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The colorimetric determination of molybdenum with polyhydric phenols:
H. BUCHWALD and E. RICHARDSON, *Talanta*, 1962, **9**, 631–637.

Summary—The use of polyhydric phenols as colorimetric reagents for molybdenum is reviewed. It is shown that any polyhydric phenol having two *ortho* hydroxyl groups can be used with equal success. The use of gallic acid or sodium 2,3-dihydroxynaphthalene-6-sulphonate has been discussed in greater detail. The practical sensitivity for molybdenum is about 0·1 μg/ml at 400 mμ.

Emission spectra from high frequency excitation—III: C. L. CHAKRABARTI, R. J. MAGEE and C. L. WILSON, *Talanta*, 1962, **9**, 639–645.

Summary—A continuous discharge at 230 megacycles, produced by a radio-frequency extra-hightension generator, in a sealed-off gas system, has been used in conjunction with a quartz prism spectrophotometer to study binary mixtures of argon and carbon dioxide· The concentrations of mixtures in the range 9 to 90% argon, and 91 to 10% carbon dioxide have been determined with a reproducibility of $\pm$3.2% absolute, expressed as a standard deviation. Determinations can be carried out in about 1 min, making the technique superior to the usual spectrographic technique. The procedure developed suggests that with improved instrumentation, ensuring constancy of source intensity, and substitution of a continuously flowing gas for the sealed-off system, it might be possible to extend the technique to mixtures of other gases and obtain better reproducibility and accuracy.

Untersuchung der Kationensorption aus Komplexanmedium—III: ZDENĚK ŠULCEK, PAVEL POVONDRA und RICHARD ŠTANGL, *Talanta*, 1962, **9**, 647–651.

Zusammenfassung—Es wurde eine neue Methode zur Trennung von Strontium und Barium unter Anwendung der Ionenaustauschchromatographie ausgearbeitet. Barium- und Strontiumionen werden an einem stark sauren Kationenaustauscher (Amberlit IR 120 in NH_4^+-Cyclus) adsorbiert, wonach Strontium mit 0,02–0,05 m DCyTE in 0,4 m Ammoniumacetat (pH 6,3–7,2) ausgewaschen wird. Im Eluat ermittelt man den Strontiumgehalt flammenphotometrisch. Bei der gleichzeitigen Bestimmung von Calcium und Strontium neben überschüssigem Barium, wäscht man Calcium mit dem gleichen Elutionsmittel bei pH 5,1 aus. Die neu vorgeschlagene Methode wurde zur Bestimmung von Strontium und Calcium in Bariummineralen, insbesondere in Schwerspat und Witherit angewendet.

Chemiluminescence of luminol and haemin; L. Erdey, W. F. Pickering and C. L. Wilson, *Talanta*, 1962, **9**, 653–659.

Summary—A study of the luminescence of haemin-luminol mixtures has shown that haemin is a chemiluminescent material, and a mechanism is proposed for the haemin-luminol reaction. The course of the reaction depends on the relative concentrations of the components and the alkalinity of the solution.

Applications of infrared spectroscopy—IX: D. M. W. ANDERSON and J. L. DUNCAN, *Talanta*, 1962, **9**, 661–666.

Summary—After determination of the total alkoxyl content (ester + ether groups) by reflux with hydriodic acid, the contribution from methyl and ethyl ester groups is found by refluxing a second sample of the compound in constant-boiling hydrochloric acid for 3 hr. Acetals cannot be distinguished from esters; the yields of alkyl chloride from propyl and butyl esters are diagnostic, although not quantitative. Certain classes of compounds, which have unusually labile ether linkages, restrict the general applicability of the method; examples of such compounds are given.

Analytical applications of infrared spectroscopy: M. AL-KAYSSI and R. J. MAGEE, *Talanta* 1962, **9**, 667–672.

Summary—Using infrared absorption spectroscopy a method has been developed which permits the identification of the following 14 anions: pertechnetate, perrhenate, thiocyanate, persulphate, perchlorate, chlorate, permanganate, periodate, ferricyanide, ferrocyanide, thiosulphate, chromate (or dichromate), molybdate and tungstate. The method is fast, sensitive and reliable compared to the corresponding laborious and time-consuming classical methods.

The spectrophotometric determination of sulphur in iron alloys: OWEN H. KRIEGE and ARTHUR L. WOLFE, *Talanta*, 1962, **9**, 673–678.

Summary—Sulphur is determined in iron alloys by evolution as hydrogen sulphide, followed by reaction with N,N-dimethyl-p-phenylenediamine and iron[III] to form methylene blue, which is measured spectrophotometrically. Replicate results are reported for acid soluble metal samples containing 0.3-230 ppm of sulphur. An evaluation of the accuracy of the methylene blue procedure was made using radio-tracer techniques.

Titrimetric analysis with chloramine-T—VIII: The chloramine-T—thallium[I] and —thiocyanate reactions: E. BISHOP and V. J. JENNINGS, *Talanta*, 1962, **9**, 679–687.

Summary—Direct oxidation of thallium[I] in chloride or bromide media at acid concentrations of 0.05 to 3.0M is too slow to permit the use of visual indicators, and potentiometric titration reveals large positive errors. Double excess back titration following oxidation in acid chloride or bromide media gives excellent results provided the excess of oxidant is limited to 0·5 ml; oxidation in the absence of bromide is preferred. No satisfactory procedure for the determination of thiocyanate other than that previously advocated[4] could be devised. Reactions with hydrazine and thiosulphate give poor results, oxidation of nitrite is unsatisfactory, and hydroxylamine and vanadium[IV] are not oxidised.

   Examples of reactions involving excess of oxidant have been examined. Determination of sulphite in which chloramine-T is used quantitatively to liberate an excess of iodine is satisfactory. Determination of 8-hydroxyquinoline and of metals precipitated as oxinates by double excess back titration in which chloramine-T is used for the quantitative generation of bromine affords excellent results. Hexacyanoferrate(II) cannot be directly titrated, but determination by double excess back titration is possible, although the results are of poor accuracy.

Studies on uronic acid materials—V: The thermal decarboxylation method of analysis: D. M. W. ANDERSON, S. GARBUTT and J. F. SMITH, *Talanta*, 1962, 9, 689–697.

Summary—The thermal decarboxylation method of determining uronic acids, proposed by Perlin, has been investigated. A specially designed oven, having good temperature stability, enabled the thermal decomposition of various compounds to be studied kinetically, with good reproducibility. Comparatively large errors can arise in the determination of the carbon dioxide evolved; these errors originate in the nature of the other volatile reaction products. Typical results are presented, and it is concluded that thermal decarboxylation does not compare favourably with the 150-min acid decarboxylation as a general analytical method.

Precipitation of nickel dimethylglyoximate from homogeneous solution The reactions of biacetyl, hydroxylamine and nickel^{II}: E. D. SALESIN, E. W. ABRAHAMSON and LOUIS GORDON, *Talanta*, 1962, 9, 699–714.

Summary—The reaction between biacetyl and hydroxylamine to form dimethylglyoxime was found to follow simple kinetics in the absence of nickel. However, with nickel^{II} present, the kinetic studies showed definite evidence for complex formation between biacetyl monoxime and nickel. This complex and others formed with nickel in the reaction mixture determines the overall rate of formation of nickel dimethylglyoximate. Supersaturation concentrations of several hundred times the equilibrium solubility of nickel dimethylglyoximate were attained in nucleation experiments. The kinetic and nucleation studies provide explanations for some previously anomalous experimental observations, *e.g.*, the persistent supersaturation in this system provides an explanation for the inability to precipitate completely small amounts of nickel^{II} with dimethylglyoxime. The yellow colour observed in the initial stage of the precipitation of nickel from homogeneous solution arises from dissolved nickel dimethylglyoximate.

A new reductimetric reagent: Iron^{II} in a strong phosphoric acid medium: Titration of uranium^{IV} with iron^{II} at room temperature: G. GOPALA RAO and SEETARAMA RAJU SAGI, *Talanta*, 1962, 9, 715–722.

Summary—The formal redox potential of the Fe^{III}/Fe^{II} couple has been determined in media of varying phosphoric acid concentration, and found to decrease steeply with increasing phosphoric acid concentration. Above a certain concentration of phosphoric acid, the difference between the formal potentials of the U^{VI}/U^{IV} and Fe^{III}/Fe^{II} couples becomes sufficiently great to enable iron^{II} to reduce uranium^{IV} even at room temperature. This is the reversal of the normal redox reaction—oxidation of uranium^{IV} by iron^{III}. A careful study of the various factors involved has enabled us to develop a new reductimetric titration of uranium^{VI} with iron^{II} in strong phosphoric acid medium (11·0 to 13·5M) at room temperature using either a potentiometric end-point or a visual end-point with methylene blue or thionine as an internal redox indicator. Because the new procedure enables the titration to be carried out at room temperature, it is more convenient than procedures involving titanium^{III} and chromium^{II} which require temperatures ranging from 60 to 90°. The new procedure has a further advantage in that it can be used for the determination of uranium^{IV} even in the presence of iron^{III} and tungsten^{VI}, using an electrometric end-point. Also, the new procedure does not require the elaborate precautions which are necessary for the preparation and storage of titanium^{III} or chromium^{II} solutions.

The hydrolysis of 8 acetoxyquinoline: DAVID ELLIOTT, LESTER C. HOWICK, BILLY G. HUDSON and WILLIAM K. NOYCE, *Talanta*, 1962, **9**, 723–724.

Summary—The rates of hydrolysis of 7-acetoxyquinoline and 8-acetoxyquinoline at 35° have been measured and are reported for the pH region from 0 to 10.

Spot test for bivalent sulphur based on pyrolysis with mercuric cyanide: FRITZ FEIGL and E. LIBERGOTT, *Talanta*, 1962, **9**, 725–727.

Summary—The test described for bivalent sulphur in organic compounds is based on the finding that hydrogen cyanide can be detected in the gas phase if the sample is heated with mercuric cyanide to 180°. The identification limits range from 5 to 50 μg. An explanation is advanced for the chemistry of the pyrolytic reaction.

Contribution to the analytical use of a standard solution of iodine trichloride: E. SCHULEK and L. LADÁNYI, *Talanta*, 1962, **9**, 727–730.

Summary—In order to establish its accurate composition, the $0.1N$ standard solution of iodine trichloride suggested by Gengrinovich has been subjected to re-investigation. It was found that iodate is responsible for 75 % and iodine monochloride for 25 % of the total oxidation power of the solution. The presence of iodine trichloride could not be detected. In terms of this knowledge of the exact composition of the solution it is possible to consider in an entirely new way the chemical reactions occurring during its use.

Chelating action of thioglycollic acid with silver: A. M. CABRERA and T. S. WEST, *Talanta*, 1962, **9**, 730–733.

Summary—The reactions between thioglycollic acid and some bivalent cations, *viz.* zinc, mercury, cadmium, lead and more particularly with silver, are studied by direct and indirect complexometric titration. New complexes are reported with zinc, cadmium and lead, and the silver complex is also formulated. The potential use of the reagent as a complexometric titrant for silver ion is hindered by the lack of suitable metallochromic indicators.

Phase titrations—I: Binary systems involving carbon tetrachloride and binary systems involving carbon disulphide: D. W. ROGERS, *Talanta*, 1962, **9**, 733–738.

Summary—The theoretical basis of phase titrations is discussed, a simple, rapid titration method is described and its errors and advantages are evaluated. Typical calibration curves are shown and related to the corresponding three component phase diagram. Data are included for the analysis of carbon tetrachloride and carbon disulphide in binary solutions with methanol, ethanol, isopropanol, dioxan and acetone, using water as the titrant. Titrations of heterogeneous systems and titrations using carbon tetrachloride as the titrant are briefly discussed and a few representative results are presented.

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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CONTENTS

THE COLORIMETRIC DETERMINATION OF MOLYBDENUM WITH POLYHYDRIC PHENOLS

H. BUCHWALD* and E. RICHARDSON†

Whitehaven College of Further Education, Cumberland, England

Summary—The use of polyhydric phenols as colorimetric reagents for molybdenum is reviewed. It is shown that any polyhydric phenol having two *ortho* hydroxyl groups can be used with equal success. The use of gallic acid or sodium 2,3-dihydroxynaphthalene-6-sulphonate has been discussed in greater detail. The practical sensitivity for molybdenum is about 0·1 μg/ml at 400 mμ.

A NUMBER of polyhydric phenols have been used as colorimetric reagents for molybdenum. It is proposed, in this paper, to show that polyhydric phenols in which there are two *ortho* hydroxyl groups may be generally used for this purpose.

Weinland and Gaisser[14] found that on treating ammonium molybdate with catechol in aqueous solution a deep red colour was produced. In neutral solution this colour arises from the formation of a chelate which requires two molecules of catechol to one of molybdenum[2,3,4,7] and is formed by any simple *ortho* dihydroxy phenol.[2,4,7] Catechol has been used for the detection[6] and determination[9] of molybdenum. Similar use has been made of pyrogallol,[1] Tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate),[15] 3,4-dihydroxybenzaldehyde[10] and tannic acid.[11,12] Halmekoski[5] used the reaction to determine catechol in the presence of excess molybdate.

Seifter and Novic[9] used a mildly alkaline (0·4% NaOH) catechol reagent which had to be stabilised with sodium metabisulphite. The colour obtained showed maximum absorption at 400 mμ, though a wide range of molybdate concentration[5] could be determined by a suitable choice of wavelength (up to 515 mμ). The sensitivity at 400 mμ was such that 1 μg of molybdenum per ml caused an optical density increase of 0·05. Beer's law was obeyed in the presence of a large excess of catechol and the colour was stable for 2 hours. Considerable interference was caused by iron[III] but none was evident from cobalt or manganese. A more critical approach to the reaction was made by Haight and Paragamian,[3] who found complications when sodium sulphite was substituted for metabisulphite as stabiliser. The reasons given for this are not very convincing, and, moreover, a correct choice of conditions can eliminate the need for a stabiliser.

Will and Yoe[15] used Tiron as their reagent and carried out a thorough study of the optimum conditions. The maximum absorption occurred at 390 mμ and Beer's law was obeyed in the presence of a large excess of the reagent. The optimum pH range of 6·5–7·5 was obtained by using a suitable buffer. The colour became slightly more intense (by 1%) over the first 6 hours, but then became completely stable and remained unaffected by temperature (15–45°). At 390 mμ, 1 μg/ml of molybdenum caused an increase in optical density of 0·07, and a practical sensitivity of 0·1 μg per ml was claimed. The effects of a large number of ions on the system were investigated and methods were suggested for determining molybdenum in various materials.

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1

The present authors have studied the reaction with twelve suitable phenols, which are listed in Table I together with data on the solvent needed to prepare a 1% solution and the discoloration produced by aerial oxidation. A more detailed study of the nature of these complexes has been published elsewhere.[2]

Any one of these phenols can be used as the colorimetric reagent. In the presence

TABLE I.—SOLVENTS FOR POLYHYDRIC PHENOLS.

No.	Phenol	Solvent for 1% solution	Colour of solution	Colour after 24 hr
I	Catechol	Water	Colourless	Pale yellow–pink
II	4-Methylcatechol	Water	Slightly yellow	Yellow–pink
III	3,4-Dihydroxybenzaldehyde	Water	Pale yellow–brown	Yellow–brown
IV	3,4-Dihydroxybenzoic acid	Water	Slightly yellow	No change
V	Tiron	Water	Colourless	No change
VI	Gallic acid	20% aqueous ethanol	Colourless	No change
VII	Pyrogallol	Water	Colourless	Yellow
VIII	2,3,4-Trihydroxybenzoic acid	20% aqueous ethanol	Slightly yellow	No change
IX	3-Methyl-6-sec-propylcatechol	30% aqueous ethanol	Yellow	Darker
X	4-Butylcatechol	30% aqueous ethanol	Yellow	Darker
XI	2,3-Dihydroxynaphthalene	20% aqueous ethanol	Slightly pink	No change
XII	Sodium-2,3-dihydroxynaphthalene-6-sulphonate	Water	Colourless	Very pale pink

of a large excess of the reagent (phenol:Mo > 25:1), Beer's law is applicable (*vide infra* and ref. 2). At a given pH and a given wavelength (in the range 400–550 mμ) the sensitivity for molybdenum is similar. The presence of up to 50% of ethanol or acetone as mutual solvents does not change the optical density. This applies for the concentrations of molybdenum normally employed in colorimetric analysis. In more concentrated solution (0·01M), molybdate forms a yellow coloration in 50% alcohol or acetone; a more complete study of this reaction is being published elsewhere.

The main objection to the use of many of these phenols is their poor colour stability in aqueous solution, but this may be overcome by using freshly prepared reagent or by stabilising, either by acidifying or with sodium sulphite. Acidifying with acetic acid to a pH around 4·5 will effectively stabilise the reagent. A second

objection to some of the phenols mentioned may be their relatively high price, but if an urgent molybdenum determination is required it is probable that at least one of the phenols mentioned will be available in the laboratory.

Gallic acid (VI) and sodium 2,3-dihydroxynaphthalene-6-sulphonic acid (XII) are stable in aqueous solution and are inexpensive; they have been chosen as examples for a more detailed description.

EXPERIMENTAL

Apparatus and reagents

Colorimetric measurements were made with a Hilger "Spekker" absorptiometer and a Unicam SP 600 spectrophotometer. Measurements of pH were carried out with a glass/calomel electrode system in conjunction with a Pye Universal pH meter.

Phenol solutions: 1% solutions of phenol VI and phenol XII were prepared from the commercially available solids without further purification. Phenol VI was dissolved in warm 20% aqueous ethanol, whilst phenol XII was dissolved in boiling water. On cooling, the solutions remained clear, but were filtered to remove any suspended matter.

Buffer solutions: Since the final colour was fairly sensitive to changes in pH the solutions had to be suitably buffered. Three buffer systems were used: (i) acetic acid–sodium acetate; (ii) potassium dihydrogen phosphate–caustic soda; (iii) potassium hydrogen phthalate–caustic soda. The concentrations used were such that on diluting the final solution the usual working strengths ($\sim$0·05M) were obtained. Various solutions were prepared according to the pH required; the quantities needed may be found in any suitable reference work (*e.g.*, Vogel[13]).

Standard molybdate solutions: two standard solutions were used from which all the working solutions were prepared:

(1) 3·9640 g of dried AnalaR sodium molybdate were dissolved in water and diluted to 1 litre. This solution contained 0·001 g/ml of molybdenum.

(2) 1·8401 g of dried AnalaR ammonium paramolybdate were dissolved in water and diluted to 1 litre. This solution also contained 0·001 g/ml of molybdenum.

Both solutions were checked by a gravimetric determination with 8-hydroxyquinoline and found to be correct and with identical molybdenum concentrations. On application of the colorimetric method, the two solutions gave identical results. The ammonium molybdate turned yellow on ageing (clear glass bottle) whilst the sodium molybdate solution remained clear and colourless.

Absorption spectra of the complexes

The absorption spectra of the complexes formed by phenols VI and XII were compared under identical conditions and are shown in Fig. 1. Both molybdate and the free phenols have negligible optical density under the same conditions in the wavelength range shown. To obtain full development of the colour, at least 10 ml of 1% reagent solution were required in each case. Fig. 2 shows the variation of optical density at 400 mμ with increasing reagent concentration, for a solution containing 10 μg of molybdenum per ml. Fig. 3 shows the variation of optical density with molybdenum concentration at two wavelengths. The straight lines indicate that Beer's law is applicable. It will be noted that by a suitable choice of wavelength a wide range of molybdenum concentrations can be covered.

Sensitivity

Using a 1-cm optical path, the practical sensitivity for both reagents is about 0·1 μg/ml of molybdenum, which is similar to that given in the works already discussed.[9,15]

Effect of pH variation

Variations in pH were brought about by altering the composition of the buffer used. Fig. 4 shows the effect of differing buffers on the optical density of the solutions. For phenol VI the optimum pH appears to be between 6·5 and 7·0. At lower pH values the optical density falls steadily, being halved at pH 4·0. At pH values above 7·0, oxidation of phenol VI occurs very quickly, leading to false results. For phenol XII the optimum pH is better defined, and falls between 6·5 and 8·0. At pH values greater than 8·0 the reagent itself turns pink and causes interference. It is noteworthy that identical results were obtained from different buffer systems.
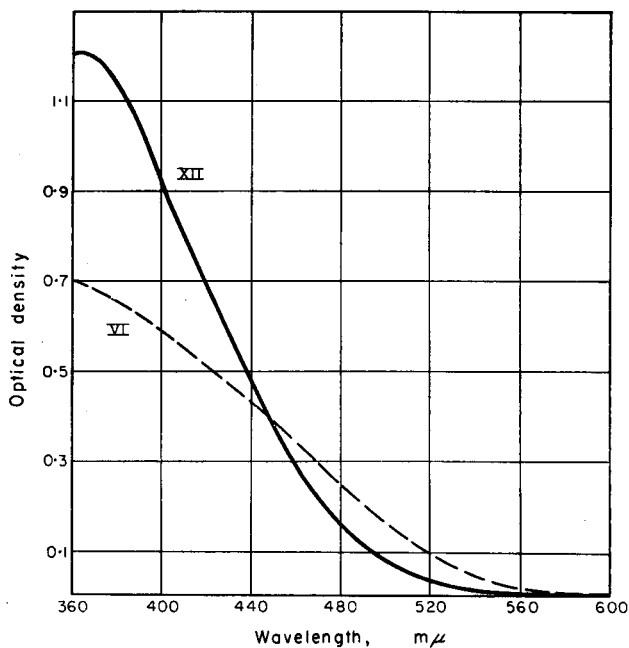
FIG. 1.—Absorption spectra of solutions containing 10 μg/ml of molybdenum and 0·002 g/ml of polyhydric phenol, buffered at pH 5·1 with acetic acid-sodium acetate.
– – – Gallic acid.
—— Sodium-2,3-dihydroxynaphthalene-6-sulphonate.
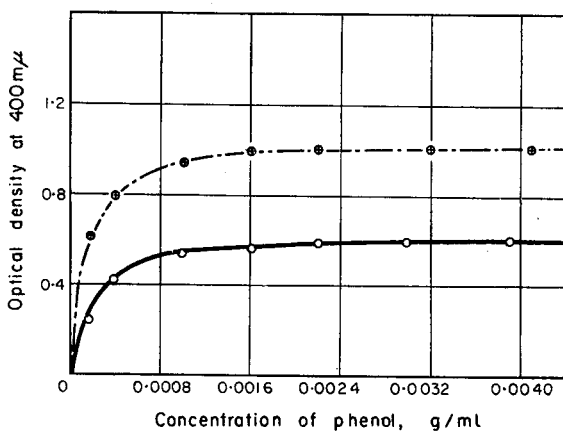
FIG. 2.—Variation of optical density at 400 mμ with concentration of polyhydric phenol. Solutions contain 10 μg/ml of molybdenum, buffered to pH 5·1 with acetic acid-sodium acetate.
○—— Gallic acid.
⊕– · – Sodium-2,3-dihydroxynaphthalene-6-sulphonate.

Fig. 4 also shows the stability of the colour with time. Phenol VI is only stable in rather acid solutions whilst phenol XII is stable below pH 6·5. To use pH ranges in which the colours are completely stable would result in a loss of sensitivity. A useful compromise is to have the pH between 5 and 6 when phenol VI is stable for a few hours and phenol XII is completely stable.

