown in any of the diagrams consists of a mechanical vacuum pump with Vacustat, a capillary manometer, a graduated hypodermic syringe and a 20-mm glass-fibre electrical heating tape operating from a low-voltage transformer at 17 watts per foot; the resistance elements are spaced closely to give even heating.

REAGENTS—

*Carbon-free water*—Distil from alkaline permanganate and then from chromium trioxide (0·2 per cent.) through a short fractionating column, taking precautions to exclude dust.

*Potassium hydrogen sulphate solution*—Dissolve 15 g of the analytical-reagent grade salt in carbon-free water, and dilute to 100 ml.

*Sulphuric acid*—Analytical-reagent grade.

*Magnesium perchlorate, anhydrous (anhydrone)*—M.A.R. grade.

*Cupric oxide*—Wire form, M.A.R. grade.

*Platinised asbestos, 5 per cent.*

*Soda-asbestos.*

*Nitrogen, high purity.*

*Oxygen, electrolytic.*

*Carbon dioxide*—A reference gas mixture of accurately known composition, containing 200 p.p.m. v/v of carbon dioxide in high-purity nitrogen. A procedure for standardisation is given below.

*Sodium carbonate solution*—Dissolve 0·4425 g of sodium carbonate, dried at 270° to 300° C, in freshly boiled water, and dilute to 250 ml.

*Potassium dichromate solution*—Dissolve 1·5 g of analytical-reagent grade potassium dichromate in 100 ml of freshly boiled 0·1 N sulphuric acid.

*Soda-lime*—Self-indicating.

STANDARDISATION OF REFERENCE GAS—

The determination of organic carbon depends on the use of a reference gas of accurately known composition. Should standardisation be necessary, the procedure described below gives an absolute measurement.

The apparatus is shown in Fig. 3. Measure exactly 1·0 ml of sodium carbonate solution into vessel A, and dilute with a few millilitres of carbon dioxide free distilled water. Evacuate gas receiver B, the volume of which is known accurately, to less than 0·5 mm of mercury. Pass nitrogen through vessel A, the anhydrone tube and the manostat until all carbon dioxide has been removed, then connect the manometer and gas receiver as shown. Open tap C, and adjust the flow of nitrogen to a suitable rate. Inject a few drops of carbon dioxide free N hydrochloric acid into the gas-entry tube with a hypodermic syringe, and continue passing nitrogen until the receiver is exactly at atmospheric pressure; then close tap C. Connect the receiver to the analyser by opening tap C, and pass some of the contents of the receiver into the analyser by pouring a suitable volume of mercury through a funnel attached to tap D; take care not to admit any air. Note the reading ($S_1$) shown by the analyser (which is not accurately adjusted at this stage), and also note the reading ($T$) given by the reference gas after passage over anhydrone.

If $M$ = weight of carbon dioxide evolved from carbonate in $\mu$g,

$p_1$ = barometric pressure in mm of mercury,

$t$ = room temperature in °C and

$V$ = volume of gas receiver B in litres, then—

$$\text{Carbon dioxide content of reference gas} = \frac{22{\cdot}4}{V} \times \frac{760}{p_1} \times \frac{273 + t}{273} \times \frac{MT}{44S_1} \text{ p.p.m.}$$

CALIBRATION OF GASHOLDER—

Introduce a known amount of carbon dioxide into the gasholder as described above (there is no need for the pressure reached to be exactly atmospheric). The gasholder is full when the float of the manostat falls away from the jet. Connect the sampling pump to the analyser; all gases are now passed into the analyser through the inlet of the pump, which offers no resistance to flow.

With the reference gas, adjust the analyser to read correctly on the chosen scale (0 to 200 p.p.m.), then purge with nitrogen. Without delay, connect the gasholder between the

pump inlet and analyser outlet, open both taps, and switch on the pump. Read the scale when equilibrium has been reached; this takes 2 to 2·5 minutes. Note the barometric pressure ($p_2$).

CALCULATION—

If $R$ = p.p.m. of carbon dioxide in reference gas,
$S_2$ = reading for gasholder contents,
$v$ = total volume of measuring system in litres,
$v_a$ = volume of measuring cell in analyser in litres,
$k$ = temperature of analyser cell in °C,
$p_2$ = barometric pressure in mm of mercury and
$x$ = weight of carbon in gasholder in $\mu$g,

then, when the reference gas is passed and the reading is $R$, the weight of carbon in the analyser cell in $\mu$g is given by the expression—

$$\frac{12}{22{\cdot}4} \times \frac{p_2}{760} \times \frac{273}{273 + k} \times Rv_a$$

and, when the contents of the gasholder are circulated and the reading is $S_2$, the weight of carbon in the analyser cell is $\frac{xv_a}{v}$ $\mu$g.

By comparing $R$ and $S_2$—

$$x = \frac{12}{22{\cdot}4} \times \frac{p_2}{760} \times \frac{273}{273 + k} \times S_2v.$$

But let F, the calibration factor for the gasholder $= \frac{12 \times 273v}{22{\cdot}4(273 + k)}$

then—

$$\mathrm{F} = \frac{760x}{S_2p_2}.$$

F can now be calculated by substituting the observed values of $x$, $S_2$ and $p_2$.

DETERMINATION OF ORGANIC CARBON—

Measure up to 50 ml of sample containing not more than 200 $\mu$g of organic carbon and not more than 330 mg of total solids into the flask. If cyanide is present, add 0·1 ml of saturated silver sulphate solution for each 50 $\mu$g of hydrogen cyanide. To samples of sea water and saline estuary water, add just enough potassium hydrogen sulphate solution to bring the pH below 5·0; for other samples, add 2 ml. Dilute, if necessary, to 10 ml with carbon-free water.

Lubricate the ground joint with sulphuric acid, connect the flask to the combustion tube, and wrap the heating tape closely round the neck of the flask and the exposed part of the combustion tube. Switch on the heating tape, and put 5 ml of potassium dichromate solution into the distillation receiver. Pass oxygen through the apparatus at a rate of 100 to 120 ml per minute until the effluent gas contains less than 3 p.p.m. of carbon dioxide (if surface-active matter is present, foaming can be prevented by warming the solution). Reduce the flow of oxygen to 10 ml per minute, connect the evacuated gasholder to the manostat outlet, bring the sample cautiously to the boil, and distil at 0·45 to 0·50 ml per minute. While the contents of the flask are reaching dryness, adjust the flow of oxygen carefully to compensate for the removal of water vapour from the system. Allow the residue to melt, adjust the flow of oxygen to 20 ml per minute, and remove the heating mantle. Heat the flask gently with a bunsen burner for about 1 minute, and then strongly for 5 minutes. Sweep out the combustion products at a rate of 45 to 50 ml per minute for 10 minutes, and then at 90 to 100 ml per minute until the gasholder is full. Close the inlet tap on the gasholder. Remove the gasholder, then fit a soda-lime guard tube to the manostat outlet, empty the distillation receiver, switch off the heating tape, and stop the flow of oxygen after allowing sufficient time for the air to be swept out of the receiver.

With the reference gas, adjust the infrared analyser to read correctly, and note the barometric pressure ($p_3$). Purge the analyser cell with nitrogen, and then connect the

gasholder in closed circuit and circulate the gas until equilibrium is reached; note the reading of the analyser ($S_3$).

Determine the blank value in the same way with 10 ml of carbon-free water.

*Calculation*—If a sample of $y$ ml gave a reading $S_3$ from a gasholder having a factor F, and the barometric pressure at the time of calibrating the analyser was $p_3$ mm of mercury, then—

$$\text{Carbon equivalent of sample} = \frac{S_3 p_3 F}{760} \mu g.$$

Subtract the carbon equivalent of the blank, also expressed in $\mu g$, and then divide by $y$ to obtain the concentration in p.p.m. of organic carbon in the sample.

NOTES—

1. Scrupulous cleanliness is essential if the blank value is to be kept reasonably constant. The combustion flask and particularly the ground joint should be washed frequently with 40 per cent. hydrofluoric acid, and the exposed part of the combustion tube, including the joint, should occasionally be heated to bright redness.

2. The manostat must be kept clean and in perfect working order.

3. The performance of the apparatus should be checked from time to time by the combustion of standard substances; if recoveries are low the most likely cause is inadequacy of the heating tape, either because it is of insufficient power or because it is not wrapped as closely as possible.

## RESULTS

The method has been tested by the combustion of the reference substances listed in Table I. Solutions of these substances were prepared with carbon-free water, except for DL-α-alanine and quinoline, which were dissolved in dilute sulphuric acid. Results obtained by the official method[1] are included for comparison.

TABLE I

RECOVERY OF ORGANIC CARBON FROM STANDARD SUBSTANCES

| Standard substance | Volume of solution, ml | Organic carbon added, μg | Organic carbon added, mg | Organic carbon found by—proposed method, μg | Organic carbon found by—official method, mg | Recovery, % |
|---|---|---|---|---|---|---|
| Sucrose | 50 | 157 | — | 158, 158 | — | 101 |
| | 10 | 204 | — | 204, 200 | — | 100, 98 |
| | 50 | — | 10·3 | — | 9·9, 10·0 | 96, 97 |
| DL-α-Alanine | 50 | 150 | — | 149, 152 | — | 99, 101 |
| | 10 | 200 | — | 200, 200 | — | 100 |
| | 50 | — | 9·7 | — | 9·3, 9·4 | 96, 97 |
| Acetic acid | 50 | 151 | — | 153, 154 | — | 101, 102 |
| | 10 | 204 | — | 204, 202 | — | 100, 99 |
| | 50 | — | 8·1 | — | 7·8, 8·0 | 96, 99 |
| Quinoline* | 50 | 149 | — | 152, 149 | — | 102, 100 |
| | 10 | 202 | — | 203, 197 | — | 100, 98 |
| | 50 | — | 10·35 | — | 9·4, 9·3 | 91, 90 |
| *S*-Benzylthiouronium chloride | 50 | 150 | — | 149, 153 | — | 99, 102 |
| | 10 | 200 | — | 200, 199 | — | 100 |
| Packaged synthetic detergent* | 40 | 96 | — | 95, 99 | — | 99, 103 |
| | 50 | — | 4·8 | — | 4·4, 5·0 | 92, 104 |

* Analysed by conventional micro-analysis.

The mean recovery of organic carbon by the proposed method for the results in Table I is 100·2 ± 1·9 per cent. These results were obtained before the large effect of sulphur dioxide on the blank value was discovered. Other substances quantitatively converted to carbon dioxide were potassium cyanide (in the presence of silver sulphate) and methane, which was introduced into the gas stream with a hypodermic syringe during the ignition. Comparative figures obtained by the two methods for several samples are shown in Table II.

It should be noted that the official method is intended primarily for samples of sewage, sewage effluents and trade wastes containing comparatively high concentrations of organic carbon. The proposed method, on the other hand, was developed specifically for determining low concentrations, although concentrations greater than 50 p.p.m. can be determined after preliminary dilution of the sample with carbon-free water.

TABLE II

COMPARISON OF RESULTS BY PROPOSED AND OFFICIAL METHODS

| Sample | Organic carbon found by— proposed method, p.p.m. | official method, p.p.m. |
|---|---|---|
| Stevenage Brook | 11·3, 11·3 | 4, 4 |
| Stevenage Brook (filtered) | 10·7, 10·8, 10·3 | 18 |
| River Thames at Datchet | 8·5, 8·5 | 6 |
| Sewage effluent A | 37·0, 36·5 | 32, 30 |
| Sewage effluent B | 23·7 | 26 |
| Sewage effluent C | 27·8 | 40 |
| Tap-water | 1·2 | 6 |
| Detergent solution | 4·8 | 8 |
| Whole algal culture | 53·2, 53·0 | 50, 48 |
| Filtrate from algal culture | 3·2, 3·0 | 2, 4 |

The fact that standard substances were recovered quantitatively when added to sea water shows that the method is satisfactory for occasional saline samples, although the sensitivity is less because of the limit on the size of sample that can be taken. This limitation is less important for samples of high organic carbon content.

The time required for a determination varies from 75 minutes for a 10-ml sample containing a small amount of inorganic carbon to 3 hours for a 50-ml sample of hard water. A determination by the official method takes 2·5 hours.

## CONCLUSIONS

The proposed method is suitable for determining low concentrations of organic carbon in fresh water. Although the method was intended primarily for fresh waters, satisfactory results have also been obtained with saline samples. Once the initial calibrations have been completed the procedure is straightforward.

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Received *March 26th*, 1962

# The Determination of Oxalic Acid in Food

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A colorimetric procedure is described for determining oxalic acid in foodstuffs. The procedure is based on the authors' previously described method for determining oxalic acid in urine. The separation of oxalic acid from food by extraction with hot acid can lead to high results owing to the conversion of carbohydrates and other compounds to oxalic acid. Extraction of the dry finely powdered food with 30 per cent. v/v hydrochloric acid at room temperature was found to give recoveries ranging from 96 to 100 per cent. with negligible conversion of the "oxalogenic" compounds to oxalic acid.

THE procedures that have been used for isolating oxalic acid from plant and animal material can be divided into three groups—

(1) Extraction of the oxalic acid from the food with cold or hot hydrochloric acid, and then extraction with ether and precipitation as the calcium salt.[1,2,3]

(2) Digestion of the food with hot concentrated sodium carbonate solution to convert oxalic acid to the soluble sodium salt, and then acidification with hydrochloric acid and precipitation as the calcium salt.[4,5]

(3) Esterification of the oxalic acid present with methanol or ethanol in hot acid solution, and then distillation and precipitation as the calcium salt.[6,7]

In each of the three methods the oxalic acid is determined by titration with a standard solution of potassium permanganate. Increased sensitivity and specificity can be achieved, however, by reducing the oxalic acid to glycollic acid and determining this substance colorimetrically with 2,7-dihydroxynaphthalene-3,6-disulphonic acid.[8]

The procedure adopted involves the extraction with cold acid of oxalate from dry finely powdered food, and then extraction with ether, precipitation as the calcium salt and colorimetric determination with chromotropic acid.[8] The method has been used by us for determining oxalic acid in a wide range of foodstuffs.[9]

## EXPERIMENTAL

Care was taken to obtain fresh samples of food, and these were analysed within 24 hours of receipt. Fruit and vegetables were stored before analysis in polythene bags to avoid loss of moisture. Analyses were also carried out on the bulked food from various 24-hour diets (subsequently referred to as "duplicate meals").

Determinations were performed on raw or cooked materials, depending on the form in which the food is customarily served. Meat (with the exception of corned beef), fish and rice pudding were supplied freshly cooked by the hospital diet kitchen. Other foods that had to be cooked were boiled with distilled water in a round-bottomed 2000-ml flask fitted with a double-walled water condenser. Duplicate meals were homogenised and diluted to 2000 ml with water; 50- to 100-ml samples were withdrawn for analysis.

The presence of large amounts of fat or casein was found to cause erroneous results. Fats were removed from meat, bacon, butter, cheese, cocoa and duplicate meals by extraction with a mixture of benzene and light petroleum. There was no loss of oxalic acid after shaking standard aqueous solutions of oxalic acid or dry powdered samples of food with the benzene - light petroleum mixture. Casein can be extracted by adjusting the pH to the iso-electric point (pH 4·6), but ultrafiltration was found to be the most satisfactory procedure for removing the interfering substances from milk.

For the initial separation of oxalic acid from food, extraction with acid was chosen in preference to esterification and distillation, as the apparatus required was less elaborate and the extraction could be performed in a shorter time. Other reasons for rejecting esterification and also digestion with sodium carbonate are discussed below.

Vigorous extraction with hot hydrochloric acid may lead to high results owing to the conversion of "oxalogenic" compounds to oxalic acid,[8] and the mildest conditions consistent with a quantitative recovery of oxalic acid were therefore sought. It was found that quantitative recovery of oxalic acid could be achieved at room temperature by shaking the dry finely ground sample with 30 per cent. v/v hydrochloric acid (see Table I). With most types of food, recovery of oxalic acid was incomplete if the concentration of hydrochloric acid was less than 3 N.

## Method

### Apparatus—

*Ether extraction apparatus and conical centrifuge tubes.*[8]

*Ultrafiltration apparatus*—This is manufactured by Messrs. Membranfilter-Gesellschaft, Göttingen, Germany, and can be purchased from Messrs. V. A. Howe & Co. Ltd., 46 Pembridge Road, London, W.11. Type Mi 5 membrane filters were used.

### Reagents—

*Benzene - light petroleum mixture*—Mix equal volumes of benzene and light petroleum (boiling range 40° to 60° C).

Other reagents were as described previously.[8]

### Procedure—

Break up a weighed amount of food into small parts by mincing, grating or homogenising with water in a M.S.E. ATO MIX 800 or other suitable blender. Dilute the homogenate to a suitable volume with water, and dry a 50- to 100-ml sample to constant weight by heating in an oven at 60° C. Grind the material to a fine powder in a glass mortar, and transfer 0·1 to 1·0 g to a glass-stoppered 25-ml graduated test-tube. Extract any fat present by shaking with two 10-ml portions of benzene - light petroleum mixture, and remove the last traces of solvent by evaporation on a bath of hot water. Add 15 ml of 30 per cent. v/v hydrochloric acid, and mix gently by inverting the tube for 5 minutes. Add solid ammonium sulphate until the solution is half saturated (38 g per 100 ml), set aside for 30 minutes, and note the volume. Spin in a centrifuge at 1200 **g** for 10 minutes, and filter the supernatant fluid through a Whatman No. 1 filter-paper. Extract 10 ml of filtrate with ether as described previously,[8] and express the result in mg of anhydrous oxalic acid per 100 g of fresh material.

### Procedure for milk—

Mix equal volumes of milk and water, and transfer 10-ml portions to collodion bags (Mi 5 membrane filter). Collect approximately 15 ml of ultrafiltrate (500 mm of mercury for 8 hours). Add sufficient concentrated hydrochloric acid to make the final solution approximately 1 N; then add solid ammonium sulphate until the solution is half saturated (38 g per 100 ml). Extract the whole sample with ether as described previously.[8]

Table I

Recovery of oxalic acid added to food

| Sample | Oxalic acid found in control, mg per 100 g | Oxalic acid added, mg | Oxalic acid found after addition, mg per 100 g | Recovery, % |
|---|---|---|---|---|
| Cabbage .. .. | 11·4 | 5·0 | 16·3 | 98 |
| Beetroot .. .. | 124·0 | 5·0 | 129·0 | 100 |
| Rhubarb .. .. | 460·0 | 50·0 | 508·0 | 96 |
| Spinach .. .. | 780·0 | 50·0 | 827·0 | 96 |
| Duplicate meal 1 .. | 1·28 | 10·0 | 11·04 | 98 |
| Duplicate meal 2 .. | 1·96 | 10·0 | 11·64 | 97 |
| | | | Mean .. | 97·5 |

## Results

### Recovery of oxalic acid from food—

The recovery of oxalic acid added to several homogenised foods and to duplicate meals was within the range 96 to 100 per cent. (see Table I). For cabbage, beetroot and spinach the oxalic acid was added to the wet homogenate, and for the remainder of the foods it was added to the dry powdered sample.

COMPARISON OF PROPOSED AND PREVIOUS METHODS—

The oxalic acid content of rhubarb was determined by the proposed method and by the procedures recommended by Kohman[3] and Andrews and Viser.[1] The agreement between the values obtained by the proposed method and by Andrews and Viser's method[1] was good, but an appreciably lower value was obtained by Kohman's method[3] (see Table II).

Results by the proposed method and Andrews and Viser's method agreed well for some foodstuffs, *e.g.*, spinach and tea, but for most foods considerable discrepancies were observed (see Table II). Generally, the values obtained by the proposed method were lower than those obtained by Andrews and Viser's method, the largest discrepancies occurring with foods having a high carbohydrate content, for example, potatoes, bread and jam.

TABLE II

COMPARISON OF PROPOSED AND PREVIOUS METHODS

| Sample | Oxalic acid found by— Kohman's method,[3] mg per 100 g | Andrews and Viser's method,[1] mg per 100 g | proposed method, mg per 100 g |
|---|---|---|---|
| Rhubarb (sample 1) | 340 | 438 | 455 |
| Rhubarb (sample 2) | — | 442 | 445 |
| Spinach | — | 783 | 780 |
| Asparagus | — | 15·1 | 1·7 |
| Potatoes, boiled | — | 39·8 | 2·3 |
| Beef, corned | — | 0·6 | 0·2 |
| Milk | — | 1·8 | 0·5 |
| Bread, white | — | 17·9 | 4·9 |
| Cornflakes | — | 30·0 | 5·6 |
| Jam, plum | — | 17·6 | 0·5 |
| Duplicate meal 1 | — | 162·8 | 82·6 |
| Duplicate meal 2 | — | 237·2 | 150·0 |

TABLE III

EFFECT OF EXTRACTION WITH HOT ACID ON THE APPARENT OXALIC ACID CONTENT OF CARBOHYDRATES

| Compound | Oxalic acid found: No heating, mg per 100 g | After heating, mg per 100 g |
|---|---|---|
| Insulin | Nil | 6·0 |
| D(+)Xylose | Nil | 8·0 |
| D(−)Fructose | Nil | 8·0 |
| Sucrose | Nil | 12·0 |
| Maize starch | Nil | 16·0 |
| Rice starch | Nil | 22·0 |
| Maltose | Nil | 26·0 |
| Potato starch | Nil | 28·0 |
| Wheat starch | Nil | 28·0 |
| Glycogen | Nil | 28·0 |
| D(−)Arabinose | Nil | 30·0 |
| Lactose | Nil | 36·0 |
| D(+)Galactose | Nil | 54·0 |
| Apple pectin | Nil | 92·0 |
| Chondroitin sulphate | Trace | 180·0 |

EFFECT OF EXTRACTION WITH HOT ACID ON THE APPARENT OXALIC ACID CONTENT OF CARBOHYDRATES—

The oxalic acid contents of various mono-, di- and polysaccharides were determined before and after the samples had been heated with hydrochloric acid under the conditions recommended by Andrews and Viser.[1] Duplicate 0·5-g samples were suspended in 10 ml of 30 per cent. v/v hydrochloric acid. The oxalic acid contents were determined by the proposed method directly on one sample and on the other after it had been heated in a boiling water bath for 5 hours.

No oxalic acid was detected in the compounds examined when the proposed method was used. Various amounts of oxalic acid were found, however, after treatment with hot acids, the highest values being observed with D(+)galactose, apple pectin and chondroitin sulphate (see Table III).

THE OXALIC ACID CONTENT OF MILK—

The oxalic acid content of milk was determined after two different techniques had been used for removing interfering constituents—

(1) Fat was removed by shaking 10 ml of milk with 5 ml of benzene - light petroleum mixture and discarding the extract. Casein and albumin were removed by adjusting the pH of the sample to 4·6, adding ammonium sulphate until the solution was saturated (76 g per 100 ml) and spinning in a centrifuge at 1200 **g** for 10 minutes.

(2) Fat was removed by shaking with benzene - light petroleum mixture, as described above. Other interfering substances were removed by ultrafiltration, as described under "Procedure for Milk," p. 699.

The results obtained in 6 determinations are summarised in Table IV, together with those published by earlier workers.

TABLE IV

OXALIC ACID CONTENT OF MILK

| Method | Number of determinations | Oxalic acid found, mg per 100 ml |
|---|---|---|
| Proposed (Method 1) .. .. .. | 4 | 0·3 to 0·7 |
| Proposed (Method 2) .. .. .. | 2 | 0·4 to 0·6 |
| Majumdar and De[11] .. .. .. | — | 1·9 |
| Grütz, Sengbusch and Timmermann[12] .. | 3 | 20·9 to 21·4 |

## CONCLUSIONS

The preliminary heating of food with hydrochloric acid is not recommended, as this gives results for oxalic acid that are too high, owing, apparently, to partial conversion of several constituents of food to oxalic acid or to compounds yielding formaldehyde under the experimental conditions used. The effect is found to be most pronounced in foods having a high carbohydrate content. Experiments reported in this and a previous communication[8] suggest that many carbohydrates are partly converted to oxalic acid in the presence of hot hydrochloric acid. Esterification with methanol and sulphuric acid might be expected to cause similar conversions; digestion with strong alkalis is known to result in the conversion of glyoxylic acid to glycolic and oxalic acids.[10]

Since many of the earlier methods involve extraction with hot acid, esterification or digestion with strong alkali, it might be expected that many of the published values for oxalate in food are high, particularly for foods having a high carbohydrate content. We have confirmed this by the analysis of some eighty different foods.[9]

Kohman's[3] method gave lower values for oxalic acid in rhubarb than did the proposed method or Andrews and Viser's method.[1] The lower value is attributed to incomplete extraction of oxalic acid from the food.

The work described here has shown that the quantitative recovery of oxalic acid from food can be achieved, with minimal conversion of oxalogenic compounds, by extracting the dried and finely powdered material with hydrochloric acid at room temperature. The quantitative recovery of added oxalic acid does not necessarily prove that there is a quantitative recovery of the oxalic acid normally present in the food, but this appears to be likely from an examination of the results shown in Table II. Thus, the values for oxalic acid in rhubarb and spinach were the same, irrespective of whether extraction with hot or cold acid was used.

The values reported by Grütz, Sengbusch and Timmermann[12] for the oxalic acid content of milk (20·9 to 21·4 mg per 100 ml) appear to be high. It is our experience that the oxalic acid content of biological fluids seldom exceeds 1·0 mg per 100 ml, and milk appears to be no exception to this.

We thank Mr. F. G. Smith, Director of the Ministry of Agriculture Experimental Horticultural Station, Cawood, Yorks., and Mr. R. E. Lambert, Catering Officer, Leeds General Infirmary, for their co-operation.

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Received *February* 22*nd*, 1962

# The Use of Glyoxal Bis-(2-hydroxyanil) in determining Microgram Amounts of Uranium

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In alkaline solution, uranium$^{VI}$ readily forms with glyoxal bis-(2-hydroxyanil) a violet complex containing two molecules of reagent to one of uranium; this reaction has been made the basis of a method for determining uranium. The complex, soluble in aqueous methanolic solution, has maximum absorption at 575 m$\mu$ and is stable in presence of ethylenediaminetetra-acetate, which suppresses formation of other metallic complexes. Phosphate and carbonate reduce the sensitivity of the method.

Complexes of glyoxal bis-(2-hydroxyanil) with metals were first prepared by Bayer,[1] who isolated crystalline compounds of zinc, cadmium, copper, nickel, manganese and the uranyl ion. Analytical use of this reagent was made by Goldstein and Stark-Mayer,[2] who developed a qualitative test for calcium, which they found formed in sodium hydroxide solution a red complex extractable into chloroform, probably as an organo-sol. They examined the effect of a large number of ions and found that, besides calcium, only copper, cobalt, nickel, cadmium and manganese formed coloured complexes. Kerr[3] found that the calcium complex with glyoxal bis-(2-hydroxyanil) was soluble in aqueous alcoholic solvents and developed a quantitative method for determining calcium. When investigating this method for use in analysing minerals, it was found that uranium seriously interfered by forming a violet complex, which, unlike the calcium complex, was stable in the presence of ethylenediaminetetra-acetic acid (EDTA).

Older colorimetric methods for determining uranium and their use in conjunction with extraction by ether from solution in nitric acid have been discussed by Harvey[4]; the alkaline-peroxide method is least subject to interference, but is relatively insensitive. More recently, arsenazo,[5] the trisodium salt of 3-(2-arsonophenylazo)-4,5-dihydroxynaphthalene-2,7-disulphonic acid, and PAN,[6,7] 1-(2-pyridylazo)-2-naphthol, have been proposed as sensitive colorimetric reagents for uranium. The complex with PAN is extracted into chloroform from alkaline solution, EDTA being used to prevent interferences; there is, however, a substantial blank value. As glyoxal bis-(2-hydroxyanil) appeared to have a high degree of selectivity for uranium, especially in presence of EDTA, and a low reagent blank value, it was thought that it might be a useful reagent for determining uranium, and such a method was investigated. During this work, my attention was drawn to a paper on the use of this reagent for determining uranium[8]; however, the conditions of pH and temperature used were different from those in the method described below.

## Experimental

Conditions for the formation of the uranium$^{VI}$ - glyoxal bis-(2-hydroxyanil) complex were broadly similar to those used by Kerr[3]; the complex was first formed in an aqueous solution containing sodium hydroxide, and the precipitate produced was dissolved by adding various alcohols. Interference from other metallic ions was suppressed by EDTA and triethanolamine.

The absorption spectra of the violet uranium$^{VI}$ complex (see Fig. 1) showed a maximum at 575 m$\mu$, and this wavelength was used in all subsequent work. Under the same conditions, the reagent formed a yellow solution (maximum absorption at 425 m$\mu$), and the blank value was therefore small. The effects of type and concentration of solvent and alkalinity were studied, and the optimum conditions found are those described under "Method."

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STABILITY OF COMPLEX IN VARIOUS SOLVENTS—

The stability of the uranium - glyoxal bis-(2-hydroxyanil) complex in 50 per cent. v/v aqueous solutions of various solvents was studied and found to decrease in the order methanol, ethanol, isopropyl alcohol, acetone; the last-named solvent decomposed the complex immediately. Methanol was therefore preferred as solvent. The stability of the complex increased with the concentration of methanol, and a solution containing 50 per cent. v/v of methanol was satisfactory.

EFFECT OF ALKALINITY—

The amount of 0·50 N sodium hydroxide used in the method was varied from 0·25 to 4·0 ml. At the lower end of the pH range so produced, colour developed slowly; at the upper end, fading of the colour was noticeable after 90 minutes. When 1 ml of 0·50 N sodium hydroxide was used, colour developed fully in less than 30 minutes and was stable for over 3 hours.

In weakly alkaline solutions produced when sodium tetraborate solution was used in place of 0·50 N sodium hydroxide, there was a pronounced decrease in the rate of formation of the complex, several hours being necessary to produce a faint colour. This difference in behaviour coincided with a change in the colour of the reagent blank solution, which was colourless when tetraborate was present and yellow in sodium hydroxide solution. This change in colour acts as a useful indicator of pH in the method, and it appears that the uranium$^{VI}$ ion reacts with the yellow form of the reagent.

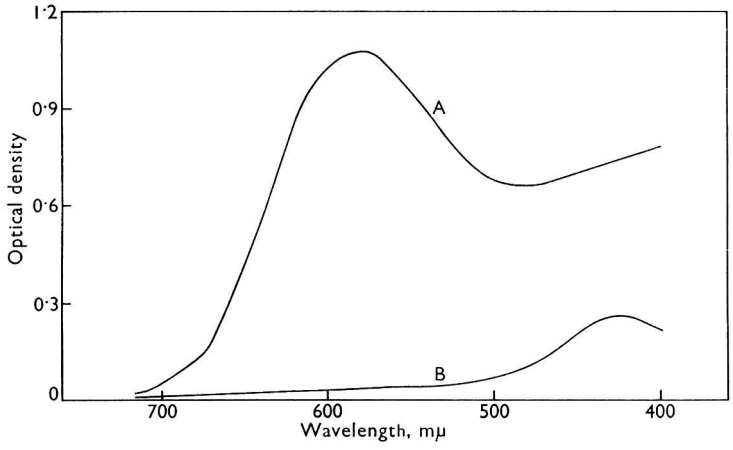


Fig. 1. Absorption spectra of uranium$^{VI}$ - glyoxal bis-(2-hydroxyanil) complex and reagent blank solution: curve A, complex formed from 500 μg of uranium (as $UO_3$); curve B, blank solution

SOLUBILITY OF URANIUM$^{VI}$ IN ALKALINE SOLUTION—

As uranium$^{VI}$ can be precipitated as uranate under alkaline conditions, the solubility of this ion was investigated; no precipitation occurred when sodium hydroxide solution was added to solutions containing 100 μg of uranium trioxide per ml (the maximum concentration used in the method). It is possible that traces of carbonate normally present in sodium hydroxide keep the uranium$^{VI}$ in solution as its carbonate complex (when barium hydroxide solution was used in place of the sodium hydroxide, a precipitate was formed).

At a concentration of 1 mg of uranium trioxide per ml, *i.e.*, ten times that used in the method, precipitation occurred with sodium hydroxide solution. Addition of carbonate prevented immediate precipitation, but, as the complexing agents EDTA and triethanolamine also had this effect, it was considered unnecessary and undesirable to add further carbonate to the sodium hydroxide solution.

FORMULA OF COMPLEX—

Preliminary work in which the slope-ratio[9] and continuous-variation[10] methods were used indicated that the complex contained two molecules of glyoxal bis-(2-hydroxyanil) to

one of uranium$^{VI}$. This was confirmed with greater precision by measuring the optical densities of solutions in which the total equivalent concentrations of uranium and reagent were kept constant, the relative amounts being varied. Different proportions of solutions 0·001 M in uranium and 0·002 M in the reagent were used, the total volume being kept at 2·00 ml. The results are plotted in Fig. 2.

## Method

### Reagents—

*Sodium hydroxide*, 0·50 N—Freshly prepare this solution from analytical-reagent grade pellets.

*Glyoxal bis-(2-hydroxyanil) solution, 0·25 per cent. w/v, in methanol*—Freshly prepared.

*Triethanolamine solution, 2 per cent. v/v, in water.*

*EDTA solution*, 0·25 M—Prepare from analytical-reagent grade disodium ethylenediaminetetra-acetate.

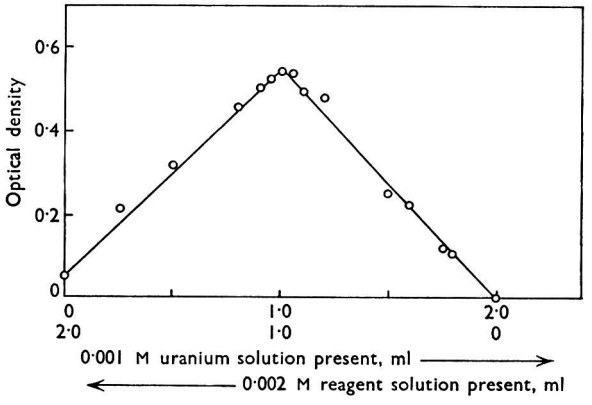


Fig. 2. Optical densities of solutions containing $x$ ml of 0·001 M uranyl nitrate, $(2 - x)$ ml of 0·002 M reagent solution, 1 ml of 0·25 M EDTA solution and 2·0 ml of 0·50 N sodium hydroxide. Final volume made up to 25 ml with 50 per cent. v/v aqueous methanol

### Procedure—

Transfer 5 ml of solution containing not more than 500 $\mu$g of uranium trioxide to a 25-ml calibrated flask, and add 1 ml of the EDTA solution. (If the acidity of the sample solution is more than 0·1 N, remove the excess of acid by evaporation, and dissolve the residue in EDTA solution.) Add 1 ml of triethanolamine solution, 2 ml of 0·50 N sodium hydroxide and 1 ml of glyoxal bis-(2-hydroxyanil) solution; mix well after each addition. Dissolve the precipitate formed by adding 12 ml of methanol, dilute to the mark with water, and mix. Set the solution aside for 1 hour, and then measure its optical density (1-cm cell) at 575 m$\mu$ against 50 per cent. aqueous methanol with a Uvispek spectrophotometer or similar instrument. Carry out control and blank experiments concurrently with the determination.

For amounts of uranium trioxide less than 100 $\mu$g, use a 0·05 per cent. w/v solution of glyoxal bis-(2-hydroxyanil). Beer's law is obeyed over the range 10 to 500 $\mu$g of uranium trioxide. The optical density for 500 $\mu$g of uranium trioxide compared with the reagent is about 1·02, the blank value being approximately 0·02.

## Interference of foreign ions

In alkaline methanolic solution, in the absence of complexing agents, certain metallic ions react with glyoxal bis-(2-hydroxyanil) and others are precipitated as hydroxides. Calcium and nickel form red complexes, that of nickel tending to be precipitated. Copper forms a greenish yellow and cobalt a yellow complex, which tends to be precipitated; manganese forms a brown precipitate. These complexes are not stable in presence of EDTA, by the use of which interference can be overcome or considerably decreased; EDTA has no effect on the uranium complex, provided that the alkalinity of the solution is maintained by adding a corresponding amount of 0·50 N sodium hydroxide.

The ions $Mg^{2+}$, $Ba^{2+}$, $Be^{2+}$, $Ti^{4+}$ and $Th^{4+}$ form white precipitates whether the reagent is present or not, and these are probably hydroxides or carbonates. (The white precipitate produced with thorium slowly turns brown over a few hours, indicating slow reaction with the reagent.) These precipitates decrease the intensity of the uranium - glyoxal bis-(2-hydroxyanil) colour, possibly by adsorption of uranium. Addition of EDTA prevents precipitation of $Mg^{2+}$, $Ba^{2+}$ and $Th^{4+}$, but $Be^{2+}$ and $Ti^{4+}$ interfere in this way and can only be tolerated in small amounts. A red solution, possibly colloidal ferric hydroxide, is produced with $Fe^{3+}$ ions; the addition of triethanolamine retains $Fe^{3+}$ in solution as a colourless complex and has no effect on the uranium complex. There is no interference from $As^{5+}$, $Al^{3+}$, $Cr^{6+}$ and $V^{5+}$.

Of the common anions, only orthophosphate and carbonate have any significant effect; these anions decreased the sensitivity of the method, probably by competing with the reagent for the uranium. (As carbonate decreases the sensitivity, freshly prepared sodium hydroxide should be used in the procedure.) Chloride, fluoride, nitrate and sulphate have no significant effect and can be tolerated in a 100-fold excess. The effects on the recovery of uranium of various ions are shown in Table I.

TABLE I

EFFECTS OF VARIOUS IONS ON RECOVERY OF URANIUM BY PROPOSED METHOD

Uranium (500 $\mu$g, as uranium trioxide) was determined in 25-ml final volumes of solution

| Compound added | Amount added, mg | Uranium found, $\mu$g | Error, % |
|---|---|---|---|
| $Al_2(SO_4)_3$, $NH_4VO_3$, $K_2Cr_2O_7$ | 4 (as $Al_2O_3$), 4 (as $V_2O_5$), 4 (as $CrO_3$) | 500 | 0·0 |
| $BaCl_2$, $MgSO_4$ | 4 (as BaO), 4 (as MgO) | 501 | +0·2 |
| $Na_2HAsO_4$ | 4 (as $As_2O_5$) | 500 | 0·0 |
| $(NH_4)_2SO_4.Fe_2(SO_4)_3$ | 1 (as $Fe_2O_3$) | 504 | +0·8 |
| $Th(NO_3)_4$ | 1 (as $ThO_2$) | 507 | +1·4 |
| $CaCl_2$ | 1 (as CaO) | 501 | +0·2 |
| $MnSO_4$ | 1 (as MnO) | 505 | +1·0 |
| | 0·1 (as MnO) | 500 | 0·0 |
| $Ni(NO_3)_2$ | 1 (as NiO) | 507 | +1·4 |
| | 0·1 (as NiO) | 501 | +0·2 |
| $Co(NO_3)_2$ | 1 (as CoO) | 519 | +3·8 |
| | 0·1 (as CoO) | 503 | +0·6 |
| $CuSO_4$ | 1 (as CuO) | 512 | +2·4 |
| | 0·1 (as CuO) | 501 | +0·2 |
| $BeSO_4$ | 0·1 (as BeO) | 500 | 0·0 |
| $Ti(SO_4)_2$ | 0·1 (as $TiO_2$) | 505 | +1·0 |
| $Na_2CO_3$ | 1 (as $CO_2$) | 495 | −1·0 |
| | 0·1 (as $CO_2$) | 498 | −0·4 |
| $(NH_4)_2HPO_4$ | 1 (as $P_2O_5$) | 483 | −3·4 |
| | 0·4 (as $P_2O_5$) | 494 | −0·8 |
| $NaNO_3$ | 50 (as $NO_3^-$) | 500 | 0·0 |
| NaCl | 50 (as $Cl^-$) | 499 | −0·2 |
| $Na_2SO_4$ | 50 (as $SO_4^{2-}$) | 503 | +0·6 |
| NaF | 50 (as $F^-$) | 496 | −0·8 |

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Received *March 28th*, 1962

# Determination of Residual Chlorine in Chlorinated Sea Water

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A spectrophotometric method is reported for determining residual chlorine in chlorinated sea water; it is based on the bleaching action of chlorine on methyl orange. Anions such as sulphate, acetate, phosphate and nitrate do not interfere. Large amounts of weak oxidising agents, such as ferric iron, cupric copper and iodine in potassium iodide, do not oxidise the indicator under the given experimental conditions. Hydrogen peroxide, potassium dichromate and hydrated manganese dioxide react slowly, and bromine and permanganate react in the same way as chlorine. The method does not measure the combined residual chlorine in the absence of bromide ion in the sample.

Sea water is used as the secondary coolant in the Canada India Reactor. This coolant is chlorinated to kill micro-organisms, and it is often necessary to determine the residual chlorine. Chlorine in water samples is generally determined by measuring the colour produced by the reaction between *o*-tolidine and the chlorine.[1] However, this method has the disadvantage that many other oxidising ions, such as ferric and manganic, react in the same manner as chlorine.

The bleaching action of chlorine on methyl orange has been used in volumetric[2,3] and visual colorimetric[4] methods. It has been reported[4] that bleaching is insensitive in the presence of substantial amounts of iron and is retarded by the presence of sulphuric, nitric or acetic acid. This paper describes the systematic development of a spectrophotometric method for determining the residual chlorine, based on the decolorisation of methyl orange.

## Experimental

### Reagents—

*Methyl orange stock solution*—A 0·05 per cent. aqueous solution was prepared from a sample of E. Merck G.R. methyl orange dried at 110° C for 2 hours. This solution was stable indefinitely.[4]

*Methyl orange working solution*—A 0·0025 per cent. solution was obtained by diluting the stock solution. This solution retained its strength for at least 1 month.

*Hydrochloric acid, chlorine free*—The commercially pure grade of acid was diluted almost to the constant-boiling mixture, and then distilled. The distillate, after the first 200 ml, was found to be chlorine free.

*Chlorine water*—Chlorine gas was bubbled through distilled water having no chlorine demand. The chlorine content was determined iodimetrically before use.

### Apparatus—

Optical-density measurements were made with a Beckman DU spectrophotometer and 10-mm Corex cells.

### Preliminary experiments—

Preliminary experiments revealed that the optical-density difference for various chlorine contents was less for Congo red than it was for methyl red or methyl orange. Further experiments were all carried out with methyl orange.

*Absorption spectrum*—Five millilitres of a 0·0025 per cent. solution of methyl orange were mixed with 1·0 ml of 6 M hydrochloric acid and diluted to 25 ml. A study of the absorption spectrum between 400 and 700 mμ (see Fig. 1) revealed a broad maximum at 510 mμ with a molecular extinction coefficient of 43,900. All further absorption measurements were made at this wavelength.

*Effect of acidity*—The acid dissociation constant of methyl orange is 3·5,[5] and it can be shown that the acid form of the indicator in 0·03 M acid is 99 per cent. dissociated; at higher acidities any further influence would be too small to be detected. Five-millilitre portions of the working solution of the indicator were adjusted to different acidities in total volumes of 25 ml by adding 6 M hydrochloric acid. There was no significant change in optical density over the range 0·024 to 0·48 M; the results were—

| | | | | | |
|---|---|---|---|---|---|
| Acidity, M .. .. | 0·024 | 0·12 | 0·24 | 0·48 | 2·40 |
| Optical density.. .. | 0·670 | 0·670 | 0·674 | 0·673 | 0·709 |

However, the optical density in 2·4 M acid was high. Hence the acidity in all further experiments was maintained at 0·24 M.

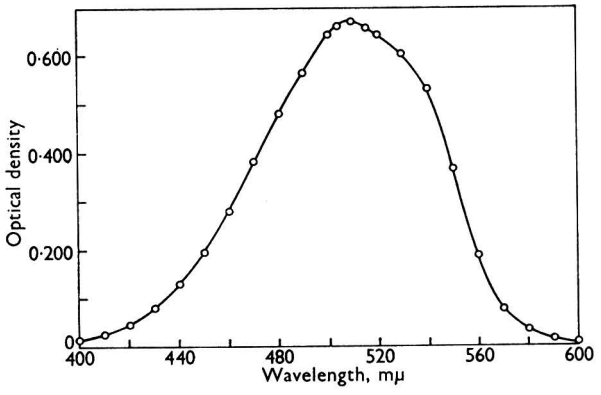



Fig. 1. Absorpt on spectrum for acidic methyl orange

RATE OF REACTION BETWEEN CHLORINE AND THE INDICATOR—

A consideration of the relative errors in the spectrophotometric measurements indicated the use of 5 ml of a 0·0025 per cent. solution of the indicator in a total volume of 25 ml. To test the rate of reaction, different amounts of chlorine were added to 5-ml portions of this solution in 25 ml, and optical densities were measured after different intervals of time; the results are shown in Table I. Reaction was complete within 2 minutes, which was the minimum time required for the manipulations.

TABLE I

RATE OF REACTION BETWEEN METHYL ORANGE AND CHLORINE

| Chlorine added, μg | Optical density ($D - D_n$)* after— 2 minutes | 10 minutes | 30 minutes |
|---|---|---|---|
| 1 | 0·020 | 0·024 | 0·022 |
| 12·5 | 0·293 | 0·290 | 0·293 |
| 25 | 0·599 | 0·600 | 0·601 |

* $D$ = Optical density of 5 ml of 0·0025 per cent. indicator solution in a total volume of 25 ml.
$D_n$ = Optical density ($D$) after reaction with chlorine.

CALIBRATION CURVE—

Five-millilitre portions of the indicator working solution were placed in separate 25-ml calibrated flasks and 1 ml of 6 M hydrochloric acid was added to the contents of each flask. A different amount of chlorine, ranging from 1 to 25 μg, was added to the contents of all the flasks except one, and the volume in each flask was made up to the mark; optical densities were then measured at 510 mμ. The $D - D_n$ values plotted against the amount of chlorine added in μg (see Fig. 2) gave a linear calibration curve.

STABILITY OF CHLORINE SOLUTIONS—

Losses on storage of gases dissolved in water were expected. To study this effect the chlorine water was suitably diluted and then standardised iodimetrically. Portions of this solution containing 8 p.p.m. of chlorine were taken at various intervals of time, and the chlorine was determined spectrophotometrically. The results shown below indicate some loss of chlorine during storage—

| Time of storage, minutes .. | 0 | 10 | 30 | 60 | 120 | 180 | 300 |
|---|---|---|---|---|---|---|---|
| Chlorine content, p.p.m. .. | 8·0 | 8·0 | 7·9 | 7·6 | 7·0 | 6·9 | 6·2 |

These losses varied according to the concentration of chlorine as well as the climatic conditions; variations are also expected in samples.

TABLE II

INTERFERENCE FROM OTHER IONS

| Chlorine taken, μg | Ion added (100 mg) | Chlorine found, μg | Difference, μg |
|---|---|---|---|
| 12·5 | Sulphate | 12·4 | −0·1 |
| | Nitrate | 12·8 | 0·3 |
| | Phosphate | 12·3 | −0·2 |
| | Acetate | 12·5 | 0·0 |

EFFECT OF FOREIGN IONS—

(*a*) The influence of some other ions on the bleaching action of chlorine on methyl orange was studied, and the results are shown in Table II. The optical-density measurements were made 10 minutes after the solutions had been mixed. It can be seen from the results that sulphate, nitrate, phosphate and acetate do not interfere.

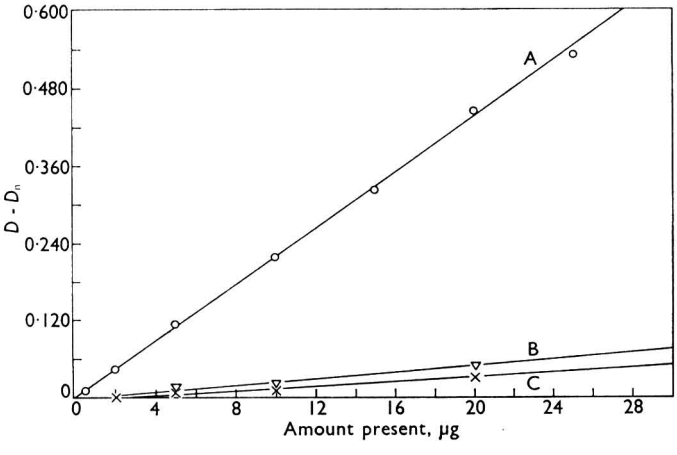



Fig. 2. Calibration graph for chlorine and bleaching effect of manganese dioxide monohydrate: curve A, chlorine; curve B, $MnO_2.H_2O$ measured 10 minutes after the reagents had been mixed; curve C, as for curve B, but measured after 30 minutes

(*b*) The bleaching effects of ferric iron, cupric copper and iodine in potassium iodide at concentrations up to 40, 10 and 1 g per litre, respectively, were studied. Each test was carried out on 5 ml of the indicator solution, and it was found that these ions did not bleach the indicator. On the contrary, they increased the optical densities by amounts quantitatively accounted for by their own absorptions at this wavelength.

Hydrogen peroxide and potassium dichromate did bleach the indicator, but the rate of bleaching was found to be slow. Potassium dichromate (5 mg) and hydrogen peroxide (3 mg) were each found to be equivalent to approximately 0·5 μg of chlorine when the reaction was allowed to proceed for about 10 minutes.

TABLE III

DETERMINATION OF CHLORINE IN SAMPLES OF PREPARED AND NATURAL SEA WATER

| Volume of sample, ml | Chlorine added, p.p.m. | Chlorine found, p.p.m. | Difference, p.p.m. |
|---|---|---|---|
| *Prepared sea water 1*†— | | | |
| 5 | 1·68 | 1·76 | +0·08 |
| 5 | 3·39 | 3·33 | −0·06 |
| 5 | 4·18 | 4·20 | +0·02 |
| 5 | 5·22 | 5·35 | +0·13 |
| 10 | 0·80 | 0·75 | −0·05 |
| 10 | 1·63 | 1·60 | −0·03 |
| 10 | 2·40 | 2·50 | +0·10 |
| 10 | 2·88 | 2·70 | −0·18 |
| 15 | 0·49 | 0·47 | −0·02 |
| 15 | 1·00 | 0·94 | −0·06 |
| 15 | 1·43 | 1·54 | +0·11 |
| 15 | 1·93 | 1·93 | 0·00 |
| *Prepared sea water 2*‡— | | | |
| 5 | 2·08 | 2·04 | −0·04 |
| 5 | 3·14 | 3·20 | +0·06 |
| 5 | 4·20 | 4·34 | +0·14 |
| 5 | 5·18 | 5·10 | −0·08 |
| 10 | 0·99 | 0·99 | 0·00 |
| 10 | 2·00 | 1·88 | −0·12 |
| 10 | 2·43 | 2·53 | +0·10 |
| 10 | 2·98 | 2·90 | −0·08 |
| 15 | 0·41 | 0·41 | 0·00 |
| 15 | 0·83 | 0·81 | −0·02 |
| 15 | 1·02 | 0·98 | −0·04 |
| 15 | 1·24 | 1·25 | +0·01 |
| *Natural sea water 1*— | | | |
| 5 | 2·16 | 0·80 | 1·36* |
| 5 | 6·48 | 4·06 | 2·42 |
| 5 | 6·92 | 4·40 | 2·52 |
| 10 | 1·08 | 0·32 | 0·76* |
| 10 | 3·24 | 0·82 | 2·42 |
| 10 | 4·32 | 1·53 | 2·79 |
| 10 | 4·54 | 2·02 | 2·52 |
| 15 | 0·72 | 0·08 | 0·64* |
| 15 | 2·88 | 0·49 | 2·39 |
| 15 | 3·45 | 0·94 | 2·51 |
| *Natural sea water 2*— | | | |
| 5 | 2·62 | 0·83 | 1·79* |
| 5 | 5·07 | 1·78 | 3·29 |
| 5 | 5·26 | 1·93 | 3·33 |
| 5 | 5·41 | 1·92 | 3·49 |
| 5 | 6·64 | 3·43 | 3·21 |
| 5 | 6·64 | 3·28 | 3·36 |
| 5 | 8·33 | 5·12 | 3·21 |
| 5 | 8·33 | 5·12 | 3·21 |
| 5 | 8·33 | 5·18 | 3·15 |

* Reaction of chlorine with oxidisable matter not complete unless excess of chlorine was added.

† Prepared sea water 1 contained (in g per kg): NaCl, 23·476; $MgCl_2$, 4·981; $Na_2SO_4$, 3·917; $CaCl_2$, 1·102; KCl, 0·664; $NaHCO_3$, 0·192; KBr, 0·096; $H_3BO_3$, 0·026; $SrCl_2$, 0·024; NaF, 0·003.

‡ Prepared sea water 2 contained (in g per kg): NaCl, 26·518; $MgCl_2$, 2·447; $MgSO_4$, 3·305; $CaCl_2$, 1·141; KCl, 0·725; $NaHCO_3$, 0·202; NaBr, 0·083.

The bleaching effect of manganese dioxide monohydrate, prepared by oxidising manganese sulphate with potassium persulphate, was tested; the monohydrate was reported to be more reactive than the anhydrous salt.[6] A slurry of the monohydrate was used, and the reaction was found to be slow (see Fig. 2).

Bromine and potassium permanganate were found to bleach the indicator as rapidly and quantitatively as did chlorine.

## METHOD

### DETERMINATION OF CHLORINE IN SAMPLES OF SEA WATER—

Two samples prepared to simulate sea water, having the compositions reported by Brujewicz and Lyman and Sverdrup, Johnson and Fleming,[7] and two samples of sea water from Bombay, all containing known amounts of added chlorine, were analysed by the procedure described below. The results are shown in Table III. The consistently low values obtained for the natural samples indicated the chlorine demand of the sea water. As the results were constant within experimental error the validity of the procedure was indicated. The results marked with an asterisk show that the reaction of chlorine with the oxidisable matter in the sea water was not complete unless an excess of chlorine was added.

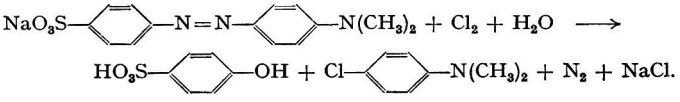
Residual chlorine present as chloramine will not react with the indicator in the absence of bromide in the samples.[8]

### PROCEDURE—

By pipette place a 5-ml portion of the sample in a 25-ml calibrated flask, add 1 ml of 6 M chlorine-free hydrochloric acid and 5 ml of methyl orange working solution, and dilute to the mark with distilled water. Prepare a corresponding reagent blank solution. Measure the optical densities of the solution against distilled water at 510 m$\mu$. Calculate $D - D_n$ for each sample, and read the corresponding amounts of chlorine ($S$ $\mu$g) from the calibration graph. The chlorine content, in $\mu$g per ml, is given by $\frac{S}{5}$.

## DISCUSSION OF THE METHOD

Methyl orange reacts with chlorine in accordance with the equation[9]—



With powerful oxidising agents such as hydrogen peroxide (30 per cent.) dissolved in glacial acetic acid, it has been reported[10] that the azo-group is oxidised to an azoxy group. Taras[4] reported that, at pH 3·0, anions such as nitrate, sulphate and acetate interfere. However, under the experimental conditions described here the reaction with peroxide was found to be slow and no interference was encountered from nitrate, sulphate or acetate.

We thank Shri Ch. Venkateswarlu for useful discussions during the progress of the work.

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Received *February 5th*, 1962

# The Determination of Iron by Solvent Extraction

## Part I. The Determination of Iron in Zone-refined Aluminium

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A method is described for determining iron contents below 15 p.p.m. in zone-refined aluminium; several improvements on earlier procedures are incorporated. Iron is extracted with isobutyl methyl ketone (hexone) from a concentrated solution of aluminium chloride of low acidity. The formation of emulsions and the slow separation of phases experienced by other workers are avoided by adjustment of phase volumes, and, by working at low acidity, extraction of aluminium chloride and hydrochloric acid is prevented. Iron is quantitatively removed from the organic phase by extraction with a buffered solution containing 1,10-phenanthroline, and the colour is measured absorptiometrically.

Methods are available for determining iron in aluminium and aluminium alloys down to the levels present in super-purity metal (aluminium produced by the British Aluminium Company Ltd. of purity not less than 99·9 per cent.) *i.e.*, 0·0015 per cent. or 15 p.p.m. These methods, in which 1,10-phenanthroline is used as colour-forming reagent, are absorptiometric and are carried out without separation of iron; the different ranges are covered by suitable selection of sample weight. The method for determining iron in super-purity aluminium can be extended down to 5 p.p.m., but at this level the blank value is of similar magnitude. At iron levels below 15 p.p.m., as in zone-refined metal, either a more sensitive reagent must be used or some preliminary separation of iron carried out.

Several phenanthroline derivatives are available commercially, some of which are more sensitive than the parent compound, *e.g.*, 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) is twice as sensitive. However, none of them is sufficiently sensitive to cope with the low concentrations present in zone-refined aluminium. An advantage of the phenanthroline derivatives is that the ferrous complexes are soluble in organic solvents and can therefore be separated by extraction. However, this technique would be unsuitable for determining the low levels of iron encountered in zone-refined aluminium, since large amounts of reagents, *e.g.*, buffer solution, would be required before the extraction stage and would consequently tend to produce high blank values.

There are three techniques for separating small amounts of iron from other elements: ion exchange, solvent extraction and co-precipitation. This paper is devoted to a consideration of solvent-extraction procedures.

Solvent extraction has long been used for separating iron, the technique being clean, simple and almost specific. Most separations are based on the extraction of the ferric chloride complex from a hydrochloric acid solution. The earliest solvent was diethyl ether[1] from 6 N hydrochloric acid, but it has several disadvantages—extraction is possible only over a limited range of acidity, the distribution ratio is low (~100), ether has a high solubility in concentrated hydrochloric acid, considerable heat is generated and total extraction is often difficult owing to photochemical reduction to non-extractable ferrous iron.

Improved results can be obtained with the less volatile di-isopropyl ether[2] or $\beta\beta'$-dichlorodiethyl ether[3]; extraction is more efficient over a wider range of acidity, volume changes owing to mutual solubility are smaller and no reduction of iron occurs.

More recently, ketones, which have distribution ratios considerably higher than those of the ethers, have been used. In particular, isobutyl methyl ketone (4-methyl-2-pentanone or hexone),[4,5] an inexpensive solvent, has found some application, particularly for the separation of large amounts of iron, *e.g.*, in the removal of iron from steel before determining other elements.

Other separations depend on the extraction of the red ferric thiocyanate colour with ether or pentanol, of the oxinate with chloroform or of the cupferrate with ether, chloroform or ethyl acetate. Another separation involves the extraction of iron from a solution at pH 1·0 with acetylacetone in chloroform.

Solvent extraction of iron has been mainly confined to the separation of milligram amounts, and little has been published on the separation of microgram amounts. The requirements for the satisfactory solvent extraction of microgram amounts of iron from a large bulk of aluminium are: (*i*) a large distribution ratio, (*ii*) the extraction should be carried out from acid solution, (*iii*) the amount of aluminium extracted should be small, (*iv*) the procedure should be simple and should not require the additions of large amounts of different reagents and (*v*) the technique should be capable of giving low blank values. From these considerations, solvent extraction of the ferric chloride complex would appear to have advantages over other solvent-extraction procedures.

Specker and Doll[4] reported distribution ratios for ferric iron between isobutyl methyl ketone and various concentrations of hydrochloric acid indicating that maximum extraction efficiency occurred at between 5 and 7 N; distribution ratios (D) of 500, ~2000 and ~5000 were obtained in 5, 6 and 7 N acid, respectively.

Similar figures were obtained by Claassen and Bastings[5] (D = 350, 3000, 7000 to 10,000 and 5000 in 5, 6, 7 and 7·5 N acid, respectively) who also reported the occurrence of emulsification preventing separation of the two phases. They overcame this by using a mixed solvent of pentyl acetate and isobutyl methyl ketone in the ratios of (1 + 2) or (1 + 1) by volume. Similar distribution ratios were obtained with the mixed solvents and with pentyl acetate over slightly higher acidity ranges. (Iron could be removed from concentrated hydrochloric acid by shaking with pentyl acetate, thus giving a useful method for purifying this reagent.) The distribution ratio was shown to be large from 500 down to 5 mg of iron in 50 ml of solution. Below this level the value fell, and, at 1 mg of iron per 50 ml, D was 1000. Lower levels of iron were not examined.