Order of adding reagents and temperature stability

Varying the order in which the reagents were added made no significant difference to the results. If the phenol was added to the molybdate and the addition was followed by pH adjustment, it took a few min before the colour became stable, depending on the conditions. It was found most convenient to add first the buffer and then the phenol to the molybdate solution, in which circumstances
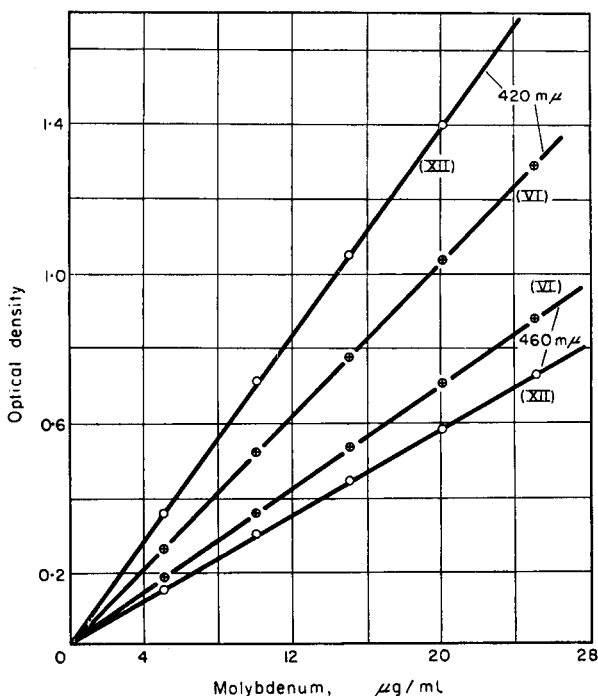
FIG. 3.—Applicability of Beer's law. Solutions contain various concentrations of molybdate in the presence of 0·002 g/ml of polyhydric phenol (Table I); buffered at pH 5·1 with acetic acid–sodium acetate.

the full colour development was practically instantaneous. In all cases the development of the colour was complete within a few min and the optical density remained constant in the temperature range 10–50°.

Effect of diverse ions

This aspect was thoroughly examined by Will and Yoe[15] in connection with Tiron, and it was found that the same ions generally interfered in the reaction with other polyhydric phenols. Those authors obtained interference by a variety of common ions such as Al^{3+} and Mg^{2+}, through precipitation of their hydroxides at pH values above 7. Such interference can easily be eliminated by using a lower pH, without any great loss in sensitivity. The only common ions which form coloured complexes with the phenols are Fe^{3+}, OsO_5^{2-}, Cu^{2+}, WO_4^{2-}, UO_2^{2+}, VO_2^{2+} and Ti. The molybdate ion can readily be separated from these ions (excepting WO_4^{2-} and OsO_5^{2-}) by passing the solution through a cation exchanger (Zeo-Karb 225) in the hydrogen form. This yields a solution of molybdic acid[6] which can be converted back to the simple molybdate by adjusting the pH with sodium hydroxide. Interference by tungstate is dependent on the pH and wavelengths used. At pH 7 the interference is negligible at wavelengths above 400 mμ but at pH 4 wavelengths above 430 mμ must be used. The

method recommended by Will and Yoe,[15] in which the Mo is first separated as the complex with α-benzoinoxime, is equally good but slightly more tedious. Common anions such as halides, nitrate, sulphate, oxalate, tartrate and those used in the buffer solutions do not interfere with the colour development.
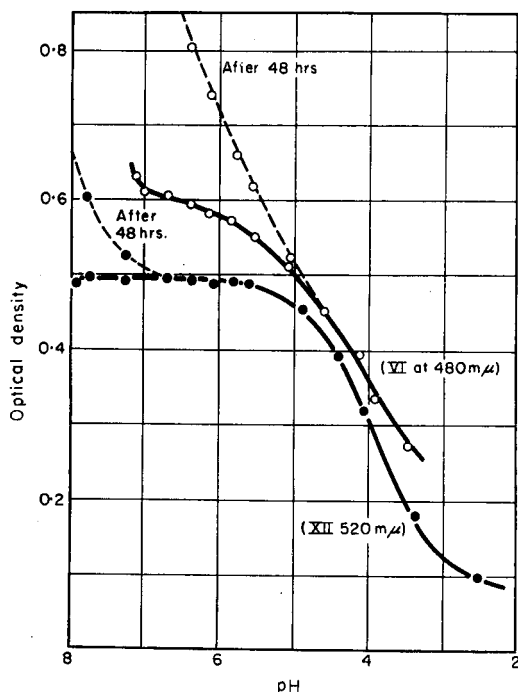
FIG. 4.—Variation of optical density with pH and time. Solutions contain 10 μg/ml of molybdenum and 0·002 g/ml of polyhydric phenol, with buffers of varying pH.

Recommended Method

Reagents

(1) *Polyhydric phenol:* A 1% solution in water or aqueous alcohol, using the purest available grade. Old or discoloured samples are best decolorised by treating a fairly concentrated alcoholic solution with activated charcoal, followed by filtering and diluting with water.

(2) *Standard molybdate:* 3·964 g of dried AnalaR sodium molybdate dissolved in water and diluted to 1 litre, giving a solution containing 0·001 g/ml of Mo. If other grades of molybdate are used these should be assayed for molybdenum by one of the standard methods.

(3) *Buffer solution:* A suitable buffer giving pH ∼5·2 may be prepared by dissolving 109 g of hydrated AnalaR sodium acetate (or an equivalent amount of the anhydrous material) in 500 ml of water, adding 10 ml of glacial acetic acid, and diluting to 1 litre.

Method

The sample is dissolved by one of the usual methods, *e.g.*, fusion, mineral acids or alkali. If any reduction of the molybdenum occurs it should be oxidised back to Mo^{VI} with concentrated nitric acid. The interfering ions are removed by one of the methods already mentioned, and the concentration of the solution is so adjusted that 5 ml contains 5–100 μg/ml of Mo. A 5-ml portion of the solution is transferred to a 25-ml graduated flask and the pH is adjusted to be as near as possible to that of the buffer solution. Five ml of the buffer solution and 10 ml of the polyhydric phenol solution are added and the volume is made up to the mark with water. The optical density of the solution is measured at 420 mμ (or with a blue filter in the case of a colorimeter) and compared with a calibration curve prepared from the standard molybdate solution. By making the optical measurements at longer wavelengths (500–600 mμ) the sensitivity can be decreased so that higher molybdate concentrations may be determined.

The present authors have used this method satisfactorily to determine the molybdenum in small quantities of various solid molybdates and heteropolymolybdates of unknown composition as well as in waste liquors containing small quantities of molybdenum.

Zusammenfassung—Die Anwendung polyhydrischer Phenole als Reagensien fur Molydän wird zusammenfassend behandelt. Es wird gezeigt, dass jedes polyhydrische Phenol mit zwei Hydroxylgruppen in Orthostellung erfolgreich verwendet werden kann. Die Verwendung von 3,4,5-Trioxybenzoesäure und 2,3-Dioxynaphthalin-6-sulfonate wird im Detail behandelt. Die Empfindlichkeit ist *ca.* 0·1 μg Mo/ml bei 400 mμ.

Résumé—Les auteurs passent en revue l'utilisation des phénols polyhydriques comme réactifs colorimétriques du molybdène. Ils montrent que tout phénol polyhydrique ayant deux groupes hydroxyle en ortho peut être employé avec une égale réussite. L'utilisation de l'acide gallique et du 2,3-dihydroxynaphthalène-6-sulfonate de sodium a été discutée en détail. La sensibilité pratique pour le molybdène est d'environ 0,1 μg par ml à 400 mμ.

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EMISSION SPECTRA FROM HIGH-FREQUENCY EXCITATION—III*

A STUDY OF ARGON-CARBON DIOXIDE MIXTURES

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Summary—A continuous discharge at 230 megacycles, produced by a radio-frequency extra-hightension generator, in a sealed-off gas system, has been used in conjunction with a quartz prism spectrophotometer to study binary mixtures of argon and carbon dioxide. The concentrations of mixtures in the range 9 to 90% argon, and 91 to 10% carbon dioxide have been determined with a reproducibility of $\pm 3.2\%$ absolute, expressed as a standard deviation. Determinations can be carried out in about 1 min, making the technique superior to the usual spectrographic technique. The procedure developed suggests that with improved instrumentation, ensuring constancy of source intensity, and substitution of a continuously flowing gas for the sealed-off system, it might be possible to extend the technique to mixtures of other gases and obtain better reproducibility and accuracy.

INTRODUCTION

A PRELIMINARY survey[1] of the emission spectra of some inorganic gases excited by high-frequency discharge indicated the possibilities of optical spectroscopy with photoelectric measurement in place of conventional photographic spectroscopy, for quantitative analysis of gas mixtures. The need for rapidity in intensity measurement makes the use of photoelectric measurement preferable to the photographic techniques, especially in the case of gases which are dissociated under the discharge (e.g. $CO_2 \rightarrow CO$) and can, therefore, be determined satisfactorily by this technique only when measurement is almost instantaneous. The photoelectric technique eliminates tedious plate calibrations and other time-consuming processes which are integral parts of the photographic technique, thereby resulting in greater speed. It also ensures greater reproducibility and accuracy, since the reproducibility and accuracy of the photographic technique is based on many variables, especially the behaviour of photographic emulsions.

This paper presents results obtained using a radio-frequency high-tension generator in conjunction with a quartz prism spectrophotometer for the study of binary mixtures of argon and carbon dioxide.

EXPERIMENTAL

Apparatus

The apparatus consists of three separate units:

(*i*) A high-vacuum train with a sealed-off gas system, all constructed from borosilicate glass. Figs. 1 and 2 are schematic diagrams of the high-vacuum system and the discharge cell, respectively. C and E are two 5-litre flasks. Argon is admitted through a mercury-bubbler, A, and the cold trap B. Carbon dioxide is admitted from the test tubes T_1 and T_2, after condensation and distillation. D is a 1-litre flask used as a reserve bulb for storage of gas mixtures. M is a vacuum-type mercury-manometer; P is a Pirani gauge; F is a cold trap to Reep mercury and water vapours from the discharge cell; I is a two-stage mercury-diffusion pump backed by a rotary oil pump, J, combined, performance of which gives a vacuum of $\simeq 10^{-4}$ mm of mercury in about 0·5 hr. X is the discharge cell of borosilicate glass with a sealed-on quartz window on the side facing the monochromator assembly. This discharge cell has the following dimensions: overall length 8·2 cm, internal diameter

* Part II—See ref. 1.
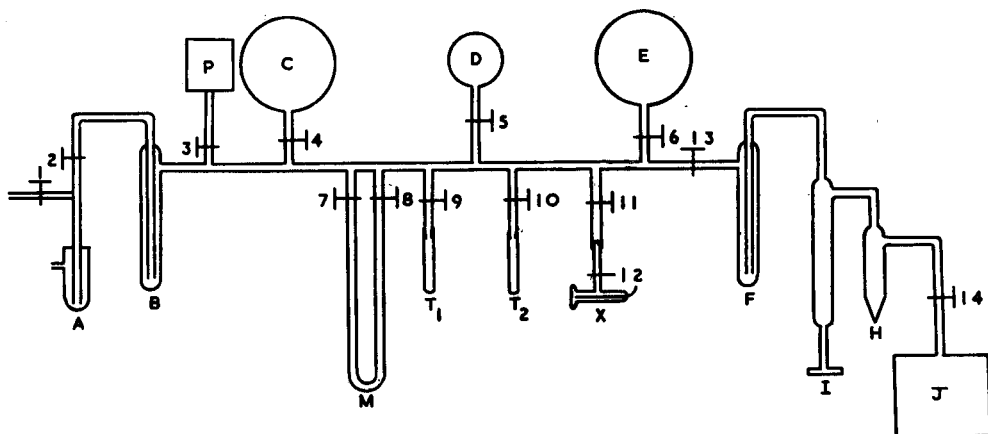
FIG. 1 Schematic diagram of high vacuum train with discharge cell

A	Mercury bubbler	T_1, T_2	Test tubes
B, F	Cold traps	J	Rotary oil pump
C, E	5-litre flasks	X	Discharge cell
D	1-litre flask	1–14	Vacuum taps
H	Mercury trap	P	Pirani gauge
I	Mercury diffusion pump	M	Vacuum type mercury-manometer
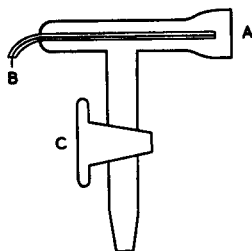
FIG. 2..—Schematic diagram of discharge cell
    A Quartz window sealed on.
    B Tungsten electrode, glass-coated.
    C Vacuum tap.

about 1 cm in the body and 2 cm at the quartz window. The quartz window is 1 mm thick, and the electrode is a glass-coated tungsten wire, diameter 1 mm.

(ii) A radio-frequency extra-high tension generator operating at about 230 megacycles for excitation. Details of this apparatus have been described elsewhere.[2] This generator has an output tuned by a variable capacitor. Discharge intensity is controlled by varying the capacitance.

(iii) A Hilger "Uvispek" photoelectric spectrophotometer with a quartz prism. Preliminary studies were carried out with the Hilger medium quartz spectrograph, E.498.

Gases

Argon: This gas was obtained from cylinders of normal commercial supply, of rated purity not less than 99·95%. It was used without further purification.

Carbon dioxide: This gas was obtained from the normal commercial supply of "Drikold", of rated purity 99·8%. It was further purified by repeated condensation and distillation using liquid nitrogen.

Gas mixing technique

The high vacuum train is pumped down to a vacuum of 10^{-4} mm of mercury. The gases for calibration mixtures are then admitted separately, one into the flask C and the other into the flask E, at pre-determined pressures. The gases are mixed in one of these flasks, by admitting the second component into it with a high backing pressure to prevent diffusion of the first component from the

mixing flask. When there is high backing pressure, mixing is fast. The mixture is left for several hr before use.

The compositions of the mixtures are determined by the partial pressures of the two components as measured at the time they are admitted, in quick succession, into the mixing chamber, at room temperature, thus eliminating the need for calibration of the volumes of the apparatus. Either the flask C or E can be used as the mixing chamber and the other as reservoir for the diluent gas. To prepare mixtures of known composition ranging from 1 to 99 % of each component, it is necessary to create a pressure differential between the gas in the mixing chamber and the diluent gas in its reservoir at the time of admission of the diluent gas into the mixing chamber. An adequate pressure differential is created by maintaining the pressure of the gas in the mixing chamber at a low level relative to the high backing pressure of the diluent gas in its reservoir. This is accomplished, for a 50:50 mixture, by maintaining, before mixing, a pressure of say, 20 cm of mercury in the mixing chamber and 60 cm of mercury in the diluent gas reservoir. To prepare other mixtures, it is necessary to have progressively higher pressures in the diluent gas reservoir as the concentration ratio departs from the 50:50 ratio. The positions of the two components in respect of the mixing chamber and the reservoir are reversed as the concentration ratio crosses the midpoint, *i.e.* 50:50, of the scale of concentration ratios.

This mixing technique introduces several minor errors: *e.g.*, (1) an error in the measurement of gas pressures with the mercury manometer; (2) an error arising from change in temperature in the mixing chamber during the mixing process; (3) the diffusion of minute quantities of the component gases out of the mixing chamber during the mixing process; (4) selective adsorption of one component of the mixture on the glass surface of the mixing chamber.

The combined effect of all these errors is to introduce into the calibration mixture an uncertainty in the exact value of the concentrations.

Preliminary studies

Preliminary studies of the mixtures were made with the quartz spectrograph, using a slit-width of 0·03 mm, an exposure time of 15 min, Ilford panchromatic HP3 plates, and a copper arc for calibrating wavelength. The object was to select those lines and band-heads which are present in the spectra of mixtures of varying concentrations and are not affected by impurity bands. The range covered by this study was from 99·0 % Ar and 1·0 % CO_2 to 0·9 % Ar and 99·1 % CO_2. Fig. 3 is a photograph of the spectra of a mixture containing Ar 15·0 % and CO_2 85·0 %. The examination of the spectra reveals the following points: (*i*) The atomic lines of Ar are present; and (*ii*) CO_2 produces very strong and persistent bands with band-heads at λ 2883 Å and λ 2896 Å, probably produced[3] by the ionised molecule CO_2^+; and also carbon monoxide bands as a result of dissociation into carbon monoxide caused by the discharge. The colour and intensity of the glow alter as the discharge continues to pass.

For calibration purposes the Ar line at λ 2942·9 Å and the CO_2^+ band, a very strong and persistent one with the band-head at λ 2896 Å, were finally selected from the many lines and band-heads examined. It may be seen from the spectra that these lines and band-heads are free from interference by impurity bands. The CO_2^+ band-head at λ 2896 Å has been used by several workers[4] for the quantitative determination of CO_2 in respiratory gases by spectrophotometric measurement of emission intensity.

This final selection was based on results obtained by examining the ratios of peak line or band-head intensities at different wavelengths for mixtures of varying concentrations. The intensity ratios were measured spectrophotometrically and their values were plotted as a function of concentration ratios, using a logarithmic scale in both cases.

Spectrographic detection limits

The spectrographic detection limits were established experimentally by photographing the spectra of mixtures of different compositions on the same photographic plate, and examining the spectra with a magnifying lens against an illuminated background, to assess the concentration sensitivity of the lines and the band-heads for analytical purposes.

This study established that the lowest limits of detection of Ar and CO_2 in their mixtures, using the Ar line at λ 2942·9 Å and the CO_2 band-head at λ 2896 Å, are of the order of 1 %. Therefore, the study of the mixtures has been limited to concentrations of 1 % to 99 %.

Procedure

The high vacuum train with the discharge cell in position, is pumped down to a pressure of 10^{-4} mm of mercury while subjected to prolonged baking with a naked flame in order to outgas the system. The gases are then admitted and mixed in the mixing chamber. The train is again pumped down to 10^{-4} mm. The sample of the mixture is admitted into the discharge cell and the discharge is switched

on. The pressure of the sample is reduced and the sample is isolated at a line-pressure of 0·50 mm, measured with a Pirani gauge. The discharge is started, and with the sample glowing, the spectrophotometer slits are opened to 0·50 mm (*i.e.*, 5 Å) The variable condenser of the generator is adjusted until the glow gives the maximum signal at the preselected wavelength. Fine adjustment of the setting of the wavelength drum is made by slowly turning the wavelength drum until maximum signal is registered. The measurement of peak intensities is immediately made; any unavoidable time-lag between the switch-on of the discharge and the measurement is kept at a minimum and is constant for all determinations.

In actual practice all these adjustments are made before the quantitative tests by using the gas from reserve volumes for setting up purposes. In this way almost instantaneous intensity readings may subsequently be made.

The intensity of emission from 100% Ar or CO_2 is made to correspond to the 100% reading of the transmittance scale on the instrument. This scale is then used to measure the emission intensity of calibration mixtures or test mixtures relative to the intensity of 100% Ar or CO_2 (as the case may be) in terms of % transmittance.

The internal standard method[5] of quantitative spectroscopy requires the presence of an element at fixed concentration in the test sample. In view of the difficulty of fulfilling this condition, the following method of analysis has been developed in the present case.

An internal standard of variable concentration was used. Thus, in the determination of Ar and CO_2, the ratios of peak intensities of the Ar line at λ 2942·9 Å and of the $CO_2{}^+$ bandhead at λ 2896 Å were found to be a linear function of their concentrations using 100% Ar or CO_2 (as the case may be) as a check. The values of intensity ratios expressed as log T_{CO_2}/T_{Ar}, were plotted as a function of the concentration ratios expressed as log $[CO_2]/[Ar]$. The term T denotes transmittance. As the values of the ratios cover a wide range, a logarithmic plot of these values spreads them more widely and also improves linearity of the calibration curve. It may be noted that equal absolute errors in log T_{CO_2}/T_{Ar} in different parts of the graph correspond to equal relative errors in concentrations; it is therefore an advantage to use this form of graph because it is desirable to maintain a uniform relative accuracy.

It takes less than 1 min to carry out the final determination.

Table I gives the experimental results which have been used to draw the calibration curve in Fig. 4. The calibration curve is nearly linear from approximately 90% Ar, 10% CO_2 to 9% Ar,
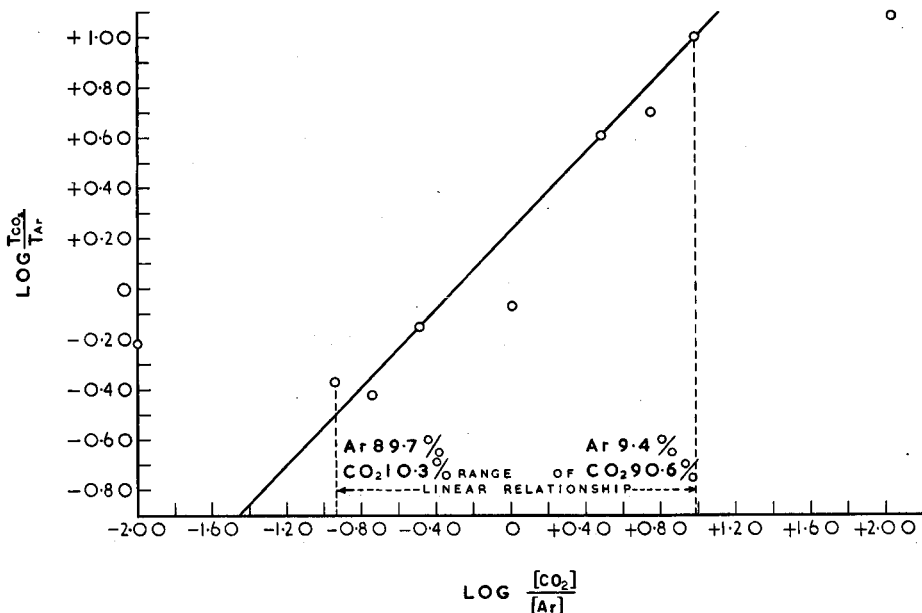
FIG. 4.—Calibration curve
Ar λ 2942·9 Å CO_2 λ 2896 Å
Slits, 0·50 mm   Pressure, 0·50 mm of Hg.

91% CO_2. The curve deviates markedly from linearity outside this range. Such departure from linearity at low and high concentrations is the result of two opposing, but unequal factors—a
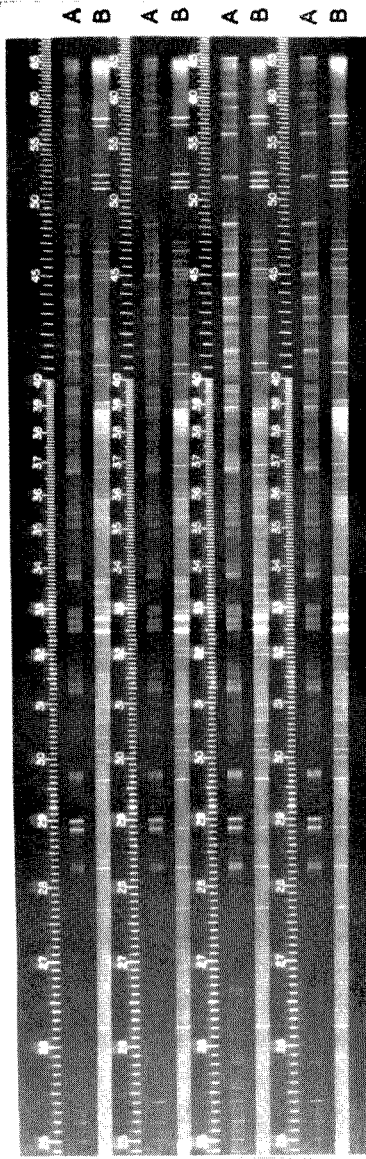
Fig. 3.—Spectra.
A Mixture of Ar, 15% and CO_2, 85%
B Copper arc

background effect which predominates at low concentrations and a self-absorption effect which predominates at high concentrations. Background has the effect of raising and self-absorption of lowering the apparent concentrations. The values of % T in Table I represent the arithmetical mean of two readings taken consecutively.