## Experimental

To examine the effect of aluminium on the efficiency of the extraction of iron with isobutyl methyl ketone, tests were made on 1-g samples of pure aluminium having iron contents in the range 10 to 65 p.p.m. by extracting twice from 40 ml of 7 N hydrochloric acid with 10-ml portions of isobutyl methyl ketone. All solutions were previously oxidised with nitric acid. (Bromine water was an unsuccessful oxidant; it was soluble in the organic phase and brominated the isobutyl methyl ketone with some reduction of iron. A similar reduction of copper was noted by Denaro and Occleshaw[6] in the extraction of metallic bromides with isobutyl methyl ketone from hydrobromic acid solutions.) Iron was extracted with water from the organic phase, and then determined absorptiometrically.

The organic phase dissolved large amounts of aluminium chloride and hydrochloric acid, and thus made it difficult to remove the iron by extraction with water; several washes were required, which resulted in excessively large volumes for the final colorimetric determination. The determination of iron in the organic phase was therefore carried out by evaporating the solution to small volume to remove the isobutyl methyl ketone and excess of acid. However, the solutions obtained were yellow owing to oxidation of organic matter; the results in the subsequent determination of iron with 1,10-phenanthroline were high. It was then discovered that iron could readily be removed from the organic phase by shaking with a mixed reagent containing sodium acetate, hydroxyammonium chloride and 1,10-phenanthroline, any free acid being neutralised by adding ammonia solution until the pH of the aqueous phase after it had been shaken was 4. Under these conditions, the complete removal of ferric iron from the organic phase is achieved owing to (*a*) reduction of iron with hydroxyammonium chloride and (*b*) formation of a complex with 1,10-phenanthroline. After several modifications the composition of the mixed reagent was adjusted so that there was sufficient acetate present to buffer the acid extracted into the organic phase, requiring only small additions of ammonia solution to produce the correct pH, sufficient hydroxyammonium chloride to reduce the iron completely and an excess of 1,10-phenanthroline for full colour development.

No difficulties arising from emulsification were experienced in separating the phases. Specker and Doll attributed this emulsification to traces of fat or grease, and Claassen and Bastings attempted to overcome it by using mixtures of isobutyl methyl ketone and pentyl acetate (2 + 1 and 1 + 1). Our investigation showed that the formation of emulsions and the slow separation of phases were caused by mutual solubilities, and occurred when equal volumes of the two phases were shaken together. This was most marked when mechanical shaking was carried out. Emulsification was readily prevented by altering the ratio of phase volumes to (1 + 2) organic - aqueous; separation was then rapid.

As previously stated, large amounts of aluminium chloride and hydrochloric acid were extracted into the organic phase and it was necessary to wash this phase with 7 N acid (rendered free from iron by extraction with isobutyl methyl ketone) before proceeding. With such small amounts of iron present there was some loss during washing, and the results, compared with those by direct determinations, were low. Successive extractions were carried out and it was observed that, after the first extraction, only small amounts of aluminium chloride and acid were removed in the subsequent extractions. This was due to the removal of acid from the aqueous phase until an equilibrium was reached at about 5 N. The result of this was that the efficiency of extraction fell exponentially, and incomplete recoveries were obtained.

A few experiments were carried out in a Craig counter-current apparatus and also in a continuous liquid - liquid extractor. However, considerable trouble was experienced owing to transfer of acid and aluminium chloride into the organic phase, and these procedures were abandoned.

Extractions were then carried out at different acidities; larger weights of sample (5 g) and a mechanical shaker were used. For the preparation of sample solutions, iron-free hydrochloric acid was prepared by the procedure described on p. 715. Aluminium chloride, present in high concentrations, acted as an efficient salting-out agent, and extractions could be carried out at acidities much lower than 7 N to obtain complete recovery of iron. Moreover, at lower acidities no aluminium chloride or acid passed into the organic phase.

Extraction of iron at low acidities is so greatly enhanced by the presence of aluminium chloride, that, at sufficiently high concentrations (4 g of aluminium, as chloride, in 100 ml of solution), no excess of acid is required. The results of a series of tests on solutions containing 1 to 4 g of aluminium, as chloride, with no excess of acid and in N hydrochloric acid in a volume of 100 ml, with 50 ml of isobutyl methyl ketone, are shown in Fig. 1. The solutions

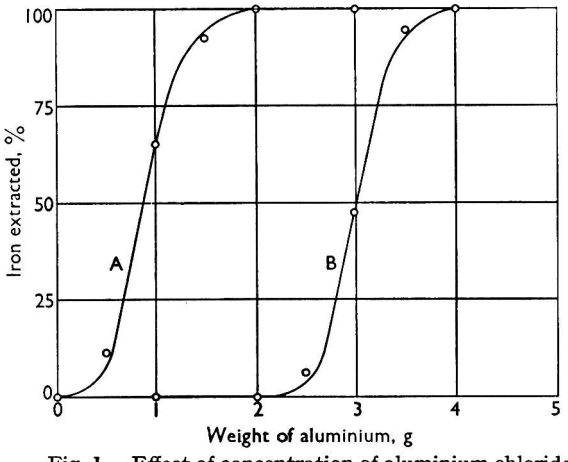


Fig. 1. Effect of concentration of aluminium chloride and acidity on the efficiency of extraction of iron with isobutyl methyl ketone: curve A, N hydrochloric acid; curve B, no excess of hydrochloric acid. (Volume of aqueous phase, 100 ml; volume of organic phase, 50 ml; weight of iron added, 7·5 $\mu$g)

of aluminium chloride were prepared from super-purity aluminium extracted several times with isobutyl methyl ketone to remove the iron. An addition of 7·5 $\mu$g of iron was made to each solution, and extractions were then carried out. The organic extracts were separated and the iron was determined absorptiometrically after extraction into an aqueous solution of mixed reagent.

Fig. 1 shows that extraction increases rapidly with increase in aluminium concentration; at a concentration of 4 g of aluminium in 100 ml, complete extraction of iron is achieved without addition of hydrochloric acid. However, the efficiency of extraction is further improved by working in solutions N in hydrochloric acid, which give complete extraction of iron from 2 g of aluminium in a volume of 100 ml.

The experiments on samples of zone-refined aluminium reported below were carried out with solutions N in hydrochloric acid and an aluminium concentration of 5 g (as chloride) in 125 ml of solution. Full details are given under "Method."

This procedure has other applications in the solvent extraction of iron, since complete extraction can be achieved by working at acidities lower than 7 N by the addition of a solution of iron-free aluminium chloride.

Increased efficiency of extraction can be explained by the common-ion effect, the removal of water molecules from the aqueous phase by the salting-out agent, and suppression of dissociation of the complex halogen acid of $Fe^{3+}$.

In view of the results obtained, the experiment was extended to cover much higher levels of iron, although not applicable to this work. Iron (150 $\mu$g) was added to a series of solutions containing from 1 to 4 g of iron-free aluminium, as chloride, in 100-ml portions of solution N or 2 N in acid, and extractions were carried out with 50-ml portions of isobutyl methyl ketone. The results in Table I show that, at this level of iron, the efficiency of extraction is high.

TABLE I

EXTRACTION OF IRON FROM ALUMINIUM CHLORIDE SOLUTIONS

| Weight of aluminium, g | Acidity | Iron added, $\mu$g | Iron found, $\mu$g | Extraction, % |
|---|---|---|---|---|
| 4 | N | 150 | 147 | 98 |
| 3 | N | 150 | 146 | 97 |
| 2 | N | 150 | 140 | 93 |
| 1 | 2 N | 150 | 140 | 93 |

TABLE II

EXTRACTION OF IRON FROM HYDROCHLORIC ACID

The volume of acid used in each test was 300 ml

| Extraction | Acid batch No. | Volume of mixed solvent, ml | Ratio of pentyl acetate to benzene | Iron extracted, $\mu$g |
|---|---|---|---|---|
| 1st | 1 | 90 | 5 to 1 | 13·4 |
| 2nd | | | | 4·7 |
| 1st | 1 | 90 | 5 to 1 | 13·4 |
| 2nd | | | | 2·4 |
| 1st | 1 | 70 | 2·5 to 1 | 12·8 |
| 2nd | | | | 1·5 |
| 1st | 2 | 75 | 2 to 1 | 45·2 |
| 2nd | | | | 1·7 |
| 1st | 2 | 150 | 2 to 1 | 40·2 |
| 2nd | | | | 3·4 |
| 1st | 2 | 75 | 2 to 1 | 40·2 |
| 2nd | | | | 4·1 |
| 1st | 2 | 150 | 2 to 1 | 39·2 |
| 2nd | | | | 2·8 |

PREPARATION OF IRON-FREE HYDROCHLORIC ACID—

An attempt was made to prepare iron-free concentrated hydrochloric acid by shaking with pentyl acetate, but the components became completely miscible after mechanical shaking for only a few minutes. The addition of benzene was found to prevent this, and, provided sufficient benzene was added, separation of acid from the organic phase was complete. Complete separation of the phases was achieved at solvent ratios in the range (5 + 1) to (2 + 1) pentyl acetate - benzene. The efficiency of extraction was high and was unaffected by changes in ratio. A (2 + 1) ratio of solvents was chosen for subsequent work with a (2 + 1) ratio of acid phase to organic phase. Iron in the organic phase was determined, as previously discussed, by extraction with a mixed reagent (acetate buffer, hydroxylamine and 1,10-phenanthroline) and the colour was measured absorptiometrically. The efficiency of the removal of iron from concentrated analytical-reagent grade hydrochloric acid is shown in Table II.

The addition of benzene to the isobutyl methyl ketone - aluminium chloride - 7 N hydrochloric acid system had a similar effect in preventing mutual solubility of the two phases, and all difficulties associated with extraction of aluminium chloride and acid into the solvent phase were overcome. This procedure was used later for determining iron in super-purity aluminium-based hardener alloys, and is reported in Part II of this series.[7]

## Method

Reagents—

*Hydrochloric acid, diluted* (1+1)—Dilute 500 ml of analytical-reagent grade hydrochloric acid, sp.gr. 1·18 (see Note 1), with 500 ml of water.

*Mercuric chloride solution, 5 per cent., aqueous.*

*Nitric acid, sp.gr.* 1·42—Analytical-reagent grade.

*Isobutyl methyl ketone.*

*Pentyl acetate - benzene mixture*—Mix 200 ml of pentyl acetate with 100 ml of benzene.

*Mixed reagent*—Mix 30 ml of 0·2 per cent. 1,10-phenanthroline solution, 30 ml of 5 per cent. hydroxyammonium chloride solution and 30 ml of 4 M sodium acetate. Dilute to 100 ml, and mix.

*Standard iron solution*—Dissolve 1·5 g of pure iron in 80 ml of diluted sulphuric acid (1 + 3) and 5 ml of nitric acid, sp.gr. 1·42, and dilute to 1·0 litre.

1 ml ≡ 1·5 mg of iron.

Dilute this solution 200-fold to give a solution containing 7·5 μg of iron per ml.

Procedure—

To a clean approximately 5-g piece of metal (see Note 2), accurately weighed and contained in a 600-ml beaker (see Note 3), add in small portions 125 ml of diluted hydrochloric acid (1 + 1) containing 15 drops of 5 per cent. mercuric chloride solution. When the violent reaction has subsided, heat gently on the edge of a hot-plate until solution is complete; add a few drops of nitric acid, and evaporate the solution until crystals of aluminium salts begin to appear. Remove from the hot-plate, and add 50 ml of water to dissolve the salts and a few drops of nitric acid to ensure complete oxidation of the iron.

Cool if necessary, pour the solution into a glass-stoppered 500-ml conical flask, wash the beaker with a few millilitres of water, and add the washings to the contents of the flask. Add 10 ml of iron-free concentrated hydrochloric acid, and dilute to 125 ml. Add 60 ml of isobutyl methyl ketone, and shake the flask mechanically for 5 minutes. Transfer the contents to a 250-ml separating funnel, and run the aqueous (lower) phase back into the conical flask, retaining the organic phase in the separating funnel. Repeat the extraction of the aqueous phase with a further 60 ml of isobutyl methyl ketone, transfer to a clean 250-ml separating funnel, and run off the aqueous layer and discard it. Combine the two ketone extracts, and drain off any residual water.

Add 10 ml of mixed reagent, and shake by hand for one minute. Transfer the lower layer containing the red ferrous - 1,10-phenanthroline complex into a 25-ml calibrated flask (see Note 4), and wash the isobutyl methyl ketone phase twice with water; add the washings to the contents of the 25-ml flask (see Note 5). Make up to the mark, mix, and measure the optical density of the solution at 510 mμ in 4-cm cells (see Note 6).

Carry out a blank determination on 145 ml of the diluted hydrochloric acid (1 + 1), omitting the mercuric chloride, as described below.

Evaporate the acid to small volume (1 to 2 ml), and dilute slightly. Add 10 ml of mixed reagent, transfer to a 25-ml calibrated flask, and dilute to the mark. Mix, and measure the optical density in the same way as for the samples.

Calibrate the instrument as described below. Measure from a microburette 0 to 5·0 ml of dilute standard iron solution (1 ml ≡ 7·5 μg of iron) into separate 25-ml calibrated flasks. Dilute each to 10 ml, add 10 ml of mixed reagent, dilute to volume, mix, and measure the optical densities under the same conditions as for the samples. A plot of optical densities against nominal iron contents give a straight line.

Notes—

1. To clean the hydrochloric acid, place 300 ml of acid (sp.gr. 1·18) and 5 drops of nitric acid (sp.gr. 1·42) in a glass-stoppered 500-ml conical flask. Mix, and add 150 ml of pentyl acetate - benzene mixture. Shake mechanically for 5 minutes. Transfer to a separating funnel, allow the phases to

separate, and run the acid (lower) phase back into the stoppered flask. Discard the pentyl acetate - benzene layer, and repeat the extraction with a second 150 ml of pentyl acetate - benzene mixture. Separate as before, and retain the clean acid for use as required.

2. To clean the sample, saw off a portion weighing about 6 g. Remove saw marks and rough irregularities from all faces with a Surform file, until a clean smooth surface is presented. Pickle the sample in hot hydrochloric acid (1 + 1), or, preferably, hot sulphuric acid (1 + 4), for several minutes, and then decant off the acid. Wash the sample twice with distilled water and finally with acetone. Dry between clean filter scrap, and weigh.

Alternatively, if turnings are required, use a clean tungsten carbide-tipped tool, and discard the first few turnings.

3. All glassware should be cleaned in aqua regia.

4. The pH of the aqueous solution should be checked at this stage and adjusted, if necessary, to approximately 4 by adding ammonia solution. If any adjustment has to be made, the solution should be returned to the separating funnel and re-shaken with the isobutyl methyl ketone. If a pH meter is not available the colour of the aqueous phase can be used as an indication of the pH, as no colour will develop if the solution is too acid. The pH can be adjusted by the dropwise addition of ammonia solution with frequent shaking of the two phases until the red ferrous colour develops.

5. This procedure covers the range of iron contents up to 7·5 p.p.m. For iron contents from 7·5 to 15 p.p.m., dilute to a final volume of 50 ml. For samples with iron contents over 15 p.p.m. the direct procedure should be used.[8]

6. If a filter photometer is used, *e.g.*, a Spekker absorptiometer, a mercury-vapour lamp with Ilford 603 filters, which isolate the mercury lines at 492 and 496 m$\mu$, is suitable.

### Interfering elements—

Zone-refined aluminium would not be expected to contain impurities at levels greater than the iron content of the sample and thus there will be no interferences with the method. However, during these investigations an examination was made of some super-purity aluminium-based hardeners containing copper, zinc and nickel. A suitable technique was evolved, based on the findings in the work described here, and is discussed in Part II of this series.[7]

### Analysis of samples—

Five samples of zone-refined aluminium having iron contents ranging from 2·1 to 7·2 p.p.m. were analysed. A standard error of $\pm$0·031 p.p.m. was obtained on 22 determinations.

## Conclusions

The method described is suitable for determining iron contents in the range 0·5 to 15 p.p.m. in zone-refined aluminium. Above this level the direct procedure can be used. The method incorporates the improvements listed below on previous methods of solvent extraction with isobutyl methyl ketone.

(1) Prevention of emulsion formation and slow phase separation by adjustment of phase volumes.

(2) Prevention of extraction of aluminium chloride and hydrochloric acid by working in solutions of low acidity.

(3) Purification of hydrochloric acid with pentyl acetate and benzene resulting in good phase separation and small loss of acid into the organic phase.

(4) Quantitative extraction of iron with isobutyl methyl ketone from concentrated solutions of aluminium chloride of low acidity.

(5) Quantitative removal of iron from the organic phase by extraction with a buffered solution containing 1,10-phenanthroline.

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Received *March 5th*, 1962

# The Determination of Iron by Solvent Extraction

## Part II. Application to Aluminium-based Hardener Alloys

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The determination of iron in super-purity aluminium-based hardeners containing copper, nickel, cobalt, chromium or zinc is described. The method involves solvent extraction with a mixture of isobutyl methyl ketone (hexone) and benzene from 7 N hydrochloric acid. The mixed solvent is preferable to isobutyl methyl ketone alone when working with small weights of sample at high acidity, as less aluminium chloride, hydrochloric acid and interfering elements are extracted. Iron is quantitatively removed from the organic phase by extraction with a buffered solution containing 1,10-phenanthroline and then determined absorptiometrically.

The determination of low concentrations of iron by solvent extraction has been discussed in Part I of this series.[1] The same technique was investigated for determining iron in super-purity aluminium-based hardener alloys, which contain elements that interfere with the photometric 1,10-phenanthroline method.

As larger concentrations of iron are present in super-purity aluminium-based hardeners than in zone-refined aluminium, smaller weights of sample can be used. Solvent extraction with isobutyl methyl ketone from solutions of aluminium chloride low in acid is then unsuitable, because of the small volume needed to give a sufficiently high concentration of aluminium chloride.

Preliminary tests on a super-purity aluminium-based copper hardener by extraction with isobutyl methyl ketone from 7 N hydrochloric acid showed that large amounts of aluminium and acid, and sufficient copper to interfere with the final colour development with 1,10-phenanthroline, were extracted into the organic phase. However, these difficulties can be overcome by extracting with an isobutyl methyl ketone - benzene solvent. The optimum ratio of isobutyl methyl ketone to benzene for efficient extraction of iron with minimum interference was found to be (2 + 1). At higher ratios, acid and aluminium were extracted in increasing amounts, whereas at lower ratios the efficiency of extraction was reduced.

The (2 + 1) solvent mixture was used to investigate the determination of iron in super-purity aluminium-based hardeners containing metals that interfere with the direct determination with phenanthroline. Copper, zinc, nickel and cobalt consume reagent and, if present in excessive amounts, must be separated before determining the iron. Chromium interferes by virtue of the colour of the chromic ion.

### Experimental

A series of experiments was carried out to determine the amounts of the separate interfering elements, copper, zinc, nickel, cobalt and chromium, that would be extracted from 7 N hydrochloric acid with the mixed isobutyl methyl ketone - benzene solvent (2 + 1). Previous work[1] had shown that, to avoid the formation of emulsions and the slow separation of phases, the ratio of acid to organic phase should be maintained at (2 + 1) for both extraction and washing. The amounts of each element extracted into the organic phase were determined by washing with 7 N hydrochloric acid and suitably analysing the washings.

#### Extraction of interfering metals with isobutyl methyl ketone - benzene—

A solution of 1 g of metal or its equivalent as chloride was prepared in 100 ml of 7 N hydrochloric acid; traces of iron were oxidised with a small amount of nitric acid. Extraction was carried out with 50 ml of (2 + 1) solvent mixture for 5 minutes on a mechanical shaker. (Shaking times of 5 minutes were probably excessive, as extraction of iron from pure solutions appeared complete within 30 seconds.) The liquids were poured into a dry separating funnel, the phases were allowed to separate, and the lower (acid) phase was run off. A small amount of solvent was then run off to wash the stem of the funnel free from the acid solution, and

discarded. The remainder of the organic layer was then run into a clean dry beaker. The separating funnel was washed to remove drops of the acid layer adhering to the walls, and dried. The solvent was returned to the funnel and washed up to three times with 100-ml portions of 7 N hydrochloric acid, shaking for one minute each time. The washings were analysed for the respective elements.

Copper was determined polarographically by using an ammonia - ammonium chloride base electrolyte, and also by the photometric diethyldithiocarbamate method. Zinc was determined polarographically in a potassium hydroxide base electrolyte. Nickel was determined gravimetrically with dimethylglyoxime. Cobalt was determined photometrically with nitroso-R salt.

The results are recorded in Table I and show the amounts of each element extracted by the mixed solvent and appearing in the acid washings. These amounts are so small that they can be tolerated in the photometric determination of iron by addition of extra phenanthroline reagent. However, a single wash with 7 N acid is sufficient to reduce their concentrations to negligible proportions.

TABLE I

EXTRACTION OF INTERFERING METALS WITH MIXED SOLVENT

Each test was carried out on 1 g of metal in 100 ml of 7 N hydrochloric acid. Extraction was carried out with 50 ml of mixed solvent and the extract was washed with 100-ml portions of 7 N hydrochloric acid

| Metal | Wash No. | Weight of metal in washings, mg | Metal extracted, % |
|---|---|---|---|
| Copper | 1 | 0·8 | 0·08 |
| | 2 | 0·04 | 0·004 |
| | 1 | 1·4 | 0·14 |
| | 1 | 1·2 | 0·12 |
| Zinc | 1 | 1·35 | 0·14 |
| | 2 | 0·25 | 0·02 |
| | 3 | Trace | — |
| Nickel | 1 | 0·93 | 0·09 |
| Cobalt | 1 | 0·53 | 0·05 |

In a solution containing chromic ions only, no colour was extracted into the organic phase and, as chromium interferes with the photometric determination of iron only by virtue of its colour, no determination of extracted chromium was carried out. Chromate ions, on the other hand, were extracted into the organic phase producing a highly coloured solvent phase and oxidation of the ketone to isobutyric acid. Chromate, if present, must therefore be converted to the tervalent state by boiling with hydrochloric acid until chlorine fumes are no longer evolved.

EXTRACTION OF COPPER UNDER VARIOUS CONDITIONS—

A comparison was made of the amounts of copper extracted (*a*) with isobutyl methyl ketone alone under the same experimental conditions as before and (*b*) with the mixed solvent from 8 N hydrochloric acid. The results are shown in Table II, and the values are much greater than those in Table I. Four washes were required to remove copper completely from the organic phase.

EXTRACTION OF COPPER IN PRESENCE OF ALUMINIUM—

To investigate the salting-out effect of aluminium chloride, prepared 50 per cent. copper hardeners, *i.e.*, 0·5 g of aluminium and 0·5 g of copper, in 7 N hydrochloric acid were extracted with mixed solvent and with isobutyl methyl ketone alone. The organic phases were evaporated to the appearance of fumes with perchloric and nitric acids, and copper was determined photometrically on portions of the solution. The results were—

| | Copper extracted, mg | Copper extracted, % |
|---|---|---|
| Isobutyl methyl ketone | 8·04 | 0·80 |
| Mixed solvent | 0·34 | 0·03 |

It can be seen that aluminium had little effect, as the results were of the same order as those in Tables I and II, although slightly lower as less copper was present.

DETERMINATION OF IRON IN PRESENCE OF COPPER—

To determine the recovery of iron in the presence of copper, a solution of 1 g of copper in 100 ml of 7 N acid was extracted several times with mixed solvent to remove traces of iron originally present. Iron (75 $\mu$g) was then added, and the solution was extracted with mixed solvent and treated in accordance with the scheme shown in Table III. The acid used for washing had previously been extracted with mixed solvent to remove traces of iron.

TABLE II

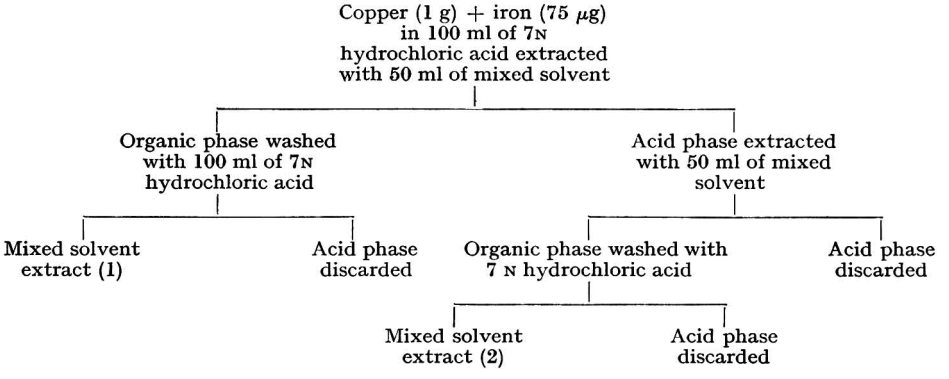
EXTRACTION OF COPPER WITH ISOBUTYL METHYL KETONE FROM 7 N HYDROCHLORIC ACID AND WITH MIXED SOLVENT FROM 8 N HYDROCHLORIC ACID

Each test was carried out on 1 g of copper in 100 ml of acid

| Solution | Wash No. | Weight of copper in washings, mg | Copper extracted, % |
|---|---|---|---|
| Isobutyl methyl ketone from 7 N acid .. | 1 | 10·6 | 1·06 |
| | 2 | 0·57 | 0·06 |
| Mixed solvent from 8 N acid .. .. | 1 | 5·4 | 0·54 |

TABLE III

SCHEME FOR DETERMINING IRON IN PRESENCE OF COPPER




The two mixed solvent extracts were shaken with mixed reagent (sodium acetate, hydroxyammonium chloride and 1,10-phenanthroline) and the iron was determined photometrically. The iron contents (75 $\mu$g added) of the two extracts were—

| | |
|---|---|
| Mixed solvent extract (1) .. .. | 75·3 $\mu$g |
| Mixed solvent extract (2) .. .. | 1·0 $\mu$g |
| Total .. .. | 76·3 $\mu$g |

DETERMINATION OF IRON IN SUPER-PURITY ALUMINIUM-BASED SAMPLES—

To check the accuracy of the method the analysis of super-purity aluminium based alloys, whose iron contents had already been determined by the direct phenanthroline method,[2] was carried out. For these samples, which contained a maximum of 0·36 per cent. of copper, the amount of copper extracted by mixed solvent would have been extremely low (based on extractions from 1 g of copper) and no acid washing of the organic phase was necessary. However, two samples were washed to determine the loss of iron. Sample weights of 1 g were used, and extractions were carried out with 25 ml of mixed solvent from a volume of 50 ml of 7 N acid. The results in Table IV show that extraction of iron was complete.

COMPARISON OF THE USE OF MIXED SOLVENT AND ISOBUTYL METHYL KETONE—

As an extension of the work, the extraction of large amounts of iron with the mixed solvent was carried out. Five-milligram portions of iron in a total volume of 100 ml from 4 to 10·8 N

in acid were extracted with 50 ml of mixed solvent, and the iron was determined absorptiometrically in the acid phases. The percentage extraction was compared with the figures obtained by Specker and Doll,[3] who used isobutyl methyl ketone alone. The results are shown in Table V.

Isobutyl methyl ketone is satisfactory over the range 4 to 8 N; above 8 N large volume changes occur and eventually there is complete miscibility of the two phases. The mixed solvent is satisfactory over the range 6 to 10·8 N with maximum extraction at 9 N, but this is not the optimum acidity, as there is a marked increase in the extraction of interfering elements when the acidity is increased above 7 N. Volume changes, which are negligible up to 7 N acid, increase with increase in acidity, and eventually there is a 40 per cent. loss of mixed solvent in concentrated acid.

No difficulties were experienced with the separation of the phases at the different acidities.

TABLE IV

DETERMINATION OF IRON IN SUPER-PURITY ALUMINIUM-BASED SAMPLES

The weight of sample taken for each test was 1 g

| Sample No. | Extraction No. | Iron found by proposed method, % | Iron found by phenanthroline method, % | Iron added, % |
|---|---|---|---|---|
| 5759 (0·36% of Cu) | 1 | 0·0131 | 0·0132† | — |
| | 2 | 0·0003 | | |
| | 3 | 0·0001 | | |
| | 1 | 0·0141 | | |
| | 1 | 0·0127* | | |
| 5759 (after extraction) + 15 μg of Fe | 1 | 0·0014 | — | 0·0015 |
| | 1 | 0·0015* | | |
| 7163/69 | 1 | 0·0028 | 0·0025‡ | — |
| | 2 | 0·0005 | | |
| | 3 | 0·0002 | | |
| | 1 | 0·0024 | | |
| | 1 | 0·0021* | | |

* Solvent extracts washed with 7 N hydrochloric acid, as outlined in Table III.
† Mean of 6 results.
‡ Mean of 4 results.

TABLE V

EFFICIENCY OF EXTRACTION OF IRON AT DIFFERENT ACIDITIES

| Normality of hydrochloric acid | Final volume of— organic phase, ml | Final volume of— acid phase, ml | Weight of iron remaining in acid phase, μg | Extraction, % | Extraction with isobutyl methyl ketone,[3] % |
|---|---|---|---|---|---|
| 4 | 50 | 100 | 1620 | 67·6 | 98·4 |
| 5 | 50 | 100 | 250 | 95·0 | 99·8 |
| 6 | 48 | 102 | 52 | $98{\cdot}9_6$ | $99{\cdot}9_5$ |
| 7 | 48 | 102 | 8·5 | $99{\cdot}8_3$ | $99{\cdot}9_8$ |
| 8 | 46 | 104 | 5·6 | $99{\cdot}8_9$ | ~99 |
| 9 | 44 | 106 | 4·8 | $99{\cdot}9_0$ | — |
| 10 | 39 | 111 | 9·3 | $99{\cdot}8_1$ | — |
| 10·8 | — | — | 64 | $98{\cdot}7_2$ | — |
| 11·3 | 30 | 120 | — | — | — |
| 7* | 44 | 106 | — | — | — |

* Final phase volumes when extraction was carried out from 100 ml of 7 N hydrochloric acid with 50 ml of isobutyl methyl ketone.

## METHOD

REAGENTS—

*Pentyl acetate - benzene mixture* (2 + 1)—Mix 2 volumes of pentyl acetate with 1 volume of benzene.

*Isobutyl methyl ketone - benzene mixture* (2 + 1) *(mixed solvent)*—Mix 2 volumes of isobutyl methyl ketone with 1 volume of benzene.

*Hydrochloric acid, diluted* (1 + 1)—Dilute 500 ml of analytical-reagent grade hydrochloric acid, sp.gr. 1·18, with 500 ml of water (see Note 1).