TABLE I. RESULTS

| Serial number | Percentage composition of samples | | $\log \dfrac{[CO_2]}{[Ar]}$ | Percentage transmittance | | $\log \dfrac{T_{CO_2}}{T_{Ar}}$ |
	Ar	CO_2		$T_{Ar} \lambda 2942.9$ Å	$T_{CO_2} \lambda 2896$ Å	
1	0·9	99·1	+2·04	2·2	26·9	+1·09
2	9·4	90·6	+0·98	1·1	11·0	+1·00
3	15·0	85·0	+0·75	16·0	80·9	+0·70
4	24·3	75·7	+0·49	17·7	71·6	+0·61
5	49·5	50·5	+0·01	25·5	21·9	−0·07
6	75·6	24·4	−0·49	54·8	38·5	−0·15
7	84·6	15·4	−0·74	53·0	20·2	−0·42
8	89·7	10·3	−0·94	61·3	25·9	−0·37
9	99·0	1.0	−2·00	27·6	16·6	−0·22

Reproducibility and accuracy

Reproducibility has been evaluated by using a synthetic standard and running a series of six samples with the same composition under identical operating conditions, with determinations spread over a period of 1 week. The results are shown in Table II. The values of T_{Ar} and T_{CO_2} represent single readings. The reproducibility, expressed as the standard deviation of six tests, is ±3·2% absolute.

For the evaluation of accuracy, it is necessary to run a series of determinations on a number of samples of accurately known composition using the calibration curve. The accuracy is limited by the uncertainty in the exact values of the concentrations in the synthetic standards and the calibration

TABLE II.—REPRODUCIBILITY

Synthetic standard containing Ar 24.3%, CO₂ 75.7%

| Serial number | Percentage transmittance | | $\log \dfrac{T_{CO_2}}{T_{Ar}}$ | Ar found, % | Mean Ar found, % | CO_2 found, % | Mean CO_2 found, % | Deviation, % | Standard deviation, $\sqrt{\dfrac{\Sigma x^2}{n-1}}$ % |
	T_{Ar} $\lambda 2942.9$ Å	T_{CO_2} $\lambda 2896$ Å							
1	15·1	61·7	0·61	24·4		75·6		2·7	
2	17·8	70·8	0·60	25·3		74·7		3·6	
3	13·5	60·3	0·65	22·8		77·2		1·1	
4	11·0	60·3	0·74	18·6		81·4		3·1	
5	15·5	72·4	0·67	22·0		78·0		0·3	
6	11·2	67·6	0·78	17·3		82·7		4·4	
					21·7		78·3		± 3·2

mixtures. Therefore, for the evaluation of accuracy, the running of synthetic standards with composition calculated from the added components and not determined independently, would accomplish nothing more than the confirmation of the validity of the calibration curve by means of samples, the composition of which are known no more accurately than those of the calibration mixtures. Because of the difficulties of obtaining gas mixtures of accurately known contents, it has not been possible to establish a general level of accuracy.

DISCUSSION

As a result of the dissociation of carbon dioxide into carbon monoxide by the running of the discharge, the apparent values for carbon dioxide change with the time of running of the discharge. Therefore, the time-lag between the beginning of the discharge and the time of taking measurement is most critical. This effect is reduced by

measuring the intensities immediately on switching on the discharge and keeping any unavoidable time-lag constant for all measurements. Satisfactory results are obtained only if this is strictly adhered to and if all other operating conditions are rigidly standardised.

Because of the "clean-up" in the electrical discharge, the intensities of emissions vary with the time of running the discharge.[6] The effect of "clean-up" in electrical discharge is to change the apparent proportions of the gases in a sample. This effect could probably be eliminated by substituting a continuously flowing gas system for the sealed-off gas system; this would ensure the feeding of fresh sample into the discharge cell at constant speed. This, however, could not be attempted with the facilities available in the present work.

The effect of all these factors has been to some extent nullified by using intensity ratios, in which the ratios of the intensities of two variable components, and not their absolute intensities, are related to concentrations. Reproducibility and accuracy may be improved by better instrumentation to ensure constancy of source intensity, and more rigid standardisation of the operating conditions (including gas pressures and the time-lag between the start of discharge and the measurement.)

Prolonged baking of the system and degassing it under high vacuum improve reproducibility and accuracy by removing from the glass surface adsorbed impurities and moisture, the variable concentrations of which may make their effect indeterminate and are, therefore, not amenable to correction.

This technique with the refinement of a flowing gas system and with improvement in instrumentation to ensure constancy in source intensity, might be extended to mixtures of other gases and volatile substances, and might give better reproducibility and accuracy.

Zusammenfassung—Eine kontinuierliche Entladung bei 230 Megacycl. (erzeugt mittels eines Radiofrequenzhochspannungsgenerators) wurde in einem abgeschlossenen System in Verbindung mit einem Quartz-prismenspectrophotometer herangezogen um binäre Mischungen von Argon und Kohlendioxyd zu studieren. Die Konzentrationen in Mischungen von 15–90% Ar und 85–10% CO₂ wurden mit einer Reproduzierbarkeit von ±5·8 (mittlerer Fehler) bestimmt. Die Bestimmung kann in etwa einer Minute durchgeführt werden, was die Methode der spektrographischen Bestimmung überlegen macht. Es ist anzunehmen, dass mit verbesserten Instrumenten, (höhere Konstanz der Erregerquelle und Ersatz des abgeschlossenen System durch einen kontinuierlichen Gasstrom) die Methode auch auf andere Gasmischungen angewendet werden kann; auch sollten dann höhere Genauigkeit und Reproduzierbarkeit erreichbar sein.

Résumé—Les auteurs ont utilisé une décharge continue à 230 méga-cycles, produite par un générateur très haute tension à fréquence radio, dans un système gazeux en tube scellé, en liaison avec un spectrophotom-ètre à prisme de quartz pour étudier des mélanges binaires d'argon et d'anhydride carbonique. Les concentrations du mélange dans le domaine 15 à 90% d'argon, 85 à 10% d'anhydride carbonique ont été dosées avec une reproductibilité de ±5,8, exprimée en déviation standard. Les dosages peuvent être réalisés en une minute envirol, ce qui rend cette technique supérieure à la spectrographie. La méthode

mise au point laisse penser que, avec un appareillage amélioré assurant la constance de l'intensité de la source et la substitution d'un gaz s'écoulant continument au système en tube scellé, il serait possible d'étendre cette technique à des mélanges d'autres gaz et d'obtenir une reproductibilité et une précision meilleure.

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UNTERSUCHUNG DER KATIONENSORPTION AUS KOMPLEXANMEDIUM—III*

CHROMATOGRAPHISCHE TRENNUNG VON STRONTIUM UND BARIUM

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Zusammenfassung—Es wurde eine neue Methode zur Trennung von Strontium und Barium unter Anwendung der Ionenaustauschchromatographie ausgearbeitet. Barium- und Strontiumionen werden an einem stark sauren Kationenaustauscher (Amberlit IR 120 in NH_4^+-Cyclus) adsorbiert, wonach Strontium mit 0,02–0,05 m DCyTE in 0,4 m Ammoniumacetat (pH 6,3–7,2) ausgewaschen wird. Im Eluat ermittelt man den Strontiumgehalt flammenphotometrisch. Bei der gleichzeitigen Bestimmung von Calcium und Strontium neben überschüssigem Barium, wäscht man mit dem gleichen Elutionsmittel bei pH 5,1 aus. Die neu vorgeschlagene Methode wurde zur Bestimmung von Strontium und Calcium in Bariummineralen, insbesondere in Schwerspat und Witherit angewendet.

DIE Untersuchung der Sorption von Erdalkalimetallen aus Lösung von ÄDTE bzw. 1,2-Diaminocyclohexan-N-N,N',N'-tetraessigsäure (DCyTE) an Ionenaustauschern[1] ergab, dass insbesondere die DCyTE ein geeignetes chromatographisches Reagens zur vollständigen Trennung von Calcium und Strontium[2] darstellt. In der vorliegenden Arbeit wird gezeigt, dass sich dieses Reagenz auch zur analogen Trennung von kleinen Mengen Strontium von überschüssigem Barium eignet und zur quantitativen Bestimmung von Strontium in Schwerspat and anderen Bariummineralen mit Erfolg angewendet werden kann.

APPARATE UND REAGENZIEN

Die Standardlösungen von Strontium und Barium wurden aus p.a. Präparaten der Fa. E. Merck, Darmstadt, DBR, bzw. der Fa. Johnson and Matthey, England, hergestellt. Als Pufferlösung wurde 1 m Ammoniumacetat verwendet, dessen pH auf den erwünschten Wert mit verdüntem Ammoniak eingestellt wurde. Ein weiterer Puffer war Triäthanolamin und sein Hydrochlorid, das sich insbesondere für den pH-Bereich von 7,2 aufwärts bewährte. Die Herstellung der Komplexbildner bzw. ihrer Lösungen und die Beschreibung der verwendeten Apparate wurden bereits in den vorangehenden Arbeiten dieser Reihe[2] behandelt.

ERGEBNISSE

Aus der gegenseitigen Lage der Sorptionskurven von Strontium und Barium aus DCyTE-Medium ist ersichtlich, dass es keinen pH-Wert, bzw. pH-Bereich gibt, in dem eines der beiden untersuchten Erdalkalimetalle als undissoziierter DCyTE-Komplex vorliegt, während die andere analoge Komplexverbindung des zweiten Metalls als vollständig dissoziiert zugegen ist. Aus diesen Grunde ist es unmöglich, die Trennung des Strontiums von Barium durch Aufguss aus DCyTE-Medium durchzuführen. Hierzu muss man sich der Ionenaustauschchromatographie bei geeignetem pH-Wert

* II. Mitteilung: *Talanta*, 1961, **8**, 705.

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bedienen. Es wurde festgestellt, dass beim Durchgang des Komplexbildners durch
die Säule das sorbierte Strontium auch bei einem solchen pH-Wert ausgewaschen
wird, bei dem die Barium-Komplexbildung praktisch ausbleibt. Es war daher nötig,
eine Waschlösung mit einem solchen pH-Wert zu finden, bei dem das Auswaschen des
Strontiums mit hinreichender Geschwindigkeit vor sich geht und das Barium zugleich
noch nicht eluiert wird. Zu diesem Zweck wurde zunächst die Trennung des Stron-
tiums und Bariums in Abhängigkeit vom pH-Wert des Elutionsmittels verfolgt. Die
beiden zu bestimmenden Metalle (5,2 mg Sr und 300 mg Ba) wurden an die Katexsäule
aus einem Volumen von 80 ml adsorbiert, nach dem Auswaschen der Säule mit Wasser
wurden die Metalle mit 0,02 m DCyTE in 0,4 m Ammoniumacetat, dessen pH-Wert
entsprechend eingestellt wurde, direkt in einem 100 ml Messkolben eluiert. In dieser
Lösung wurden Strontium flammenphotometrisch und Barium spektralanalytisch[3]
bestimmt.

Aus den so gewonnenen und in Tab. I. zusammengefassten Ergebnissen geht
hervor, dass es in dieser Weise möglich ist Strontium von überschüssigem Barium

TAB. I. pH ABHÄNGIGKEIT DER CHROMATOGRAPHISCHEN TRENNUNG VON STRONTIUM UND BARIUM
Elution mit 0,02 m DCyTE im 0,4 m Ammoniumacetat.
Sr = 5,2 mg; Ba = 300,0 mg.

pH der Elutionslösung		Sr gefunden %	Ba in der Strontium-fraction, % aus der gesamten Barium-menge
Anfangswert	Endwert nach der Elution		
6,3	6,2	99,5	0,05
6,6	6,45	99,2	0,05
7,0	6,75	99,0	0,05
7,3*	7,3	99,3	0,05
7,4	70,5	99,2	0,05
7,8	7,60	99,0	0,20
8,45	8,20	99,0	12,50

* 0.25 m Triäthanolamin HCl auf pH 7,3 gebracht.

innerhalb des pH-Bereiches von 6,3–7,8 verlässlich abzutrennen. Unter diesen
Bedingungen sind die Bariummengen in der Strontiumfraktion kleiner als 0,05% des
ursprünglichen Bariumgehaltes. Es ist daher möglich, das in der Säule zurückgehalt-
ene Barium mit einem geeigneten Reagenz auszuwaschen und mittels einer passenden
analytischen Methode zu bestimmen. Den optimalen pH-Bereich realisiert man
entweder mit Hilfe von mit Ammoniak eingestelltem Ammoniumacetat, oder mit 0,25 m
Triäthanolamin, dessen pH-Wert man mit Salzsäure auf den Wert von 7,0–7,5
einstellt.

Wegen des ziemlich geringen Puffervermögens der Ammoniumacetat-Lösung
kommt es beim Auswaschen des Strontiums d.h. bei der Bildung des Sr-DCyTE-
Komplexes, infolge des Freiwerdens von Wasserstoffionen zu einer geringen pH-
Änderung (s. Tab. I), die jedoch auf die Vollständigkeit des Auswaschens des Stron-
tiums beim angegebenen Volumen des Elutionsmittels ohne Einfluss ist. Ferner wurde
festgestellt, dass die flammenphotometrische Bestimmung von Strontium aus komplex-
bildendem Medium im angegebenen pH-Bereich durch pH-Änderung nicht beein-
flusst wird.

Auf Grund dieser Ergebnisse wurde zur quantitativen Trennung des Strontiums von überschüssigem Barium die nachfolgende Vorschrift ausgearbeitet:

Eine in 80 ml etwa 0,5–10 mg Strontium und bis 300 mg Barium enthaltende Lösung wird mit einer Durchlaufgeschwindigkeit von 2 ml min^{-1} . cm^{-2} an der Katexsäule adsorbiert und die Säule wird mit 30–50 ml Wasser ausgewaschen. Dann wäscht man die Säule mit 20–40 m 0,4 m Ammoniumacetat von pH–Wert 7,2 bis zum konstant bleibenden pH–Wert der ausfliessenden Lösung aus. Hierauf eluiert man das Strontium mit 100 ml 0,02–0,03 m DCyTE in 0,4 m Ammoniumacetat von pH 7,2 aus. Das Eluat sammelt man in einem 100 ml Messkolben und bestimmt das Strontium flammenphotometrisch. Die Auswertung geschieht mit Hilfe einer Eichkurve die man an Hand von Strontium-Standardlösungen, die die gleichen Mengen DCyTE und Pufferlösung wie die zu analysierende Probe enthalten, herstellt. Einige Ergebnisse der Trennung von synthetischen, Barium und Strontium enthaltenden Gemischen sind in Tab. II wiedergegeben. Aus der gleichen Tabelle entnimmt man, dass auch beim Verhältnis Sr:Ba 1:300 die Fehler der Bestimmung kleiner als 1 % sind.

DER EINFLUSS VON BEGLEITELEMENTEN

Die beschriebene Trennung von Strontium und Barium war vor allem auf die Analyse von Schwerspat, Witherit und einigen bariumhaltigen Silikaten gezielt. Daher wurde auch der Einfluss der in den obigen Mineralen vorkommenden Begleitelemente untersucht.

TAB. II. BESTIMMUNG VON STRONTIUM NEBEN ÜBERSCHÜSSIGEM BARIUM
Elution mit 0,03 m DCyTE im 0,4 m Ammoniumacetat
Ba = 300 mg; pH = 7,2

Sr, *mg*		Differenz, %
gegeben	gefunden	
10,40	10,38	−0,19
8,32	8,24	−0.94
7,28	7,26	−0,28
6,24	6,24	±0,00
5,20	5,20	±0,00
4,16	4,16	±0,00
2,08	2,09	+0,48
1,04	1,04	±0,00

Die eigentliche Sorption und chromatographische Trennung der beiden Elemente wird durch zu hohe, beim Sodaaufschluss in den Analysengang eingetragene Mengen von Natriumionen gestört. Die entstandenen Erdalkalicarbonate enthalten nach mehrmaligem Auswaschen mit Ammoniumcarbonat nur wenig Natrium, das die Strontiumbestimmung nicht beeinflusst. Diese kleinen Natrium mengen wirken sich jedoch auf die eventuelle Calciumbestimmung störend aus. In einem solchen Fall muss man die Erdalkalicarbonate in verdünnter Säure lösen und nochmals mit Ammoniumcarbonat fällen.

Falls die Probe neben Strontium und Barium auch Calcium enthält, trennt man zunächst chromatographisch das Calcium mit 0,02–0,05 m DCyTE in 0,4 m Ammoniumacetat von pH 5,1 ab. Da das Calcium in den erwähnten Mineralen nur in Mengen von unterhalb 1 % vorkommt, genügen zu seiner quantitativen Abtrennung 100 ml dieser Lösung. Den Calciumgehalt kann man unmittelbar aus dem Eluat flammenphotometrisch bestimmen. Gleichzeitig mit Calcium wird auch Magnesium eluiert.

Die am Kationenaustauscher adsorbierten Eisen(III)-ionen werden unter den beschriebenen Bedingungen wahrscheinlich infolge der langsamen Bildung des Hydroxokomplexes nur zum Teil eluiert, jedoch wird die nachfolgende flammenphotometrische Strontiumbestimmung mit diesen Eisenmengen (1 % Sr neben 7 % Fe) nicht

gestört. Bei grösseren Eisen- und besonders Aluminiummengen ist es vorteilhaft, die dreiwertigen Metalle durch Sorption aus Citratpuffermedium (pH 3 bis 3,5) abzutrnnen[4]. In diesem Medium bilden die drei, bzw. vierwertigen Metalle anionische Citratkomplexe, die am Ionenaustauscher nicht adsorbiert werden.

PRAKTISCHE ANWENDUNG

Etwa 0,5 g fein zerriebenes Mineral schliesst man etwa 20–30 min. lang mit 3 g wasserfreier Soda auf, kühlt ab und lässt die Schmelze in warmem Wasser gut zerfallen. Die abgeschiedenen Carbonate und Hydroxyde sammelt man auf dem Filter und wäscht sie 5-mal mit 1 % igem Ammoniumcarbonat aus. Hierauf löst man den Niederschlag in möglichst wenig verdünnter Salzsäure. Aus der vorwiegend Erdalkalimetalle enthaltenden Lösung entfernt man die Säure durch Abdampfen auf kleines Volumen, macht dann mit verdünntem Ammoniak alkalisch und fällt in der Wärme mit 20–30 ml 10 % igem Ammoniumcarbonat die Erdalkalien.

Variante A: Analyse von mineralogisch separierten Schwerspatsorten: den durch Filtrieren abgetrennten Niederschlag löst man in möglichst wenig Salzsäure, verdünnt auf 80–100 ml und lässt die Lösung durch die Katexsäule mit der bereits erwähnten Durchlaufgeschwindigkeit fliessen. Zuletzt wäscht man die Säule mit 50 ml Wasser aus.

Variante B: Für technische Schwerspatsorten und Bariumalumosilikate: den Carbonatniederschlag löst man in Salzsäure, dampft zur Trockne ab und entfernt in üblicher Weise die Kieselsäurereste. Alsdann versetzt man die Lösung mit 1 g Citronensäure und stellt den pH unter potentiometrischer

TAB. III. DIE STRONTIUMBESTIMMUNG IN NATÜRLICHEN SCHWERSPATEN

Probe	Sr gefunden, %	Sr durch Kontrollmethoden bestimmt, %	Bemerkung
I	0,91[6]	0,89[a] 0,93[b]	Durchschnitt aus 11 Bestimmungen; Standart- abweichung $\sigma = \pm 0,85\%$
II	0,60 0,59[c]	0,65[a]	Durchschnitt aus 6 Bestimmungen
III	0,77	0,80[a]	Durchschnitt aus 3 Bestimmungen

[a] spektralanalytisch.   [b] chemisch.   [c] Eisen als Citratkomplex abgetrennt.
Bei der Probe Nr. I wurde der Calciumgehalt nach der beschriebenen Methode
0,11 % bestimmt, spektralanalytisch 0,10 % gefunden.

Kontrolle auf den Wert von 3–3,5 ein. Hierauf sorbiert man die Erdalkalien bei einer Durchlaufgeschwindigkeit von 1,5–2 ml. min^{-1}. cm^{-2} und wäscht zum Schlusse die Säule mit 50 ml Wasser aus.

Bestimmung von Calcium: Die Säule wäscht man mit 0,4 m Acetatpuffer von pH 5,1 aus bis das Eluat den gleichen pH-Wert aufweist. Das sorbierte Calcium eluiert man mit 100 ml 0,02-0,05 m DCyTE in 0,4 m Ammoniumacetat von pH 5,1 aus. Das Eluat fängt man in einen 100 ml Messkolben auf und bestimmt den Calciumgehalt flammenphotometrisch. Die Auswertung des Calciumgehaltes geschieht mit Hilfe einer Eichkurve, die man an Hand von Calciumstandardlösungen, die sowohl das Komplexan als auch die Pufferlösung enthalten, hergestellt hat.

Bestimmung von Strontium: Die Kolonne wäscht man mit 30 ml Wasser und mit 0,4 m Ammoniumacetat von pH 7,2 aus. Das sorbierte Strontium eluiert man dann mit 100 ml 0,02 m DCyTE in 0,4 m Ammoniumacetat des gleichen pH-Wertes. Das Eluat wird wiederum in einen 100 ml Messkolben aufgefangen und das Strontium wird photometrisch nach der bereits erwähnten Weise bestimmt. Die Durchlaufgeschwindigkeit beträgt sowohl bei der Calciumbestimmung als auch bei der Strontiumbestimmung 1–1,5 ml. min^{-1}. cm^{-2}.

Das am Ionenaustauscher zurückgehaltene Barium kann man entweder mit ammoniakalischer ÄDTE vom pH 10 oder mit 3 m HCl auswaschen und seine Bestimmung im Eluat am besten komplexometrisch[5] durchführen.

Die obige Strontiumbestimmung in Schwerspat wurde durch Analyse von synthetischen Gemischen und durch wiederholte Analyse von 3 natürlichen Schwerspatsorten beglaubigt. Die Probe Nr. 1 war ein separiertes sehr reines und nur Spuren von Verunreinigungen enthaltendes Mineral, die Probe Nr. 2 enthielt 15% Siderit. Die Probe Nr. 3 war ein 5% Fluorit enthaltender Schwerspat. Die in Tab. III zusammengefassten Ergebnisse zeigen, dass die Methode gut reproduzierbare, mit den Ergebnissen der Spektralanalyse und mit dem deklarierten Gehalt übereinstimmende Werte liefert. Ihr Vorteil gegenüber den bisher zu diesem Zweck verwendeten Methoden ist vor allen Dingen in der Einfachkeit und Schnelligkeit der praktischen Ausführung zu sehen.

Wenn es sich nur um die schnelle Strontiumbestimmung handelt, so kann man die obenbeschriebene Ammoniumcarbonatfällung auslassen. Die durch den Sodaaufschluss entstandenen Carbonate können direkt nach Auswaschen und Auflösung (in verdünnter Salzsäure) an dem Kationenaustauscher sorbiert werden.

Übersetzt von A. Emr, Prag.

Summary—A new method, using ion-exchange chromatography, has been developed for the separation of strontium and barium. The ions are adsorbed on a strong acid exchanger (Amberlite IR 120 in the ammonium form). Strontium is eluted with 0·02–0·05M 1,2-diamino-cyclohexane-N,N',N''-tetra-acetic acid (DCyTA) in 0·4M ammonium acetate (pH 6·3–7·2), and is determined in the eluate by flame-photometry. For the simultaneous determination of calcium and strontium in the presence of excess barium, the calcium is removed by the same eluent at pH 5·1. This method has been applied to the determination of strontium and calcium in barium minerals such as barytes and witherite.

Résumé—Les auteurs ont mis au point une nouvelle méthode de chromatographie d'échange d'ions pour la séparation du strontium et du baryum. Les ions sont adsorbés sur un échangeur acide fort (Amberlite IR 120 sous forme ammonium). Le strontium est élué par de l'acide 1,2 diaminocyclohexane N,N,N′,N′-tétracétique (DCyTA) 0,20–0,05 M dans l'acétate d'ammonium 0,4 M (pH 6,3–7,2) et est dosé dans l'éluat par photométrie de flamme. Pour le dosage simultané du calcium et du strontium en présence d'un excès de baryum, le calcium est éliminé par le même éluant à pH 5,1. Cette méthode a été appliquée au dosage du strontium et du calcium dans des minerais de baryum comme les barytes et la withérite.

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CHEMILUMINESCENCE OF LUMINOL AND HAEMIN

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Summary—A study of the luminescence of haemin-luminol mixtures has shown that haemin is a chemiluminescent material, and a mechanism is proposed for the haemin-luminol reaction. The course of the reaction depends on the relative concentrations of the components and the alkalinity of the solution.

THE brilliant chemiluminescence emitted by luminol (3-aminophthalhydrazide) on oxidation in an alkaline medium is well known and this phenomenon has been studied for many years. The chemiluminescence shown by phthalhydrazide derivatives when oxidised by sodium hypochlorite was studied by Zellner and Dougherty[1] in 1937, and a series of studies on the luminescence of luminol has been published by Weber and coworkers.[2–10] The latter series was mainly concerned with the effect of different catalysts and inhibitors on the intensity of light emitted by luminol when oxidised by hydrogen peroxide. The behaviour of luminol in the presence of potassium hexacyanoferrate(III) as catalyst has also been studied.[11,12]

Luminol was introduced as a chemiluminescent indicator for the titration of acids by bases by Kenny and Kurtz;[13] and Erdey and his coworkers[14,15] have used this reagent as a chemiluminescent indicator in a variety of redox titrations. Luminol is not a satisfactory indicator for the titration of bases by acids because the indicator is irreversibly oxidised in an alkaline medium in the presence of the catalysts normally used to increase the intensity of luminescence, *e.g.* haemin. However, it has recently been observed[17] that a mixture of fluorescein and luminol may be used as a reversible chemiluminescent indicator for acid-base titrations provided that the temperature of the solution is 60° at the beginning of the titration.

Attempts have since been made to eliminate the need for an elevated temperature by adding a small amount of catalyst. This aim has not been achieved but subsequent studies on the luminol-haemin system have nevertheless provided some interesting results which, it is felt, are worth reporting and discussing.

EXPERIMENTAL

To alkaline solutions ($0.001N$ to $1N$ sodium hydroxide) containing 1 ml of 6% hydrogen peroxide were added 1 or 2 ml of luminol solution ($5.7 \times 10^{-4}M$). These mixtures were then added to varying volumes of haemin solution ($1.3 \times 10^{-5}\ M$) and mixed thoroughly. The volume of alkali present was adjusted to give a total volume of 10 ml after mixing. The mixing was carried out in a dark room, and both the duration of the chemiluminescence and its relative intensity were measured.

In some tests haemin was replaced by sucrose, glycerol or glucose (1-g quantities) in warm solution, and in other tests the luminol was eliminated.

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RESULTS

The results of all of these comparative tests may be summarised as follows:

(1) The rate of fading of the normal blue chemiluminescence was slowest in approximately $0.01N$ sodium hydroxide solution. The rate was just slightly faster in more dilute solutions but fading was extremely fast in $0.1N$ and $1N$ sodium hydroxide solutions.

(2) For a given concentration of luminol in $0.01N$ sodium hydroxide, the intensity of the light emitted increased with the amount of haemin added, although the colour persisted for longer periods with smaller additions of haemin.

(3) In alkalinities of $0.01N$ and less, the chemiluminescence ceased because of the loss of the catalytic effect of the haemin present. The addition of further haemin to such solutions resulted in the return of blue luminescence.

(4) In alkalinities of $0.1N$ or greater, the luminol was destroyed in the luminescent reaction. Luminescence was restored by adding more luminol.

(5) The rate of the initial reaction varied with the concentration of haemin at the time of mixing.

(6) After the original blue light had faded from solutions of alkalinity less than $0.02N$, a pale yellowish-green light was observed. In many cases the light could be observed as bright specks on suspended particles in the solution; these slowly collected at the bottom of the vessel.

(7) Warm (60°) alkaline solutions of haemin oxidised by hydrogen peroxide emitted weak greenish chemiluminescence of very short duration. The duration of this chemiluminescence was increased by adding glycerol to the original solution.

(8) The intensity of the pale blue luminescence obtained by oxidising alkaline solutions of luminol with hydrogen peroxide (without catalysts) increased with temperature. The intensity was further enhanced if sucrose, glucose or glycerol was present during the heating. On cooling the luminescence faded, but the rate of fading was slower in the presence of the carbohydrates.

(9) Provided that the acid solutions are initially heated to 60°, a mixture of 1 ml of 1% luminol and 1 ml of glycerol is a suitable chemiluminescent indicator for the titration of acids by bases. When hot base solution is titrated by acid the results are low, because of the formation of acid through oxidation of the glycerol. The error is lessened by adding the glycerol to the hot alkali just before titration.

DISCUSSION

The first three of the above findings are in agreement with the conclusions of Weber, Rezek and Vouk.[3] These workers measured the intensity of the luminescence of luminol under different conditions using a photoelectric circuit. The concentration of luminol used by Weber and his coworkers was about ten times greater than that used in the present investigation, but comparable concentrations of haemin were used in both cases. In the haemin-catalysed reaction, the maximum brilliance was obtained with concentrations of sodium hydroxide between $0.025N$ and $0.05N$, and the maximum half-life was obtained in $0.015N$ sodium hydroxide solution. At low concentrations of catalyst, the maximum intensity was found to vary with the concentration of catalyst. With alkalinites up to $0.04N$ sodium hydroxide, all of the catalyst was altered irreversibly in the course of the reaction and the other components (hydrogen peroxide and luminol) were probably partially but by no means

completely destroyed in the reaction. For example, the addition of fresh catalyst to a number of samples 7 min after the initial luminescence reaction resulted in further bright luminescence, the intensity of this second emission being about 75% of the intensity of the original emission.

Using sodium hypochlorite as the oxidising agent, Zellner and Dougherty[1] observed a maximum emission intensity in $0.015N$ sodium hydroxide solutions. The intensity of luminescence decreased with increasing alkalinity, being reduced to about one-tenth of the maximum intensity in $0.5N$ sodium hydroxide solution.

The rate of oxidation of luminol by sodium hypochlorite was followed by measuring the volume of nitrogen liberated. This was found to accelerate markedly with hydroxyl ion concentration, e.g. the time required for half of the total nitrogen gas to be evolved was 4.9 min in $0.17N$ sodium hydroxide, 2.8 min in $0.33N$ sodium hydroxide and 0.9 min in $0.5N$ sodium hydroxide.

The evidence of accelerated destructive oxidation with increasing alkalinity gives an explanation for the fourth observation in this current study, namely, the destruction of luminol in the luminescent reactions using alkalinities greater than $0.1N$.

The hydroxyl ion concentration of the test solution can influence the luminescence reaction in a number of ways. Weber[2,3] has shown that the carbonyl form of luminol is required for the oxidation of luminol. At pH 8 about 5% of luminol is present in this form, and the transformation is complete at pH 12.6. When hydrogen peroxide is present, the concentration of the ion ($H_2O_2 \cdot OOH^-$) also reaches a maximum concentration at about the same pH.[18] Hence the maximum intensity of luminescence observed in solutions having an alkalinity of about $0.02N$ sodium hydroxide may perhaps be attributed in a large part to the presence in maximum possible concentration of these two reacting species.

The composition of the catalyst, haemin, can also vary with the alkalinity of the solution. In the presence of excess alkali, haemin (ferri-proto-porphyrin) forms a bivalent anion of ferri-proto-porphyrin hydroxide in which two carboxyl groups of the propionic acid side chains are ionised and the iron is bound to the hydroxyl group of the base and to one mole of water as well as to the four nitrogen atoms in the haemin molecule.[19] The existence of this hydroxide complex explains the suspended particles noted in observation (6) where such particles appeared as a source of yellow-green chemiluminescence.

Weber[6] has related the catalytic effects of iron complexes such as haemin to the behaviour of the co-ordination valencies not bound to the nitrogen of the original molecule. Thus, with haemin, both the fifth and sixth valences of the iron[III] may be catalytically active. At the same time, replacement of the water from these co-ordination sites by more strongly bound ligands (e.g. CN^-, OH^-) inhibits the catalytic effect. Weber considers that the catalyst can exhibit two kinds of oxidation action: (a) as a peroxidase, and (b) as a catalase. In the first case, one mole of hydrogen peroxide acts on the substrate to form luminol peroxide, which then forms an intermediate addition complex with the catalyst. This complex quickly decomposes in the presence of water to give an oxidation product of luminol, free catalyst and hydroxyl ions. In the second case, the luminol peroxide is in turn oxidised by another mole of hydrogen peroxide, resulting in the formation of the same oxidised species of luminol as before, a higher concentration of hydroxyl ions and the liberation of atomic oxygen with dehydration of the substrate. In the formation of the peroxide

catalyst complex, the O of the luminol peroxide is bound to the free (sixth) co-ordination valence of the iron^{III} in the catalyst.

The formation of an intermediate addition complex has also been postulated by the present authors[17] to explain the behaviour of the luminol-fluorescein system. The observation made in this present study, that haemin is a chemiluminescent material, would indicate a substantial similarity between the two systems. When oxidised separately in alkaline solutions, haemin and fluorescein both chemiluminesce very weakly and require further excitation by heat.[16] Luminol alone is also a weak emitter unless heated. However, a mixture of luminol with either of the other two compounds emits brilliant luminescence. When fluorescein is the additive the emitted light is green, and with haemin the emitted light is bright blue.

All three compounds are known to form oxygen complexes and it has been suggested that removal of the bound oxygen can leave a molecule in an excited triplet state. Reversion of the molecule to a singlet state may then result in the release of the excess energy in the form of light.[25] The formation of oxygen complexes has been stated to favour singlet-triplet transformation; and the existence of a triplet state with haemin has been proved.[23]

The stable complex formed between haemin and hydrogen peroxide has been examined, and has been found to contain one mole of haemin and two moles of hydrogen peroxide.[20] A polarographic study led to the conclusion that only undissociated hydrogen peroxide molecules take part in the reaction and combine with the haemin.[21] On the other hand, the action of haemin in speeding up the evolution of oxygen from hydrogen peroxide has been analysed and discussed on the basis of three reactions:

$$(a) \; Cat. + H_2O_2 \;\; = Cat. \; O + H_2O$$

$$(b) \; Cat. + 2H_2O_2 = Cat. \begin{smallmatrix}O\\O\end{smallmatrix} + 2H_2O$$

$$(c) \; Cat. \begin{smallmatrix}O\\O\end{smallmatrix} \qquad = Cat. \;\; + O_2$$
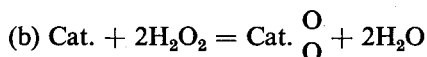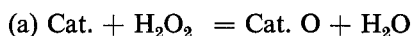
where Cat. is the catalyst. Reactions (a) and (b) were considered to reach rapid equilibrium while reaction (c) was postulated as a slow step.[22]

On the basis of all of this evidence, the following is proposed as the mechanism of the luminol-haemin reactions observed in this latest study, the symbols LU and HEM being used to represent molecules of luminol and haemin, respectively.

$$LU + (H_2O_2 \cdot OOH^-) \longrightarrow LUO_2 + OH^- + H_2O \qquad (1)$$

$$HEM + 2H_2O_2 \longrightarrow HEMO_2 + 2H_2O \qquad (2)$$
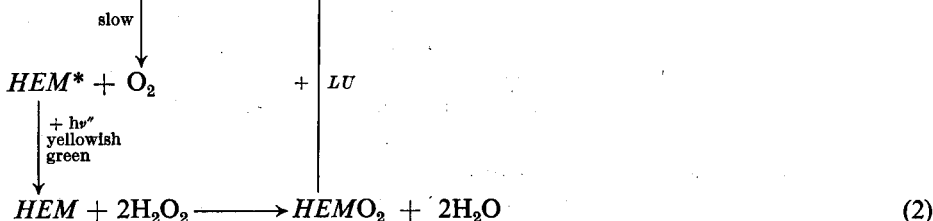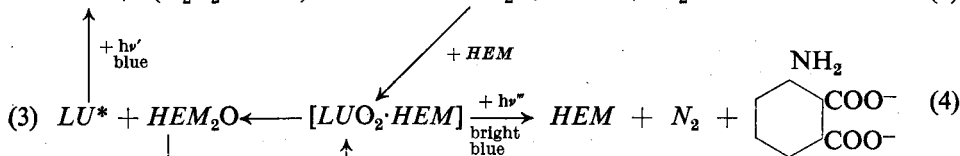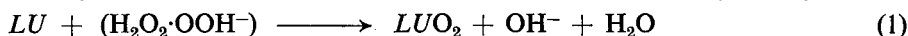
The relative importance of the competing reactions is controlled by the pH of the solution and the concentration of reactants.

Since it has been shown[21] that only undissociated hydrogen peroxide molecules react with haemin, the importance of reaction (2) will increase as the pH of the solution is lowered. On the other hand, since luminol reacts preferably with the $(H_2O_2 \cdot OOH^-)$ ion, reaction (1) should reach maximum importance at pH values around 12 to 13. The liberation of nitrogen from oxidised luminol solutions has been observed to be accelerated by increased pH, hence reaction (5) will become increasingly important with increasing hydroxyl concentration in the solution.

In dilute alkaline solutions, e.g. $<0 \cdot 01N$ sodium hydroxide, the haemin-luminol reaction can be considered to follow the course of reactions (2) and (3) or (1) and (3), the relative importance of each depending on the exact pH. When luminol is present in excess, reaction (1) will be favoured, particularly at pH values of the order of 12 to 13. Increasing the concentration of haemin present will increase the rate of intermediate complex formation and thus increase the initial maximum intensity.

Kobozev[22] postulated that the decomposition of $HEMO_2$ is a slow process, and this slow step can be considered to influence the duration of luminescence. The speckles of greenish-yellow light observed in the solutions after the fading of the blue luminol colour can be attributed to the chemiluminescence of the activated haemin formed on decomposition of the $HEMO_2$. The decomposition product lacks catalytic properties and it may be suggested that both the fifth and sixth co-ordinate valencies of iron are occupied by hydroxyl ions, thus reducing both the solubility and the co-ordinating power of the compound.

Increasing the H_2O_2 content of the reaction mixture will tend to favour reaction (2), thus reducing the amount of haemin available to form an association complex with luminol peroxide. This in turn means less light emission, as has been observed by Weber.[6]

As the alkalinity of the test solutions is increased reaction (4) becomes more important, and light emission is accompanied by an increasing degree of destruction of the luminol. Above pH 12, however, the concentration of $(H_2O_2 \cdot OOH^-)$ is reduced, and this reduces the intensity of emission by inhibition of reaction (1). In the absence of free hydrogen peroxide the haemin molecule should remain virtually unchanged and retain its catalytic properties. This is supported by experiment, because the addition of further luminol to extinguished solutions of alkalinity greater than $0 \cdot 1N$ sodium hydroxide results in a return of the bright blue luminescence.

The above mechanism postulates three types of emitted light. The existence and characteristics of that emitted in reaction (4) is well known and requires no further discussion. The yellowish-green light attributed to activated haemin has been observed when haemin is oxidised by hydrogen peroxide in hot alkaline solution, as well as in the mixed indicator study. The greater persistence of this emission in the presence of luminol is analogous to the phenomena observed previously with fluorescein-luminol mixtures. When oxidised alone fluorescein luminesced very weakly, but in the presence of luminol brilliant green light was emitted with little apparent destruction of the luminol. In fact, oxidation of an alkaline mixture of haemin, luminol and fluorescein with hydrogen peroxide yields bright green light, not blue as obtained in the absence of fluorescein.

The third colour is the blue postulated for the deactivation of the luminol species

in reaction (3). The possibility of such an emission is indicated by the behaviour of alkaline peroxide solutions containing luminol when they are heated in the presence of glycerol or sugars. Heating the luminol solution alone causes a marked increase in intensity of a deep blue radiation and this intensity is further increased in the presence of glycerol or sugars. As long as the temperature remains constant, the intensity remains constant and there is no marked destruction of the luminol in the sense of equation (4). On cooling, the intensity decreases (slowly in the presence of the carbohydrates) but it can be restored by further heating.

This behaviour can be explained by conclusions similar to those reached by Parker and Hatchard.[24] These workers used a high-sensitivity spectrophotometer to study the very weak, long-lived emission spectra of eosin in glycerol and ethanol. The visible band of long-lived luminescence was found to be delayed fluorescence produced by thermal agitation of the eosin from the triplet to the excited singlet level. The probabilities of inter-system crossing from the upper singlet to triplet, and from triplet to upper singlet state, were found to be of the same order of magnitude, being greater in glycerol than in the more fluid ethanol.

The luminol-glycerol reaction can thus be ascribed to the formation of the triplet state by thermal decomposition of the luminol peroxide formed during the oxidation process followed by transition of the molecule from the triplet state to an excited singlet level state, the probability of this latter transition being increased by the presence of glycerol. This need for thermal agitation from the triplet to the upper singlet state explains the observation that the intensity of chemiluminescence of uncatalysed luminol, fluorescein, eosin or haemin increases with temperature. In mixed indicator systems, the activation barrier may be overcome by energy transfer during the formation of intermediate complexes, and thus reactions can proceed more rapidly at lower temperatures.

CONCLUSIONS

The chemiluminescent light emitted on oxidation of a luminol-haemin system is undoubtedly from a triplet-singlet transition in the luminol molecule. The intermediate reactions responsible for the excitation of the luminol can, however, be varied by the experimental conditions. The main intermediate is a luminol-oxygen-haemin complex. In mild alkaline conditions most of this complex appears to dissociate leaving the oxygen with the haemin, but under stronger alkaline conditions the oxygen is retained by the luminol with the simultaneous evolution of nitrogen.

There are also competing reactions responsible for the formation of the intermediate association complex. The actual course of the chemical reactions responsible for the activation of luminol therefore varies with the concentrations of luminol, haemin, hydrogen peroxide and alkali present.

In alkaline conditions, the chemical reactions destroy either the luminol or the haemin and hence a mixture of these two cannot be used for the titration of bases by acids. However, since fluorescein is not affected by the alkaline conditions, a mixture of fluorescein-luminol has been found to be a suitable indicator for this type of reaction. The use of a luminol-glycerol mixture as a chemiluminescent indicator was only partially successful, since sufficient glycerol can be oxidised to give an error in the volume of acid required in the titration at the elevated temperature necessary for chemiluminescence.

Zusammenfassung—Untersuchung der Luminiszenz von Hämin-Luminol Mischungen haben gezeigt, dass Hämin eine chemiluminiszente Substanz ist. Ein Mechanismus für die Hämin-Luminol Reaktion wird vorgeschlagen. Der Reaktionsverlauf scheint von der relativen Konzentration der beiden Komponenten und von der Alkalität der Lösung abzuhängen.

Résumé—Une étude de la luminescence de mélanges hemine-luminol a montré que l'hemine est une substance chimioluminescente; les auteurs proposent un mécanisme pour la réaction hemine-luminol. La marche de la réaction dépend des concentrations relatives des composants et de l'alcalinité de la solution.

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APPLICATIONS OF INFRARED SPECTROSCOPY—IX*

THE DIFFERENTIATION OF ESTERS AND ACETALS FROM ETHERS IN THE ZEISEL ALKOXYL REACTION

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Summary—After determination of the total alkoxyl content (ester + ether groups) by reflux with hydriodic acid, the contribution from methyl and ethyl ester groups is found by refluxing a second sample of the compound in constant-boiling hydrochloric acid for 3 hr. Acetals cannot be distinguished from esters; the yields of alkyl chloride from propyl and butyl esters are diagnostic, although not quantitative. Certain classes of compounds, which have unusually labile ether linkages, restrict the general applicability of the method; examples of such compounds are given.

THE Zeisel alkoxyl determination gives the total alkoxyl content of a compound, and does not differentiate[1] between esters, acetals, alcohols and ethers; such information would be useful in structural studies on complex molecules.

Analytical methods for esters[2] and acetals[3] have been reviewed: colorimetric[4] and oximation[5] methods for determining acetals, ketals and vinyl ethers continue to be described. Differences in reaction-rate can sometimes be used to analyse mixtures of organic compounds containing the same functional group.[6,7] The Zeisel reaction-time for quantitative yields of alkyl iodide from methoxy and ethoxy compounds is so rapid, however (approx. 15 min for methyl iodide) that kinetic differentiation between esters and ethers is not feasible (*cf.* ref. 8).

Methods for the determination of methanol, methyl esters and methyl ethers were considered in an early review,[9] and the determination of glycosidic methoxyl was investigated by Hoffpanir and Reeves.[10] The use of hydrobromic acid as a demethylating agent is well known;[11,12] when it was found[13] that constant-boiling hydrobromic acid produced alkyl bromides quantitatively from esters and ethers almost as quickly as hydriodic acid formed the corresponding iodides (*cf.* refs. 12 and 14), the rates of reaction in constant-boiling hydrochloric acid were investigated. Quantitative yields of the corresponding alkyl chloride were obtained from methyl or ethyl esters and acetals in 3 hours; in that time, only trace amounts of alkyl chloride were produced from true ethers (*e.g.*, 0·05 moles from vanillin, 0·12 moles from 2,3-dimethoxybenzaldehyde, 0·02 moles from phenacetin) (*cf.* ref. 15). This modification to the Zeisel reaction therefore gives the possibility of differentiating between esters and ethers.

EXPERIMENTAL

The reagents, reaction conditions and apparatus used for determination of total alkoxyl, using constant-boiling hydriodic acid, were as described elsewhere.[16] The ester content is found by refluxing a sample (sufficient to yield 1–4 mg of alkyl chloride) for 3 hr with constant-boiling hydrochloric acid (6 ml) to which approx. 0·25 g of phenol has been added.

The alkyl chloride evolved is determined by the infrared method, using the manometric method of calibration:[17] laboratories not equipped with an infrared spectrometer can use a modified Fujiwara method.[18]

No difficulty was experienced with volatile alcohols, acetals and esters when the reaction conditions proposed by Anderson and Duncan[16] were used (cf. refs. 19 and 20).

RESULTS

The method has been applied to a wide range of methoxy and ethoxy compounds having (a) ether groups only, (b) ester groups only, and (c) ether and ester groups in various combinations. Some typical results are shown in Tables I and II, together with the structural deductions possible had only the molecular weight of the compound been known.

Whilst the method is clearly applicable to many compounds, it is not of general applicability. Several classes of compound contain abnormally reactive ether groups, which are labile in constant-boiling hydrochloric acid. The following examples of these have been encountered in this work, and others doubtless exist (cf. ref. 12):

(1) *Substituted urea salts*, such as X and XI.

$$C_6H_5 \cdot NH \cdot C = NH_2^+ Cl' \qquad C_6H_5 \cdot NH \cdot C = NH^+ \cdot C_6H_5 \cdot Cl'$$
$$\underset{OCH_3}{|} \qquad\qquad\qquad \underset{OC_2H_5}{|}$$

X   XI
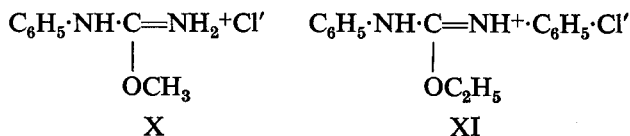
(2) *Certain methoxy-pyrimidines*[21] *and -pyridines.*[22]

(3) *Flavone derivatives*[23] containing alkoxyl substituents at position 5. Thus 3,5,7, 3',4'-pentaethoxy-6-methoxyflavone (XII) gives 1 mole of ethyl chloride (from position 5) when treated with hydrochloric acid, and 1 mole of methyl iodide + 5 moles of ethyl iodide on reflux with hydriodic acid.

XII
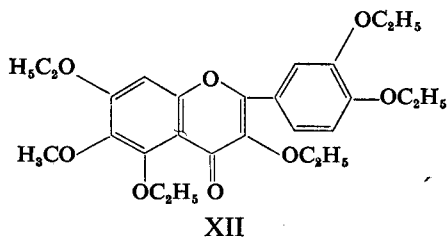
Reaction with constant-boiling hydrochloric acid is therefore a diagnostic test for alkoxyl substituents at position 5 in flavones if it is known (infrared spectroscopy) that ester groups are not also present in the molecule.