*Nitric acid, sp.gr.* 1·42—Analytical-reagent grade.

*Mixed reagent*[1]—Mix 30 ml of 0·2 per cent. 1,10-phenanthroline solution, 30 ml of 5 per cent. hydroxyammonium chloride solution and 30 ml of 4 M sodium acetate. Dilute to 100 ml, and mix.

*Standard iron solution*—Dissolve 1·5 g of pure iron in 80 ml of diluted sulphuric acid (1 + 3) and 5 ml of nitric acid, sp.gr. 1·42, and dilute to 1·0 litre.

1 ml ≡ 1·5 mg of iron.

Dilute this solution 200-fold to give a solution containing 7·5 μg of iron per ml.

PROCEDURE—

Dissolve 1 g of metal in 25 ml of diluted hydrochloric acid (1 + 1), and add a few drops of nitric acid to oxidise the iron. Carry out at the same time a blank determination by the same procedure and with the same amounts of reagents.

Evaporate until crystals appear (10 ml for the sample; 1 to 2 ml for the blank determination), and add 31 ml of hydrochloric acid and water to give a total volume of 50 ml; warm to dissolve, and cool to room temperature (see Note 2).

Extract for 5 minutes on a mechanical shaker with 25 ml of mixed solvent, and then run off the lower (acid) phase from the separating funnel.

Carry out a second extraction with 25 ml of mixed solvent. Again separate the acid phase, and discard. Combine the two organic phases (see Note 3).

Add to the organic phase a few millilitres of water and 10 ml of mixed reagent, and shake for 30 seconds to extract iron. Run off the aqueous phase into a 25-ml calibrated flask (see Note 4), wash the organic phase with water, and add the washings to the contents of the flask. Dilute the aqueous phase to the mark with water.

Measure the optical densities at 510 mμ in 4-cm cells (see Note 5).

Calibrate the instrument as described below. Measure from a microburette 0 to 5·0 ml of dilute standard iron solution (1 ml ≡ 7·5 μg of iron) into separate 25-ml calibrated flasks. Dilute each to 10 ml, add 10 ml of mixed reagent, dilute to volume, mix, and measure the optical densities under the same conditions as for the samples. A plot of optical densities against nominal iron contents gives a straight line.

NOTES—

1. To clean the hydrochloric acid, place 300 ml of hydrochloric acid (sp.gr. 1·18) and 5 drops of nitric acid (sp.gr. 1·42) in a glass-stoppered 500-ml conical flask. Mix, and add 150 ml of pentyl acetate - benzene mixture. Shake mechanically for 5 minutes. Transfer to a separating funnel, allow the phases to separate, and run the acid (lower) phase back into the stoppered flask. Discard the organic layer, and repeat the extraction with a second 150 ml of pentyl acetate - benzene mixture. Separate as before, and retain the clean acid for use as required.

2. These conditions cover iron contents up to 0·014 per cent. For iron contents >0·014 per cent., use a smaller weight of sample. When interfering elements exceed 50 per cent., add 62 ml of hydrochloric acid, and dilute the solution to 100 ml.

3. If the organic phase is coloured owing to the presence of copper, or if the concentration of interfering elements is high, wash the organic layer with 100 ml of 7 N hydrochloric acid. Separate and discard the acid layer (7 N acid can be cleaned by shaking with mixed solvent).

4. The final volume is varied according to the iron content—
For iron up to 0·0035 per cent., dilute to 25·0 ml.
For 0·0035 to 0·0070 per cent., dilute to 50·0 ml.
For 0·0070 to 0·014 per cent., dilute to 100·0 ml.

5. If a filter photometer is used, *e.g.*, a Spekker absorptiometer, a mercury-vapour lamp with Ilford 603 filters, which isolate the mercury lines at 492 and 496 mμ, is suitable.

## CONCLUSIONS

1. The mixed solvent is preferable to isobutyl methyl ketone alone for extracting iron from super-purity aluminium-based hardeners containing elements that interfere with the photometric 1,10-phenanthroline method (copper, zinc, nickel, cobalt and chromium).

2. Usually, the amount of interfering element extracted with the iron into the organic phase is sufficiently small to permit the determination of iron in its presence without interference.

3. When the initial concentration of interfering element is high, a single wash with 7 N hydrochloric acid suffices to remove the interfering element almost completely without loss of iron.

4. Optimum conditions for extraction occur at 7 N acid. At this concentration extraction of iron is complete and extraction of the interfering element is low.

5. Maximum extraction of iron with mixed solvent occurs in 9 N acid compared with 7 N acid for isobutyl methyl ketone alone.

6. Volume changes are negligible for extractions from 7 N acid and increase with increase in acidity.

7. No difficulties occur in the separation of the phases if the ratio of acid to organic phase is maintained at (2 + 1). With ratios of (1 + 1) and less, emulsification and slow separation of phases occur.

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1. Jackson, H., and Phillips, D. S., *Analyst*, **1962**, **87**, 712.
2. The British Aluminium Company Limited, Publication No. 405, London, 1961, p. 166.
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Received *March 5th*, 1962

# Differential Electrolytic Potentiometry

## Part VII.* The Interpretation of Current-Potential-Temperature Relationships of Antimony Electrodes in Neutral Solution

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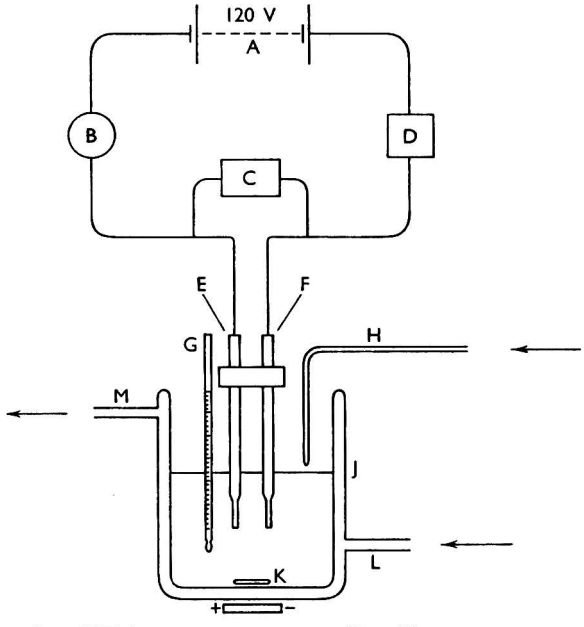
The application of differential electrolytic potentiometry to acid - base titrations with antimony electrodes has been employed to develop a method for investigating the mechanism of differential electrolytic potentiometry. Equations are derived that relate the differential potential at the end-point of a titration to the temperature of the solution and to the current used.

The application of differential electrolytic potentiometry to ion-combination reactions leading to the formation of sparingly ionised solvent molecules has been described.[1] The precision and accuracy of the method were established for all types of acid - base reactions in aqueous media at various dilutions for optimum values of the differentiating current. The forms of




| | |
|---|---|
| A = H.T. battery | G = Thermometer |
| B = Milliameter | H = Nitrogen inlet |
| C = pH meter | J = Jacketed beaker |
| D = Decade resistance box | K = Magnetic stirrer |
| E = Anode | L = Water inlet |
| F = Cathode | M = Water outlet |

Fig. 1. Apparatus and circuit for the determination of $E_\Delta$

the anodic, cathodic and differential titration curves were also established. It was realised that the nearly perfect reversibility of the reaction and the fast response speed of the antimony electrodes afforded a unique opportunity for studying the variation of the differential potential with current, temperature, pH and other variables both quickly and simply. This paper

*Part VI of this series appeared in *Analyst*, 1962, **87**, 467.

deals with the construction and interpretation of current - potential - temperature curves at pH 7 in the presence of a neutral salt of a strong acid and a strong base, *i.e.*, at the equivalence-point of any strong acid - strong base titration. Potentials determined at this point will represent the maximum height of the differential peak for the corresponding titration.

## Experimental

### Apparatus—

The vessel used to contain the salt solution was made from a 400-ml beaker sealed by the rim inside an 800-ml beaker. Two side-arms were fitted so that water could be circulated around the space between the beakers to keep the contents of the inner beaker at constant temperature. Two antimony electrodes labelled anode and cathode of area 0·126 sq. cm were positioned in the inner beaker. The differential potential was measured as before[1] with an E.I.L. 23A direct-reading pH meter, and the current was varied by altering the resistance on a decade resistance box. The solution was protected from air as much as possible by a cover fitted over the beaker, and nitrogen was blown continuously on to the surface of the solution. Water at controlled temperature was supplied by a Frigidaire refrigerator unit containing a five gallon tank of water, above-ambient temperatures being provided by two 250-watt heating bulbs immersed in the tank. A large paddle kept the water circulating in the tank and the heating or refrigeration were controlled by a mercury - toluene regulator via a Sunvic electronic relay. Any temperature between 0° and 50° C could be maintained in the tank to $\pm 0{\cdot}05°$ C. The water was circulated through the jacketed beaker by means of the pump of a Circotherm unit. The temperature of the test solution was monitored by a thermometer graduated in tenths, and the stability achieved was $\pm 0{\cdot}1°$ C. A diagram of the apparatus is shown in Fig. 1.

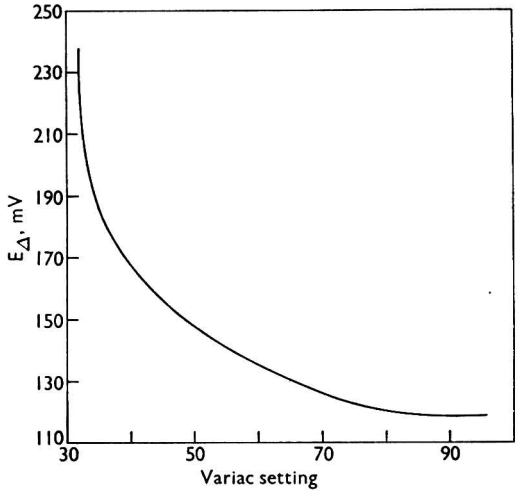



Fig. 2. Effect of stirring rate on $E_\Delta$

### Influence of stirring rate on differential potential—

The potential developed across the anode and cathode was found to depend on the rate at which the solution was stirred. This effect is well known for antimony electrodes,[2] and is to be expected in a diffusion-controlled process. However, as shown in Fig. 2, in which the potential is plotted against the setting of the Variac controlling the magnetic stirrer, a constant potential is reached at a high stirring rate, so that all subsequent determinations of potential were made while stirring at just below cavitation speed.

### Method—

The containing vessel was well washed and rinsed with carbon dioxide free distilled *water*,[1] placed in position with the nitrogen turned on, and charged with 200 ml of carbon

dioxide free *water* and about 0·5 g of AnalaR potassium sulphate. The two antimony electrodes were immersed in the solution, and the pumping unit was started. The initial current passed was set at $5 \times 10^{-7}$ amp at 50° C, and 30 minutes were allowed for the constant temperature and potential to reach equilibrium. The current was then varied by successive increments of about $2 \times 10^{-7}$ amp, and the resultant potential was recorded. After a set of readings had been taken with increasing current, a second set with decreasing current was taken to check on electrode hysteresis. Potentials in the middle of the current range usually reached equilibrium within 3 minutes. At both high and low currents up to 15 minutes was needed for equilibration. When a complete set of readings at 50° C had been made, the thermostat was adjusted to 40° C, and the series repeated. This was continued at various temperatures down to 0° C.

TABLE I

VARIATION OF DIFFERENTIAL POTENTIAL AT 20° C

| Resistance, megohms | Differential potential,* mV | Differential potential,† mV | Current, $I_\Delta$, amps |
|---|---|---|---|
| 500 | 98 | 101 | $2{\cdot}40 \times 10^{-7}$ |
| 350 | 123 | 123 | $3{\cdot}43 \times 10^{-7}$ |
| 250 | 139 | 141 | $4{\cdot}80 \times 10^{-7}$ |
| 200 | 150 | 151 | $6{\cdot}00 \times 10^{-7}$ |
| 150 | 163 | 165 | $8{\cdot}09 \times 10^{-7}$ |
| 120 | 176 | 178 | $1{\cdot}00 \times 10^{-6}$ |
| 100 | 187 | 188 | $1{\cdot}20 \times 10^{-6}$ |
| 80 | 200 | 201 | $1{\cdot}50 \times 10^{-6}$ |

* Current increasing.
† Current decreasing.

## RESULTS

The results of a typical series of determinations are shown in Fig. 3, in which the differential potential ($E\Delta$) is plotted against the differential current at 20° C. The results of a hysteresis check are shown in Table I. In general, the potentials were reproducible to $\pm 2$ mV in the current range shown. At higher currents fluctuations of $\pm 20$ mV were encountered, and at lower currents the electrode response to change of ballast resistance

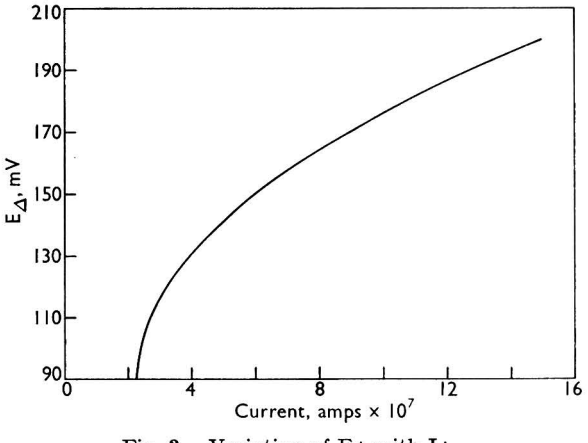



Fig. 3. Variation of $E\Delta$ with $I\Delta$

was sluggish. When $E\Delta$ was plotted against $\log_{10} I\Delta$ over the current range for which the potentials were reproducible, a straight line was obtained (see Figs. 3 and 4). The differential potential decreases with increase in temperature and decrease in current. The decrease is roughly such that a current increase of about one order of magnitude is required to counteract a 50° C rise in temperature.

## Discussion of results

The fact that the variation of $E\Delta$ with $\log_{10}I\Delta$ is linear over a wide current range encouraged the belief that an analysis of these results might lead to a theoretical interpretation of differential electrolytic potentiometry that would be of use both in predicting new phenomena and in explaining previous results. Later papers will show that this belief has been justified. This paper deals merely with establishing certain empirical data and some theoretical observations that have a bearing on later work.

For the linear portion of the curves—

$$E\Delta = k_1 \log_{10} I\Delta + k_2(T) \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where $E\Delta$ = differential potential (volts),
$I\Delta$ = differential current (amps) and
$k_1$ = slope (volts).

Since the isotherms are parallel within the limits of experimental error, the slope $k_1$ is independent of temperature. The intercept on the potential axis, $k_2$, is temperature dependent and can be defined as the value of $E\Delta$ at T ° C when $I\Delta$ is equal to unity.

From equation (1), when $E\Delta = 0$,

$$k_2(T) = -k_1 \log_{10} I_0 \quad .. \quad .. \quad .. \quad .. \quad (2)$$

Values of $k_2$, $k_1$ and $I_0$ are shown in Table II.

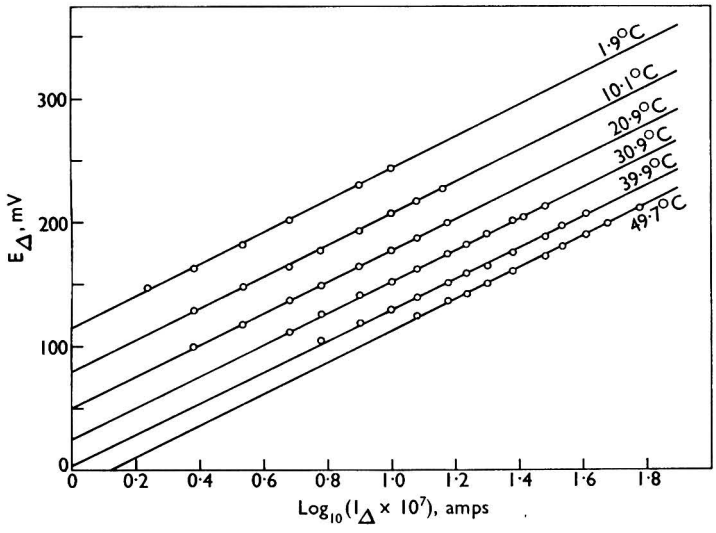



Fig. 4. Variation of $E\Delta$ with $\log_{10}(I\Delta \times 10^7)$ in the temperature range 0° to 50° C

For the complete evaluation of equation (1), the dependence of $k_2$ on temperature must be elucidated. When $k_2$ was plotted against $\log_{10}k_w$, a straight line resulted, so the relation must be of the form—

$$k_2 = k_3 \log_{10} k_w + k_4 \quad .. \quad .. \quad .. \quad .. \quad (3)$$

$k_3$ and $k_4$ were determined from the graph

$$-k_3 = +\ 0{\cdot}0766 \text{ volts}$$
$$-k_4 = +\ 0{\cdot}138 \text{ volts}$$

where $k_4$ is defined as the value of $k_2$ in volts at the temperature at which $k_w = 1$.

TABLE II

DATA DERIVED FROM FIG. 4

| T, °A | $\frac{1}{T}$ | $Log_{10}T$ | $k_2$, volts | $Log_{10}k_2$ | $I_0$, amps $\times 10^7$ | $Log_{10}I_0$ | $I_0^{5/3}$ | $I_0^2$ | $k_w \times 10^{15}$ | $Log_{10}k_w$ | $k_1$, volts |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 275·1 | 0·00364 | 2·4395 | 1·008 | 0·0033 | 0·1248 | $\bar{8}$·0962 | $6{\cdot}714 \times 10^{-14}$ | $1{\cdot}557 \times 10^{-16}$ | 1·450 | −14·84 | 0·1289 |
| 283·3 | 0·00353 | 2·4523 | 0·971 | $\bar{1}$·9872 | 0·2353 | $\bar{8}$·3712 | $1{\cdot}929 \times 10^{-13}$ | $5{\cdot}526 \times 10^{-16}$ | 3·020 | −14·52 | 0·1274 |
| 294·1 | 0·00340 | 2·4684 | 0·942 | $\bar{1}$·9741 | 0·3976 | $\bar{8}$·5995 | $4{\cdot}633 \times 10^{-13}$ | $1{\cdot}581 \times 10^{-15}$ | 7·59 | −14·12 | 0·1274 |
| 304·1 | 0·00329 | 2·4830 | 0·917 | $\bar{1}$·9624 | 0·6247 | $\bar{8}$·7957 | $9{\cdot}835 \times 10^{-13}$ | $3{\cdot}903 \times 10^{-15}$ | 15·85 | −13·80 | 0·1269 |
| 313·1 | 0·00319 | 2·4956 | 0·894 | $\bar{1}$·9513 | 0·9303 | $\bar{8}$·9686 | $1{\cdot}910 \times 10^{-12}$ | $8{\cdot}654 \times 10^{-15}$ | 29·51 | −13·53 | 0·1263 |
| 322·9 | 0·00312 | 2·5091 | 0·876 | $\bar{1}$·9425 | 1·3100 | $\bar{7}$·1173 | $3{\cdot}379 \times 10^{-12}$ | $1{\cdot}716 \times 10^{-14}$ | 56·23 | −13·25 | 0·1269 |

RELATION BETWEEN $I_0$ AND $k_w$

An interesting relation betweeen $I_0$ and $k_w$ was revealed by combining equations (2) and (3)—

$$-k_1 \log_{10} I_0 = k_3 \log_{10} k_w + k_4 \quad .. \quad .. \quad .. \quad .. \quad (4)$$

Let—

$$k_4 = k_3 \log_{10} k_5 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

then—

$$-k_1 \log_{10} I_0 = k_3 \log_{10} k_w k_5 \quad .. \quad .. \quad .. \quad .. \quad (6)$$

The ratio $k_1$ to $k_3 = 1{\cdot}665$ so—

$$I_0^{5/3} = k_w k_5 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

This relation was tested by plotting $I_0^{5/3}$ against $k_w$, and a straight line was obtained passing through the origin. There is thus a direct simple relation between $I_0$ and $k_w$, and between $k_2$ and $\log k_w$, over the temperature range investigated. Any theory of the mechanism of differential electrolytic potentiometry must involve the proof of these relations.

## THE MECHANISM OF DIFFERENTIAL ELECTROLYTIC POTENTIOMETRY

The mechanism of differential electrolytic potentiometry has not hitherto been closely examined, largely due to the fact that early work[3] was concentrated on irreversible and partially irreversible redox reactions, which are not susceptible to rapid determinations of peak heights on change of differential current or to easy understanding of end-point conditions.

The use of salt solutions to simulate exact reproducible end-point conditions, the almost perfectly reversible electrode reactions and the better data available on the physico-chemical constants of the $H_3O^+ - OH^- - H_2O$ system, have made the application of differential electrolytic potentiometry to pH titrations an adaptable method for the investigation of the mechanism of the process itself.

The most obvious approach is from the aspect of electrolysis. The minute differential current causes local concentration of hydrogen ions in the vicinity of the anode and of hydroxyl ions at the cathode. These concentrations will be proportional to the current producing them. Since the electrodes are chosen to respond to the ions that are surrounding them, a Nernstian potential is set up proportional to the concentration of these ions in the layers immediately adjacent to the surface of the electrodes. It is necessary, therefore, to account for the concentration of the ions in these layers in terms of the magnitude of the current passed. The factors referred to below must be considered.

(*a*) ELECTRODE REACTION—

It has been pointed out[1] that the exact choice of electrode reaction is unimportant, since the current yield is identical for all feasible reactions. It will be seen later that the exact value of $E_0$ is irrelevant also. The most plausible electrode reaction would seem to be—

$$\text{Cathode: } Sb_2O_3 + 6H^+ + 6\epsilon \rightleftharpoons 2Sb + 3H_2O \quad .. \quad .. \quad .. \quad (8)$$

$$\text{Anode: } 2Sb + 3H_2O \rightleftharpoons 6H^+ + 6\epsilon + Sb_2O_3 \quad .. \quad .. \quad .. \quad (9)$$

At the anode surface there will be a higher net concentration of hydrogen ions than in the bulk of the solution and at the cathode surface a higher net concentration of hydroxyl ions.

(*b*) DIFFUSION—

Evidently a concentration gradient will exist at the anode and cathode such that hydrogen ions from the anode and hydroxyl ions from the cathode diffuse into the bulk of the solution. As a first approximation it will be assumed that the two rates of diffusion are of the same order. This is a justifiable assumption at pH 7, where the concentration gradients may be taken to be identical.

(*c*) ELECTROMIGRATION—

Transport of active ions may be neglected under the prescribed conditions because of the relatively high concentration of inactive ions produced from the supporting electrolyte present in the solution.

(*d*) RATE OF STIRRING—

Agitation of the solution will affect the local concentrations of ions at the electrode surface, and hence the potential (see Fig. 2). The fact that a constant potential is established above a certain minimum stirring rate gave grounds for assuming that there is a layer immediately adjacent to the electrode surfaces unaffected by agitation of the solution. Since all measurements were conducted at a rate of stirring above this minimum, the stirring speed can be neglected as a variable in this treatment.

(*e*) pH OF THE SOLUTION—

It will be assumed that the pH of the bulk of the solution is $-\log_{10}k_w^{\frac{1}{2}}$. If the solution has a pH much lower or higher than this, then no significant net concentration of ions at either electrode can occur and no differential potential is recorded. This is a natural consequence of the logarithmic nature of the dependence of potential on concentration. Thus a change of concentration of $H^+$ ions at the cathode from $10^{-7}$ to $10^{-5}$ M resulting from the production of a concentration of $9{\cdot}9 \times 10^{-6}$ M, leads to a potential change of 120 mV, whereas a similar change of concentration at pH 4 leads to a potential change of only 2·4 mV. The presence of buffer in the solution leads to a zero differential potential because the concentration changes in the region of the electrodes are nullified by the buffer system. This accounts qualitatively for the existence of the differential peak. At the end-point of a titration the concentration difference between the anode and cathode exerts its strongest effect on the potential between them, and this effect rapidly diminishes on either side of the end-point, as $[OH^-]_C$ and $[H^+]_A$ diverge further from equality, producing the well known form of the differential curve.

It will be assumed, therefore, that the production of hydrogen ions at the anode will be balanced by an equivalent production of hydroxyl ions at the cathode, so at pH 7—

$$[OH^-]'_C = [H^+]'_A \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10)$$

where $[OH^-]'_C$ = increase in concentration of hydroxyl ions at the cathode and
$[H^+]'_A$ = increase in concentration of hydrogen ions at the anode.

Since the magnitude of these concentrations is a function of the current producing them, we have—

$$[OH^-]'_C = [H^+]'_A = f(I\Delta) \quad .. \quad .. \quad .. \quad .. \quad (11)$$

If the effect of diffusion as a factor in controlling the electrode surface concentrations is also assumed to be equivalent at each electrode at pH 7, then $f(I\Delta)$ will be a linear function, and we can write—

$$[OH^-]'_C = [H^+]'_A = k_6 I\Delta \quad .. \quad .. \quad .. \quad .. \quad (12)$$

where $k_6$ is a proportionality constant. The total concentration at each electrode must also include the ions present due to the ionisation of water, so—

$$[OH^-]_C = [OH^-]'_C + [OH^-]_B \quad .. \quad .. \quad .. \quad .. \quad (13)$$

and—

$$[H^+]_A = [H^+]'_A + [H^+]_B \quad .. \quad .. \quad .. \quad .. \quad (14)$$

where $[H^+]_A$ = actual concentration of hydrogen ion at the anode surface and
$[H^+]_B$ = concentration of hydrogen ion in the bulk of the solution.

From the fact that the potential - pH curves of both anode and cathode can be superimposed on the zero-current electrode curve[1] by a shift along the volume axis only, it will be seen that the Nernst relation is followed by both electrodes, and, further, no significant change in electrode reaction can occur. So if $E_A$ and $E_C$ designate the potentials of anode and cathode, respectively, then—

$$E_A = E_0 + \frac{RT}{nF}\log_e[H^+]_A \quad .. \quad .. \quad .. \quad .. \quad .. \quad (15)$$

$$E_C = E_0 + \frac{RT}{nF}\log_e[H^+]_C \quad .. \quad .. \quad .. \quad .. \quad .. \quad (16)$$

By combining equation (15) with equations (14) and (12), we obtain—

$$E_A = E_0 + \frac{RT}{nF}\log_e(k_6 I\Delta + [H^+]_B) \quad .. \quad .. \quad .. \quad (17)$$

Similarly—

$$E_C = E_0 + \frac{RT}{nF}\log_e \frac{k_w}{[H^+]_B + k_6 I_\Delta} \quad .. \quad .. \quad .. \quad (18)$$

The differential potential is now given by $E_A - E_C$, *i.e.*—

$$E_\Delta = \frac{RT}{nF}\log_e \frac{(k_6 I_\Delta + [H^+]_B)^2}{k_w} \quad .. \quad .. \quad .. \quad .. \quad (19)$$

ESTIMATION OF $k_6$—

A value for $k_6$ can be obtained from the Nernst equation for an individual electrode. At 20° C with a differential current of $5 \times 10^{-7}$ amp a potential of 0·140 volt is generated. Assuming anode and cathode contribute equally to this, each electrode must be displaced 0·070 volt from the potential it would display at pH 7 if no current were passed. If $E_N$ denotes the potential of the indicator electrode at pH 7, then—

$$E_N = E_0 + \frac{RT}{nF}\log_e 10^{-7} = E_0 - \frac{7 \times 2{\cdot}303RT}{nF} \quad .. \quad .. \quad .. \quad (20)$$

Let—

$$E_A = E_N + 0{\cdot}070 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (21)$$

By combining equations (21) and (15), we obtain—

$$\log_{10}[H^+]_A = \frac{0{\cdot}070 \times nF}{2{\cdot}303RT} - 7 = -5{\cdot}813$$

so—

$$[H^+]_A = 1{\cdot}54 \times 10^{-6} \text{ moles per litre.}$$

By inserting this value into equation (14) and combining with equation (12), we obtain—

$$k_6 = 2{\cdot}88.$$

## RELATION BETWEEN $E_\Delta$ AND $I_\Delta$

Reverting to equation (19), it can now be seen that for currents of $5 \times 10^{-7}$ amp and above, $[H^+]_B$ can be neglected in comparison with $k_6 I_\Delta$, hence—

$$E_\Delta = \frac{2{\cdot}303RT}{nF}\log_{10}\frac{(k_6 I_\Delta)^2}{k_w} \quad .. \quad .. \quad .. \quad .. \quad (22)$$

From equation (22)—

$$E_\Delta = 0 \text{ when } I_0^2 = \frac{k_w}{k_6^2} \quad .. \quad .. \quad .. \quad .. \quad (23)$$

However, the plot of $I_0^2$ against $k_w$ was non-linear, therefore $k_6$ must be temperature dependent. Combining equations (23) and (7), we obtain—

$$-\log_{10}k_6 = \tfrac{3}{5}\log_{10}k_5 + \tfrac{1}{10}\log_{10}k_w \quad .. \quad .. \quad .. \quad .. \quad (24)$$

Inserting equation (24) in equation (22) and rewriting—

$$E_\Delta = \frac{2 \times 2{\cdot}303RT}{nF}\log_{10}I_\Delta - \frac{6 \times 2{\cdot}303RT}{5nF}\log_{10}k_w - \frac{6 \times 2{\cdot}303RT}{5nF}\log_{10}k_5 \quad .. \quad (25)$$

Comparing this with the empirical equations (1), (3) and (5)—

$$E_\Delta = k_1\log_{10}I_\Delta + k_3\log_{10}k_w + k_3\log_{10}k_5 \quad .. \quad .. \quad .. \quad (26)$$

From theoretical considerations an equivalent expression has been obtained for $E_\Delta$ that is directly comparable with the empirical equation.

Thus—

$$-k_3 \equiv \frac{6}{5} \times \frac{2{\cdot}303RT}{nF} = 0{\cdot}071 \text{ volt,}$$

which compares with the experimental value of 0·0766 volt.

And—

$$k_1 \equiv \frac{2 \times 2{\cdot}303RT}{nF} = 0{\cdot}118 \text{ volt at } 20° \text{ C,}$$

which compares with the value of 0·127 volt obtained experimentally. The apparent independence of $k_1$ with temperature is explicable with the more elaborate theoretical treatment to be discussed in a later communication.

By simplifying equation (25), we obtain—

$$E = \frac{6 \times 2{\cdot}303RT}{5nF} \log_{10} \frac{I_\Delta^{5/3}}{k_5 k_w} \quad .. \quad .. \quad .. \quad .. \quad (27)$$

Equation (27) represents approximately the dependence of the differential potential at the equivalence-point on the differential current when antimony electrodes are used. The equation is not general since $k_6$, and hence $k_5$, will depend on the area of the electrodes and on the diffusion coefficients of the active ions. It is not valid in the presence of buffers or at pH values greatly differing from 7. It does, however, show that the mechanism proposed for differential electrolytic potentiometry has some justification, and it affords a starting point for the development of the more general equation embracing diffusion under acid and alkaline conditions.

MINIMUM CURRENTS—

An interesting corollary to equation (19) arises when the differential current is reduced to a level where $k_6 I_\Delta \ll [H^+]_B$.

$$E_\Delta = \frac{2{\cdot}303RT}{nF} \log_{10} \frac{(k_6 I_\Delta + [H^+]_B)^2}{k_w} \quad .. \quad .. \quad .. \quad (19)$$

so—

$$E_\Delta \simeq 0 \text{ when } [H^+]_B = k_w^{\frac{1}{2}}.$$

This means that there is a minimum current below which it is impracticable to conduct a differential electrolytic potentiometric titration, given by—

$$I_{min.} \ll \frac{k_w^{\frac{1}{2}}}{k_6} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (28)$$

Under the conditions used in this work the minimum current was therefore about $1{\cdot}0 \times 10^{-8}$ amp. This was roughly confirmed in practice, but it should be noted that equation (19) applies only to moderately high currents and is invalid at low currents. However, the indications are that the minimum current is dependent on the square root of the dissociation constant for a reversible bimolecular ion-combination reaction, and for the general reaction—

$$nA^- + mB^+ \rightleftharpoons B_mA_n$$

it can be shown that—

$$I_{min.} \ll \frac{n^n k^{1/m+n}}{m^m} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (29)$$

where k is the dissociation constant of $B_mA_n$. This relationship has been noted in other parts of this work.[4]

We thank Electronic Instruments Ltd. for their interest in and support of this work and for the loan of instruments. One of us (G.D.S.) gratefully acknowledges the support of an Electronic Instruments Ltd. Research Fellowship.

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Received *March 30th*, 1962

# A Cell Design for Radio-frequency Titrimetry

By A. H. COLLINS

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The type of cell normally used in radio-frequency titrimetry consists of a beaker having metal electrodes clamped to its outside surfaces. For such cells, the range of the titrimeter can be extended by increasing the frequency employed. By interpretation of an equivalent circuit, a capacitively coupled cell has been designed that, when used at a frequency of about one megacycle per second, has a range and sensitivity only obtainable at much higher frequencies with conventional cells. The construction of the cell is simple, and, apart from the measuring device, the only ancillary equipment required is a circulating pump of low volume that acts as a stirrer.

Many difficulties encountered in the measurement of electrolytic conductivity can be overcome by using external electrodes and coupling into the electrolyte either capacitively or inductively. In radio-frequency titrimetry, this method is used for the detection of end-points of titrations in media that would be deleterious to immersed electrodes. A typical application is for precipitation titrations such as those in which silver nitrate is used. Although various circuits have been employed for detecting end-points, derivation of an equivalent electrical circuit shows that two main factors influence the sensitivity and operating range of all titrimeters that have capacitive coupling. One of these factors, namely the frequency employed, has been used extensively to improve the performance of titrimeters; early models operated at a few Mc/s,[1] whereas in some recent examples the frequency exceeds 100 Mc/s.[2] The other factor is cell design, a subject that has received little attention. This paper describes how theoretical considerations can lead to the design of a simple cell that provides ample range and sensitivity at relatively low frequencies.

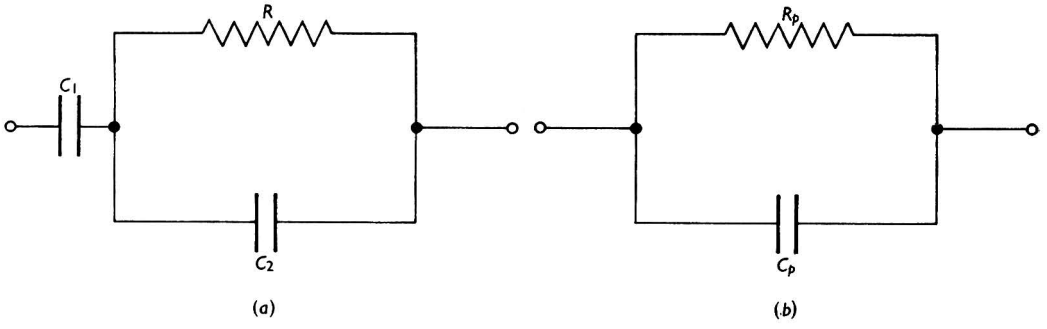


Fig. 1. *(a)* Equivalent circuit ($C_1$ is the coupling capacitance; $C_2$ and R are the capacitance and resistance, respectively, of the liquid); *(b)* simplified circuit as seen by measuring device

Design considerations—

Cells described in the literature generally consist of glass or plastic vessels around which are wrapped two metal bands acting as electrodes. The radio-frequency signal from the detector is therefore capacitively coupled to the liquid in the vessel. In less common arrangements the input signal is inductively coupled.

The theory of capacitively coupled cells has been discussed by reference to an equivalent electrical circuit.[3,4,5] Reilley and McCurdy[4] analysed the equivalent circuit shown in Fig. 1 (*a*) and thereby predicted the shapes of the response curves (see Fig. 2), which they verified by experiment. They also derived expressions for the positions of the minima in $R_p$ curves and points of inflexion in $C_p$ curves. For the design of a titrimetric cell, however, an objective study of the equivalent circuit and the response curves will suffice.

The electrical circuit of an R.F. titrimeter is based on the detection of changes in $R_p$ or $C_p$, or complex functions of these variables. Ideally, both $R_p$ and $C_p$ should vary linearly with the composition of the liquid (*i.e.*, $R$ and $C_2$). In most analytical applications, changes take place in cell resistance, $R$, owing to variations in electrolyte concentration occurring during a titration. The argument developed below is, however, equally applicable when detection is based on variations of cell capacitance, $C_2$.

In Fig. 1, the series capacitor $C_1$ is reponsible for the restricted range over which $R_p$ varies linearly with $R$. In designing a titrimeter cell, it is important, therefore, to minimise the influence of this coupling capacitance by making its reactance extremely small compared with the impedance of the cell liquid ($R$ and $C_2$). Ideally, as the reactance of $C_1$ is made to approach zero, $R_p$ approximates to $R$ and $C_p$ approximates to $C_2$. Since the reactance of $C_1$ is $X_1 = 1/\omega C_1$ (where $\omega = 2\pi f$ and $f$ = frequency in c/s), the design rules listed below can be applied—

(1) Make $C_1$ as large as possible by increasing the effective electrode area and decreasing the thickness of dielectric (*i.e.*, the cell walls).

(2) Make $\omega$ as large as possible by using higher frequencies.

(3) Make the impedance of the liquid as high as possible by using a cell of elongated shape (*i.e.*, having a large cell constant).

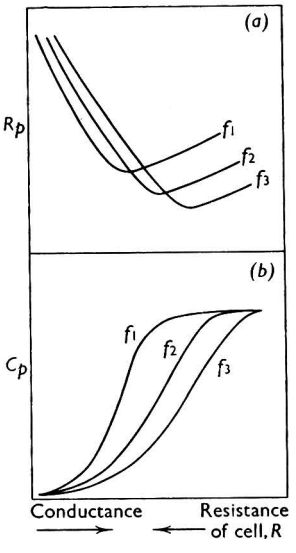


Fig. 2. Response curves of $R_p$ and $C_p$ against R: frequencies $f_3 > f_2 > f_1$

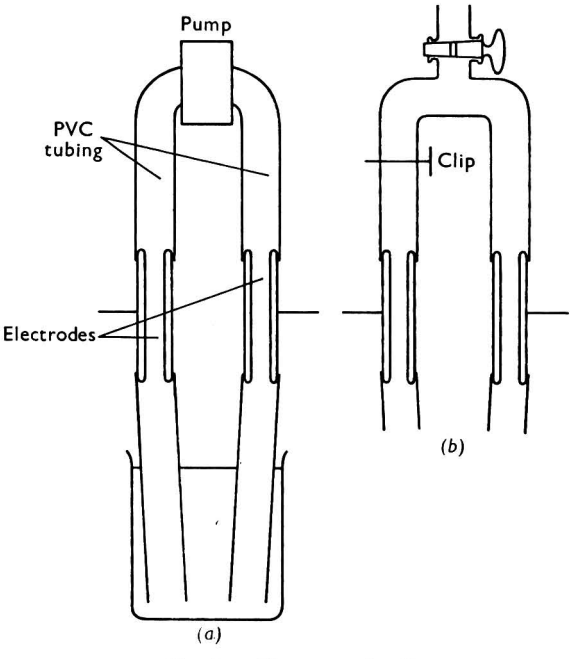


Fig. 3. Diagrams of cells

When detecting changes in $R$, sensitivity is reduced at higher frequencies owing to the shunting effect of $C_2$. It is therefore advisable to maintain as low a frequency as possible while utilising geometrical considerations to effect improvements in sensitivity and range of linearity.

A cell design that does fulfil the above theoretical requirements is shown diagrammatically in Fig. 3 (*a*). The solution under examination is continuously circulated through a pump and two lengths of tubing with their ends dipping in the reservoir, which can be a beaker or any convenient container. The electrodes are two pieces of metallic tubing; they are inserted into the stream at a convenient point and insulated from it by a thin layer of dielectric material. The choice of dielectric depends upon the liquids being examined, and could be one of the common plastics. The thickness of this layer can be of the order of 0·001 inch, which compares favourably with the wall thickness of a beaker. The use of such a circulatory

system obviates the need for a stirrer and ensures that the impedance of the liquid is high compared with that of the coupling capacitance. Further, the electrodes do not have to fit any special containers, and, by utilising various gauges of flexible tubing, a wide range of liquid volumes can be handled. In order that the circulatory system should have minimal volume, the pump used should have a peristaltic action. The volume in the system could then be as small as a few millilitres.

## Experimental

The characteristics of the cell were investigated by direct measurements of $R_p$ and $C_p$ with a radio-frequency admittance bridge (type LE 300, Hatfield Instruments Ltd.). The bridge was supplied by a signal generator (type 802A, Dawe Instruments Ltd.), and the balance of the bridge was detected with a radio-receiver (model 680X, Eddystone).

Electrodes were made from 3-inch lengths of $\frac{3}{16}$-inch bore copper tubing, internally coated with a surface-coating epoxy varnish (Araldite 985E). Several coats of varnish were applied by alternate dipping and stoving, and continuity of the film was checked by filling the tubes with mercury and measuring the leakage current through the varnish insulation. The final thickness of the film was approximately 0·002 inch. The electrodes were held $1\frac{1}{2}$ inches apart in a wooden clamp and were connected to the R.F. bridge terminals by the

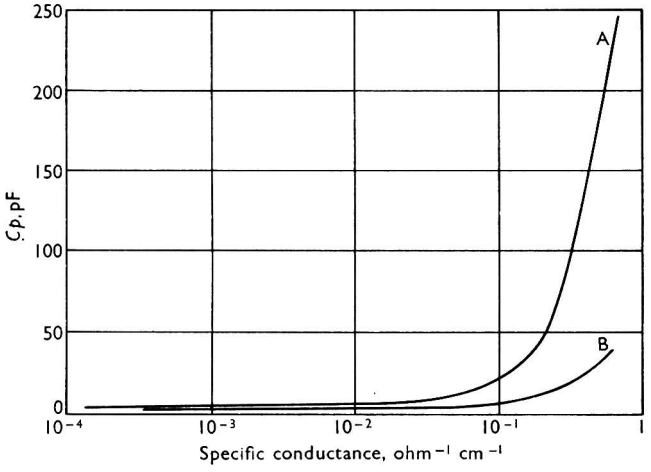


Fig. 4. Graph of $C_p$ against conductance: curve A, 800 kc/s; curve B, 3 Mc/s

shortest possible leads. As continuous circulation was not necessary for an investigation of the cell characteristics, the circulatory system was simulated by the arrangement shown in Fig. 3 (*b*). Before a reading was taken on the bridge, liquid from the beaker was sucked into both limbs via the T-piece and stopcock; one of the tubes was then clipped-off as shown.

Values of $R_p$ and $C_p$ across the bridge terminals were obtained over the range of concentrations of sulphuric acid from 0·001 to 5 N. Two frequencies were employed, namely, 3 Mc/s and 800 kc/s, and the results were plotted as shown in Figs. 4 and 5. The corresponding values of cell impedance, $Z$, were plotted on Fig. 5 for easy comparison. They were calculated from the relation—

$$Z = \frac{R_p}{\sqrt{1 + \omega^2 C_p^2 R_p}}$$

It is clear from these graphs that the cell permits discrimination between the resistive and reactive components of its simplified equivalent circuit over wide ranges of electrolyte conductance. The close proximity of the $R_p$ and $Z$ curves further indicates that the cell design tends to reduce the effect of the coupling capacitance. In fact, at frequencies greater than 800 kc/s, the minima in the $R_p$ curves have been displaced to values of specific conductance that would be rarely encountered in practice. It is only by using highly conductive

electrolytes, such as sulphuric acid, that the curves can be drawn. For most other electrolytes, a linear response to changes in concentration could be obtained over the maximum working range at still lower frequencies.

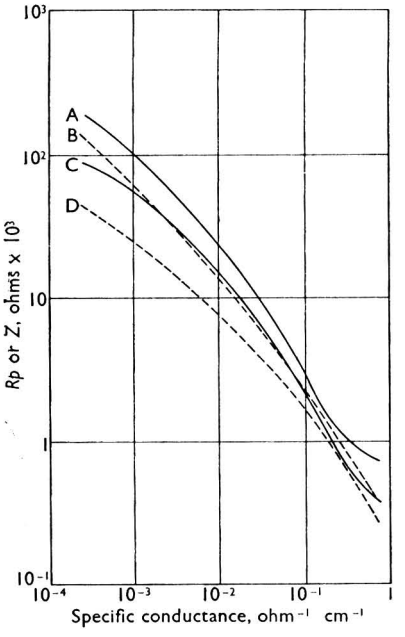


Fig. 5. Graph of $R_p$ and $Z$ against conductance: curve A, values of $R_p$ at 800 kc/s; curve B, values of $Z$ at 800 kc/s; curve C, values of $R_p$ at 3 Mc/s; curve D, values of $Z$ at 3 Mc/s

## Conclusions

In a radio-frequency titrimeter, it is important that the measured parameters should vary linearly with electrolyte concentration. Ideally, the cell impedance should approximate closely to the resistance of the electrolyte. By using the simple cell described, this condition can be approached without the use of excessively high frequencies. Other advantages of the design arise from its versatility and the fact that a separate stirrer is not required.

I thank the Director and Council of B.S.I.R.A. for permission to publish this paper.

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Received *March 7th*, 1962

# A Simple Chromatographic Gas-analysis Apparatus

By G. BLAKEMORE

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A gas analysis apparatus suitable for routine determinations is described. It is possible to carry out a complete analysis, including the determination of individual hydrocarbons present in gases manufactured from petroleum products.

During the last few years there has been a rapid increase in the use of petroleum products for the manufacture of town gas. Methane, from mine drainage and from natural gas, and also a variety of refinery gases have been used to enrich the gas. These practices have resulted in a wider range of hydrocarbon gases ($C_2$, $C_3$ and $C_4$) being present in town gas.

Conventional gas-analysis apparatus[1] will only indicate the total saturated and unsaturated hydrocarbon content. Since a more detailed analysis was required, the possibility of producing an inexpensive apparatus suitable for routine analysis and capable of determining all gases present in concentrations down to 0·1 per cent. was investigated.

Modification of an Orsat or a Bone and Wheeler apparatus to permit each hydrocarbon to be absorbed separately was not practicable, and so chromatographic methods were considered. All the constituents of town gas can be detected by a katharometer, with an inert gas, such as helium, as a carrier, whereas a more sensitive method for detecting hydrocarbons is by the hydrogen flame detector or the flame-ionisation detector. These methods were rejected, as they were considered unsuitable for routine works tests.

In the work carried out by Janák[2] and applied to refinery gas by Boreham and Marhoff,[3] the sample was carried forward by carbon dioxide on to a chromatographic column. On leaving the column, the carrier gas was absorbed in a nitrometer and the volume of each gas eluted was measured in a burette. It is obviously impossible to determine the carbon dioxide content of a gas by Janák's method, and also no chromatographic column was found that would separate oxygen and nitrogen. It was therefore decided to construct the apparatus in two sections: (*a*) the Birmingham-type Orsat section for determining carbon dioxide and oxygen and (*b*) the Janák section for all other constituents.

Since this work was completed, an extremely sensitive piston-type volume detector has been described by Brown and Satsmadjis,[4] but so far no success has been obtained from its use owing to the effects of surface tension.

## Apparatus

The Orsat - Janák apparatus shown in Fig. 1 was designed and constructed. It is made in two separate sections: (1) three Orsat absorption pipettes, $P_1$, $P_2$ and $P_3$, connected to a 100-ml gas burette and (2) the chromatographic section where the carrier gas, supplied at a steady rate of 40 ml per minute from a cylinder of carbon dioxide, flows through the gas-sampling unit and then through either of two 16-foot long chromatographic columns into the carbon dioxide absorption unit connected to a 5-ml gas burette. It was assumed that the apparatus would be used in a laboratory where the variations in temperature during an analysis would be negligible.

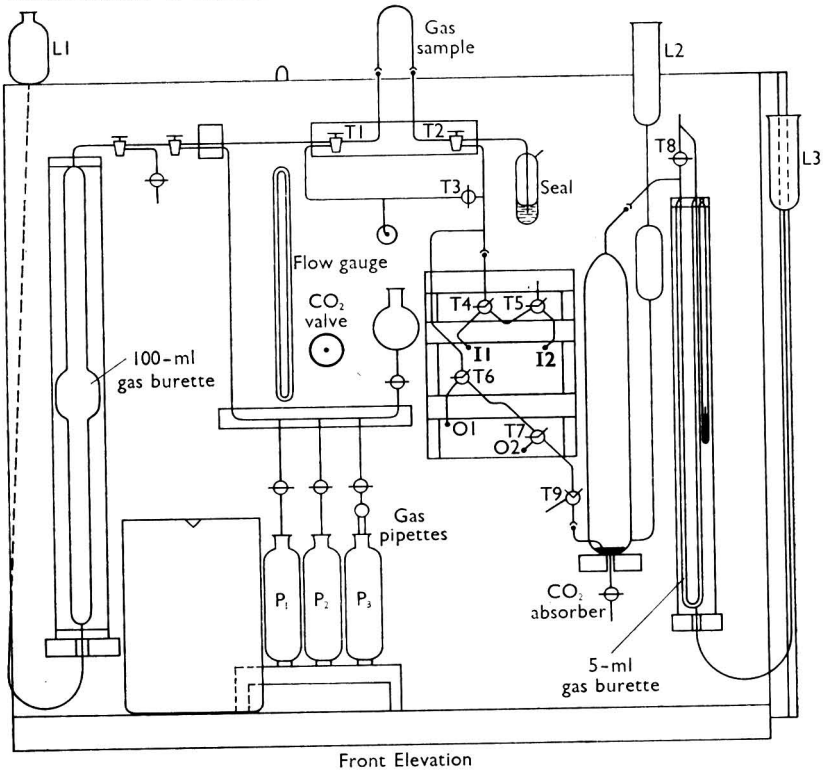
## Experimental

### Carrier gas—

Commercial carbon dioxide in cylinders was found to contain impurities insoluble in potassium hydroxide solution, but it can be partly purified by blowing off about $\frac{1}{5}$ of the contents of a cylinder. In this way, the insoluble impurity is reduced to less than 0·1 per cent.

### Gas-sampling unit—

The simple by-pass unit is such that capillary U-tubes of different sizes can be connected into the system by means of spherical joints, and thus samples of different volumes can be introduced. The capacity of each capillary U-tube is determined by filling it with mercury and weighing. The unit can be vented to atmosphere through a water seal.



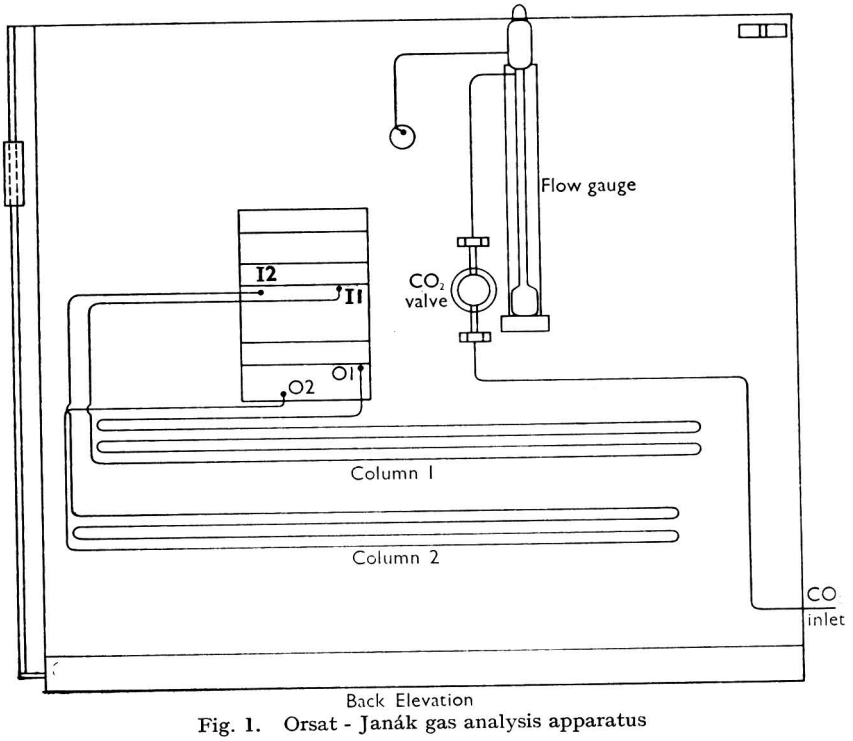




Fig. 1. Orsat - Janák gas analysis apparatus

CHROMATOGRAPHIC COLUMNS—

Columns filled with silica gel, activated alumina, activated charcoal, molecular sieve, 20 per cent. w/w of hexadecane on brickdust, 20 per cent. w/w of dimethylsulpholane on brickdust and 20 per cent. w/w of diethyldigol on brickdust were investigated.

The most suitable columns were: (1) activated charcoal (Sutcliffe, Speakman & Co. Ltd., type C), 40 to 60 mesh, for separating permanent gases. Retention times with 16-foot columns are—

*Hydrogen*—3 minutes.
*Oxygen and nitrogen*—6·5 minutes.
*Carbon monoxide*—8·5 minutes.
*Methane*—17 minutes.

(2) Activated alumina (Peter Spence Ltd., type 5A), 40 to 60 mesh, for separating $C_2$ and $C_3$ hydrocarbons. Retention times with 16-foot columns are—

*Permanent gases*—4·25 minutes.
*Ethane*—7·25 minutes.
*Ethylene*—8·25 minutes.
*Propane*—13·5 minutes.
*Propylene*—20·5 minutes.
*Isobutane*—27 minutes.
*n-Butane*—32·5 minutes.
*Isobutene and But-1-ene*—54 minutes.
cis-*Butene*—60 minutes.
trans-*Butene*—66 minutes.

(3) Twenty per cent. w/w of diethyldigol on brickdust (Johns Manville, C22), 40 to 60 mesh, for separating $C_3$ and $C_4$ hydrocarbons. Retention times with 16-foot columns are—

*Permanent gases*—2·5 minutes.
*Ethane and ethylene*—3·5 minutes.
*Propane*—6 minutes.
*Propylene*—7·25 minutes.
*Isobutane*—10 minutes.
*n-Butane*—14·25 minutes.
*Isobutene and But-1-ene*—17 minutes.
cis-*Butene*—20·5 minutes.
trans-*Butene*—23·5 minutes.

As oxygen and nitrogen are eluted together, oxygen must be determined in the Orsat section of the apparatus in the usual way and nitrogen then determined by difference. Each column is 16 feet long and is constructed by joining four 2-foot glass U-tubes, of 6-mm bore, by means of small capillary U-tubes and poly(vinyl chloride) tubing. Connections are by spherical joints to permit columns to be changed easily. The columns lie horizontally at the rear of the apparatus.

SELECTION OF CHROMATOGRAPHIC COLUMNS—

Two columns can be connected to the apparatus. The choice is normally activated charcoal for separating permanent gases and either of the two columns mentioned above for separating hydrocarbons.

If a column of charcoal is used for a long time, the strongly absorbed hydrocarbon gases will begin to be eluted in the normal way and give an apparent increased amount of insoluble impurity in the carrier gas. When this column is used, therefore, the gas flow must be reversed through it during idle periods, *e.g.*, overnight, so that these gases are removed.

CARBON DIOXIDE ABSORPTION UNIT—

The outlet tube from the chromatographic columns dips into a mercury seal and the carrier gas is absorbed in 50 per cent. w/w solution of potassium hydroxide. The diameter of the levelling bottle, $L_2$, is large compared with the diameter of the capillary tube leading to the burette, thus minimising the effect of changes in the volume of solution.

Between analyses, the outlet gas from the column is vented to the atmosphere through tap $T_9$.

MEASURING BURETTE—

A 5-ml grade A burette, graduated in 0·02 ml, forms one limb of a U-pressure gauge that has a levelling bottle fitted to a slide.

Before an analysis, the burette is set to zero by means of tap $T_8$.

As $C_5$ gases, acetylenes and aromatics are either soluble in potassium hydroxide solution or condense in the absorption unit, these gases cannot be determined with this apparatus.

## METHOD

REAGENT SOLUTIONS—

*Sulphuric acid, 5 per cent. v/v*—As retaining liquid for the 100-ml gas burette.

*Potassium hydroxide solution, 40 per cent. w/v*—For absorption pipette $P_1$.

*A (2 + 1) mixture of potassium hydroxide, 40 per cent. w/v, and pyrogallic acid solution, 30 per cent. w/v*—For absorption pipette $P_2$.

*Potassium bromide solution, 5 per cent. w/v*—Saturate with bromine and then dilute (1 + 1) with water; for absorption pipette $P_3$.

*Sodium chloride solution, saturated*—As retaining liquid for 5-ml gas burette.

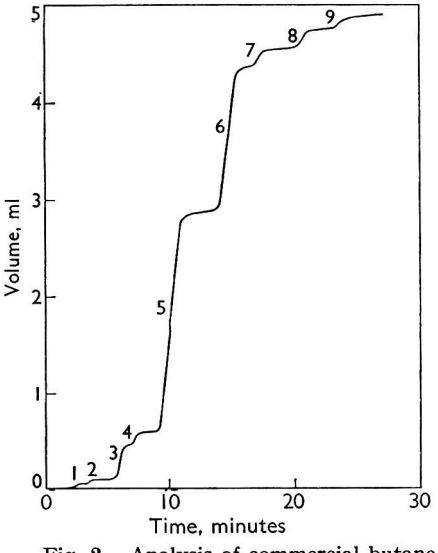



Fig. 2. Analysis of commercial butane: 1, permanent gases; 2, ethane *plus* ethylene; 3, propane; 4, propylene; 5, isobutane; 6, n-butane; 7, but-1-ene *plus* isobutene; 8, *trans*-but-2-ene; 9, *cis*-but-2-ene

TAP LUBRICANT—

It is recommended that a lubricant prepared as described below, which does not absorb hydrocarbon gases, be used on taps $T_1$, $T_2$, $T_4$, $T_5$, $T_6$ and $T_7$.

Heat a mixture of dextrin, mannitol and glycerol in the proportions of 30 : 7 : 60, stirring until the mixture boils. Allow to cool, with occasional stirring.[5]

PROCEDURE—

The procedure for each chromatographic column is described below.

Admit 100 ml of sample into the 100-ml gas burette, and pass approximately 95 ml of it fairly rapidly through the Janák gas-sampling unit fitted with a U-tube of the required volume and then through the water seal to atmosphere, so enclosing a sample of known volume between taps $T_1$ and $T_2$. Close tap $T_3$, open taps $T_1$ and $T_2$, and allow the carrier gas to pass the sample through the appropriate chromatographic column. Read the volume of gas collected in the 5-ml gas burette to the nearest 0·01 ml every half minute, and plot a graph of volume

eluted against time. Correct the volume of each component eluted for the amounts of impurities in the carrier gas, and calculate the concentration of each component to the nearest 0·1 per cent. A typical elution - time graph is shown in Fig. 2.

While this chromatographic separation is proceeding, measure a further 100 ml of sample into the 100-ml gas burette, and determine in the Orsat section of the apparatus the concentration of carbon dioxide and oxygen and, if required, the easily brominated unsaturated hydrocarbons.

## Results

Comparative analyses of a town gas have been carried out on a Bone and Wheeler apparatus and on the Orsat - Janák apparatus described. Results are shown in Tables I and II; some other results are shown in Tables III and IV.

### Table I

Analysis of town gas by Orsat - Janák apparatus

The volume of sample was 4·605 ml; activated charcoal column

| | Carbon dioxide, % | Oxygen, % | Unsaturated hydrocarbons, % | Hydrogen, % | Oxygen + nitrogen, % | Carbon monoxide, % | Methane, % | Nitrogen (by difference), % |
|---|---|---|---|---|---|---|---|---|
| Average .. .. | 4·5 | 0·3 | 2·7 | 48·8 | 8·3 | 23·0 | 11·1 | 8·0 |
| Standard deviation (8 determinations) | — | — | — | 0·20 | 0·19 | 0·21 | 0·14 | — |

### Table II

Comparative analyses of town gas

| | Carbon dioxide, % | Oxygen, % | Unsaturated hydrocarbons, % | Hydrogen, % | Carbon monoxide, % | Methane, % | Ethane, % | Nitrogen, % |
|---|---|---|---|---|---|---|---|---|
| Bone and Wheeler apparatus .. | 4·3 | 0·5 | 2·8 | 49·0 | 22·8 | 10·4 | 2·1 | 8·1 |
| Orsat - Janák apparatus .. | 4·5 | 0·3 | 2·7 | 48·8 | 23·0 | 11·1 | — | 8·0 |

### Table III

Determination of hydrocarbons in commercial butane

Column packed with 20 per cent. w/w of diethyldigol on brickdust

| Sample .. .. .. .. | Commercial butane | Commercial butane (1 per cent.) in air |
|---|---|---|
| Sample volume, ml .. .. .. | 4·605 | 16·45 |
| Permanent gases, % .. .. | 0·5 | — |
| Ethane + ethylene, % .. .. | 0·4 | — |
| Propane, % .. .. .. | 8·3 | 0·1, 0·2, 0·1, 0·1 |
| Propylene, % .. .. .. | 3·6 | Nil, Nil, <0·1, <0·1 |
| Isobutane, % .. .. .. | 45·8 | 0·5, 0·5, 0·4, 0·4 |
| n-Butane, % .. .. .. | 32·0 | 0·3, 0·3, 0·3, 0·3 |
| Butene, % .. .. .. .. | 9·1 | 0·1, 0·1, 0·1, 0·1 |

## Conclusions

It appears that, with the apparatus described, results are repeatable to within ±0·3 per cent. for a 5-ml sample and ±0·1 per cent. for a 15- to 20-ml sample.