(4) *Certain dimethoxy compounds,*[24] such as the *N*-benzene-sulphonyl derivative of XIII.

XIII
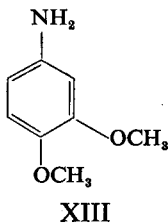
TABLE I.

| Compound | Reflux with hydriodic acid | | | | Reflux with hydrochloric acid | | | | Deductions |
| | total methoxyl, % | | total ethoxyl, % | | ester methoxyl, % | | ester ethoxyl, % | | |
	Theory	Found	Theory	Found	Theory	Found	Theory	Found	
Vanillin	20·4	20·4	—	—	0	0·9	0	0·5	ether groups only.
Phenacetin	—	—	25·2	25·1	—	—	—	—	
Yohimbine HCl	7·94	7·92	—	—	7·94	7·67	—	—	ester groups only.
Ethyl-p-nitrobenzoate	—	—	23·1	22·9	—	—	23·1	22·7	
"Ruelene" (I)	10·7	10·5	—	—	10·7	10·5	—	—	
"Ronnel" (II)	19·3	19·3	—	—	19·3	19·0	—	—	
"Menazon" (III)	22·1	21·4	—	—	22·1	21·2	—	—	
"Mecarbam" (IV)	—	37·4	41·0	40·6	18·7	19·2	41·0	40·1	
Methyl anisate	37·4	37·4	—	—	18·7	19·2	—	—	methyl ether and ester groups, ratio 1:1
Methyl-3:4-dimethoxy-benzoate	47·4	47·3	—	—	15·8	16·1	—	—	methyl ether and ester groups, ratio 2:1
Reserpine	30·6	30·4	—	—	5·10	5·36	—	—	methyl ether and ester groups, ratio 5:1
Methyl mangifate trimethyl ether (V)	29·7	29·3	—	—	7·43	7·71	—	—	methyl ether and ester groups, ratio 3:1
Ethyl-α-ethoxy-propionate	—	—	61·6	61·2	—	—	30·8	31·7	ethyl ether and ester groups, ratio 1:1

$$H_3C-C(CH_3)(CH_3)-\text{—}C_6H_4\text{—}O-P(=O)(OCH_3)-NHCH_3$$

I

Cl, Cl, Cl –C₆H₂– O–P(=S)(OCH₃)OCH₃

II

$$H_2N-C\cdots N\cdots C-CH_2-S-P(=S)(OCH_3)OCH_3,\ H_2N-$$

III

$$H_5C_2O\!\!-\!\!P(=S)(OC_2H_5)\!-\!S-CH_2-CO-N(CH_3)-COOC_2H_5$$

IV

H₃CO, H₃CO, OCH₃, OCH₃, C₃H₅(OH)COOCH₃, OH (xanthone)

V
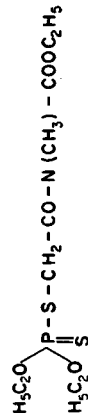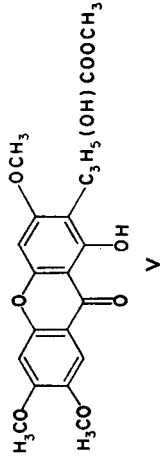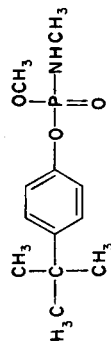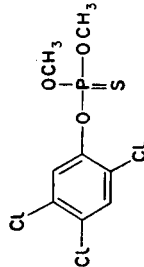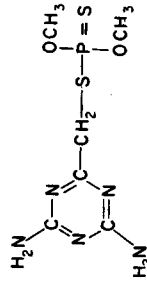
TABLE II

Compound	Reflux with hydriodic acid				Reflux with hydrochloric acid				Deductions
	total methoxyl, %		total ethoxyl, %		ester methoxyl, %		ester ethoxyl, %		
	Theory	Found	Theory	Found	Theory	Found	Theory	Found	
Methyl-3-ethoxy-4-methoxybenzoate	29·5	29·3	21·4	21·1	14·7	15·0	—	—	methyl ester, methyl and ethyl ether, ratio 1:1:1.
Ethyl-3:4-dimethoxy-benzoate	29·5	29·3	21·4	21·6	—	—	21·4	20·8	all ethoxyl present as ester, all methoxyl as ether. Ratio of methoxy/ethoxy = 2/1.
(VI)	10·0	10·3	14·5	14·1	—	—	14·5	13·9	all ethoxyl present as ester, all methoxyl as ether. Ratio of methoxy/ethoxy = 1/1.
(VII)	26·0	26·0	—	—	13·3	13·0	—	—	methoxy only; ratio of ester/ether = 1/1.
2-hydroxy-5-methoxy-w4:6-triethoxy-acetophenone (VIII)	10·4	10·6	45·3	44·7	—	—	—	—	methoxy and ethoxy, present as ethers only. Ratio = 1/3.
Ethyl angolensin (IX)	10·3	10·0	15·0	14·8	—	—	—	—	methoxy and ethoxy, present as ethers only. Ratio = 1/1.

CO(CH₂)₂—CO—CH₂—COOC₂H₅
(VI)

CO(CH₂)₂—COOCH₃
(VII)

(VIII)

(IX)
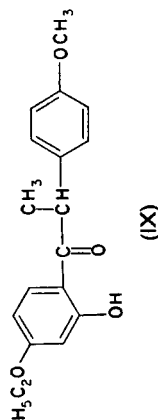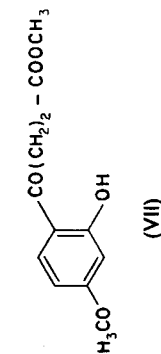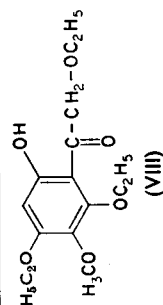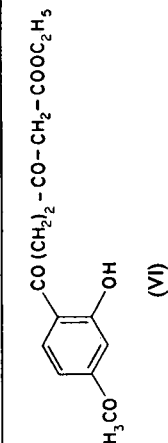
(5) *Compounds containing tertiary butyl*[25] *groups.* Two effects must be distinguished: (*a*) non-alkoxy tert-butylated compounds yield alkyl halide, so giving an anomalous reaction; (*b*) in certain alkoxy tert-butylated compounds, such as tert-butylated-*p*-hydroxyanisole, both the tert-butyl and alkoxyl groups are labile so that the compound does not react like a true ether. In addition, high alkoxyl results are given if a method which does not differentiate between methyl and tert-butyl halides is used (*cf.* refs. 8 and 26).

(6) *Methyl glycosides and* O-*methyl carbohydrate derivatives.* A method for differentiating between methyl ester groups at C_6 and methyl linkages at C_2, C_3 and C_4 would be of great value in investigations of plant gums[27] and pectins; investigations of mild de-alkylating reagents[22] are in progress.

Propyl and butyl esters give non-quantitative yields of the corresponding alkyl chloride (approx. 70% for propyl, 30% for butyl chloride) even when zinc chloride is added to the reaction mixture. It is well-known, however, that propyl and butyl ethers react much more slowly in acid solutions than methyl or ethyl ethers. Small yields of propyl and butyl chlorides on reflux with constant-boiling hydrochloric acid therefore indicate the presence of the corresponding ester groups. (The exceptional case of tert-butyl groups has already been mentioned.)

Zusammenfassung—Nach Bestimmung des geamten Alkoxylgehaltes (Ester- und Ätherguppen) mittels Rückflussdestillation mit Iodwasserstoffsäure, wird der Anteil der Methyl- und Äthylgruppen durch Rückflussdestillation (3 Stunden) mit konstant siedender Salzsäure bestimmt. Acetale können von Äthern nicht differenziert werden. Die Ausbeuten der Alkylchloride von Propyl- und Butylestern sind nicht quantitativ, haben aber diagnostischen Wert. Gewisse Klassen von Komponenten mit besonders labilen Ätherbindungen begrenzen die allgemeine Anwendbarkeit der Methode. Beispiele für solche sind mitgeteilt.

Résumé—Après dosage de la teneur totale en alcoyle (groupes ester + éther-oxyde) par reflux avec l'acide iodhydrique, la contribution des groupes esters méthylique et éthylique est déterminée en chauffant au reflux un deuxième échantillon du composé dans de l'acide chlorhydrique bouillant constamment pendant trois heures. Les acétals ne peuvent pas être distingués des éther-oxydes; les rendements en chlorure d'alcoyle à partir des esters propylique et butyrique sont déterminés, bien que non quantitatifs. Certaines catégories de composés, qui possèdent des liaisons étheroxyde inhabituellement labiles, restreignent l'application générale de la méthode; des exemples de tels composés sont donnés.

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ANALYTICAL APPLICATIONS OF INFRARED SPECTROSCOPY

IDENTIFICATION OF POLYATOMIC INORGANIC ANIONS

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Summary—Using infrared absorption spectroscopy a method has been developed which permits the identification of the following 14 anions: pertechnetate, perrhenate, thiocyanate, persulphate, perchlorate, chlorate, permanganate, periodate, ferricyanide, ferrocyanide, thiosulphate, chromate (or dichromate), molybdate and tungstate. The method is fast, sensitive and reliable compared to the corresponding laborious and time-consuming classical methods.

ALTHOUGH a large number of investigations of inorganic compounds by infrared absorption spectroscopy has been carried out, few applications of this technique to systematic qualitative analysis have been attempted. Hunt et al.,[1] studied the infrared absorption spectra of 64 natural minerals and compounds, while Miller and Wilkins[2] carried out their investigations on a number of inorganic salts, building up an excellent catalogue for 159 compounds.

In the present work infrared spectroscopy was used in the systematic identification of the following anions: pertechnetate, perrhenate, thiocyanate, persulphate, perchlorate, chlorate, permanganate, periodate, ferricyanide, ferrocyanide, thiosulphate, chromate (or dichromate), molybdate and tungstate.

All of the foregoing anions form compounds of the type $(Phenyl)_4AsX$, where X is the anion, and the method used is based on the precipitation of the anions with tetraphenylarsonium chloride (TPAC), followed by the mixing of the precipitate with potassium bromide. From the mixture a disc was prepared. This disc, when placed in the infrared spectrophotometer, produced spectra which permitted the identification of the anions present.

EXPERIMENTAL

Apparatus and reagents

The infrared spectra were recorded on a Perkin-Elmer ('Infracord') Spectrophotometer, Model 137.

The potassium bromide discs were prepared with a Perkin-Elmer die using an 'Apex' hydraulic press with a 10-ton capacity on a ram of $2\frac{1}{2}$-inch diameter. Before use, the potassium bromide, which was Analytical Reagent grade, was dried at 150° for 24 hr. The tetraphenylarsonium chloride was supplied by L. Light and Co., Ltd. A 10% aqueous solution was used.

All other chemicals used in the work were AnalaR.

Procedure

1. Dissolve an appropriate amount (about 5–50 mg) of the anion mixture in approximately 3 ml of water or suitable solvent in a 20-ml centrifuge tube. Add sufficient solid sodium chloride to make the solution about $1M$. Neutralise with ammonia solution and add 0·5 ml in excess. Heat the solution, centrifuge and discard any precipitate formed.

2. Add to the clear solution an excess of 10% tetraphenylarsonium chloride reagent. Mix the contents for a few min and centrifuge. To the supernatant liquid add 1 more drop of TPAC reagent to ensure that precipitation is complete. Decant into a second centrifuge tube, wash the precipitate

with 1 ml of $1M$ sodium chloride solution and centrifuge once more. Decant the washings into a second centrifuge tube. Dry the precipitate by placing the tube in a water bath maintained at a temperature of 50–60°. Connect the tube to a vacuum pump. This prevents decomposition of some complexes. The precipitate will contain thiocyanate, persulphate, perchlorate, chlorate, perrhenate, pertechnetate, permanganate and periodate, if these anions were present in the original mixture.

3. Scrape out the precipitate with a small spatula and break up any lumps which may have formed. Weigh out 1–3 mg of the precipitate and approximately 300 mg of potassium bromide. Transfer to an agate mortar. Grind the mixture to a fine state of division and place in the die.
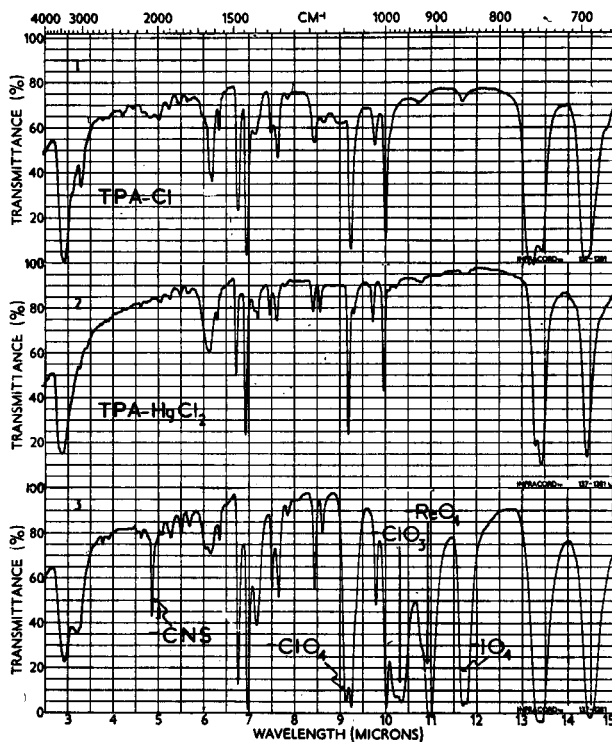
FIG. 1. 1—Tetraphenylarsonium chloride (TPAC). 2—Tetraphenylarsonium chloro-mercuriate. 3—Tetraphenylarsonium complexes of thiocyanate, perchlorate, chlorate, perrhenate and periodate.

Evacuate the assembled die for 2 min and apply a total pressure of 10 tons for a period of 5 min. Dismantle the die and fix the disc with a special holder in the beam of the 'Infracord' spectrophotometer using a disc of potassium bromide in the reference beam. Record the spectrum over the range 3–15 μ. The characteristic bands of each anion are shown in Figs. 1, 2 and 3.

4. Divide the supernatant liquid from the TPAC precipitation into 2 parts. To one part add a small strip of litmus paper and neutralise the solution with 1:1 hydrochloric acid, adding a drop in excess. The formation of a precipitate in this operation indicates the presence of ferrocyanide, ferricyanide, thiosulphate, chromate (or dichromate), molybdate and tungstate.

Centrifuge and add 1 drop of TPAC reagent to ensure complete precipitation. Treat the precipitate as outlined above, and record the spectrum over the range 3–15 μ. The spectra are shown in Figs. 1, 2 and 3.

5. If chromate, molybdate and tungstate are present, their interference may be eliminated by adding to the second portion of the solution approximately 0·1 g of sodium citrate or citric acid and treating the solution as under (4) above.

RESULTS AND DISCUSSION

Tetraphenylarsonium chloride was introduced as an analytical reagent by Willard and Smith.[3] It forms precipitates under different conditions with a large number of

ions, *e.g.* iodide, bromide, fluoride, bismuth[III], platinum[IV], gold[III], palladium[IV], tin[IV], zinc[II], cadmium[II], thallium[III], mercury[II], the metallic complexes of thiocyanate and other groups, as well as with the polyatomic anions examined in this study. The solubilities of these precipitates range from fairly soluble, *e.g.* chlorate, thiosulphate, ferrocyanide, ferricyanide, and tungstate, to sparingly soluble, *e.g.* perrhenate, pertechnetate, perchlorate, *etc.* If the former groups of anions are present in microgram quantities, then complete precipitation will be assisted by the presence of the latter group which behaves as a carrier. The method is reasonably sensitive, 10 μg or even less of perrhenate, pertechnetate, thiocyanate and periodate in a 300-μg potassium bromide disc can be detected, and it is possible to detect amounts of less than 100 μg of the fairly soluble precipitate such as chlorate and thiosulphate.

The characteristic infrared spectra of polyatomic inorganic compounds under normal conditions are caused by rotation in addition to the lattice vibrations and their absorption bands are, in general, broad and in some cases ill-defined. This makes their identification difficult, particularly in mixtures. Exceptions are the simple or complex cyanides which exhibit sharp bands from C–N stretching frequencies.

The characteristic bands of the polyatomic anions examined in this study are attributable to either metal-oxygen frequencies, as in perrhenate, or to non-metal-oxygen frequencies, as in persulphate, *etc.* It was found that most of the metal-oxygen frequencies fall within the range of 9–11 μ.[4] The advantages of using TPAC as a precipitant for the isolation of the anions prior to infrared absorption studies can be summarised as follows:

(1) The reagent forms ion-association complexes with a large number of ions. These complexes are mostly insoluble and can be separated from other interfering ions.

(2) Although the reagent has a comparatively high molecular weight and is composed of several groups, it exhibits a relatively simple infrared spectrum and has few strong absorption bands. These cause no interference with any of the anions investigated in the present study.

(3) The bonds between the anions and the TPA ion are covalent in character, which leads to sharper bands with less overlapping than obtained with the pure inorganic compounds. Perrhenate, pertechnetate, and permanganate (when complexed with TPAC) exhibit strong bands at 10·94, 11·09, and 11·02 μ.

Perrhenate, pertechnetate and permanganate

It is quite easy to identify perrhenate, pertechnetate and permanganate (Fig. 2) if present singly, but identification can be difficult if these anions are present together in a mixture.

From the infrared spectra of these anions it is evident that they are isomorphous and the presence of one strong band may mean that they are monomers. The strong bands are assignable to metal-oxygen stretching frequencies (M = O). These complexes are soluble in chloroform.

Molybdate and tungstate

These two anions show several absorption bands at longer wavelengths (Fig. 3). The intensities of the bands are variable. This may be explained on the basis that these ions exist as polymers, the presence of several bands arising from M—O—M—O continuous structures.[4] The variability of the bands can also be attributed to the
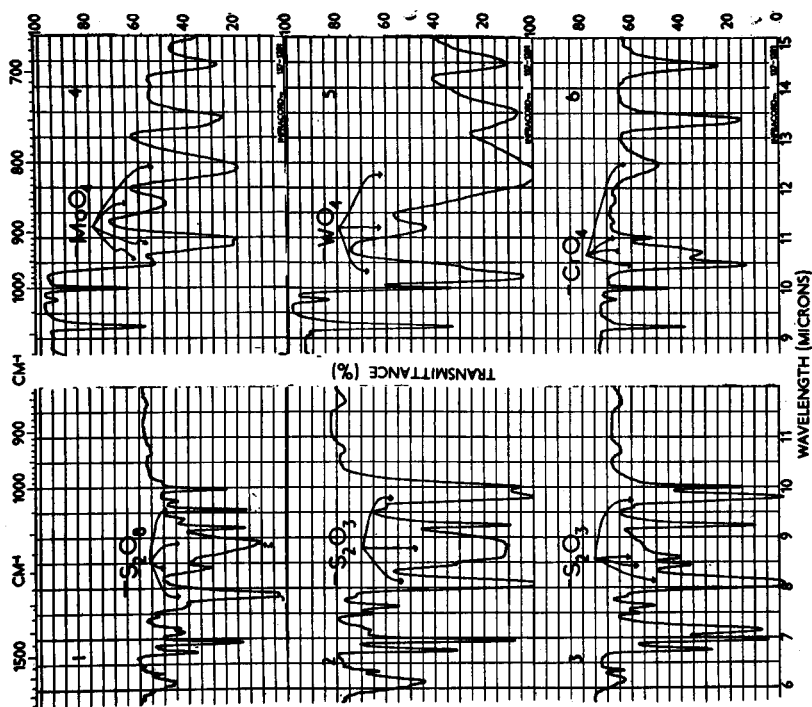
FIG. 3. 1—Tetraphenylarsonium persulphate. 2—Tetraphenylarsonium thiosulphate (from neutral solution). 3—Tetraphenylarsonium thiosulphate (from slightly acidic solution). 4—Tetraphenylarsonium molybdate. 5—Tetraphenylarsonium tungstate. 6—Tetraphenylarsonium chromate (or dichromate).
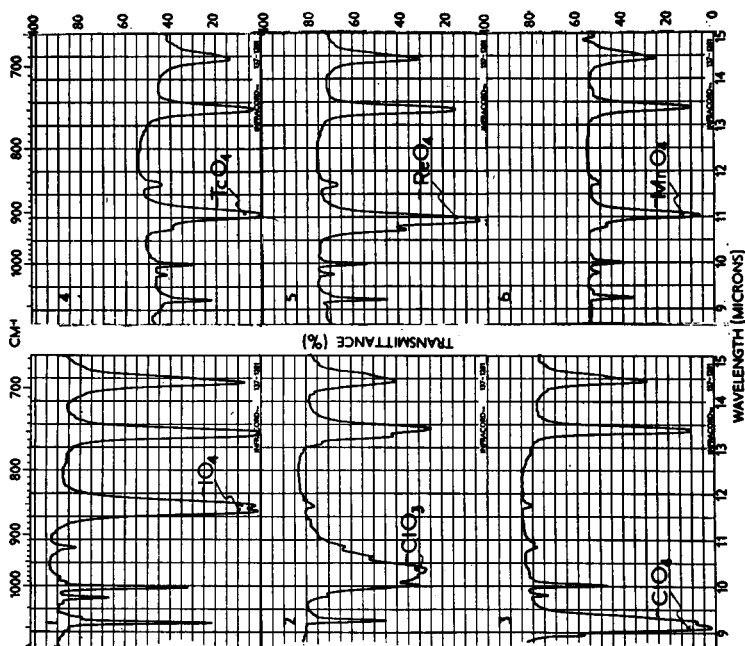
FIG. 2. 1—Tetraphenylarsonium periodate. 2—Tetraphenylarsonium chlorate. 3—Tetraphenylarsonium perchlorate. 4—Tetraphenylarsonium pertechnetate. 5—Tetraphenylarsonium perrhenate. 6—Tetraphenylarsonium permanganate.

variability of composition of the complexes under different conditions. Identification can be difficult, especially when present with chromate ions. These complexes are insoluble in chloroform. Addition of citrate ion prevents the precipitation of molybdate and tungstate complexes.

Chromate (or dichromate)

The procedure outlined permits the identification of chromate (or dichromate) ion which is characterised by a strong band at 10·48 μ and other variable bands (Fig. 3). The disappearance of the absorption bands on the addition of citrate ions can be used as a confirmation of the presence of molybdate and tungstate ions. On the other hand the treatment of chromate ion with iron[II] sulphate and the consequent elimination of the strong band at 10·48 μ can be regarded as a confirmation of the presence of this ion.

Ferrocyanide and ferricyanide

Ferrocyanide and ferricyanide ions form precipitates from a slightly acidic medium, and the infrared spectra of their precipitates show strong and sharp bands at 4·65 and 4·74 μ, respectively. Although these two bands are close to each other there is no overlapping, which permits their individual identification when present in approximately equal amounts.

Perchlorate and chlorate

The perchlorate ion forms a stable complex and exhibits a strong and sharp band at 9·12 μ. Although this band and that exhibited by the reagent at 9·24 μ partially overlap, the identification of microgram quantities of perchlorate ion is still easy (Fig. 1). The chlorate ion which forms a fairly soluble complex with TPAC exhibits a strong and broader band at 10·35 μ. The broadness may be explained by the assumption that the bonding between the chlorate ion and TPA ion is less covalent in character than in the other cases discussed. To identify a microgram amount of chlorate ion by the infrared technique, a carrier such as the perchlorate ion must also be present.

Persulphate and thiosulphate

The persulphate ion forms an apparently stable complex with TPAC which is insoluble in water. This ion shows several strong bands (Fig. 3).

Thiosulphate ion forms a fairly soluble complex with TPAC under neutral and slightly acidic conditions. The complex formed in neutral solution exhibits three absorption bands at 8·08, 8·78, and 9·8 μ. The band at 8·78 μ is variable and broad. When the complex is formed in a slightly acidic medium the broad band at 8·78 μ splits into two weaker bands.