A Bone and Wheeler apparatus would almost certainly give more accurate results for the permanent gases, but would only give an average carbon number for the saturated hydrocarbon gases. The versatility of the Orsat - Janák apparatus, however, successfully fills the gap between the absorption type of apparatus and the more sensitive methods of chromatographic detection, and the apparatus is now being used by junior staff in works laboratories in the West Midlands Gas Board's area.

TABLE IV

TYPICAL ROUTINE ANALYSES

| Sample No. | 6 | 7 |
|---|---|---|
| Carbon dioxide, % | 5·3 | 25·6 |
| Oxygen, % | 1·1 | 0·2 |
| Unsaturated hydrocarbons, % | 5·5 | 4·2 |
| Hydrogen, % | 39·2 | 51·8 |
| Nitrogen, % | 9·0 | 7·2 |
| Carbon monoxide, % | 32·1 | 4·1 |
| Methane, % | 5·4 | 4·4 |
| Ethane, % | 1·3 | 1·0 |
| Ethylene, % | 4·2 | 3·3 |
| Propane, % | 0·1 | 0·1 |
| Propylene, % | 1·4 | 1·1 |
| Isobutane, % | <0·1 | Nil |
| n-Butane, % | <0·1 | <0·1 |
| Butene, % | 0·3 | 0·3 |

I thank Mr. A. Harbige for his assistance in the construction of the apparatus described and Mr. E. T. Pickering, Area Chief Chemist, and the West Midlands Gas Board for permission to publish this paper.

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Received *January 18th*, 1962

# A Study of the Emission Spectra of Arsenic, Antimony and Bismuth from the Reaction Zone of Acetylene-Oxygen Flames*

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Arsenic, antimony and bismuth emit a number of rather sensitive emission lines in the reaction zone of a rich acetylene - oxygen flame when the analyte is dissolved in an organic solvent. The lines have been tabulated with the logarithmic slope and corresponding concentration range of the stronger lines. For the arsenic line at 235·0 mμ, the emission sensitivity is 2·2 μg per ml, for the antimony line at 252·8 mμ, 1·0 μg per ml and for the bismuth line at 223·1 mμ, 6·4 μg per ml. The optimum working conditions and inter-element effects have been explored, and the excitation mechanism is discussed. The use of a light-guide facilitates observations of the reaction zone and improves the net signal and the signal-to-background ratio.

Lines of several elements that are absent or very weak in the mantle of the flame appear in unusual strength in the spectrum of the reaction zone of a rich acetylene - oxygen flame. These are primarily elements of high excitation potential and high ionisation potential. In this investigation the emission spectra of arsenic, antimony and bismuth have been examined and optimum working conditions and inter-element effects explored. Rather sensitive lines were also observed for cadmium, mercury, platinum and tin.

Lundegårdh[1] noticed ultraviolet lines in the spectrum of the inner cone of an air - acetylene flame, a fact also reported by Mavrodineanu and Boiteux[2] and Alekseeva and Mandel'shtam.[3] Lundegårdh also noted that long exposure times were required for some of the lines, a difficulty overcome in this study by the use of organic aerosols to enhance the emission intensity. Recently, Buell[4] has reported useful emission from the reaction zone of an oxygen - hydrogen flame when the analyte is dissolved in a hydrocarbon. Fassel, Curry and Kniseley[5] have utilised a rich acetylene - oxygen flame to elicit the line spectra of the rare earths. The troublesome effect of the continuous radiation from the reaction zone can be minimised by the use of a light-guide.[6]

## Apparatus and reagents

A Beckman DU spectrophotometer with a model 9220 flame attachment and model 4304 photomultiplier unit was used. The medium-bore acetylene - oxygen burner could be raised or lowered from its normal position by a rack-and-pinion mount. Results were recorded on a 10-mV Bristol recorder, having a ⅔-second pen response, by means of the Beckman energy recording attachment. Brooks Rotameters (Sho-Rate model 1356) were used to regulate the flow of gases. The ratio of oxygen flow to acetylene flow was adjusted to 1·5; the oxygen pressure was 10 lb per sq. inch.

Standard solutions of the individual metals were prepared by dissolving a known weight of metal in 48 per cent. hydrobromic acid, and then diluting to an appropriate volume with isobutyl methyl ketone (hexone). To achieve complete miscibility in some instances, 10 per cent. by volume of methanol was incorporated in the solvent.

## Results and discussion

The lines observed for the elements studied and the emission sensitivities of the more intense and useful lines are recorded in Table I. A ratio of oxygen flow to acetylene flow of 1·5 offered a maximum degree of excitation. For some of the lines the emission sensitivities, reported by Gilbert[7,8] from studies with isopropanol solutions sprayed into an air - hydrogen flame, are included. Roughly, the emission sensitivity is the concentration of element

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required to give a net signal of 0·1 mV at the specified instrument settings. It approximates the definition given for detection limits by Gilbert, as the shot noise was about 1 per cent. at a time constant of 1 second. The relative excitation of the emission lines of an individual element remains unaltered in the two types of flames, but the emission intensities appear slightly larger in the oxygen - acetylene flame for arsenic and slightly smaller for the antimony and bismuth lines.

Arsenic, antimony and bismuth attained their maximum intensity at a height of 6 to 8 mm above the tip of the burner, as shown in Fig. 1. The region of maximum intensity is rather sharply localised 2 to 3 mm above the inner cone of the flame; it closely parallels the emission pattern of the carbon atomic line. Broida[9] showed that abnormal conditions for an oxygen - acetylene flame persisted 2 mm beyond the inner cone. With the particular flame employed, the inner cone terminated about 3 mm above the tip of the burner. The reaction zone is

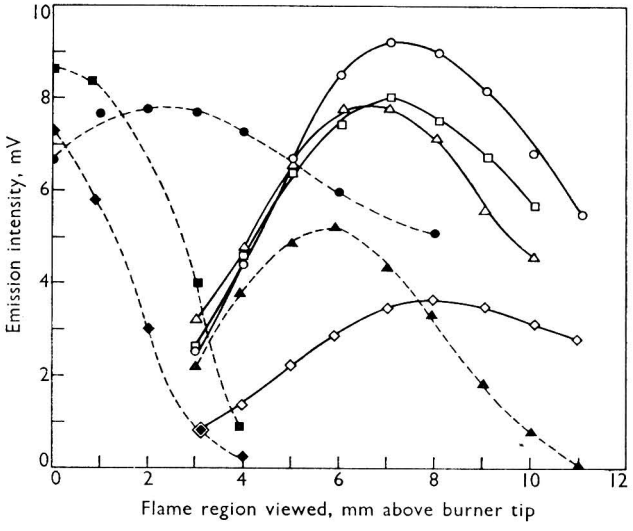


Fig. 1. Emission intensity as a function of flame region viewed. Individual analytes contained 200 μg of arsenic per ml, 80 μg of antimony per ml, 500 μg of bismuth per ml and 100 μg of tin per ml, each in isobutyl methyl ketone. Slit width, 0·13 mm; dynode voltage on 1P28, 60 volts; ERA % adjust, 50. ○, 235·0-mμ arsenic line; □, 252·8-mμ antimony line; △, 223·1-mμ bismuth line; ◊, 243·0-mμ tin line; ●, 306·7-mμ OH band head; ■, 431·5-mμ CH band head; ◆, 516·5-mμ $C_2$ band head; ▲, 247·8-mμ carbon line

rendered visible by the blue colour due to the CH and $C_2$ band systems. With the concave backing mirror covered, the burner was aligned by means of the atomic line of carbon at 247·8 mμ. The use of a light-guide[6] facilitated location of the region of maximum emission and increased both the net signal and the signal-to-background ratio.

Generally, observations of spectra from the reaction zone must be confined to wavelengths shorter than 260 mμ. In this region the reaction zone exhibits only the atomic emission of carbon at 247·8 mμ and a continuous background owing to the incandescent carbon particles and to the non-quantised processes of dissociation, association and ionisation. The slit width can be increased to at least 0·13 mm (equivalent to spectral band widths that vary from 0·1 to 0·2 mμ in the interval from 220 to 260 mμ) and still retain a sufficient degree of resolution and signal stability. Above 260 mμ the OH band system becomes troublesome.

EXCITATION MECHANISM—

The chemical activity of the flame (chemi-luminescence) obviously must be an important factor. Lundegårdh[1] pointed out that the high reduction potential of the reaction zone

induced emission from the negative elements, whereas the high oxidation potential of the mantle is more suitable for the emission of the positive elements of low ionisation potential. Thus the sensitivity of the spectra would appear to depend to a large extent on the position of the flame in relation to the optical axis of the spectrophotometer.

As shown in Fig. 1, the relative excitation of the carbon atomic line, as a function of the flame region viewed, parallels closely the pattern observed for the emission lines of arsenic, antimony, bismuth and tin. The excitation energy of the carbon line is 7·7 eV. Consequently, the presence of the carbon line in emission in the reaction zone of a rich acetylene - oxygen flame indicates that conditions of extremely high energy prevail in and immediately above the reaction zone. The excitation energies of the atomic lines are 6·6 eV for the arsenic line at 235·0 mμ, 6·12 eV for the antimony line at 252·8 mμ, and 5·55 eV for the bismuth line at 223·1 mμ; the dissociation energies of the monoxides are 4·9 eV for arsenic, 3·8 eV for antimony and 3·5 eV for bismuth. The monoxide flame bands are all weak or obscure, since the reaction zone of a rich acetylene - oxygen flame is reactive enough to dissociate the oxides and has sufficient energy to excite the atomic lines of these elements.

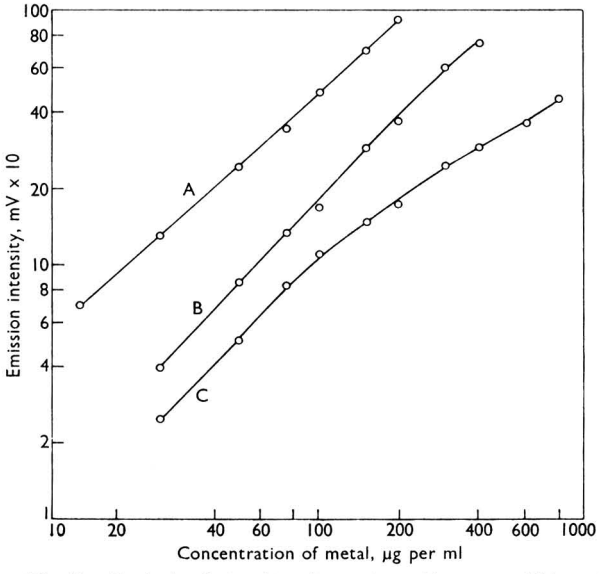


Fig. 2. Emission intensity of arsenic, antimony and bismuth lines from solutions of isobutyl methyl ketone as a function of concentration: curve A, 252·8-mμ antimony line; curve B, 235·0-mμ arsenic line; curve C, 223·1-mμ bismuth line

It seems fairly certain that the temperature of the reaction zone, which is lower than that of the mantle, cannot account for the spectra observed. In fact, Robinson[10] failed to detect these elements in the mantle of an oxygen - cyanogen flame. The energy requirements for excitation must arise from chemical reactions during the initial phases of the combustion process. Two hypotheses seem applicable. The parallelism between the intensity of the atomic spectra and the carbon line might be due to the dominance of the reaction (suggested by Sternberg[11]) of atomic carbon vapour with a monoxide of the metal to give carbon monoxide and an excited metal atom. Since the dissociation energy of carbon monoxide is 11·1 eV, this reaction will always be able to impart excess energy to the metal atom, although the amount of excess energy seems somewhat low for arsenic. However, Broida and Shuler[12] suggested that the CH, $CH_2$, etc., formed in the reaction zone react with atomic or molecular oxygen to give carbon monoxide. The large amount of energy from this reaction is imparted to the stabilising collision partner, such as water, which makes the reaction possible by carrying off the excess of energy (7·1 eV). This collision partner in turn excites a metal atom on subsequent collision. The CH emission fell off before the metal lines attained their maximum brilliance (see Fig. 1); this supports the latter hypothesis.

SPECTRAL INTERFERENCES—

Since the spectra under discussion are line spectra in the deep ultraviolet region, where the Beckman DU quartz spectrophotometer affords good resolution, specificity is generally excellent. The pair of bismuth lines at 222·8 and 223·1 mμ are completely resolved only at slit widths of 0·04 mm or less; however, the overlap at the base of the two lines at slit widths of less than 0·13 mm does not preclude the use of the stronger line at 223·1 mμ. The 228·8-mμ arsenic line suffers direct interference from the cadmium line at 228·8 mμ and

TABLE I

EMISSION LINES OBSERVED IN THE REACTION ZONE

Emission sensitivities for air - hydrogen - propanol flame estimated from values given by Gilbert and the relationship; 10 (detection limit) = emission sensitivity. Values in brackets taken from Gilbert[7]

| Element | Wavelength, mμ | Emission sensitivity with— AH flame,* μg per ml per 0·1 mV | Emission sensitivity with— OA flame,† μg per ml per 0·1 mV | Logarithmic slope | Concentration range, μg per ml |
|---|---|---|---|---|---|
| Arsenic | 228·8 | 6·0 | — | (1·0) | (20 to 200) |
| | 235·0 | 3·3 | 2·2 | 1·1 | 25 to 150 |
| Antimony | 231·2 | 0·50 | — | (0·8) | (10 to 100) |
| | 252·8 | 0·55 | 1·0 | 0·9 | 12 to 200 |
| | 259·8 | 0·35 | — | (1·0) | (10 to 100) |
| Bismuth | 206·2 | | | | |
| | 211·0 | | | | |
| | 213·4 | | | | |
| | 222·8 | 6·0 | 11·5 | — | — |
| | 223·1 | 3·3 | 6·4 | 1·1 | 25 to 70 |
| | | | | 0·5 | 250 to 750 |
| | 227·7 | 30 | — | (1·0) | (100 to 1000) |
| | 240·1 | — | — | | |
| | 289·8 | 2·8 | — | | |
| Cadmium | 228·8 | — | 4·2 | | |
| Mercury | 253·6 | — | 2·5 | | |
| Platinum | 246·7 | | | | |
| | 248·7 | — | 200 | | |
| | 262·8 | — | 100 | | |
| | 265·9 | — | 15 | | |
| Tin | 221·0 | — | 26 | | |
| | 224·6 | | | | |
| | 226·9 | | | | |
| | 231·7 | | | | |
| | 233·5 | | | | |
| | 235·5 | | | | |
| | 242·2 | | | | |
| | 243·0 | — | 1·6 | | |
| | 248·3 | — | 17 | | |
| | 254·7 | | | | |
| | 257·2 | | | | |
| | 270·7 | | | | |
| | 284·0 | | | | |
| Zinc | 213·8 | — | 77 | | |

* Air - hydrogen flame with isopropanol solutions.
† Oxygen - acetylene flame with isobutyl methyl ketone solutions.

the tin line at 228·7 mμ; the specificity factor[13] is 13·3. The tin line at 235·5 mμ and the nickel line at 234·5 mμ could interfere with the arsenic line at 235·0 mμ if the slit width ever exceeded 0·3 mm.

WORKING CURVES—

The curvature of working curves is a matter of interest. When the net intensity against concentration is plotted in logarithmic co-ordinates for each emission line, a slope of unity

indicates that the working curve is linear and a slope of 0·5 that it is parabolic. The logarithmic slope of several lines and the concentration range to which the slope applies are listed in Table I. Coupled with the emission sensitivity, the linear portions of the working curves provide sufficient signal strength for the arsenic line at 235·0 m$\mu$ and the antimony line at 252·8 m$\mu$, neither of which are ground state lines; the double bismuth lines, both resonance lines, show incipient self-absorption at rather low concentrations of bismuth (see Fig. 2).

MUTUAL INTERFERENCES—

A study was conducted on the possible mutual interference of arsenic, antimony and bismuth. Concentrations of antimony, up to at least 500 $\mu$g per ml, did not affect arsenic. However, arsenic depressed the emission of antimony by approximately 2 $\mu$g per ml (80 $\mu$g of antimony per ml were present in the test) for each 100 $\mu$g of arsenic per ml present. Bismuth exerted only a slight inhibitory effect on the emission intensity of antimony; approximately 1 per cent. when 400 $\mu$g of bismuth per ml were present with 80 $\mu$g of antimony per ml. Bismuth was unaffected by the presence of 500 $\mu$g of arsenic or antimony per ml.

No extensive tests were conducted with other metals. However, tin at concentrations of 1000 $\mu$g per ml did not affect arsenic, but zinc repressed arsenic by approximately 1 per cent. per 100 $\mu$g of zinc per ml present.

SUMMARY—

A flame-spectrophotometric method of analysis is definitely feasible for determining arsenic, antimony and bismuth. To achieve adequate emission sensitivity, it is necessary to introduce the analyte as an organic aerosol into a rich acetylene - oxygen flame and observe the spectra emitted from the reaction zone. The use of selective solvent-extraction methods is indicated,[14] and in this manner interfering elements can also be eliminated or, at least, their concentrations decreased. Possible extractions include arsenic with potassium xanthate, sodium diethyldithiocarbamate or the diethylammonium salt of diethyldithiocarbamate, antimony with hydrochloric acid and bismuth as the iodide complex or with di-n-butyl phosphorodithioic acid.[15]

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Received *February 28th*, 1962

# The use of a Light-guide in Flame Spectrophotometry*

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A hollow light-guide constructed from polished aluminium tubing was used for the examination of various regions in the flame, particularly the reaction zone of an acetylene - oxygen flame. The signal-to-background ratio of many emission lines was improved, and the signal strength was about doubled.

To examine the emission spectra of elements in the reaction zone of flames, a light-guide was constructed providing a method of viewing a selected portion of the flame and excluding radiation from other regions of the flame. The light-guide, 140 mm long and 6 mm in diameter, was placed between the burner and the mirror at the entrance to the monochromator of a Beckman DU flame spectrophotometer. The mounting bracket is shown in Fig. 1; similar mountings could be constructed for other commercial flame spectrophotometers. The bracket was inserted between the exit port of the burner housing and the entrance port of the DU monochromator. Adjusting screws provided a means of centering the light-guide on the optical axis between the burner and the entrance mirror. A tapped hole in the slit plate of the monochromator accommodated a retaining screw for the bracket. When properly aligned, the mounting bracket could be removed without disturbing the alignment of the light-guide when further insertions were to be made.

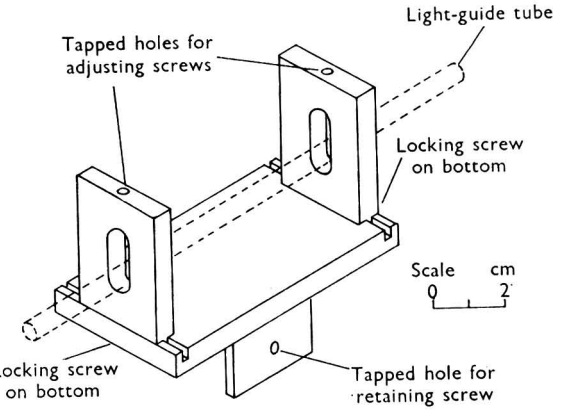


Fig. 1. Light-guide mounting bracket for Beckman DU flame spectrophotometer

Early work was done with a solid rod of Pyrex or silica (below 350 m$\mu$) glass, but absorption and radiation losses were severe, particularly in the far ultraviolet region. A hollow light-guide was more satisfactory for transmitting the radiation from selected portions of the flame to the entrance light-port of the monochromator. A hollow tube will transmit a light beam by multiple reflections from its inner surface. Highly polished aluminium tubing will reflect about 90 per cent. of the incident light over the wavelength region from 200 to 1000 m$\mu$. A glass tube silvered on the inner surface was also suitable. Light-guides have been used for the transmission of infrared radiation,[1] and a radiation pyrometer has been developed incorporating a sapphire rod as light-guide.[2] The mathematical treatment of the reflection, absorption and scattering of a light beam traversing a cylindrical rod or tube is complex[3] and will not be discussed.

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## Experimental

To ascertain the appearance of an observed light signal when a light-guide was used, the experiment described below was performed. A beam of light of known diameter emanating from a tungsten lamp and passing through apertures of various diameters was allowed to fall on a barrier-layer photocell after transmission through the light-guide. The light beam was moved vertically in front of the entrance of the light-guide, which is analogous to raising or lowering the point of observation in a flame, and the relative response of the photocell was recorded (see Fig. 2). The solid angle intercepted by the light-guide was varied by moving the lamp away from or closer to the entrance of the light-guide along a horizontal line. No significant difference in the intensity of the light signal could be detected when the source was placed 7 or 30 mm from the entrance of the light-guide. Transmitted signals from an identical, but non-reflecting, light-guide were one-third as strong.

Although the concave backing mirror in the burner housing was covered, the signal strength was about doubled when the light-guide was employed. The light-guide compensated for the loss of signals caused by the backing mirror during normal operations.

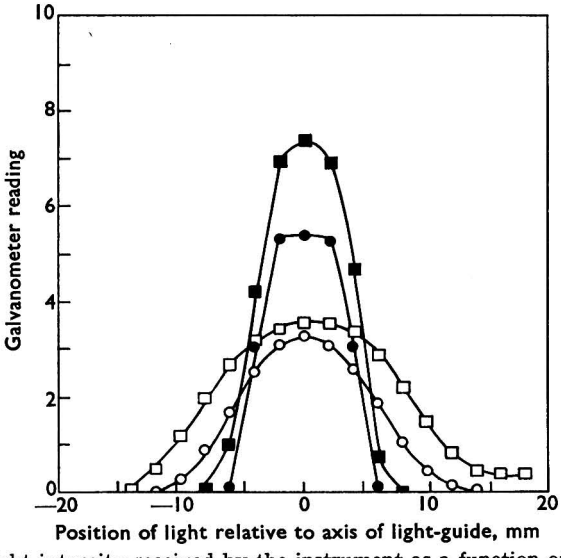


Fig. 2. Relative light intensity received by the instrument as a function of the position of the light source. The axial centre of the light-guide (or focal point) is represented by the zero point on the abscissa; negative distances represent positions below the axial centre. Squares represent readings taken with a light source whose diameter was 2·38 mm; circles are readings when the diameter was 1·59 mm. Solid circles and squares are readings taken with the light-guide in position; open circles and squares are readings without the light-guide. Diameter of light-guide was 6·0 mm

## Alignment procedure

One alignment procedure resembles that described in the Beckman Instruments Inc. instruction manual.[4] Remove the phototube housing and sample compartment from the monochromator chassis. Project light from the tungsten lamp through the exit slit of the monochromator, and adjust the light-guide until a perfectly circular area of light is observed on a piece of white paper held at the end of the light-guide and directly over the tip of the burner. Deviation from a concentric position results in a distorted light pattern owing to lack of balance in the distribution of the light reflected from the walls of the light-guide. This method of alignment is necessary only when aligning the light-guide initially.

The second method of alignment utilises the emission of the carbon atomic line at 247·8 mμ, which reaches its maximum intensity in the reaction zone and closely parallels the maximum emission of many metallic lines.[5] Adjust the gas pressure and flow rate of the acetylene and oxygen to their optimum values, and then raise or lower the burner by means of a rack-and-pinion device until the carbon line exhibits a maximal emission reading. Reference to

plots of relative emission readings of particular element lines as a function of flame region viewed permits a final adjustment to be made. Alternatively, the optimum flame region of the burner can be selected while aspirating a standard solution of the analyte.

Alignment of the light-guide is critical when observing emissions from the narrow reaction zone of a flame. Vertical shifts of only 1 or 2 mm may result in a variation of signal strength exceeding 80 per cent. of the maximum strength.

## Signal-to-background ratio

The use of the light-guide improves the signal-to-background ratio of many emission lines, particularly lines whose maximum intensity is attained in a restricted region of the flame. Several signal-to-background ratios are listed in Table I. Lines of moderate absolute intensity will not have to contend with as strong a background signal; consequently, detection limits will be improved. In some instances the slit width can be increased; this provides more signal strength without sacrificing signal stability.

### Table I

Signal-to-background ratios with and without use of a light-guide

| Element | Wavelength, mμ | Signal-to-background ratio— with light-guide | Signal-to-background ratio— without light-guide |
|---|---|---|---|
| Arsenic .. .. .. | 235·0 | 1·1 | 0·58 |
| Bismuth .. .. .. | 223·1 | 0·75 | 0·65 |
| Carbon .. .. .. | 247·8 | 0·88 | 0·26 |
| Chromium .. .. | 520·6* | 1·6 | 0·63 |

* Centre of unresolved triplet.

## Conclusions

The use of the light-guide proved valuable for examination of various regions in the flame, particularly the reaction zone of an acetylene - oxygen flame, which could be sharply defined. A degree of amplification was obtained that was independent of the signal-receiving and signal-amplifying circuitry. Optimum flame regions could be selected for observing the chosen spectrum line of any element. Also, improvement was achieved in the ratio of signal-to-background. In this manner rather sensitive emission lines of arsenic, antimony, bismuth, cadmium, mercury, platinum and tin have been studied.[5]

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Received *February 28th*, 1962

# Notes

## THE DETERMINATION OF URANIUM METAL IN PRODUCTS FROM THE REDUCTION OF URANIUM OXIDES WITH MAGNESIUM

In the production of uranium metal by the reduction of uranium oxides with magnesium, it is necessary to determine the amount of metal in the reduction product in order to determine the efficiency of the reduction. The reduction product has been shown to contain, as well as uranium metal, significant amounts of uranium oxides ($UO_2$ and $U_3O_8$), uranium carbides, magnesium uranates, magnesium metal and magnesium oxide. Because of the rather complex nature of this product, a procedure employing either the solubility or insolubility of the metal or the other constituents of the product appeared to offer the most promising approach.

The solution of uranium metal in bromine - ethyl acetate solutions under reflux has been described.[1] This solvent system has been found satisfactory for the extraction of uranium metal from samples of reduction products.

### Experimental

#### Preliminary studies—

After the extraction of uranium metal into a bromine - ethyl acetate solution, extraction of the uranium from the organic solution into an aqueous solution was preferred to isolation by evaporation of the solvent. Tests showed that the extraction of uranium from a bromine - ethyl acetate solution with water[2] was not particularly satisfactory for solutions containing about 1 g of uranium. A total of 500 ml of water, in 50-ml portions, was required to extract this amount of uranium from a 20 per cent. v/v bromine - ethyl acetate solution. By using a 5 or 10 per cent. w/v solution of sodium carbonate, complete extraction of 1 g of uranium was achieved with three 50-ml extractions.

In order to inhibit the formation of free acids during extractions, magnesium oxide[2] was added to each test solution.

Since the reduction products contained several uranium compounds, it was necessary to determine the solubility of each of these compounds in order to find the most suitable conditions under which the uranium metal could be extracted from the sample without interference.

Because of the small particle size of the samples, a Whatman No. 50 filter-paper was used, with suction, to filter off the residue after leaching the sample. Buchner funnels were unsuitable for supporting the filter-paper, as the nature of the paper allowed small amounts of the residue to creep underneath it into the filtrate. The use of a Millipore Filter Holder (Millipore Filter Corp., Bedford, Mass., U.S.A.) fitted with Whatman No. 50 filter-paper was found to be satisfactory for filtering these samples.

#### Solubility of uranium oxides and magnesium uranate—

The solubilities of $UO_2$, $U_3O_8$ and $U_4O_9$ were found to be low in both 10 and 20 per cent. v/v bromine - ethyl acetate solutions. In the solvent boiling under reflux about 0·2 per cent. of each oxide was soluble after one hour, and, at 25° C, the solubility of each oxide decreased to approximately 0·02 per cent. after 4 hours' leaching.

Magnesium uranate ($MgUO_4$) showed about 0·2 per cent. to be soluble in the 20 per cent. solvent boiling under reflux, and 0·05 per cent. at 25° C. Since the solubilities of these compounds at 25° C were so low, the determination of solubilities at lower temperatures was considered unnecessary.

#### Solubility of uranium carbide—

Chemical analysis of the uranium carbide used in these experiments gave 92·9 per cent. of U, 5·3 per cent. of C and 3·4 per cent. of $UO_2$. X-ray diffraction showed the major portion to be UC, with a small minor portion of $UC_2$ and a trace of $UO_2$.

The solubility of the uranium carbide sample in the 20 per cent. v/v bromine - ethyl acetate solution boiling under reflux was of the order of 20 per cent. after 1 hour and 30 to 45 per cent. after 2 hours. Consistent results could not be obtained. The solubility of this compound at temperatures from 25° to −30° C are shown in Table I.

#### Solubility of uranium metal—

The uranium metal used was in the form of small chips. Oxide was removed by washing with nitric acid. The metal was then washed with water, dried, and used immediately.

Uranium metal was found to be readily soluble in 20 per cent. v/v bromine - ethyl acetate solution boiling under reflux. The rate of solution decreased as the temperature was lowered. At 25° C, 1 g required 15 to 30 minutes for complete solution; at −30° C, 3 hours were required to dissolve 0·5 g of the metal.