Thiocyanate

Thiocyanate ion forms an insoluble precipitate with TPAC in alkaline and acidic media. It shows a strong and sharp band at 4·85 μ which permits the identification of a few μg in a 300-mg potassium bromide disc (Fig. 1).

Periodate

With TPAC in acidic or alkaline media this ion forms a precipitate which shows a strong absorption band at 11·68 μ (Fig. 2).

It is worthy of note that the TPA complexes of most of the anions examined in this work show two very weak absorption bands at approximatley $10\cdot8$ μ and $11\cdot7$ μ. In no case, however, did these bands ever interfere with the detection of perrhenate, pertechnetate, permanganate or periodate. Comparison of the spectra of the anions concerned and that of the reagent removes any misinterpretation which might arise.

Other anions

TPAC forms precipitates with fluoride, bromide and iodide, which interfere in the precipitation of the anions studied in the present work. Fortunately, however, the halide complexes of (TPAC) show spectra which are similar to (TPAC) in the region from 3–15 μ.

The halo-complexes of some metallic ions, such as $(Hg\,Cl_4)^{2-}$, with the TPA ion form precipitates which do not exhibit a significant band in the working region (Fig. 1). If, therefore, these ions are present, no interference in the identification of the other anions arises.

Zusammenfassung—Eine infrarotspektrophotometrische Methode wurde entwickelt um die folgenden 14 Anionen rasch, empfindlich und zuverlässig zu bestimmen und das besser und schneller als nach klassischen Methoden: Pertechnat, Perrhenat, Thiocyanat, Persulfat, Perchlorat, Chlorat, Permanganat, Perjodat, Ferri- und Ferrocyanid, Thiosulfat, Chromat (und Dichromat), Molybdate und Wolframat.

Résumé—Les auteurs ont mis au point une méthode de spectroscopie d'absorption infra-rouge permettant l'identification des 14 anions suivants: pertechnétate, perrhénate, thiocyanate, persulfate, perchlorate, chlorate, permanganate, périodate, ferricyanure, ferrocyanure, thiosulfate, chromate (ou bichromate), molybdate et tungstate. La méthode est rapide, sensible et fidèle par comparaison avec les méthodes classiques correspondantes longues et laborieuses.

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THE SPECTROPHOTOMETRIC DETERMINATION OF SULPHUR IN IRON ALLOYS

METHYLENE BLUE METHOD

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Summary—Sulphur is determined in iron alloys by evolution as hydrogen sulphide, followed by reaction with N,N-dimethyl-p-phenylenediamine and iron^{III} to form methylene blue, which is measured spectrophotometrically. Replicate results are reported for acid soluble metal samples containing 0·3-230 ppm of sulphur. An evaluation of the accuracy of the methylene blue procedure was made using radiotracer techniques.

INTRODUCTION

Traces of sulphur have a marked effect on the physical properties of steel and other iron-base alloys; consequently, the accurate determination of small amounts of sulphur in these materials is of considerable importance. Traditional techniques for this analysis may be summarised as follows: (1) precipitation of sulphur as barium sulphate following solution of the sample in an oxidising medium; (2) combustion of the sample in oxygen and absorption of the sulphur oxides in an aqueous iodine solution, followed by measurement of the sulphur by a redox titration or by a colorimetric technique; or (3) evolution of hydrogen sulphide from a hydrochloric acid solution of the sample followed by absorption and determination of the sulphide by a redox titration. These techniques were found to be unsatisfactory for the determination of less than 10 ppm of sulphur when sample size was limited to 5 g or less. The use of more than 5 g of sample is impractical by the combustion technique; and dissolution of a sample of this size is slow and introduces large quantities of other elements.

The method herein proposed involves the reaction between sulphide, N,N-dimethyl-p-phenylenediamine and iron^{III}, which produces the intense blue colour of methylene blue. While this system has been known for some time[1,2,6] it has not previously been applied to the determination of sulphur in ferruginous materials. Fogo and Popowsky[3] first used modern spectrophotometric instrumentation in the study of the methylene blue techniques. The experimental conditions suggested by their work were applied in our laboratory to the determination of 2–250 μg of sulphur in 0·1–4 g of iron-base alloys. Recently, Gustafsson[4] investigated thoroughly a number of variables in the methylene blue system, including temperature, acidity, various anions, traces of heavy metals, ageing time, reagent concentrations and air-oxidation.

APPLICABILITY

This procedure may be used to determine sulphide sulphur in any sample in which the sulphide is soluble in dilute hydrochloric acid. Materials studied thus far include a variety of iron alloys and manganese. If the sulphur is present as the sulphate, the

reduction solution technique detailed by Gustafsson[5] is used before determining the sulphur.

<div align="center">EXPERIMENTAL</div>

Reagents

All reagents are prepared with de-ionised water rather than with distilled water.

Ferric Chloride: 6·2 g of $FeCl_3 \cdot 6H_2O$ in 400 ml of 1·2N hydrochloric acid.

Hydrochloric Acid: 6N.

Nitrogen, Liquid: Used as the source for all gaseous nitrogen because of excessive oxygen in tank nitrogen.

N,N-Dimethyl-p-phenylenediamine Monohydrochloride: 0·5 g in 500 ml of 6N hydrochloric acid.

Potassium Iodate: Standard solution, 0·03N, containing 20 g of potassium iodide in 1 litre of water.

Sodium Hydroxide: 12 g in 100 ml of water.

Starch Solution: 1 g in 100 ml of water.

Zinc Acetate: 10 g in 1 litre of water.

Apparatus

See Fig. 1. The Westinghouse Electric Corporation will make and provide equipment of this type if required.

Preparation of standard curve

1. Dissolve 3·5–4·0 g of water-washed crystals of $Na_2S \cdot 9H_2O$ in about 500 ml of cooled freshly-boiled water.

2. Bubble gaseous nitrogen through the solution in a stoppered bottle for 15 min.

3. Store this solution under a slight nitrogen pressure.

4. Remove 2 ml of the sulphide solution through a serum stopper and place in a stoppered 250-ml flask containing 50 ml of cooled, freshly-boiled water.

5. Add 1 ml of starch solution and 10 ml of 6N HCl through a serum stopper.

6. Titrate without delay with the KIO_3 solution until a permanent blue colour is obtained.

7. Repeat steps 4, 5 and 6 until a constant value for the titre of the sulphide solution is obtained. (This solution is stable for 3 weeks under nitrogen.)

8. Prepare a dilute sulphide solution by transferring 3 ml of the standard solution to 497 ml of cooled, boiled distilled water, which has been flushed with nitrogen for 30 min. (This solution is stable for 3 days under nitrogen.)

9. Add 50 ml of the $Zn(C_2H_3O_2)_2$ solution and 2 ml of the NaOH solution to the absorption flask.

10. Add 0, 1, 2, 3, 4, 5, or 6 ml of the dilute sulphide solution to the absorption flask.

11. Add, through the serum stopper, 10 ml of N,N-dimethyl-p-phenylenediamine, and swirl until a clear solution is obtained. Temperature should be 24 ± 3°.

12. Add 2 ml of $FeCl_3$ solution through the serum stopper, shake vigorously for 5 sec and age for 15-20 min out of direct sunlight.

13. Transfer the solution to a 100-ml volumetric flask and dilute to volume.

14. Measure the optical density in 2-cm cells at 670 mμ versus water with a Beckman DU Spectrophotometer.

15. Plot results to obtain a standard curve.

16. For lower concentrations of sulphur prepare a similar curve using 10-cm cells.

Analysis of samples

1. Clean samples by swirling with benzene, then with acetone, then air dry.

2. Weigh a sample containing 2-35 μg of sulphur and place in a clean digestion flask.

3. Prepare the absorption flask by adding 50 ml of $Zn(C_2H_3O_2)_2$ solution and 2 ml of NaOH solution.

4. Assemble distillation apparatus and sweep system for 30 min at a moderate rate with nitrogen. Also outgas 50 ml of 6N hydrochloric acid with nitrogen for 30 min.

5. Admit water to the condenser, add the outgassed HCl to the reaction flask through the dropping funnel, close stop-cock, and increase the temperature gradually until the boiling point of the solution is reached. (Avoid excessive foaming by control of temperature.)

6. After the sample has dissolved completely, continue sweeping for 60 min. (Occasionally dark material of low density remains undissolved. This is primarily silicon, and may be neglected.)

7. Disconnect absorption flask, close exit tube, add 10 ml of N,N-dimethyl-p-phenylenediamine through the serum stopper and swirl until a clear solution is obtained. Temperature should be 24 ± 3°.

8. Add 2 ml of $FeCl_3$ solution through the serum stopper, shake vigorously for 5 sec, and age for 15-20 min out of direct sunlight.
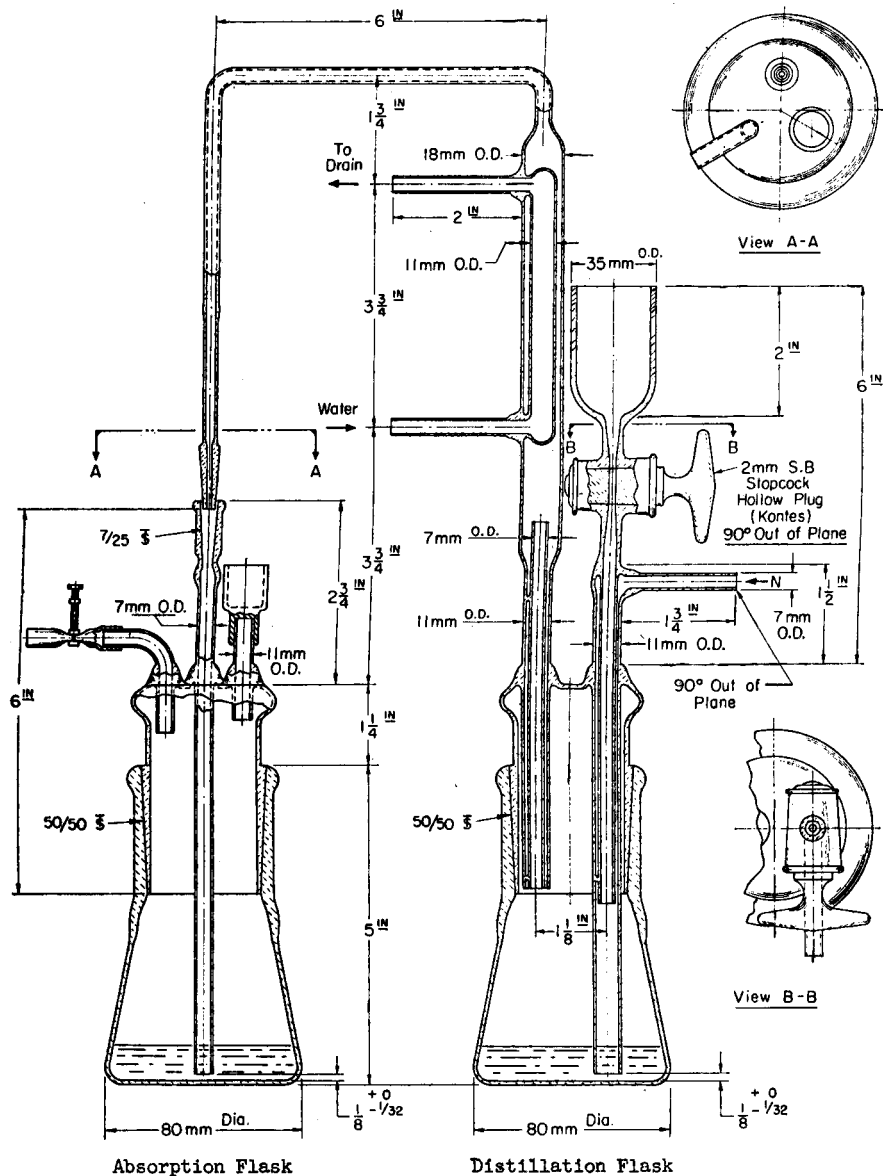
FIG. 1.—Sulphur distillation apparatus.

9. Transfer the solution to a 100-ml volumetric flask and dilute to volume.

10. Measure the optical density with a Beckman DU Spectrophotometer in 2-cm cells at 670 mμ versus water. Use 10-cm cells for low concentrations of sulphur.

11. Subtract optical density of a blank from observed optical density and compare with standard curve to obtain the weight of sulphur in the sample.

RESULTS AND DISCUSSION

Distillation technique

A study was made to determine if sulphur was lost during the solution and distillation phases of the procedure. A second receiver containing zinc acetate and

sodium hydroxide was connected to the first ·absorption flask and a sample containing 20 μg of sulphur was dissolved and distilled in the usual manner. No sulphur was detected in the second absorption flask. To determine if any sulphide sulphur was retained in the initial reaction vessel an iron-base alloy, doped with radiotracer ^{35}S, was dissolved in an oxidising medium, treated with a known amount of sulphuric acid, and then·with barium chloride to precipitate barium sulphate. This precipitate had a specific activity of 10,000 counts per min. A second portion of this alloy was dissolved with hydrochloric acid in the distillation apparatus and the hydrogen sulphide distilled in the normal manner. The residue in the reaction flask was then oxidised and treated with the same amount of sulphuric acid and barium chloride as the first sample. The specific activity of this precipitate was only 5 counts per min with the same counting geometry, thus demonstrating that only a negligible amount of sulphur remained undistilled.

Insoluble residue

Certain iron-silicon alloys did not dissolve completely in constant-boiling hydrochloric acid, but formed dark-coloured flakes of material in addition to the usual silica. This material gradually became translucent upon exposure to air and was identified as silicon metal. To ascertain if sulphur was retained by this material, or by the silica, several samples were treated with a few ml of hydrofluoric acid in addition to the hydrochloric acid usually used to dissolve these materials. The sulphur content of samples dissolved with hydrofluoric and hydrochloric acid combinations was found to be identical with that obtained for samples dissolved with hydrochloric acid alone.

Interferences

Gustafsson[4] has discussed the effect of traces of heavy metals on the determination of sulphur by the methylene blue procedure. We found that when water distilled from copper was used in reagent preparation, low results were obtained for small amounts of sulphur. This interference can be eliminated by using de-ionised water rather than distilled water for all reagents. The effect of distilled water is shown in Table I.

TABLE I.—THE EFFECT OF DISTILLED WATER ON THE
DETERMINATION OF SULPHUR

| | Concentration of sulphur, *ppm* | |
Sample No.	De-ionised water	Distilled water
356-299	2·6	0·3
8228-172-3	3·4, 3·3	1·1
8238-166-T	1·7	0·4, 0·4
379-295-8	3·1, 2·6	1·4

Accuracy

In the absence of satisfactory iron standards in the low sulphur range, an evaluation of the accuracy of the methylene blue method was made with the help of radiochemical measurements. An iron-base alloy was strip-annealed until it was virtually sulphur free. It was then treated with iron sulphide containing ^{35}S and annealed to ensure homogeneity. This master sample was analysed for sulphur by the methylene

blue technique, and in addition the specific activity was measured. Portions of the master sample were then strip-annealed under varying conditions to produce samples containing different concentrations of sulphur. By measuring the specific activity of the annealed samples, a totally independent check of the chemical method of analysis was made. Results are given in Table II.

TABLE II.—A COMPARISON OF SULPHUR RESULTS BY
RADIOCHEMICAL AND METHYLENE BLUE METHODS

	Concentration of sulphur, *ppm*	
Sample No.	Radiochemical	Methylene blue
Master alloy		21·4*
A	3·4	3·9, 3·8
B	6·1	6·1, 6·0
C	1·0	1·5, 1·5
X	0·29	0·48, 0·24, 0·38, 0·20, 0·27, 0·34
Y	0·07	0·39, 0·25

* This value was checked to within 1 ppm by combustion analysis.

The correlation coefficient between the two methods in Table II is 1·04, with a 95% Confidence Interval of 0·97–1·10 assuming no error in the radiochemical measurements. The actual confidence interval may be a bit larger since duplicate radiochemical determinations differed by about 10%.

Precision

Replicate results for a number of samples of iron-base alloys and manganese were obtained in order to ascertain the precision of the methylene blue method for sulphur when applied to these materials. Many of the samples were analysed by two chemists using different sets of apparatus in different laboratories. In most cases duplicate determinations were made on two or more days. Representative results are given in Table III.

TABLE III.—THE DETERMINATION OF SULPHUR IN MANGANESE AND IRON ALLOYS
BY METHYLENE BLUE METHOD

Sample	Concentration of sulphur, *ppm*	
Manganese-2	230, 225	
Manganese-1	132, 142	
Iron-2	23·8, 21·6, 20·2, 19·2, 21·9, 22·7	s = 1·7
Iron-5	11·1, 10·9, 11·1	
Iron-8	3·4, 3·4	
	Analyst A 0·9, 0·7, 0·8, 0·9, 0·9	
Iron-ASTM-No. G		s = 0·1
	Analyst B 0·7, 1·0, 0·9, 0·8, 0·8	

Zusammenfassung—Schwefel in Eisenlegierungen wird bestimmt durch Entwicklung von Schwefelwasserstoff. Letzterer wird mit N,N-dimethyl-p-phenylendiamin und Ferriion zur Reaktion gebracht und das gebildete Methylenblau spektrophotometrisch gemessen. Resultate für Schwefelgehalte von 0·3 bis 230 p.p.m. in säurelöslichen Metall-proben werden mitgeteilt. Die Genauigkeit der Methylenblaumethode wurde mittels einer Radiotracertechnik überprüft.

Résumé—Les auteurs dosent le soufre dans les alliages de fer par dégagement à l'état d'acide sulfhydrique, suivi d'une réaction avec la N,N-diméthyl-p-phénylènediamine et le fer ferrique pour former le bleu de méthylène; ce dernier est déterminé par spectrophotométrie. Des résultats sont donnés pour des échantillons métalliques solubles dans les acides contenant 0,3 à 230 p.p.m. de soufre. Les auteurs ont évalué la précision de la méthode à l'aide de traceurs radioactifs.

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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—VIII*

THE CHLORAMINE-T—THALLIUM[I] AND —THIOCYANATE REACTIONS AND SOME FURTHER APPLICATIONS EMPLOYING EXCESS OF REAGENT

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Summary—Direct oxidation of thallium[I] in chloride or bromide media at acid concentrations of 0.05 to 3.0M is too slow to permit the use of visual indicators, and potentiometric titration reveals large positive errors. Double excess back titration following oxidation in acid chloride or bromide media gives excellent results provided the excess of oxidant is limited to 0·5 ml; oxidation in the absence of bromide is preferred. No satisfactory procedure for the determination of thiocyanate other than that previously advocated[4] could be devised. Reactions with hydrazine and thiosulphate give poor results, oxidation of nitrite is unsatisfactory, and hydroxylamine and vanadium[IV] are not oxidised.

Examples of reactions involving excess of oxidant have been examined. Determination of sulphite in which chloramine-T is used quantitatively to liberate an excess of iodine is satisfactory. Determination of 8-hydroxyquinoline and of metals precipitated as oxinates by double excess back titration in which chloramine-T is used for the quantitative generation of bromine affords excellent results. Hexacyanoferrate(II) cannot be directly titrated, but determination by double excess back titration is possible, although the results are of poor accuracy.

DIRECT titrations with chloramine-T of thallium[I] in "dilute" hydrochloric acid in the presence of "excess" potassium bromide using methyl orange as indicator,[2] and in 0·07 to 0·7M hydrochloric acid in a bromide concentration of 1·4M by the potentiometric method[3] have been reported. A precision of about 1 % was achieved. Titration in 3–5M hydrochloric acid with the aid of iodine monochloride as a reaction intermediate has already been scrutinised.[4] Titration in iodide media is not possible, because thallium[III] oxidises iodide. Reactions in chloride and bromide media have been critically examined, and reaction conditions established in the present study.

Thiocyanate has been determined with chloramine-T by the tedious and rather imprecise method of addition of an excess of reagent to the thiocyanate in bicarbonate buffer, standing for 4 hr, addition of excess iodide, acidification with hydrochloric acid, and titration of the liberated iodine with thiosulphate.[5] Thiocyanate has also been titrated potentiometrically in neutral or dilute boric acid solution at an elevated temperature.[6] A careful examination of the titration in 3–5M hydrochloric acid using iodine monochloride as a reaction intermediate has already been reported.[4] This gives excellent and highly accurate results, and is the only satisfactory method for determination of thiocyanate with chloramine-T.

A considerable number of other reactions have been critically examined during the course of the present investigation. In many cases chloramine-T has proved convenient and accurate in use, and three typical examples of different modes of employment are given in illustration: one (sulphite) wherein chloramine-T is used for quantitative generation of iodine which is the active oxidant; one (oxine) of quantitative bromination in which chloramine-T is substituted for bromate; and one [hexacyanoferrate(II)] using chloramine-T as a substitute for cerium^{IV}. In others, e.g. hydroquinone, iron^{II}, no significant advance on previous work can be offered. The investigation of the iron^{II} reaction, for instance, substantially confirms the work of Poethke and Wolf.[7]

Certain reactions proved unprofitable.[8] Hydrazine gives inaccurate and unreproducible results,[1] though the reaction is utilisable in routine analysis. A similar marked divergence from the behaviour of bromate occurs in the failure of chloramine-T to oxidise hydroxylamine in bromide media even with the aid of molybdenum catalysts. Nor does chloramine-T oxidise vanadium^{IV}, although it will oxidise vanadium^{III}. The reaction with nitrite is unsatisfactory. Although under suitable conditions chloramine-T oxidises thiosulphate substantially to sulphate, and the reaction, like that with hydrazine, can be employed in routine work,[9] a side reaction producing the oxidation resistant tetrathionate ion results in a reaction deficiency of about 2%,[10,11] causing errors of about 0·2 to 0·5%. The oxidation of xanthate sulphur to sulphate, and the determination of xanthates and through them carbon disulphide, is likewise of a lower order of precision,[12] but has been found useful in agreement with Murthy's claims.[13,14]

EXPERIMENTAL

Apparatus and Reagents

The preparation and standardisation of solutions of chloramine-T,[15] arsenic^{III},[15] thallium^{I}[4] and thiocyanate[4] have been described. Indicators[16] and other reagents[17] and the quantitative and titrimetric apparatus and reagents[15] have been specified. The following reagents are additional to those previously used.

8-*hydroxyquinoline*: A 0·025M solution was prepared by dissolving 7·258 g of the AnalaR solid in 10 ml of AnalaR hydrochloric acid and dilution to 2 litres. The solution was standardised against primary standard 0·01667M potassium bromate.[18,19] A 10–20% excess of bromate solution is added to a 20-ml aliquot of oxine solution in a titration bottle to which has been added 10 ml of 1·0M potassium bromide and 10 ml of hydrochloric acid. After thorough mixing, a 10-ml aliquot of primary standard 0·05M arsenic^{III} solution is added and the excess back titrated with bromate using 1 ml of 0·1% α-naphthoflavone[18] or 0·3 ml of 0·1% rosaniline hydrochloride[19] as indicator (factor: 0·9987, 0·9997, 0·9990).

Potassium hexacyanoferrate(II): A 0·1M solution was prepared from the AnalaR trihydrate in water containing 0·04% of AnalaR sodium carbonate, and standardised by titration in 0·5M sulphuric acid with standard 0·1M cerate^{IV} solution using o-phenanthroline-iron^{II} sulphate as indicator[20] (factor: 1·1096, 1·110, 1·110).

Cerium^{IV}: An approximately 0·1M solution prepared from AnalaR ammonium hexanitratocerate (IV) in 0·5M sulphuric acid by the method of Smith,[21] and standardised against primary standard 0·05M arsenic^{III} solution in 0·5M sulphuric acid using osmic acid (3 drops of 0·01M) as catalyst and o-phenanthroline-iron^{II} sulphate as indicator.[22]

Sodium sulphite: An approximately 0·03M solution prepared from the AnalaR heptahydrate. The solution was standardised against primary standard 0·025M potassium iodate through 0·1M thiosulphate standardised[15] against the same iodate solution. An aliquot of the iodate solution is treated with an excess of iodide and acidified to 2·0M with hydrochloric acid. An aliquot of the sulphite solution is pipetted into this solution, and the excess iodine back titrated with thiosulphate[23] (factor: 0·0303, 0·0303, 0·0303).