TABLE I

SOLUBILITY OF URANIUM CARBIDE IN BROMINE - ETHYL ACETATE SOLUTIONS

| Temperature, °C | Extraction time, hours | Bromine - ethyl acetate solvent, % v/v | UC soluble, % |
|---|---|---|---|
| 25 | 0·5 | 20 | 5·8 |
| | 1 | | 10·2 |
| | 2 | | 16·1 |
| | 4 | | 17·8 |
| | 0·5 | 10 | 6·3 |
| | 1 | | 10·5 |
| | 2 | | 17·1 |
| | 4 | | 18·1 |
| | 0·5 | 5 | 6·1 |
| | 1 | | 10·3 |
| | 2 | | 16·5 |
| | 4 | | 17·3 |
| 0 | 1 | 20 | 5·7 |
| | 2 | | 9·9 |
| | 4 | | 10·5 |
| | 1 | 10 | 6·5 |
| | 2 | | 8·5 |
| | 4 | | 11·6 |
| −10 | 1 | 20 | 4·2 |
| | 2 | | 6·8 |
| | 4 | | 7·5 |
| −20 | 1 | 20 | 3·5 |
| | 2 | | 4·2 |
| | 4 | | 5·0 |
| −30 | 1 | 20 | 1·3 |
| | 2 | | 1·8 |
| | 4 | | 2·6 |

TABLE II

EXTRACTION OF A SAMPLE OF REDUCTION PRODUCT WITH 20 per cent. v/v BROMINE - ETHYL ACETATE SOLUTION

| Temperature, °C | Extraction time, minutes | Uranium extracted, % | Temperature, °C | Extraction time, minutes | Uranium extracted, % |
|---|---|---|---|---|---|
| 25 | 10 | 27·3 | −10 | 60 | 39·0 |
| | 20 | 49·7 | | 120 | 44·4 |
| 30 | 30 | 49·4 | | 180 | 47·0 |
| | 45 | 50·5 | −20 | 60 | 33·9 |
| | 60 | 49·9 | | 120 | 40·6 |
| | 120 | 50·8 | | 180 | 42·7 |
| 0 | 30 | 42·0 | −30 | 60 | 26·0 |
| | 60 | 45·8 | | 120 | 33·3 |
| | 90 | 47·8 | | 180 | 37·3 |
| | 120 | 49·0 | | 240 | 40·3 |
| | 180 | 50·0 | | 360 | 48·2 |
| | 240 | 50·5 | | | |

EXTRACTION OF A SAMPLE OF REDUCTION PRODUCT—

Weighed portions of a sample of a product from the reduction of $UO_2$ with a mixture of magnesium metal and magnesium chloride were leached for different lengths of time with 20 per cent. bromine - ethyl acetate solution at temperatures ranging from 25° to −30° C. Approximately 0·5-g samples were used and the volumes of solvent were 100 ml. Table II shows the results of these experiments.

At 25° C, all the uranium metal was extracted in about 30 minutes. As the temperature was decreased the time required for maximum extraction increased; for 0°, −10°, −20° and −30° C the approximate times were 3, 4, 5 and 6 hours, respectively.

EXTRACTION OF URANIUM METAL FROM A SYNTHETIC REDUCTION PRODUCT—

A synthetic reduction product was prepared by intimately mixing known amounts of uranium carbide, magnesium uranate ($MgUO_4$), $UO_2$ and $U_3O_8$. Before extraction, uranium metal chips, free from oxide, were added to a weighed portion of the mixture. The final approximate composition of the mixture was: uranium metal, 50 per cent.; uranium carbide, 30 per cent.; magnesium uranate, 10 per cent.; $UO_2$, 5 per cent.; $U_3O_8$, 5 per cent. Extraction of the samples was carried out at 25° C with 20 per cent. bromine - ethyl acetate solution. The results (see Table III) show that between 30 and 45 minutes are required to extract completely the metal from the mixture. Extraction beyond this time gives an increasing positive result, so that, after 2 hours' extraction, 107 per cent. recovery is obtained. This is due to the solubility of the uranium carbide.

TABLE III

EXTRACTION OF A SYNTHETIC REDUCTION PRODUCT WITH 20 per cent. v/v BROMINE - ETHYL ACETATE SOLUTION AT 25° C

| Uranium metal added, % | Uranium carbide added, % | Extraction time, minutes | Uranium metal recovered, % |
|---|---|---|---|
| 51·4 | 29·1 | 10 | 34·8 |
| 50·5 | 29·6 | 20 | 69·5 |
| 52·2 | 28·6 | 30 | 94·5 |
| 51·7 | 28·9 | 45 | 101·6 |
| 50·2 | 29·8 | 60 | 103·5 |
| 50·5 | 29·6 | 90 | 104·5 |
| 49·1 | 30·5 | 120 | 106·8 |

TABLE IV

TYPICAL RESULTS OBTAINED BY THE PROPOSED METHOD ON SAMPLES OF REDUCTION PRODUCTS

| Sample | Uranium metal found, % |
|---|---|
| A | 51·7, 51·7, 51·9, 51·3, 51·8, 50·7 |
| B | 50·1, 49·7 |
| C | 56·1, 56·3 |
| D | 32·6, 32·2 |

## METHOD

REAGENTS—

*Bromine - ethyl acetate solution*—A 20 per cent. solution of bromine in anhydrous ethyl acetate.

*Sodium carbonate solution, 5 per cent. w/v.*

*Magnesium oxide.*

PROCEDURE—

Weigh a suitable sample into a clean dry 250-ml beaker. Add about 0·1 g of magnesium oxide and 100 ml of the bromine - ethyl acetate solution. Cover with a watch glass, and, with a magnetic stirrer, stir as rapidly as possible without splashing, for 30 minutes. Filter through a Whatman No. 50 filter-paper, with suction, and wash the residue thoroughly with ethyl acetate. Transfer the filtrate to a 250-ml separating funnel, and extract with three 25-ml portions of the sodium carbonate solution, shaking for 1 minute for each extraction. It is essential to shake cautiously at first, and to release the pressure in the funnel frequently. Acidify the aqueous extracts with nitric acid, and boil to remove all the bromine. Cool, and dilute to a suitable volume. Determine the uranium by any convenient method. In this laboratory either a fluorimetric or colorimetric procedure is used.

## RESULTS AND DISCUSSION

Table IV shows some typical results obtained on samples from the reduction of uranium oxides with magnesium metal.

Large amounts of uranium carbide in the sample will tend to give a positive error, but, as the extraction time is kept to a minimum, the error should not be serious.

Amounts of magnesium oxide greater than that recommended will increase the time of filtration considerably. Volumes of 100 ml of solvent, rather than smaller volumes, were taken because they permitted more efficient stirring, without splashing.

A coating of oxide on the uranium metal does not appear to inhibit the extraction of uranium, although the rate of solution may be somewhat decreased.

The solubility of uranium carbide is not a direct function of the bromine concentration in the solvent, as is shown by the results in Table I. Little difference in solubility is given with 20 and 5 per cent. solutions for a given extraction time and temperature. For this reason it was considered necessary to use the 20 per cent. solvent, because of the necessity to dissolve the uranium metal in the shortest possible time, so that the uranium carbide would not give high results.

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# THE TITRIMETRIC DETERMINATION OF VANADIUM IN CHROMITE

The standard titrimetric methods for determining chromium in chromite do not distinguish between vanadium and chromium.[1] Consequently, a method for determining vanadium in chromite has long been required. The formidable nature of chromite* appears to have resulted in few methods, apart from the usual spectrographic methods and Ryan's recent colorimetric method,[2] being described. Few reliable figures for the vanadium content of chromite have been published, although Goldschmidt[3] mentions that 0·1 per cent. (as vanadium) may occur.

The proposed method is simple, rapid and fairly accurate; it involves no separations and is believed to have produced fairly reliable results for vanadium in chromite. It is similar in approach to Willard and Fenwick's method,[4] but is unique in the use of the peroxo-titanium complex as a selective reagent for vanadium.

## Experimental

Known amounts of chromium$^{III}$ and iron$^{III}$ (as chlorides), peroxo-titanium complex (prepared as described below), vanadium$^{V}$ (as standard vanadium$^{V}$ solution) and sulphuric acid in 60 to 65 ml of solution were heated to boiling in a 250-ml conical flask; 3 ml of 20-volume hydrogen peroxide were added, the solution was boiled for 2 to 3 minutes, and then cooled. Seven millilitres of titration acid (see "Reagents, p. 756) were added, and the solution was titrated amperometrically ("dead-stop" method) with 0·004 N ferrous sulphate. The recovery of vanadium as vanadium$^{V}$ was calculated by comparison with the titre for an untreated aliquot of vanadium$^{V}$ solution.

## Results—

The almost quantitative (>99 per cent.) recovery of vanadium as vanadium$^{V}$ when the peroxo-vanadium complex is decomposed by boiling at acidities of less than 0·02 M[5] suggests that this might provide a simple basis for the determination of vanadium by titration with ferrous iron.

However, in the presence of chromium, some chromium$^{VI}$ is formed, which leads to apparent recoveries of vanadium$^{V}$ greater than 100 per cent.; in the presence of iron, greatly decreased recovery of vanadium$^{V}$ is obtained, which is relatively unaffected at high acidity by the presence of chromium. Some results are shown in Table I.

* A typical chromite might contain 45 per cent. of $Cr_2O_3$, 15 per cent. of $Fe_2O_3$, 1 per cent. of $TiO^2$ and 0·15 per cent. of $V_2O_3$; or about 150 mg of chromium, 50 mg of iron, 3 mg of titanium and 0·5 mg of vanadium per 0·5 g. The remainder consists mainly of oxides of aluminium, magnesium and silicon, and may include small amounts of calcium, barium, manganese and nickel.[1]

The presence of iron and chromium would clearly prevent this approach to the determination of vanadium if it were not for the remarkable influence of titanium, which forms the peroxo-titanium complex under the conditions used, and whose presence was found to restore the almost quantitative recovery of vanadium$^{V}$; here the similarity, both in stability constant[6] and in the conditions and ease of formation, between the peroxo-titanium and peroxo-vanadium complexes may be significant. The decomposition of peroxo-titanium yields titanium$^{IV}$, which is not reduced by ferrous iron.

As with the decomposition of peroxo-vanadium, the decomposition of peroxo-titanium in the presence of chromium leads to the formation of chromium$^{VI}$; however, the amount of chromium$^{VI}$ formed was found to decrease rapidly with increasing acidity and iron concentration (see Table II). As expected, the apparent recovery of vanadium$^{V}$ was dependent on the titanium concentration, but non-critical conditions giving negligible blank values and good recovery of vanadium$^{V}$ were easily determined (see Table III).

TABLE I

APPARENT RECOVERY OF VANADIUM AS VANADIUM$^{V}$

Each sample was boiled with 60 to 65 ml of sulphuric acid of the appropriate normality

| Sample | Vanadium$^{V}$ recovered in presence of— 0·1 N sulphuric acid, % | 0·2 N sulphuric acid, % | 0·3 N sulphuric acid, % | 0·6 N sulphuric acid, % |
|---|---|---|---|---|
| 2·4 mg of vanadium | 98·8 to 99·1 | — | 97 | — |
| 2·4 mg of vanadium + 2 mg of chromium | 99·6 to 100·3 | — | — | — |
| 2·4 mg of vanadium + 25 mg of chromium | — | — | 97·5 | — |
| 2·4 mg of vanadium + 250 mg of chromium | 108 to 115 | — | — | — |
| 2·4 mg of vanadium + 250 mg of chromium + 1 g of iron | 97·9 to 100·4 | — | — | — |
| 0·44 mg of vanadium | — | 98 | — | 94 |
| 0·44 mg of vanadium + 300 mg of iron | — | — | — | 78 |
| 0·44 mg of vanadium + 50 mg of chromium | — | — | — | 78 |
| 0·44 mg of vanadium + 300 mg of iron + 150 mg of chromium | — | 120 | — | 79 |

TABLE II

CHROMIUM$^{VI}$ PRODUCED

Each solution contained 150 mg of chromium and 10 mg of titanium in 60 to 65 ml in the absence of vanadium

| Concentration of sulphuric acid, N | 0·25 | 0·42 | 0·53 | 0·61 | 0·99 | 1·80 |
|---|---|---|---|---|---|---|
| Chromium$^{VI}$ produced, as percentage of 0·44 mg of vanadium, in presence of— | | | | | | |
| 50 mg of iron | 71 | 17 | 4·3 | 4·1 | 0·14 | 0·0 |
| 300 mg of iron | — | — | — | 0·3 | — | — |

TABLE III

APPARENT RECOVERY OF 0·44 mg OF VANADIUM AS VANADIUM$^{V}$

Each solution contained 150 mg of chromium and 300 mg of iron in 60 to 65 ml

| Concentration of sulphuric acid, N | 0·6 | | | | | 0·7 | | 1·0 |
|---|---|---|---|---|---|---|---|---|
| Titanium present, mg | 0 | 5 | 10 | 15 | 20 | 20 | 40 | 20 |
| Recovery of 0·44 mg of vanadium, % | 78 | 92 | 93 | 97·8 | 102·2 | 97·3 | 98·4 | 96·5 |
| Apparent recovery of vanadium (in absence of vanadium), % | 0·05 | — | 0·3 | — | 8·9 | 0·3 | — | — |

It can be seen from Table III that an acidity of 0·6 to 0·7 N with 15 mg of titanium would be expected to give satisfactory results for vanadium. This has been confirmed (see Table IV), but to improve the tolerance to titanium and sulphuric acid the acidity was increased to 0·8 to 0·9 N and the amount of titanium to 30 mg; the recovery of vanadium$^{V}$ was not significantly changed by these modifications (see Table IV).

The latter conditions were employed for the analysis of five chromites by the procedure described below; the results are shown in Table V. According to Goldschmidt,[3] vanadium is likely to be present in chromite as vanadium$^{III}$; consequently, the results are expressed as per cent. of $V_2O_3$.

TABLE IV

DETERMINATION OF VANADIUM IN SYNTHETIC SAMPLES

| Sample A | | | | Sample B | | | |
|---|---|---|---|---|---|---|---|
| Vanadium added,* mg | Vanadium found, mg | Error, % | Remarks | Vanadium added,* mg | Vanadium found, mg | Error, % | Remarks |
| 0·854 | 0·826 | −3·3 | — | 0·437 | 0·419† | −4·0 | —‡ |
| 0·437 | 0·431 | −1·3 | — | 0·437 | 0·436† | −0·2 | — |
| 0·437 | 0·419 | −4·1 | 10 mg of Ti in sample | 0·437 | 0·424† | −3·1 | 40 mg of Cr in sample |
| 0·437 | 0·430 | −1·5 | 20 mg of Ti in sample | 0·0262 | 0·0276† | +5·5 | — |
| 0·175 | 0·167 | −4·7 | — | 0·0026 | 0·0019† | −27 | —‡ |
| 0·0875 | 0·0881 | +0·7 | — | Nil | 0·0002 | — | —‡ |
| Nil | 0·0001 | — | 10 mg of Ti in sample | Nil | 0·0002 | — | 45 mg of Ti in sample‡ |
| Nil | 0·0014 | — | 20 mg of Ti in sample | Nil | 0·0002 | — | —§ |

Sample A: 150 mg of chromium, 300 mg of iron and 15 mg of titanium; acidity 0·67 N; volume 60 ml.
Sample B: 150 mg of chromium, 300 mg of iron and 30 mg of titanium; acidity 0·85 N; volume 60 ml.
* 0·437 mg of vanadium corresponds to 0·13 per cent. of $V_2O_3$ in 0·5 g of chromite.
† Corrected for blank value.
‡ 2·5 g of analytical-reagent grade boric acid added.
§ 2 mg of manganese, 2 mg of molybdenum, 30 mg of phosphorus and 2·5 g of analytical-reagent grade boric acid added.

TABLE V

DETERMINATION OF VANADIUM IN CHROMITE

| Chromite | $Cr_2O_3$ present, % | $Fe_2O_3$ present, % | $V_2O_3$ found by— proposed method, % | $V_2O_3$ found by— colorimetric method,† % |
|---|---|---|---|---|
| Chrome refractory* .. .. | 37 | 16 | 0·179, 0·177 | 0·165, 0·171 |
| Turkish chrome ore .. .. | 39 | — | 0·161, 0·165 | — |
| Chrome-magnesite brick .. | 24 | 12 | 0·098, 0·118 | — |
| Chromite (origin unknown) .. | 53 | 15 | 0·125, 0·123 | 0·11 |
| Chrome-magnesite refractory.. | 30 | — | 0·087, 0·073 | 0·039, 0·042 |

* Standard sample No. 103 of the U.S. National Bureau of Standards. The vanadium content of this sample is not given on the certificate, but a footnote contains the statement "titration corrected for 0·08 vanadium content of the refractory." Whether this means 0·08 per cent. of V, 0·08 per cent. of $V_2O_3$ or 0·08 per cent. of $V_2O_5$ is not clear, but has been taken to mean 0·08 per cent. of V[7]; 0·08 per cent. of V ≡ 0·12 per cent. of $V_2O_3$.
† Values obtained by Ryan (unpublished work) with benzoylphenylhydroxylamine.[2]

## METHOD

REAGENTS—

*Iron solution*—Dissolve 25 g of analytical-reagent grade ferric chloride, $FeCl_3.6H_2O$, in water, and dilute to 100 ml.

*Peroxo-titanium solution*—Dissolve 5·6 g of recrystallised potassium titanyl oxalate in 10 ml of water in a tall 150-ml beaker; add 15 ml of diluted analytical-reagent grade sulphuric acid (1 + 1) and 10 ml of nitric acid, evaporate to fumes for 10 minutes, and set aside to cool. Dissolve the residue in 30 ml of 20-volume hydrogen peroxide, and dilute to about 100 ml. Immerse the beaker in cold water, and add solid sodium hydroxide in small portions, with stirring to complete the dissolution between additions, until the colour has faded to pale orange (on further treatment it becomes yellow and then colourless); immediately decant the liquid into a beaker, and slowly add 35·0 ml of 98 per cent. w/w analytical-reagent grade sulphuric acid with stirring. Dilute the cold solution to exactly 250 ml, and set aside overnight before use. It is stable for at least one week.

*Titration acid*—To 50 ml of water add 25 ml of analytical-reagent grade orthophosphoric acid and 25 ml of analytical-reagent grade sulphuric acid.

*Ferrous sulphate*, 0·004 N—Dissolve 0·30 g of analytical-reagent grade ferrous sulphate, $FeSO_4.7H_2O$, in water, add 12 ml of diluted analytical-reagent grade sulphuric acid (1 + 1), and dilute to 250 ml. Standardise before use by amperometric titration against freshly prepared standard dichromate.

PROCEDURE—

Fuse 0·5 g of the chromite with 4·0 g of analytical-reagent grade hydrated sodium tetraborate and 6·0 g of analytical-reagent grade anhydrous sodium carbonate in a 30-ml platinum crucible. Extract the cold fused mass with 25 ml of water and 9·0 ml of accurately diluted (1 + 1) sulphuric acid.

To the cold solution add 3 ml of 20-volume hydrogen peroxide; when the blue colour due to peroxo-chromium has dispersed, add a further 3 ml of peroxide; if the blue colour returns, repeat the addition. Stir, and add 5 N sodium hydroxide dropwise until a faint permanent precipitate is formed; about 5 ml will be required. (The object at this stage is to attain a sufficiently low acidity that the subsequent addition of peroxo-titanium solution will give the required final acidity (0·85 to 0·90 N); an excess of acid is preferable to a deficiency. The operation is hindered by the deep colour of the solution, and the use of a pH meter is advantageous. Addition of sodium hydroxide before the first addition of hydrogen peroxide is not permissible, as a reasonable acidity is required for the successful decomposition of the peroxo-chromium complex.)

To the cold solution add 5·0 ml of iron solution, transfer to a wide-mouthed 250-ml conical flask, and dilute accurately, either by weighing or by the use of a measuring cylinder, to 50 ± 1 ml with water. Add 10·0 ml of peroxo-titanium solution, and heat to boiling for a few minutes. Add 3 ml of 20-volume hydrogen peroxide with swirling, boil gently for 2 to 3 minutes, and cool. (If boric acid separates out, redissolve by warming and dilution.)

Add 7 ml of titration acid, and titrate amperometrically ("dead-stop" method with an applied potential difference of 300 mV) with 0·004 N ferrous sulphate from a 5-ml microburette.

1 ml of 0·004 N ferrous sulphate ≡ 0·0600 per cent. of $V_2O_3$ in 0·5 g of chromite.

## DISCUSSION OF THE METHOD

The end-point could usually be graphically determined to within ±0·001 ml of 0·004 N ferrous sulphate in a total volume of 80 ml, and the observed titres were between 1·5 and 3·0 ml.

The recovery of vanadium$^V$ from synthetic samples containing the equivalent of 0·01 to 0·25 per cent. of $V_2O_3$ in 0·5 g of chromite is generally in the range 95 to 100 per cent. No reliable standard chromites were available, but the values for the $V_2O_3$ content obtained by the proposed method are in fairly good agreement with those obtained by Ryan with benzoylphenylhydroxylamine; they varied from 0·08 to 0·18 per cent., average 0·13 per cent., or from 2·5 to 4·5 per cent. of the $Cr_2O_3$ content.

The blank value is low and is independent of the presence of boric acid and of at least the equivalent of 0·5 per cent. of MnO, 0·5 per cent. of $Mo_2O_3$, 30 per cent. of $P_2O_5$ and 5 per cent. of $TiO_2$ in 0·5 g of chromite. The levels of added iron and titanium are sufficient to swamp any variation of these between normal chromites.

The studies reported were made at the Imperial College of Science and Technology, London, S.W.7. I thank Assistant Professor L. S. Theobald for helpful discussion and samples of chromites, Dr. D. E. Ryan for permission to quote his unpublished results, and Imperial Chemical Industries Ltd. (Billingham Division) for the award of a Bursary, during the tenure of which the main part of this work was carried out.

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## A SOLVENT SYSTEM FOR THE ONE-DIMENSIONAL SEPARATION OF HEXOSE PHOSPHATES ON FILTER-PAPER CHROMATOGRAMS

ONE-DIMENSIONAL,[1,2] two-dimensional[3,4,5,6] and circular[7] paper-chromatographic methods have been described for the separation of the phosphorylated intermediates of metabolism. However, no single-solvent system, particularly with one-dimensional development, permits clear resolution between glucose monophosphates and fructose mono- and diphosphates.[1 to 9] A new solvent system has been developed by us that permits a satisfactory separation of glucose-1-phosphate, glucose-6-phosphate, fructose-6-phosphate and fructose-1,6-diphosphate by the one-dimensional descending-solvent technique.

### METHOD

The solvent mixture was prepared by mixing 80 volumes of *t*-butanol, 5 volumes of 50 per cent. formic acid and 20 volumes of water. Whatman No. 1 chromatography paper strips measuring 12 cm × 38 cm were used. (Pre-washing of the paper with ethylenediaminetetra-acetic acid did not offer any significant advantage.) Portions (10 to 20 $\mu$l) of 0·05 to 0·1 M solutions of samples of phosphate esters, in the form of sodium or potassium salts, were applied to the paper. The chromatogram was developed with the solvent descending for about 48 hours at 20° to 25° C; at the end of this period the solvent front just reached the lower edge of the paper. Slight variation in temperature affected the rate of flow of the solvent, but not the resolution of the spots. The chromatograms were dried in air and treated with Wade and Morgan's spray reagent[2] as modified by Runeckles and Krotkov.[10] All the phosphate esters were located in the first half of the paper and the spots were fairly compact. The relative distances from the centres of each spot to the centre of the orthophosphate spot are shown in Table I.

TABLE I

POSITION CONSTANTS OF HEXOSE PHOSPHATES

| Compound | Position constant |
|---|---|
| Orthophosphate | 100 |
| Fructose-1,6-diphosphate | 14 |
| Glucose-6-phosphate | 40 |
| Glucose-1-phosphate | 45 |
| Fructose-6-phosphate | 59 |

### RESULTS

The orthophosphate spot moves faster than any of the hexose phosphate esters. Fructose-1,6-diphosphate has the lowest position constant, providing a clear separation from hexose monophosphates. Fructose-6-phosphate moves ahead of glucose phosphates and can therefore be easily identified. Glucose-1-phosphate and glucose-6-phosphate move fairly close to each other, but can be separated by allowing the solvent to overflow. The system possesses the advantage that it is not too acidic, the solvent components can be removed from the paper fairly easily and that the use of the tertiary alcohol avoids esterification during development.

One of us (D.P.A.) thanks the Scientific Research Committee, U.P., Allahabad, for financial assistance.

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Received *March 22nd*, 1962

## STABILISATION OF SULPHIDE IN AQUEOUS SOLUTION

MICROGRAM amounts of sulphide are necessary for use as standards in the spectrophotometric determination of atmospheric hydrogen sulphide.[1] Standard aqueous sodium sulphide (1·0 μg per ml as sulphide) was found to lose its sulphide content in less than 5 minutes at room temperature. A method for stabilising aqueous sulphide, depending on the use of gum arabic or gum ghatti, was suggested by the junior author.

Gums have been used for some time for stabilising sulphide and other precipitates. More than 50 years ago Schidrowitz and Goldsbrough[2] noted that 10 mg of gum acacia (a synonym for gum arabic) added to 10 ml of a test solution were sufficient to hold as much as 2 mg of antimony, as $Sb_2S_3$, in colloidal condition, and that the colour was proportional to the concentration. Beam and Freak[3] and Bamford[4] made improvements to this method for the determination of antimony, and retained the use of gum arabic.

Moseley, Rohwer and Moore[5] employed both gelatin and gum tragacanth as protective colloids for stabilising copper diethyldithiocarbamate for the quantitative determination of minute amounts of copper. Hoar[6] used gum arabic for the same purpose.

In the late 1930's, Jacobs[7,8] used gum ghatti for stabilising lead sulphide and antimony sulphide for determining small amounts of lead and antimony in food.

Zinzadze[9] used gum arabic for stabilising the phosphate molybdenum blue formed by reduction with stannous chloride.

More recently, Willard, Mosher and Boyle,[10] West and Compere[11] and Miller, Geld and Quatinetz[12] used gum arabic for stabilising copper rubeanate.

### METHOD

PROCEDURE—

A solution of lead acetate (approximately 26 μg of lead per ml) was prepared and analysed polarographically. By pipette, 25 ml of this solution were put into a 100-ml calibrated flask. Two millilitres of a 5 per cent. solution of gum arabic in water and then a 50-ml portion of a solution containing 2·0 μg of sulphide per ml (prepared from sodium sulphide and standardised by iodimetric titration) were added. The suspension was subsequently diluted to 100 ml with distilled water to produce a "solution" containing 1·0 μg of sulphide per ml.

EVALUATON OF STABILITY—

The methylene blue - cadmium hydroxide method[1] was used to evaluate the stability of the suspension. Two millilitres of the 1·0 μg per ml suspension were treated with the reagents, and the optical density of the resulting blue solution was read at 670 mμ on a Beckman B spectrophotometer against a reagent blank. Portions of the suspension were analysed at intervals over a period of 2 days.

### RESULTS

The optical densities of the suspension at various times after preparation were—

| Time, hours .. .. .. | ⅔ | 2½ | 2¾ | 4⅓ | 5 | 22⅔ | 48 |
|---|---|---|---|---|---|---|---|
| Optical density .. .. | 0·101 | 0·103 | 0·109 | 0·105 | 0·101 | 0·106 | 0·099 |

After the suspension had stood for 2 days at room temperature in a glass-stoppered flask, its optical density decreased by not more than 2 per cent. The results indicate that the suspension is stable for at least 2 days. The slight variation found in the optical density is within the experimental error of the analytical method used.

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Received *March 12th*, 1962

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## CALIBRATION OF THE WAVELENGTH SCALE ON SPECTROPHOTOMETERS BY SAMARIUM AND NEODYMIUM CHLORIDES

For calibrating the wavelength scale on spectrophotometers, no method is superior to those in which mercury lamps or other lamps emitting line spectra are used. If spectral lamps are not available or if they cannot be fitted to the photometer, other calibrating procedures have to be used.

The absorption spectra of the rare-earth metals seem especially well suited to this purpose. The salts of these metals have many absorption peaks in the near ultraviolet, visual and near infrared regions of the spectrum.

Table I

Absorption maxima of samarium and neodymium chlorides

The letters used for the peaks are the same as those used on Figs. 1 and 2. Temperature 20° to 30° C. The tolerances are those given for the Beckman DU spectrophotometer by the manufacturer

| Peak | Wavelength of peak for samarium chloride,* mμ | Wavelength of peak for neodymium chloride,* mμ |
|---|---|---|
| a | 344·5 ± 0·2 | 512·0 ± 0·6 |
| b | (354·5) | 521·75 ± 0·6† |
| c | 362·25 ± 0·2 | 574·75 ± 0·7‡ |
| d | 374·3 ± 0·3 | 627·5 ± 0·8 |
| e | 390·5 ± 0·4 | 678 ± 1 |
| f | 401·5 ± 0·4† | 731 ± 1 |
| g | 407·0 ± 0·4 | 740 ± 1‡ |
| h | 415·25 ± 0·4 | 794 ± 1‡ |
| i | (417) | (801) |
| k | 441·0 ± 0·5 | 865 ± 1‡ |
| l | (451) | |
| m | 463·25 ± 0·5‡ | |
| n | 478·5 ± 0·5 | |

* All wavelengths can be used for calibration.
† Most accurate and easy to use.
‡ Especially well suited to calibration purposes.

That the rare-earth metals are not in general use as standards for wavelength settings is probably due to the impure products that have been on the market. These elements and their salts are now available in a high state of purity after purification by ion-exchange methods, and they are relatively inexpensive.

Samarium and neodymium chloride have especially been studied in this laboratory. The exact wavelengths of the peaks obtained with two Beckman DU spectrophotometers and carefully checked with a mercury lamp are shown in Table I. No shift in the wavelengths of the peaks could be observed at temperatures between 20° and 30° C.

The wavelengths were checked both with a standard spectrophotometer and an instrument supplied with photomultiplier accessories giving very narrow effective bandwidths. All values obtained with the two photometers were within the tolerances shown in Table I. It should be

emphasised that the wavelengths shown in Table I, because of the bandwidths employed, differ slightly from those obtained with a high resolution spectrograph.

The chemicals used were samarium$^{III}$ chloride (purity 99·96 per cent.) and neodymium$^{III}$ chloride (purity 99·8 per cent.) both obtained from Dr. Theodor Schuchardt, München, Germany. The salts contained unknown amounts of water.