Procedure

The techniques of potentiometric[15,17] and visual indicator[15] titration have been described. For thallium and thiocyanate equivalence point volumes of 200 ml for potentiometric and 100 ml for

visual indicator titrations were used, due allowance being made for washings, and the concentrations specified are referred to the equivalence point. Details of the other techniques are as follows.

Double excess back titration

This technique has been mentioned[15,17] and employed in various titrimetric processes.[8,19] It is useful for reactions which are too slow to allow direct titration, but which can be made quantitative by the use of an excess of the initial titrant. It consists in the addition of an excess of the initial titrant *A* followed after the appropriate reaction interval by an excess of a second reagent *B* and titration of the second excess by means of the initial titrant *A*. Reagent *B* is chosen to react rapidly and so be directly titratable with *A*. This has the advantages of employing only one standard solution, of a single filling of a single burette with *A*, and of allowing the addition of a regulated amount of *A*, such as 23 or 27 ml which is not readily measurable by pipette, and which, moreover, need not be accurately measured because the same burette-full is to be used in completing the titration. If the standard solution is *A*, then the titre of the amount of *B* added can be determined by blank titration of an amount of *B* similar to that used in the determination; when *B* is also a standard solution, the titre may be calculated directly. The consumption of *A* by the substance to be determined is calculated by subtraction of the titre of *B* from the total consumption of *A*. If the standard solution is *B*, then a similar process affords a standardisation of *A* contiguous with the determination, a process occasionally convenient for use with titrants of poor stability.

This technique has frequently been of value with chloramine-T and is illustrated in the determination of thallium[1], 8-hydroxyquinoline and metal oxinates [method (a)] and hexacyanoferrate(II). Single excess back titration is illustrated in the determination of sulphite and 8-hydroxyquinoline [method (b)].

Determination of sulphite

Transfer to a titration bottle an aliquot of standard chloramine-T solution equivalent to about twice the amount of sulphite to be determined. Add 100 ml of water, 5 ml of $2M$ hydrochloric acid and 1 g of potassium iodide. Add an aliquot of the sulphite solution (discharge of the pipette in the normal fashion caused no significant error, so that delivery of the solution with the pipette tip immersed in the iodine solution is unnecessary), stopper the bottle, shake and allow to stand for 1 min. Remove and rinse the stopper, and titrate the excess iodine with standard thiosulphate solution, adding 2 ml of 1% starch solution as indicator near the end-point.

Determination of 8-hydroxyquinoline

Transfer to a titration bottle an aliquot of oxine solution (20 ml of $0.025M$) or a solution of the metal oxinate precipitate in hydrochloric acid. Add 10 ml of $10M$ hydrochloric acid (less the amount used to dissolve the precipitate) and 1 g of potassium bromide. Add from a burette a 15% excess (23 ml) of standard chloramine-T, stopper the bottle, shake and allow to stand for 5 min. Determine the excess of bromine by either of the following methods:

(a) *Double excess back titration.* Add an excess (10 ml of $0.05M$) of standard arsenic[III] solution and a further 5 ml of $10M$ hydrochloric acid. Titrate the excess arsenic[III] with the chloramine-T remaining in the burette. Use 1 ml of 0.1% α-naphthoflavone added about 1 ml before the equivalence point, or 0.2 ml of 0.1% p-ethoxychrysoïdine as indicator. Determine the arsenic blank under the same conditions.

(b) *Single excess back titration with thiosulphate.* Add 2 g of potassium iodide and back titrate the liberated iodine with standard thiosulphate solution using starch as indicator.

Determination of hexacyanoferrate(II)

Double excess back titration with chloramine-T and arsenic[III]. Transfer an aliquot (20 ml of $0.1M$) of hexacyanoferrate(II) solution to a titration bottle, add 2 ml of $2M$ hydrochloric acid and run in a 50% excess (30 ml of $0.05M$) of standard chloramine-T solution from a burette. Stopper, shake and allow to stand for 10 min. Add an aliquot of standard arsenic[III] solution in excess of the excess of oxidant, 15 ml of $10M$ hydrochloric acid and 1 g of potassium bromide. Titrate the excess of arsenic[III] with the chloramine-T remaining in the burette, using 0.2 ml of 0.1% methyl orange added 1 ml before the equivalence point as indicator. Determine the arsenic blank under the same conditions.

RESULTS AND DISCUSSION

Determination of thallium[I]

Thallium[I] may be accurately determined by titration with bromate[24] in a hydrochloric acid medium with or without the addition of bromide or by the Andrews procedure with iodate.[25,26] In the presence of chloride or bromide, thallium[I] chloride

or bromide is precipitated and reacts only slowly with chloramine-T. The use of colour indicators such as methyl orange[2] and bordeaux has, therefore, proved impracticable in direct titration. Potentiometric titration has been investigated under a variety of conditions.
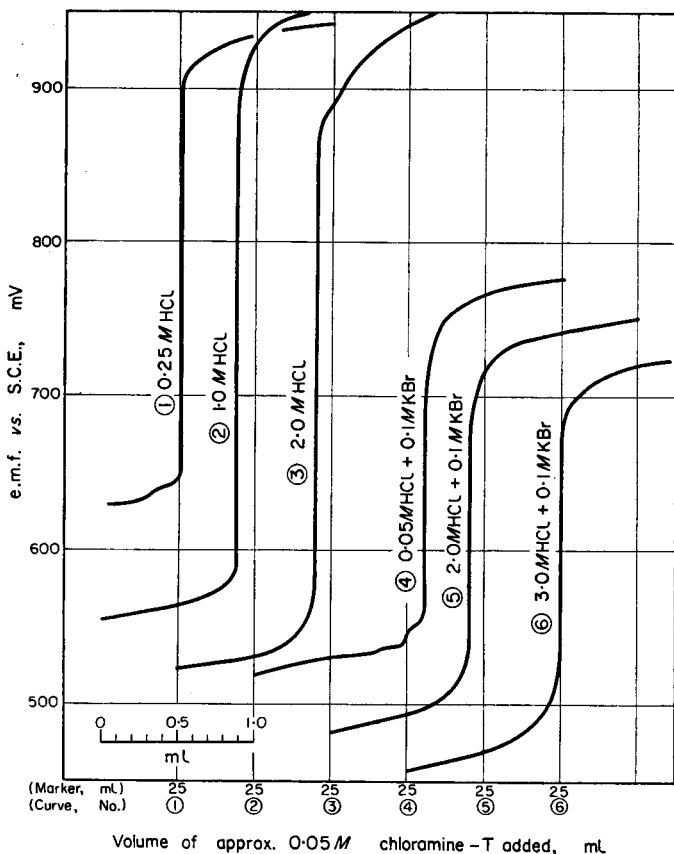
FIG. 1.—Direct titration of 25-ml aliquots of approx. $5 \times 10^{-2}M$ thallium[I] at an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

TABLE I—POTENTIOMETRIC TITRATION OF
THALLIUM[1] WITH CHLORAMINE-T IN
VARIOUS MEDIA

Concentration, M		End-point,	Error
HCl	KBr	ml	%
0·25	—	25·02	+0·81
1·0	—	24·87	+0·20
2·0	—	24·89	+0·28
0·05	0·1	25·12	+1·21
2·0	0·1	24·91	+0·36
3·0	0·1	24·98	+0·65

Calculated equivalence point: 24·82 ml.

(a) *Potentiometric titration in hydrochloric acid.* The curves are shown in Fig. 1, and give large and sharp breaks in potential, but the results given in Table I are all high. The reaction was slow in all titrations, though the potentials were steady in 1 and 2M acid before the end-point. In 0·25M acid the potentials were unstable. After the end-point in all titrations the potentials became steady.

(b) *Potentiometric titration in hydrochloric acid containing potassium bromide.* The effect of an equivalence point concentration of 0·1M bromide was examined at hydrochloric acid concentrations from 0·05 to 3·0M.

In acid concentrations of 0·05 to 1·0M, the reaction was too slow to be analytically useful. However, since reaction at low acid concentrations has been advocated,[3] a titration was conducted in 0·05M acid, in which the chloramine-T was added rapidly up to within 1 ml of equivalence, ignoring the production of a large temporary excess of volatile bromine which slowly reacted with the precipitate. The accuracy attained by this method was comparable to that previously claimed,[3] but was inferior to that achieved in higher acid concentrations. In 2–3M acid the reaction was sufficiently fast to permit titration in the normal manner. The potential changes are large and sharp (Fig. 1), but the results are still high. Potentials were steady before the end-point and equilibrated rapidly thereafter.

Direct titration in hydrochloric acid solution, with or without the addition of bromide, is subject to errors of at least +0·2% and cannot, therefore, be recommended.

Determination with chloramine-T by the Andrews procedure has, however, proved to give excellent results,[4] under the proper conditions.

Since direct titration proved inaccurate, oxidation with excess of chloramine-T followed by determination of the excess of oxidant and hence the net consumption of oxidant by thallium[I] was examined under a variety of conditions by the double excess back titration method (*vide supra*). Oxidations in the presence and absence of bromide were compared and the amount of excess oxidant, the acid concentration and the time of oxidation were investigated.

(c) *Oxidation in hydrochloric acid.* A variable amount of 10M hydrochloric acid with water to make an oxidation volume of 100 ml was added to an aliquot of the thallium solution in a titration bottle followed by a variable excess of chloramine-T, the bottle stoppered, shaken and allowed to stand for 1–5 min. Then 10 ml of standard arsenic[III] solution and 10 ml of 1M potassium bromide were added and the titration completed in an equivalence point volume of 150 ml with chloramine-T using rosaniline as indicator.[15,16] The results in Table II indicate that in 1–2M acid, with an excess of 0·5–1·0 ml of oxidant and a reaction time of 1 min or more, the method gives errors of less than 0·1%, which is as good as the preferred method.[4]

(d) *Oxidation in hydrochloric acid at a bromide concentration of* 0·1M. The method is similar to the previous one, except that the bromide (10 ml of 1·0M) is added along with the hydrochloric acid. With an excess of 0·3 to 0·5 ml of oxidant in 1–2M acid and a reaction time of at least 1 min, the results (Table II) are equally as good as the previous ones, but with a greater excess of oxidant, the positive errors increase rapidly.

The double excess back titration procedure is, therefore, capable of giving results of an accuracy of 0·05%, and is recommended for this determination. Though there is little to choose between the alternative methods under the proper conditions, initial oxidation in the absence of bromide is preferred. This reaction affords yet

another instance of the failure of chloramine-T as a substitute for bromate in direct titration.[15,24]

Determination of thiocyanate

Though it is possible that the methods noticed above involving prolonged action of excess oxidant in bicarbonate buffer[5] or potentiometric titration at elevated temperature[6] may give acceptable results, neither is convenient. Attempted titrations with chloramine-T in hydrochloric acid of various concentrations, with or without the addition of bromide were unsuccessful because of the slowness of the reaction. Reaction with excess of oxidant under similar conditions followed by a double excess back titration or a single excess back titration were equally unsuccessful, with reaction times of up to 30 min. In view of the excellent results achieved in 3–5M hydrochloric acid in the presence of iodine monochloride for both potentiometric and visual indicator titrations with chloramine-T,[4] other methods were not pursued.

TABLE II—DETERMINATION OF THALLIUM[I] WITH CHLORAMINE-T BY DOUBLE
EXCESS BACK TITRATION

Excess of chloramine-T added, ml	Volume of 10M HCl used, ml	Period of standing, min	Total titration, ml	Chloramine-T equivalent to Tl[I], ml	Error %
Method (a)					
0·5	10	1	34·83	24·83	+0·04
0·5	10	5	34·84	24·84	+0·08
1·0	10	1	34·84	24·84	+0·08
0·5	20	1	34·83	24·83	+0·04
0·7	15	3	34·83	24·83	+0·04
Method (b)					
0·3	10	1	34·83	24·83	+0·04
0·5	10	1	34·84	24·84	+0·08
0·5	10	5	34·84	24·84	+0·08
0·5	20	1	34·83	24·83	+0·04
0·8	10	1	34·86	24·86	+0·16
1·0	10	1	34·88	24·88	+0·24

Chloramine-T titre of arsenic[III] solution added: 10·0 ml; calculated total titration volume: 34·82; calculated titre of thallium[I] solution: 24·82 ml.

Determination of sulphite

It is not possible to determine sulphite by direct titration in acid solution because both the volatility of sulphur dioxide and the direct and induced air oxidation of sulphite lead to low results. Chloramine-T proved no exception. Similar errors in lesser degree arise on rapid addition of excess oxidant to the sulphite solution prior to back titration of the excess. Errors are minimised by the addition of the neutral sulphite to an excess of oxidant, acidified if necessary before or after the addition.

Such a method proved very satisfactory with chloramine-T, used to liberate an excess of iodine from an acidified iodide solution, the excess being back titrated with thiosulphate as described above. The results for the factor of a sulphite solution (0·0303, 0·0303, 0·0303M) compare favourably with the parallel method[23] using standard iodate.

Determination of 8-hydroxyquinoline and of metal oxinates

The use of standard bromate quantitatively to generate known amounts of free bromine from acidified bromide solutions for the quantitative bromination of aromatic amino and hydroxy compounds is well known. The use of chloramine-T as a replacement for bromate in similar reactions has been investigated and has been found successful. The conditions and procedure are similar to those employed for

TABLE III—TITRATION OF 8-HYDROXYQUINOLINE
WITH CHLORAMINE-T

Method	Indicator	Factor	Error, %
(a)	α-naphthoflavone	1·000	+0·09
(a)	p-ethoxychrysoïdine	0·9995	+0·04
		1·0005	+0·14
(b)	starch	1·000	+0·09
		1·000	+0·09
		1·001	+0·19
		1·000	+0·09

Factor of the 0·025M 8-hydroxyquinoline by bromate titration: 0·9991.

TABLE IV—DETERMINATION* OF METALS BY
PRECIPITATION OF THE METAL OXINATE
FOLLOWED BY TITRATION OF THE OXINE BY
METHOD (a) USING ROSANILINE AS INDICATOR

Metal	Taken, mg	Found, mg	Error, %
Zn	16·00	15·91	−0·56
	16·00	15·93	−0·44
	4·00	4·01	+0·25
	4·00	4·02	+0·50
Co	15·00	14·96	−0·27
	15·00	15·06	+0·40
	3·75	3·78	+0·80
	3·75	3·76	+0·27
Al	4·50	4·56	+1·33
	4·50	4·51	+0·22
	1·125	1·13	+0·44
	1·125	1·12	−0·44

* Determinations made by first year undergraduate students in E.B.'s laboratories.

bromate. As an example, the doubly useful determination of oxine and its metal complexes is given in illustration.

Bromination of oxine proved to be too slow to permit direct titration, even with the reversible indicator α-naphthoflavone, so that a double excess back titration procedure [method (a) above] using arsenic[III] to remove the initial excess of bromine,[19] and a single excess procedure [method (b) above] using iodide and thiosulphate were examined. Both methods give excellent results in good agreement with the bromate results, as shown in Table III.

A number of metals were precipitated as oxinates by established procedures, the washed precipitates dissolved in hydrochloric acid and the equivalent oxine titrated

by method (a) using rosaniline as indicator for the final titration. The results obtained by undergraduate students were satisfactory as shown in Table IV.

Oxine and its metal complexes can, therefore, be determined accurately by bromination using chloramine-T in place of bromate. A preference for the double excess back titration procedure is expressed.

Determination of hexacyanoferrate(II)

Again, direct titration proved to be too slow to permit the use of visual indicators, so that the double excess back titration procedure was investigated. By the method described above, values for the factor of a $0.1M$ hexacyanoferrate(II) solution of 1·105, 1·105 and 1·105 were obtained, showing an error of -0.5% with respect to the figures given by direct titration with cerium[IV]. Though the reproducibility (precision) is good, the accuracy is poor, and the method has little to recommend it other than economy in the expense of the reagent used.

Zusammenfassung—Die direkte Oxydation von Thallium(I) in chlorid- oder bromidhaltiger Lösung bei Säurekonzentration von 0·05 bis 3·0 m ist zu langsam um die Verwendung visueller Indicatoren zu gestatten und die potentiometrische Anzeige gibt stark positive Fehler. Eine der Oxydation folgende doppelte Rücktitration gibt ausgezeichnete Ergebnisse, wenn darauf geachtet wird, dass der Überschuss an Oxydans 0·5 ml nicht überschreitet; Oxydation in Abwesenheit von Bromid wird vorgezogen. Keine andere Methode zur Bestimmung von Thiocyanate als die bereits früher vorgeschlagene[4] kann empfohlen werden. Die Reaktion mit Hydrazin und Thiosulfat gibt schlechte Resultate, die Oxydation von Nitrit verläuft nicht zufriedenstellend und Hydroxylamin und Vanadin(IV) werden nicht oxydiert.

Beispiele, bei denen Überschuss an Oxydans angewendet wurde, wurden studiert. Die Bestimmung von Sulfit, bei der Chloramin-T angewandt wird um quantitativ einen Überschuss von Jod zu erzeugen, verläuft zufriedenstellend. Die Bestimmung von Metallen über-ihre Oxinate mittels doppelter Rücktitration gibt hervorragende Resultate (Chloramin T wird zur quantitativen Erzeugung von Brom verwendet). Ferrocyanid kann nicht direkt titriert werden. Bestimmung mittels doppelter Rücktitration ist möglich, doch sind die Resultate nicht sonderlich gut.

Résumé—L'oxydation directe du thallium(I) en milieu chlorure ou bromure à des concentrations d'acide de 0,05 à 3,0 M est trop lente pour permettre l'utilisation d'indicateurs visuels, et le titrage potentiométrique révèle de grandes erreurs positives. Le titrage en retour-d'un double excès suivant l'oxydation en milieu acide, chlorure ou bromure donne d'excellents résultats à condition que l'excès d'oxydant soit limité à 0,5 ml; l'oxydation en l'absence de bromure est préférée. Aucune méthode satisfaisante, pour le dosage du thiocyanate, autre que celle qui a été recommandée antérieurement (4) ne pourrait être imaginée. Les réactions avec l'hydrazine et le thiosulfate donnent de mauvais résultats, l'oxydation du nitrite n'est pas satisfaisante, l'hydroxylamine et le vanadium(IV) ne sont pas oxydés.

Des exemples de réactions mettant en jeu un excès d'oxydant ont été examinés. Le dosage du sulfite, dans lequel la chloramine T est utilisée pour libérer quantitativement un excès d'iode, est satisfaisant. Le dosage de 8-hydroxyquinoléine et de métaux précipités à l'état d'oxinates, par titrage en retour d'un double excès, dans lequel la chloramine T est utilisée pour la production quantitative de brome, donne d'excellents résultats. Le ferrocyanure ne peut être titré directement, mais le dosage par titrage en retour est possible, bien que les résultats aient une mauvaise précision.

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STUDIES ON URONIC ACID MATERIALS—V*

THE THERMAL DECARBOXYLATION METHOD OF ANALYSIS

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Summary—The thermal decarboxylation method of determining uronic acids, proposed by Perlin, has been investigated. A specially designed oven, having good temperature stability, enabled the thermal decomposition of various compounds to be studied kinetically, with good reproducibility. Comparatively large errors can arise in the determination of the carbon dioxide evolved; these errors originate in the nature of the other volatile reaction products. Typical results are presented, and it is concluded that thermal decarboxylation does not compare favourably with the 150-min acid decarboxylation as a general analytical method.

VARIOUS aspects of the acid decarboxylation of uronic acid groups have been investigated[1,2,3] in attempts to improve the accuracy and reliability of this analytical reaction,[4] which is important in carbohydrate chemistry. The formation of potentially acidic vapours, such as methyl chloride and methyl formate, gives a source of error; a knowledge of these products is also important in studies of the reaction mechanism. A comprehensive study[5] was therefore made of the volatile reaction products from some 80 carbohydrate materials and related compounds: a vapour-phase infrared method[6] showed that the products included furan, 2-methylfuran, acetone, methylethylketone, diethylketone, acetaldehyde, propionaldehyde, chloral, methyl formate, methyl chloride and dimethylformal, although not all of these are formed from any one sugar residue. Acetone was known to be an acid decomposition product of rhamnose[7] and other sugars,[8] but the formation of some of the other compounds was unexpected. They have, however, been found subsequently[9] as products of the thermal decomposition of various carbohydrate materials. Under other experimental conditions the formation of other volatiles has also been reported, e.g., methyl glyoxal, acetol and diacetyl from reducing sugars,[10] maltol and isomaltol[11] from the pyrolysis of starch.

There have been many studies of the formation of pyrodextrins[12,13] and the production of volatile organic compounds during thermal decomposition is, of course, well known[14] (cf. ref. 9). This formation of organic vapours by chemical reaction must be distinguished from the desorption of physically retained organic solvents. Although the latter effect has long been recognised,[15] and further examples continue to be reported,[16] it is now known[17] that solvent-retention continues up to the temperature at which the carbohydrate concerned begins to decompose. A knowledge of the pretreatment of the sample is therefore important in thermal decomposition studies.

Differential thermal analysis has been applied to starches[18] and other polysaccharides;[19] it has been suggested that decarboxylation causes a small endothermic

*Part IV: D. M. W. Anderson, A. M. Bews, S. Garbutt and N. J. King, J. Chem. Soc., 1961, 5230.

reaction observed for uronic acid materials at 145–155°. Although these temperatures are only slightly higher than those at which carbohydrate decomposition was observed to begin,[17] they are some 100° lower than the decomposition temperatures proposed for the thermal decarboxylation method[20] of estimating uronic acids.

Since it appeared that Perlin's method[20] has not been widely adopted or studied further (*cf.* ref. 20), an examination of its applicability appeared to be a logical extension of our studies. This paper presents some results which show that thermal decarboxylation is inferior, for several practical reasons, to the acid decarboxylation reaction as a quantitative method[2,3] for the analysis of uronic acid contents.

EXPERIMENTAL

Design of apparatus

In Perlin's experiments,[20] the method of heating involved the refluxing of vapours. Whilst this method offers the advantage that over-heating cannot possibly occur, it is restrictive, since a continuous range of temperatures cannot be studied. Moreover, the absolute reaction temperature could not be established:[20] the reaction conditions are critical[13] in this type of investigation.

Preliminary investigations[5] revealed that careful experimental design would be required to give minimum temperature equilibration times with run-to-run reproducibility at absolute temperatures. Successive refinements with different designs of apparatus showed that, after the required stability of oven temperature was achieved, the following factors were also critical: (a) stabilisation of rate of flow-gas, (b) pre-heating of flow-gas to the required reaction temperature, (c) reproducible location of samples at the same position within the oven, (d) measurement of the actual sample temperature during the decomposition.

The apparatus finally satisfying all these requirements is represented diagramatically in Fig. 1. With its use, the rate of decomposition of a particular sample was reproducible to within ±2%.
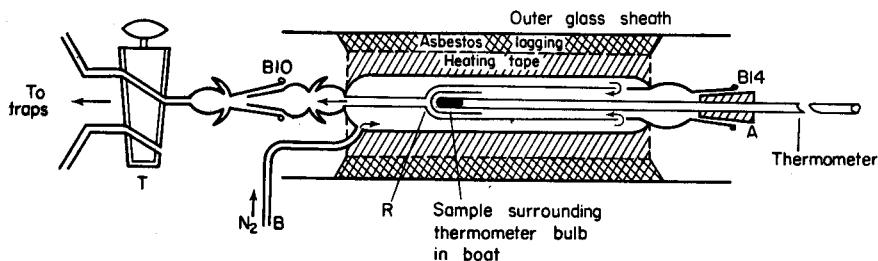
FIG. 1.—Construction of thermal decomposition apparatus.