The optical density at 374·3 m$\mu$ (peak d) for samarium chloride was 0·795 when 1·310 g were dissolved in 3 ml of 1 N hydrochloric acid (1-cm cells). Neodymium chloride gave an optical density of 1·020 when 0·270 g was dissolved in 3 ml of N hydrochloric acid and read at 521·75 m$\mu$ (peak b).

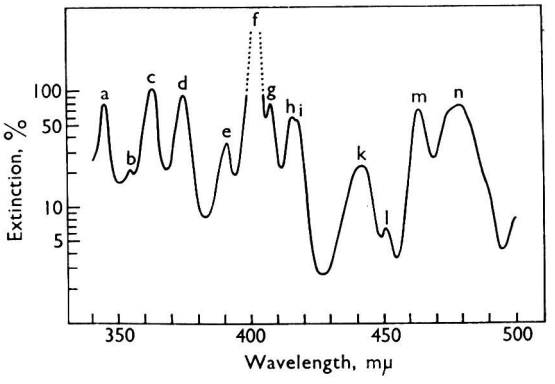


Fig. 1. Absorption spectrum for samarium chloride (for details of peaks, see Table I)

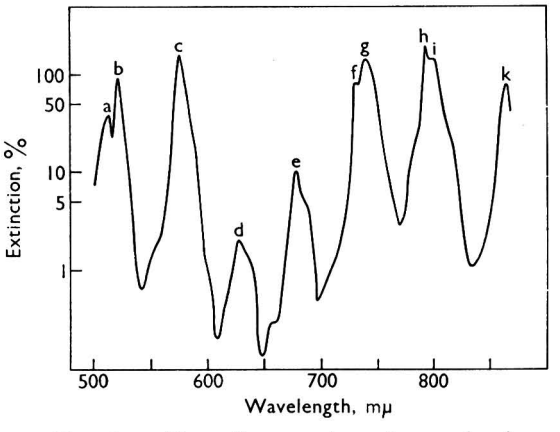


Fig. 2. Absorption spectrum for neodymium chloride (for details of peaks, see Table I)

Figs. 1 and 2 show the absorption curves measured with the Beckman DU spectrophotometer at 24·5° to 25·5° C. For samarium chloride, peak d (374·3 m$\mu$) was set to 100 per cent.; the optical densities observed were 0·948, 0·947, 0·922, 0·945 and 0·954. For neodymium chloride, peak b (521·75 m$\mu$) was chosen as 100 per cent.; the optical densities observed were 0·506, 0·508, 0·503, 0·497 and 0·497.

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Received *December 28th*, 1961

## A SIMPLE METHOD OF DETERMINING RADIOACTIVE ISOTOPES BY SOLID COUNTING

When determining radioactive isotopes by solid counting, it is frequently necessary to precipitate the radioactive substance from a fairly large volume of solution. The difficulty then arises of collecting the active material in a reproducible manner in the form of a solid layer suitable for placing beneath the end-window counter. The difficulty is particularly prevalent when analysing biological materials, as the amount of carrier will vary from sample to sample, giving precipitates of different thicknesses. Constant-thickness precipitates of many of the radioactive isotopes used in biological studies can, however, be obtained easily by making up the concentration of the carrier to a fixed level.

Phosphorus, for example, can be precipitated in an acid extract of plant material as either ammonium or quinolinium molybdophosphate, and a volumetric determination would give the concentration of $^{31}P$. Standard orthophosphate solution, sufficient to bring the $^{31}P$ to a constant weight, is then added to the titrated solution, and a reprecipitation in a shallow sintered crucible suitable for counting allows the concentration of $^{32}P$ to be determined.

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## THE DETERMINATION OF TRACES OF LEAD IN DRINKING WATER

The authors of a Note[1] in the May, 1962, issue of *The Analyst* under the above title appear to have completely overlooked my paper "The Estimation of Lead in Drinking Water"[2] published 22 years ago, otherwise they could hardly have stated that "The sulphide method is not applicable to water containing organic matter and iron." It was the precise object of my paper to show how, by means of wet oxidation, it was possible to apply the sulphide method to peaty waters naturally coloured by organic matter and occurring in many parts of the West Riding of Yorkshire. This was a problem, moreover, for which the well known water expert of his day, J. C. Thresh, and others had failed to find a satisfactory solution. As regards precision, the standard amount of lead adopted either in the form of solution or represented in B.D.H. colour discs also ranged from 10 $\mu$g upwards, and quantitative recovery of lead added as nitrate to 500 ml of Leeds City water was effected. Any traces of iron present are prevented from causing interference by the ammonium citrate normally added to the final solution. Moreover, there is no indication that any of the various eight waters to which lead was added by the authors or the two found to possess it in the ordinary way were coloured by organic matter. This may or may not be so, but the contention may be that the new method would yield satisfactory results in any case.

1. Abbott, D. C., and Harris, J. R., *Analyst*, 1962, **87**, 387.
2. Manley, C. H., *Ibid.*, 1940, **65**, 403.

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Received *May 21st*, 1962

# Book Reviews

A Laboratory Handbook of Pulp and Paper Manufacture, incorporating the Fourth Edition of Steven's "Paper Mill Chemist." By Julius Grant, M.Sc., Ph.D., F.R.I.C. Second Edition. Pp. viii + 523. London: Edward Arnold (Publishers) Ltd. 1961. Price 80s.

When Dr. Grant reviews and reports, we have come to expect a clear presentation of the facts given in an easily readable and understandable form. His mastery of this technique is clearly illustrated in his book, particularly in his handling of complex and difficult subjects such as packaging, plastics, toxicity evaluation and statistics.

The author's aim in preparing the second edition of his book is covered in the preface. Seventeen years have elapsed between the first and second editions, and it is agreed that this period of time has been "momentous" for the pulp and paper industry. To quote: "These advances have, of course, had wide repercussions in the subject matter of this book." There are 78 additions to the text, many being only a few sentences or paragraphs. The main additions come under the headings of printability, packaging, plastics, statistics, water and effluents. After studying the book it is difficult to appreciate how recent advances have radically changed the useful contents of the laboratory handbook. Laboratory work in the main has changed little and the majority of tests are well covered in the first edition.

Some justification for the remarks can be found in the highly specialised field of laboratory work. The paper mill chemist cannot hope to continue to be fully informed on all aspects of specialised investigation and testing. Some applications are of limited interest to him and the equipment necessary is often expensive and not always available. The techniques can, for certain applications, be of great value and coverage of these subjects does allow critical assessments to be made.

The section on electron microscopy is an example. An electron microscope must continue to be a curiosity for most chemists, but its possibilities and limitations are particularly important when all members of the Research Association are in a position to have any problem examined by this technique. The question of toxicity is in a similar category and the book gives an understanding of the testing methods and also a means of interpreting the results quoted.

The expanded statistics section gives a clear explanation of the mathematical techniques and their applications. It is certainly broad enough in scope, without being complicated, to allow the use of statistical methods in both laboratory testing and certain machine applications.

Recent legislation is demanding continual improvement of paper-mill effluents. The section on this subject is particularly valuable. It covers most of the important points and gives all the necessary background for the start of investigational work. The criticisms of the B.O.D. tests are fully justified.

Esparto cooking in Britain is shrinking and there seems little justification for introducing details on the composition of esparto wax extractable during the cleaning process. Similarly, expansion of the section on rag treatment appears to be unnecessary. However, with the advent of greater competition from the Scandinavian countries the treatment of waste paper becomes of increasing importance and the additions to this section are welcomed.

As a pulp importing country Britain must obtain maximum value for money and the increased emphasis on pulp evaluation is essential. Difficulties encountered by every paper mill in this field are illustrated by the section on sampling pulp for moisture content. It is regrettable that, although the coverage is admirable, there is little new information to help the sorely tried mill chemist who has to decide whether to risk submitting a pulp consignment to arbitration in the event of discrepancies.

Laboratory beating techniques in connection with pulp evaluation are important and it is admitted that for some pulps the Lampén mill method of beating is not reliable. No better alternative, however, is suggested.

Methods used for determinations of fibre length are often based on personal preference, but screening now seems to be almost completely superseded by fibre measuring and counting. It is difficult to understand why it is considered necessary to describe a screening method. Microscopical methods are critically reviewed and the clearer way of presenting the "weight factor" table of some common papermaking fibres should be helpful.

Testing of clays is a difficult task, their properties often being influenced by pH. The testing method covered does not include this point.

The information given on the evaluation and testing of retention aids and optical bleaching agents is sketchy and inadequate in view of the increased importance and use of both these items.

The need for accurate measurement of consistency on the paper machine is now urgent. Because of increasing production speeds and emphasis on controlling quality the more important aspects of this measurement are continuous indication of consistency and also its control. Unfortunately, these items have not been covered. These production trends also mean that more attention must be paid to keeping production units in good condition. The recommended method of measuring pressure between calender bowls is an important contribution.

The use of synthetic fibres for paper machine felts is now accepted and the present position is admirably summarised. However, Dr. Grant states that felts containing synthetic fibres tend to "blind" more readily than wool and mark the paper to a greater degree. From numerous

enquiries from papermakers using felts containing synthetic fibres it would appear that these views are not generally accepted.

Tub sizing as described is seldom used and any newcomer to the industry will find it disturbing to learn that there is no index reference to "sizepress." The unit is referred to only in passing and in view of its ever increasing use is worthy of greater description.

Other items that would appear to be worthy of inclusion in a laboratory handbook are: rheological measurement in connection with coating mixes particularly in view of the increasing number of on-machine installations, beta-ray gauges for determination of substance both on the machine and in the laboratory, and the use of the xenon lamp as a light source for the evaluation of light fastness.

The staining techniques for the identification of fibres and cooking methods are important. Different chemical treatments are now used on one type of wood and it is no longer valid to conclude that a certain treatment has been given to the fibre because of the latter's cellular structure. The lack of advance in this field is illustrated by the fact that only one new stain has been added to the list given in the first edition.

On the subject of physical testing, reference is made to the Van der Korput tensile tester as a dynamic instrument. However, it should be stated that the instrument can also be used for measuring static tensile and stretch.

A few lines are devoted to the testing for silicones, but anyone who has attempted to establish their presence will realise that such an exercise is not easy. The remarks do not in any way indicate the difficulties involved.

The first publication of this book had to conform to the War Economy Standard and the lifting of this restriction on paper usage has resulted in a clearer, more easily read text, better spacing and superior reproductions of drawings and photographs. The use of a glossy paper, however, can be most annoying especially when reading in a position illuminated from a number of different sources. Further, this book will often be opened and used on a laboratory bench. Any liquid accidentally splashed on to the pages will result in a dull stain. If the book is closed while the page is still damp with water the effect will be sticking of one page to another.

Mill chemists are notorious at obtaining the wrong answer when using rapid methods of calculation. To avoid the possibility of some future annoyance to a mill manager or papermaker it should be pointed out that the machine production formula on p. 230 should include substance in lbs D.C. 480's (compare Table 37, p. 503). J. B. HEATON

AN INTRODUCTION TO INFRARED SPECTROSCOPY. By Dr. WERNER BRÜGEL. Translated from the German original by A. R. KATRITZKY and A. J. D. KATRITZKY. Pp. xvi + 419. London: Methuen & Co. Ltd., New York: John Wiley & Sons Inc. 1962. Price 55s.

The development of analytical chemistry during the last 20 years has been characterised by the introduction and general acceptance of a wide range of physical methods that have helped solve problems, which either could not have been undertaken or would have taken much longer to solve by the older chemical procedures. Infrared-absorption spectroscopy is a leader among the newer techniques and is one of the most powerful tools available to-day for the rapid identification and measurement of an organic compound. Infrared spectroscopy is, however, a rapidly expanding subject and it is difficult for a student to gain a comprehensive picture of both the theoretical and practical aspects of the subject. An authoritative book that provides an up-to-date account in English of all aspects of infrared spectroscopy is therefore assured of a welcome. This volume, which sets out to meet these requirements, is largely a translation of the second German edition (1957) of Dr. W. Brügel's well known "*Einführung in die Ultrarotspektroskopie*"; some new material and about 70 additional references have been included.

The volume is divided into four main sections, which deal in turn with (1) basic theory, including an account of rotation - vibration spectra of small molecules in the gaseous state, (2) instrumentation and experimental techniques, covering radiation sources and detectors, monochromators and gas analysers, and describing the principal features of modern American, British and German commercial infrared spectrophotometers, (3) practical applications in structural diagnosis and quantitative analysis, and the uses of polarisation, reflection and microscope techniques in infrared spectroscopy and (4) special applications, including absorption-band frequency correlations for the commoner functional groups, the examination of polymers and inorganic compounds, and special effects, such as hydrogen bonding and rotational isomerisation. This

book covers a much wider field than, but is in many ways complementary to, L. J. Bellamy's monograph ("The Infrared Spectra of Complex Molecules," Methuen & Co. Ltd., London, Second Edition, 1958); the latter ignores the theoretical and instrumental aspects of infrared spectroscopy, but provides a more detailed account of structural correlations. Dr. Brügel's book disappoints in having relatively few references to work published since 1957; recent work on aromatic and heterocyclic compounds, a field in which Dr. A. R. Katritzky, one of the translators, has had special experience, is adequately reviewed.

The translation has been well done and the book can be recommended to all students and to chemists who require a reliable account of both the theory and the practical applications of infrared spectroscopy. The volume is well produced and has few printing errors. It is, perhaps, to be regretted that in his introduction, the author mentions the pioneering work on infrared spectroscopy conducted in Germany and America, but does not refer to the equally important work undertaken in this country.

J. E. PAGE

THE CHROMATOGRAPHY OF STEROIDS. By I. E. BUSH, M.A., Ph.D., M.B., B.Ch. Pp. xxii + 437. Oxford, London, New York and Paris: Pergamon Press Ltd. 1961. Price 80s.

Although the chromatography of steroids has been the subject of many books and reviews in recent years, never has theory been so successfully blended with practice as in the present volume. The shortcomings of an approach to this field not soundly based on theory are lucidly exposed by Professor Bush. In spite of dealing with a rapidly expanding subject this book will prove invaluable both as a reference work and laboratory manual and will undoubtedly remain so for a long time.

However, the scope is limited in that examples are not drawn from bile acids, sapogenins, cardiac aglycones and steroid alkaloids, although the author states justifiably that the general principles he emphasises throughout should be applicable to the investigation of these less familiar steroids. Discussion of partition chromatography, especially on paper, occupies considerably more space than that of adsorption chromatography. Even so the latter is adequately covered considering it is less often used and its basic theory not well developed. One might have expected mention of chromatography on impregnated glass-fibre sheets, a not too recent development offering some unique advantages.

The basic theory of partition chromatography is discussed at length. Numerous examples are drawn from many branches of biochemistry to show that chromatographic behaviour is a consequence of general laws and can be treated on a quantitative basis. The application of these general principles to the chromatography of steroids is illustrated and discussed with reference to the types of systems in use. Discussion of factors influencing chromatographic behaviour, such as chemical structure and solvent - steroid interaction, is more than adequate and to the point.

The author has drawn on his own considerable experience in describing with a wealth of detail the apparatus used and the many techniques involved in obtaining the best results from chromatography. The methods of estimation of steroids by direct automatic scanning of paper chromatograms after treatment with suitable reagents are described at great length on the justification that they are more rapid and convenient than conventional colorimetric procedures and yet almost as accurate. The ever increasing use of double-isotope labelling methods is only described briefly being, in the author's opinion, unnecessary. This may sometimes be so, but the availability of steroids and reagents with high specific radioactivities minimises many of the extra complications while increasing the precision and time and labour saved.

The chapter outlining procedures for structure determination of unknown steroids utilising chromatography combined with modifying steps is excellent, as is that dealing with the application of these techniques to typical analytical problems such as the isolation and estimation of cortisol in blood or aldosterone in urine. The comprehensive appendices include purification of solvents and reagents, details of microchemical reactions for steroids, detection of steroids on paper chromatograms and many others even including the cleaning of glassware.

As in many first editions some misprints have escaped correction in the proof reading. Thus the year of a reference quoted in the text does not always correspond with that given in the reference list and there is a strange omission of both legend and title from the figure on p. 187. However, these are minor flaws in an otherwise outstanding and thoroughly recommendable book.

DENNIS A. SHAW

ADVANCES IN SPECTROSCOPY. Edited by H. W. THOMPSON, C.B.E., F.R.S. Volume II. Pp. xii + 483. New York and London: Interscience Publishers Inc. 1961. Price $13.00; 98s.

Authoritative monographs on nine topics in spectroscopy form the subject matter of the second volume of this series, of which the first has already received notice in this journal (*Analyst*, 1960, **85**, 532). The high standard set in the earlier volume is well maintained; a broad range of interests is catered for by those phases of the subject that now receive attention, as will be appreciated from a list of the contents.

Application of atomic-absorption spectroscopy to chemical analysis (A. Walsh); Spectra of flames (A. G. Gaydon); X-ray spectroscopy (H. Friedman); Nuclear-magnetic resonance (R. E. Richards); Infra-red spectra of crystals (W. Vedder and D. F. Hornig); Refraction of gases in the infra-red (J. H. Jaffe); Infra-red spectra of micro-organisms (K. P. Norris); Ultra-violet absorption spectra of proteins and related compounds (G. H. Beaven); Some recent developments in the theory of molecular energy levels (H. C. Longuet-Higgins).

As in the earlier volume, the various articles are complete in themselves, written by acknowledged experts in the various fields and each well provided with literature references. It may be noted that there is appreciably more subject matter to interest the practising analyst than there was in the first volume.

The editor is to be congratulated on his selection of contributors and in once more producing so well balanced a collection of informative articles. The many readers who have welcomed the first two of these "Advances" will look forward to the third, which "should make it possible to complete a survey of other established fields and to include a few of the very recent developments."

B. S. COOPER

TECHNIQUES IN FLAME PHOTOMETRIC ANALYSIS. By N. S. POLUEKTOV. Authorised translation from the Russian by C. NIGEL TURTON, B.Sc., Ph.D., and TATIANA I. TURTON, B.A. Pp. xiv + 219. New York: Consultants Bureau Enterprises Inc. 1961. Price $9.50.

Few satisfactory text-books of flame photometry have so far been published in English. This volume is a welcome addition.

The initial sections deal with the theoretical basis of flame photometry, apparatus and general analytical procedures and the latter half of the book with the determination of individual elements.

The translators are to be congratulated in that there are few signs that this is a translation; the English style is simple and direct.

This book provides a useful introduction to the Russian literature, and analysts interested in flame photometry will find it a helpful addition to their libraries; however, the clarity with which the theoretical basis of the method is discussed make this text an excellent introduction for those unfamiliar with the subject. It is recommended.

IAIN MACINTYRE

EXPERIMENTAL THERMOCHEMISTRY. Volume II. Prepared under the auspices of I.U.P.A.C. by the Subcommission on Experimental Thermochemistry. Edited by H. A. SKINNER. Pp. xx + 457. New York and London: Interscience Publishers Inc. 1962. Price 107s.

After the publication of "Experimental Thermochemistry" in 1956, a second volume was prepared by a similar I.U.P.A.C. Subcommission on Experimental Thermochemistry. This book contains nineteen chapters. The first five of these, an introductory survey and four chapters on the particular techniques applicable to metals, organic fluorine, organic bromine and organometallic compounds, deal with combustion bomb calorimetry in which oxygen is used, with special reference to the moving-bomb technique. Next are two chapters on the use of fluorine as oxidant in bomb and in flame calorimetry. Then there are eight chapters on reaction calorimetry: introduction, design of reaction calorimeters, heats of hydrogenation and of halogenation, heats of hydrolysis, heats of polymerisation, high temperature reactions and heats of formation, solution calorimetry and silicate thermochemistry, and heats of mixing the constituents of binary liquid mixtures. The remaining four chapters deal with the problems peculiar to metallurgical and alloy thermochemistry, recent progress in microcalorimetry, biochemical and zoological thermogenesis as studied by microcalorimetry, and heats of biochemical reactions.

Not only will the combination of the first and second volumes provide a valuable text-book and reference book for all serious workers in the field of thermochemistry, for the second volume is an almost perfect complement of the first, but also the lucid explanations of methods for deriving quantitative information about the energetics of chemical change in biochemical and metallurgical systems will render this pair of volumes of interest to a much greater scientific readership. What the first volume lacked in application to inorganic and biochemistry, this volume discusses adequately, as well as expanding on the relatively recent methods involving fluorine and micro-calorimetric procedures. The book abounds with examples of procedures, with diagrams of apparatus and of electronic circuitry, and with tables and summaries of thermochemical publications. Little repetition is evident, but some overlapping with the first volume exists. Different numbering of steps unfortunately occurs in the several computation forms (the Washburn reduction type) used in analysis of the results from bomb experiments. The criticism that there are numerous references to chapters in the first volume is not wholly relevant, because many of the chemists interested in this volume will already have obtained the previous volume. The writing and the editing are otherwise generally good. Volume II of "Experimental Thermochemistry" is thus a useful book and a necessary companion to Volume I; together they constitute the modern definitive work in thermochemistry. J. F. OGILVIE

REAGENT CHEMICALS AND STANDARDS. By JOSEPH ROSIN. Fourth Edition. Pp. viii + 557. Princeton, N.J., New York, Toronto and London: D. Van Nostrand Company Inc. 1961. Price $14.50; 112s. 6d.

This edition follows closely the pattern of the third edition, which was reviewed in *The Analyst*, 1956, **81**, 731. The main difference is an enlargement by some thirty specifications for chemicals not previously included. With a total of over 600 specifications, the publication is one of the most comprehensive of its kind.

The new items include ten of the "essential" amino acids, and the tests prescribed for these substances are intended to ensure their suitability for use as reference standards, but no chromatographic or microbiological criteria are invoked. The vitamins nicotinic acid, riboflavin and thiamine hydrochloride are also newly introduced as reference substances. Other miscellaneous additions are ethoxyethanol, ceric sulphate, n-hexane, lead tetra-acetate, murexide, sodium tetraphenylboron and tetrahydrofuran.

The very wide coverage of this compilation allows it to serve a useful purpose as a supplement to official and proprietary publications of similar character, and this function is of particular importance in the U.S.A., where the standards of the American Chemical Society cover a comparatively restricted range of 234 reagents. W. C. JOHNSON

GAS CHROMATOGRAPHY. By JOHN H. KNOX. Pp. viii + 126. New York: John Wiley & Sons Inc.; London: Methuen & Co. Ltd. 1962. Price 15s.

Some of the older generation of chemists tend to resent the present as an age of push-button chemistry, and it is true that the development of modern instrumentation allows certain otherwise complicated routine analyses to be carried out rapidly and accurately by trained, if unqualified, assistants, but the routine has still to be devised by one possessing the requisite fundamental knowledge and experience. This is nowhere more the case than in gas chromatography, where the problems of appropriate column filling, carrier gas, temperature and detector have first to be solved. For these, a knowledge of the fundamental theoretical background and of the factors that determine the desirable properties of the materials used is essential. This monograph provides this knowledge for gas chromatography. It deals with the underlying fundamental principles and theory of the subject; specific applications in analytical chemistry are not included. After an introduction, chapters deal with the theory of the process, columns and column packings, detectors, ancillary equipment and additional methods, such as multiple columns and temperature programming. Gas-chromatographic methods are rapidly becoming essential in all analytical laboratories and it is equally essential that the chemist charged with their application should be familiar with the theoretical background. This he can be by the study of this excellent monograph. J. I. M. JONES

# Publications Received

THE DITHIOCARBAMATES AND RELATED COMPOUNDS. By G. D. THORN and R. A. LUDWIG. Pp. viii + 298. Amsterdam and New York: Elsevier Publishing Company. 1962. Price Dfl. 20.

MISES AU POINT DE CHIMIE ANALYTIQUE PURE ET APPLIQUÉE ET D'ANALYSE BROMATOLOGIQUE. Edited by J.-A. GAUTIER. Dixième Série. Pp. 257. Paris: Masson et Cie. 1962. Price 55 NF.

CHEMICAL ANALYSIS: THE WORKING TOOLS. Volumes I, II and III. Edited by C. R. N. STROUTS, H. N. WILSON and R. T. PARRY-JONES, with the assistance of J. H. GILFILLAN. Second Edition. Pp. xx + 467 (volume I), xii + 479 (volume II) and xii + 273 (volume III). Oxford University Press. 1962. Price (3 volumes) £7 7s.

THE PRACTICE AND SCIENCE OF BREADMAKING. By D. W. KENT-JONES, Ph.D., B.Sc., F.R.I.C., and E. F. MITCHELL. Third Edition. Pp. x + 312. Liverpool: The Northern Publishing Co. Ltd. 1962. Price 50s; $8.

CHROMATOGRAPHIC REVIEWS: PROGRESS IN CHROMATOGRAPHY, ELECTROPHORESIS AND RELATED METHODS. Volume 4. Edited by MICHAEL LEDERER. Pp. viii + 184. Amsterdam and New York: Elsevier Publishing Company. 1962. Proce Dfl. 25.

BNF ANALYTICAL CONFERENCE, MALVERN, 1961. Pp. 120. London: The British Non-Ferrous Metals Research Association. 1962. Price 50s.

ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY FOR 1961. Volume LVIII. Pp. vi + 529. London: The Chemical Society. 1962. Price 40s.

INFLUENCE OF ANIMAL STRAIN SELECTION AND CONDITIONING ON BIOLOGICAL EXPERIMENTS AND ASSAYS. January 16, 1962. Pp. iv +32. London: The Pharmaceutical Press. 1962. Price 5s.

*Report of a Symposium organised by the Department of Pharmaceutical Sciences of the Pharmaceutical Society of Great Britain at the Society's Headquarters.*

DETECTION AND MEASUREMENT OF NUCLEAR RADIATION. By G. D. O'KELLEY. Pp. viii + 138. Washington, D.C., U.S. Department of Commerce, Office of Technical Services. 1962. Price $1.50.

*Nuclear Science Series: NAS–NS–3105. Radiochemical Techniques.*

PAPER CHROMATOGRAPHIC AND ELECTROMIGRATION TECHNIQUES IN RADIOCHEMISTRY. By R. A. BAILEY. Pp. vi + 48. Washington, D.C., U.S. Department of Commerce, Office of Technical Services. 1962. Price 50 cents.

*Nuclear Science Series: NAS–NS–3106. Radiochemical Techniques.*

PRACTICAL PHARMACEUTICAL CHEMISTRY: QUANTITATIVE ANALYSIS. By A. H. BECKETT, D.Sc., Ph.D., F.P.S., F.R.I.C., and J. B. STENLAKE, D.Sc., Ph.D., F.P.S., F.R.I.C. Pp. viii + 378. London: The Athlone Press. 1962. Price 63s.

SPECTROSCOPY. Edited by M. J. WELLS. Pp. viii + 305. Oxford, London, New York and Paris: Pergamon Press, distributors for The Institute of Petroleum. 1962. Price 63s.

*Report of the Conference by The Hydrocarbon Research Group of the Institute of Petroleum and held in London, March* 1962.

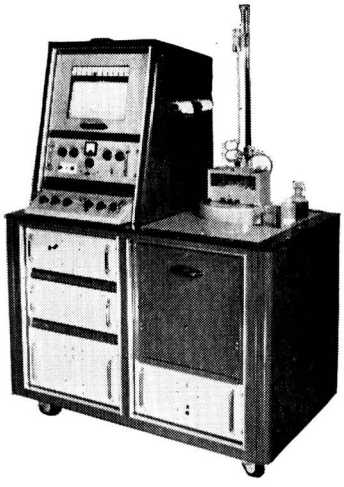
DEOXYRIBONUCLEIC ACID: STRUCTRE, SYNTHESIS AND FUNCTION. Pp. xii + 235. Oxford, London, New York and Paris: Pergamon Press. 1962. Price 60s.

*Proceeding of the 11th Annual Reunion of the Société de Chimie Physique, June,* 1961.

## Errata

JUNE (1962) *issue,* p. 466, Table II, 1st line under column headings. *For* "$V_f \simeq 60$ ml" *read* "$V_0 = 60$ ml."

*Ibid.,* p. 466, Table II, 2nd line under column headings. *For* "$V- = 35$" *read* "$V_f \simeq 35$."



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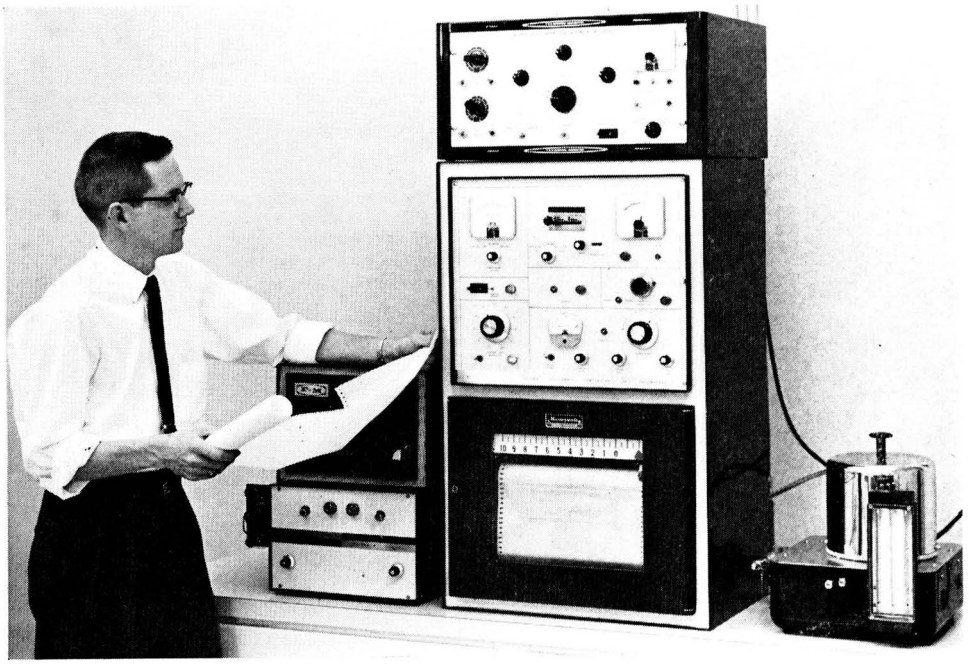

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Volume 87. No. 1038, Pages 689 - 768 September, 1962

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THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

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Printed and Published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England. **Communications to be addressed to the Editor, J. B. Attrill, 14 Belgrave Square, London, S.W.1.** Enquiries about advertisements should be addressed to Walter Judd Ltd., 47 Gresham Street, London, E.C.2.

Entered as Second Class at New York, U.S.A., Post Office