Constructional details: The internal dimensions are a function of the size and shape of the sample-boat which, in turn, is dictated by the weight of sample necessary for the production of suitable quantities of carbon dioxide. Suitable sample weights were 30 mg for uronic acids and polyuronides, 100 mg for non-uronides. The boat must be sufficiently deep to contain the increased volume occupied by the samples upon decomposition: porcelain boats, 35 × 12 × 6 mm, were suitable.

By grinding off one end (the "hook" end) of a boat, a form of long-handled weighing-spoon was made, with a thermometer, bound to the boat by several turns of platinum wire, acting as the handle: samples were added carefully so as to surround the mercury bulb. A tightly-fitting rubber stopper was positioned on the thermometer stem at a part of the scale where readings were not required. The position chosen dictated the effective length of the "weighing spoon" handle; the constriction in the bore of the oven was positioned during manufacture so as to provide a locating device against which samples could be positioned centrally and reproducibly within the oven at its hottest part.

Heating: The external dimensions of the oven, 17 cm × 2.3 cm, were chosen so that its whole surface could be wound with a heating tape, 30″ long, 1″ broad ("Electrothermal" type HT 350). The heating tape was lagged with a layer of asbestos tape, and enclosed within an open-ended tightly-fitting glass sleeve, 25 cm long and 4 cm in diameter, which enclosed the whole assembly from A to B. Temperatures could be varied within the range 140–300° by adjustment of the Variac which supplied the continuous heating voltage. For particular temperatures, long- and short-period temperature variation did not exceed ±1° after several hours had been allowed for the establishment of equilibrium conditions.

Flow-gas: Cylinder nitrogen ("N.O.F." grade), dried and freed of traces of carbon dioxide by passage through scrubbing towers, was used. The flow-rate was established at 15 ml per min by means of two needle valves, a capillary-tube buffer system, and a calibrated Rotameter. For some experiments, residual traces of oxygen (approx. 20 ppm) in the cylinder gas were also removed by passage through a "Nilox" purifier (Southern Instruments Ltd.). Inclusion of the nitrogen inlet system within the jacketed heating assembly ensured that the flow-gas was correctly pre-heated.

Use of apparatus

Determination of the carbon dioxide evolved: Kinetic measurements were facilitated by a two-way stop-cock system and matched pairs of traps, as described.[21] Determinations were made (a) titrimetrically using a titration-cell designed[2] for carbon dioxide titrations, (b) gravimetrically, using conventional analytical adsorption tubes, (c) by infrared spectroscopy,[6] using the manometric calibration method.

Use of sulphuric acid bubblers: In some experiments, as indicated below, the gas-stream from the oven was led through a conventional gas-bubbler before determination of the carbon dioxide.

Detection of carbon monoxide: Standard colorimetric reactions[22] were used. The molybdenum blue method could not be used when sulphur dioxide was also present (cf. ref. 22, p. 347), and the palladous chloride method was therefore employed.

Identification of the volatile products: For each compound studied separate runs, using samples of 500 mg, were made so that the volatile products (before and after passage through the sulphuric acid bubbler) could be trapped in liquid nitrogen[23] and subsequently examined by the vapour-phase infrared technique.[6] (Cf. ref. 17).

Procedure: With the nitrogen flow-rate stabilised at 15 ml per min and with a thermometer-handled weighing-spoon in position, the oven temperature was allowed to equilibrate (usually overnight) at the required temperature. The weighing-spoon was withdrawn and allowed to cool, stop-cock T (Fig. 1) being closed so that the flow of nitrogen, emerging at A, prevented air from entering the oven. The sample, weighed by transfer from a suitable weighing-scoop, was added to the thermometer-spoon so as to surround the thermometer-bulb. The thermometer-spoon was replaced carefully in the oven, and stop-cock T opened. Preliminary experiments with water had established the internal volume (V ml) of the system from restriction R to T; $V/15$ min after opening T was taken as the zero-time for the kinetics. The sample reached the pre-established equilibrium temperature of the oven after about 5 min (cf. ref. 20). Thus results quoted below for "20 min at 255°" are, in effect, for 5 min heating over the range 0–255° + 15 min heating at 255°.

Origin of samples

The samples of glucurone and galacturonic acid monohydrate had 97% and 96% purity, respectively, by acid decarboxylation,[3] and have been described.[21] The alginic acid, pectic acid and pectin were commercial samples, for which acid decarboxylation[3] gave 79%, 61% and 57% respectively: the pectic acid and pectin contained 0.1% and 6.5%, of methoxyl, respectively. The sample of *Acacia seyal*[24] gum contained 12% of glucuronic acid, and 1% of methoxyl.

The non-uronic samples studied were of commercial origin and were chromatographically pure.

RESULTS AND DISCUSSION

1. Uronic acids and polyuronides

Fig. 2 (dotted curves) shows the results obtained titrimetrically for decomposition at 255°; for temperatures between 255° and 280° the initial rate of evolution of carbon dioxide was faster, but the curves levelled off more quickly, so that the total yields were not significantly greater. Above 280°, however, the decomposition mechanism apparently changes, since the yields of carbon dioxide were considerably increased. Thus, after decomposition for 1 hr at 300°, titrimetric determinations indicated apparent uronic acid contents of 96%, 107% and 87% for glucurone, galacturonic acid and alginic acid respectively.

The titrimetric values for the yield and rate of evolution of carbon dioxide at 255° were much less than were reported by Perlin.[20] The experiments were therefore repeated, the carbon dioxide being determined gravimetrically. The apparent yields of carbon dioxide, as shown in Fig. 2 (full lines) agreed much more closely with Perlin's

values, the acid decarboxylation values for galacturonic acid and alginic acid—but not for glucurone—now being attained in approx. 20 min. Reasons for the large discrepancy between the titrimetric and gravimetric results had therefore to be found.

Investigation of the volatile reaction products: Carbon monoxide was detected colorimetrically, in agreement with Perlin.[20] Vapour-phase infrared spectroscopy showed that, after removal of carbon dioxide and water, the volatile products included acetone and other carbonyl compounds. Although these were formed in considerable quantity (*cf.* Perlin's "distillable oils") they were evidently of low volatility and their identification lay outside the applicability of the vapour-phase spectroscopic method.
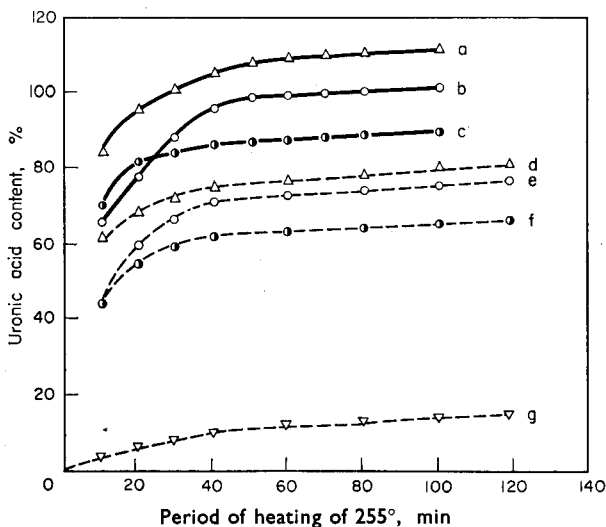
FIG. 2.—Rate of evolution of carbon dioxide from uronic compounds at 255°

Curve (*a*) galacturonic acid ⎫
     (*b*) glucurone   ⎬ gravimetric determination
     (*c*) alginic acid   ⎭   of carbon dioxide

Curve (*d*) galacturonic acid ⎫
     (*e*) glucurone   ⎪ titrimetric detetermination
     (*f*) alginic acid   ⎬   of carbon dioxide
     (*g*) *Acacia seyal* gum ⎭

When these reaction products were passed through a sulphuric acid bubbler, spectroscopy showed that although the carbonyl compounds had been removed, sulphur dioxide and increased quantities of carbon monoxide, together with traces of carbon dioxide, were now present in the carrier-gas emerging from the bubbler. Evolution of these acidic gases continued for several hours after the end of a run. The thermal decomposition products must therefore include significant quantities of formic acid and other organic acids (*cf.* ref. 22, p. 347).

Infrared estimations of the amounts of carbon dioxide present in the mixture of acidic decomposition products indicated that direct titrimetric determinations gave the most reliable estimation of the actual carbon dioxide content. Titrimetric results are considerably higher if a sulphuric acid bubbler is used, as shown in Table I; the increased apparent uronic acid content results from the acidic gases evolved from the scrubber.

Fig. 1 also shows the corresponding figures for gravimetric determinations. Without a sulphuric acid bubbler, the result is virtually the total of all the volatile products: insertion of the bubbler gives lower results, which, however, are still high as a result of the acidic vapours released from the bubbler. A measure of these is given in Table I, column (c). When this is applied as a correction to column (e), the values expressed in columns (a) and (f) are, for experiments of this kind, in reasonable agreement with the estimations given by the specific infra-red method.

TABLE I. DEPENDENCE OF THE APPARENT PERCENTAGE URONIC ACID CONTENT ON THE METHOD OF ESTIMATING THE CARBON DIOXIDE EVOLVED*

| | Titrimetric | | | Gravimetric | | | |
Compound	(a) Without H_2SO_4 scrubber	(b) With H_2SO_4 scrubber	(c) Difference (b–a)	(d) Without H_2SO_4 scrubber	(e) With H_2SO_4 scrubber	(f) Corrected Value (e–c)	Spectroscopic
Glucurone	73	84	11	99	88	77	70–75
Galacturonic acid	77	91	14	109	97	83	75–80
Alginic acid	64	72	8	87	77	69	65–70

* All results quoted refer to decarboxylation at 255°for 1 hr.

TABLE II. APPARENT PERCENTAGE URONIC ACID CONTENT OF SOME SUGARS

Sugars	Thermal Decarboxylation at 255°				Decarboxylation in 19% HCl		
	30 min	60 min	90 min	120 min	50 min	100 min	150 min
Glucose	3·2	5·8	7·1	8·6	1·0	1·6	1·9
Galactose	2·5	5·8	6·2	8·4	1·4	2·2	2·9
Mannose	3·2	6·6	7·3	8·9	2·1	3·0	3·5
Arabinose	3·6	6·0	6·3	6·7	0·9	1·4	1·8
Xylose	4·7	6·6	8·5	9·7	1·1	1·4	1·6
Rhamnose	4·1	6·4	7·5	8·3	1·9	2·7	3·2
Fucose	5·2	6·7	7·4	8·2	1·2	2·1	2·8

TABLE III. APPARENT PERCENTAGE URONIC ACID CONTENT OF GLUCOSE ON THERMAL DECOMPOSITION AT DIFFERENT TEMPERATURES

Temp., °C	Period of heating, min			
	30	60	90	120
245	0·6	2·5	4·1	5·7
255	3·2	5·8	7·1	8·6
265	4·1	7·6	9·8	11·0

2. *Non-uronic, non-methylated sugars*

Direct titrimetric determinations of the carbon dioxide evolved at 255° gave the results shown in Table II. These results are similar to those reported by Perlin,[20] who found apparent uronic acid contents of "about 3% in 15 min" for reducing sugars.

When the values found are compared in Table II with values obtained by the 150-min acid decarboxylation method,[3] however, it is apparent that the thermal decomposition method gives relative errors which are considerably greater for most of the common sugars studied.

· *Temperature-dependence of the decomposition:* Table III lists the results found by direct titration for glucose at 245°, 255° and 265°.

Volatile decomposition products other than carbon dioxide and water: (*a*) For glucose, galactose and mannose, only trace amounts of volatile products were formed, the main component being acetaldehyde. Gravimetric experiments, with and without sulphuric acid scrubbing, showed that the results were only marginally greater than those quoted in Table II.

(*b*) For arabinose, rhamnose and fucose, however, much larger amounts of acetaldehyde were formed, and gravimetric results were up to 50% higher than those

TABLE IV. COMPARISON OF THE APPARENT PERCENTAGE URONIC ACID CONTENTS OF METHYLATED COMPOUNDS AS FOUND BY DIFFERENT METHODS

Compound	Thermal decomposition for 1 hr at 255°			Decarboxylation for 2·5 hr in 19% HCl		Spectros-copy
	Volatile decompn. products	Titrimetric detn.	Grav. detn.	Volatile decompn. products	Titrimetric detn.	
2:3:4:6-tetra-*O*-methyl glucose	carbon dioxide methyl formate	*	*	carbon dioxide methyl chloride	1·7	0·8
3-*O*-methyl-glucose	carbon dioxide methyl formate	*	*	carbon dioxide methyl formate methyl chloride	2·4	0·8
α-Methyl-glucoside	carbon dioxide methyl formate	*	*	carbon dioxide methyl formate methyl chloride	3·1	1·4
Pectic Acid	carbon dioxide acetaldehyde	59	68	carbon dioxide furan methyl formate	61·8	60–61
Pectin	carbon dioxide methyl chloride methyl formate	54·0	63·0	carbon dioxide furan methyl formate methyl chloride	57·0	55–56

* Determinations not possible on these compounds, which volatilise before extensive decomposition begins.

shown in Table II, *e.g.*, for 1 hr reaction at 255°, arabinose gave 9·4% and rhamnose gave 10% apparent uronic acid content.

3. *Methylated sugars and polysaccharides*

Although 2,3,4,6-tetramethyl-D-glucopyranose is more stable than D-glucose in acid solution,[25] methylated sugars yield acidic decomposition products on acid decarboxylations.[1] Table IV shows some typical results for 150-min acid decarboxylation,[3] infrared experiments showing that >50% of the apparent acidity is through volatile products other than carbon dioxide.

As a result of the effects already discussed, gravimetric determinations of methylated polysaccharides give high results.

4. Minimum temperature required for effective thermal decarboxylation

Our results have indicated that thermal decomposition is markedly temperature-sensitive in the range 245°–265°, with a distinct change in the decomposition mechanism above 280°. Carbohydrate materials begin to decompose[17] at about 130°, and the suggestion[19] that decarboxylation of uronic acid groups occurs at 145–155° made us investigate if any analytically useful, more specific, decarboxylation reaction would be given at lower decomposition temperatures.

For *Acacia seyal* gum, heating for 2.5-hr periods at each of 165°, 180° and 200° gave apparent uronic contents of 0·7%, 1·0% and 2·8%, respectively. For alginic acid evolution of carbon dioxide became detectable at 140° and estimable on heating for 2 hr at 145°; the results of various experiments are shown in Table V.

These experiments were sufficient to show that (*a*) the extent of decomposition depends on the uronic material studied, and (*b*) the time required for complete thermal decarboxylation would be much greater than the 150-min required for acid decarboxylation. The investigations were therefore discontinued, although it appears that the very small endothermic reaction observed by Chesters and Thomson[19] at 145–155° cannot result directly from "decarboxylation",

TABLE V. THERMAL DECOMPOSITION OF ALGINIC ACID

Decomposition temp., °C	Period of heating, hr	Apparent uronic acid, %
165	2·5	11·2
165	16	41·6
180	2·5	40·0
200	2·5	51·0

CONCLUSIONS

Decomposition at 255° for 20 min gave quantitative results for galacturonic and alginic acids if a *gravimetric* finish was used. The results are distinctly time-dependent (see Fig. 2) and considerable over-decarboxylation can occur. Furthermore, the rate of evolution of carbon dioxide varies for different compounds; the required yield of carbon dioxide is only given after 40 min for glucurone and after 60 min for *Acacia seyal* gum. In no case was a quantitative yield obtained in 15 min at 255°, as was reported by Perlin.[20] The reason for this is difficult to understand. The time taken for samples to attain the oven temperature was very similar to that reported by Perlin: the temperatures reported here were actual *sample* temperatures, not nominal oven or retort temperatures; the zero-time used for the kinetic measurements was corrected to allow for the internal volume of the oven, which had no "dead-space".

In investigations of this kind, the reaction kinetics and the results may be dependent on the apparatus design, on the surface area of the sample, and on its rate of increase in temperature; in agreement with Perlin,[20] all that can be done is to ensure, by careful apparatus design, that all the reaction conditions and variables are closely reproducible from run to run for different compounds.

The amounts of carbon monoxide detected agreed with those reported.[20] The nitrogen flow-gas used in most of our experiments contained approx. 20 ppm of

oxygen; when this was removed the results, as reported,[20] were not significantly altered.

It is of fundamental importance that when only the acidity from carbon dioxide is measured, thermal decarboxylation is not complete in 2 hr at 255°. The considerable differences between the gravimetric and titrimetric results are a consequence of the volatile reaction products which accompany the carbon dioxide; these products affect the gravimetric determination to a large extent. It is of interest that the volatilisable reaction products react slowly in cold concentrated sulphuric acid, liberating acidic vapours which give an additional source of error.

These facts must be considered together with the marked temperature- and time-dependence of the reaction, the differing reaction-times required for different compounds, and the relatively larger errors caused by side-reactions and the decomposition of non-uronic materials. Thermal decarboxylation, in our experience, does not compare favourably with acidic decarboxylation as a reliable reaction of general applicability for the analysis of materials containing uronic acid groups.

Zusammenfassung—Die von Perlin vorgeschlagene Methode zur Bestimmung von Uronsäure durch thermische Decarboxylierung wurde untersucht. Ein speziell konstruierter Ofen, mit besonders hoher Temperaturkonstanz, gestattete die thermische Zersetzung verschiedener Verbindungen mit guter Reproduzierbarkeit kinetisch zu studieren. Verhältnismässig grosse Fehler können bei der Bestimmung der entwickelten Kohlensäure auftreten. Resultate werden mitgeteilt und es wird geschlossen, dass die thermische Decarboxylierung mit der 150-Minuten-Säuredecarboxylierung als allgemeine analytische Methode nicht konkurrieren kann.

Résumé—Les auteurs ont étudié la méthode de décarboxylation thermique des acides uroniques, proposée par Perlin. Un four conçu spécialement, ayant une bonne stabilité de température, permettait d'étudier cinétiquement la décomposition thermique de différents composés, avec une bonne reproductibilité. Des erreurs comparativement grandes peuvent se produire dans le dosage de l'anhydride carbonique dégagé; ces erreurs dépendent de la nature des autres produites de réaction volatils. Des résultats caractéristiques sont donnés et les auteurs concluent que la décarboxylation thermique ne peut être comparée favorablement à la décarboxylation acide pendant 150 minutes comme méthode analytique générale.

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PRECIPITATION OF NICKEL DIMETHYLGLYOXIMATE FROM HOMOGENEOUS SOLUTION

STUDIES OF THE REACTIONS OF BIACETYL, HYDROXYLAMINE AND NICKEL[II]

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Summary—The reaction between biacetyl and hydroxylamine to form dimethylglyoxime was found to follow simple kinetics in the absence of nickel. However, with nickel[II] present, the kinetic studies showed definite evidence for complex formation between biacetyl monoxime and nickel. This complex and others formed with nickel in the reaction mixture determines the overall rate of formation of nickel dimethylglyoximate. Supersaturation concentrations of several hundred times the equilibrium solubility of nickel dimethylglyoximate were attained in nucleation experiments. The kinetic and nucleation studies provide explanations for some previously anomalous experimental observations, *e.g.*, the persistent supersaturation in this system provides an explanation for the inability to precipitate completely small amounts of nickel[II] with dimethylglyoxime. The yellow colour observed in the initial stage of the precipitation of nickel from homogeneous solution arises from dissolved nickel dimethylglyoximate.

IN a previous investigation, the precipitation of nickel dimethylglyoximate from homogeneous solution was used[1] as the basis of a gravimetric analytical method for nickel[II]. In the reaction, in which dimethylglyoxime is generated in ammoniacal nickel solution, a yellow colour is formed in the solution before the precipitation of the nickel chelate. The yellow colour could be made to persist for over an hour before the appearance of the solid phase. In addition, it was also found that the presence of nickel[II] had a catalytic effect upon the reaction between biacetyl and hydroxylamine, *i.e.*, dimethylglyoxime was produced in the early stages of the reaction faster than when nickel[II] was absent from the solution.

Investigations were therefore undertaken to provide information about the reactions taking place in solution before and during the precipitation of nickel dimethylglyoximate.

REAGENTS AND APPARATUS

The nickel and biacetyl stock solutions used in these investigations were prepared as described previously.[1] The dimethylglyoxime (Distillation Products Co., Rochester, N.Y.) was used in very dilute aqueous solutions without further purification.

The biacetyl monoxime (Distillation Products Co.) contained some dimethylglyoxime which could not effectively be removed by successive recrystallisations from aqueous solution. It therefore became necessary to prepare a biacetyl monoxime solution free of dimethylglyoxime.

Preparation of biacetyl monoxime solution

A small amount of the impure biacetyl monoxime was dissolved in 200 ml of distilled water. Five g of ammonium chloride and 10 ml of nickel[II] stock solution were added to the biacetyl monoxime solution. The pH was then adjusted to approximately 7·5 with ammonium hydroxide, and the solution was allowed to stand for several hours before the precipitate was removed by filtration. The filtrate was then acidified with hydrochloric acid and extracted with three successive 25-ml portions of diethyl ether to separate the biacetyl monoxime from nickel[II] and the other inorganic material. The combined ether extracts were extracted with three successive 25-ml portions of 1*N* sodium hydroxide

solution in order to transfer the biacetyl monoxime (as the anion) back into aqueous solution. The combined alkaline extracts were neutralised with 6N hydrochloric acid. The addition of an ammoniacal nickel solution to a test portion of the resulting biacetyl monoxime solution did not produce the characteristic red precipitate of nickel dimethylglyoximate.

Purification of hydroxylamine hydrochloride

The reagent grade hydroxylamine hydrochloride (J. T. Baker Chemical Co., Phillipsburgh, N.J.) used in the kinetic and nucleation experiments was purified by recrystallisation from ethyl alcohol solution containing a small amount of water; the product was then dried over sodium hydroxide and anhydrous calcium chloride in a desiccator.

All other chemicals used in this study were reagent grade.

Apparatus

All pH measurements were made with a Beckman Model 9600 pH meter calibrated with a Beckman pH 7 buffer solution (No. 3581).

The polarographic studies were made with a Sargent Model XXI polarograph. The electrolysis vessel was thermostatted at $30 \cdot 0 \pm 0 \cdot 2°$.

The spectrophotometric studies were made with a Cary Model II spectrophotometer equipped with a thermostatted cell compartment.

PROPERTIES OF THE YELLOW SPECIES

In the absence of nickel, the reaction between biacetyl and hydroxylamine did not result in the formation of the yellow colour. Because the colour was only observed when nickel was present, it was apparent that it was caused by complex formation between nickel and one of the components in the reaction mixture. When a very dilute aqueous solution of dimethylglyoxime was added to a very dilute aqueous ammoniacal nickel solution, a yellow colour was observed before precipitation. The absorption spectra, from 4000 to 2200 Å, of this yellow solution and that obtained from a PFHS (precipitation from homogeneous solution) experiment were identical. This indicated that complex formation between nickel and dimethylglyoxime was responsible for the yellow colour.

When the component in the coloured aqueous solution was extracted by chloroform, the organic phase showed a spectrum identical to that of nickel dimethylglyoximate dissolved in chloroform. The extinction coefficients for the component in chloroform and in water were determined from colorimetric analysis of the nickel content of the yellow solutions with 2,3-quinoxalinedithiol.[2] On the assumption that 1 atom of nickel is present in each molecule, the extinction coefficient ($1 \cdot 70 \times 10^3$) for the component extracted into the chloroform phase matched very well the extinction coefficient for nickel dimethylglyoximate in chloroform ($1 \cdot 72 \times 10^3$). It was found that when aqueous ammoniacal solutions containing nickel dimethylglyoximate crystals were heated nearly to boiling, yellow-coloured solutions were produced which exhibited spectra again identical to that obtained for the previously described yellow aqueous solution.

If nickel dimethylglyoximate were to dissociate into a 1:1 complex and free dimethylglyoxime, as indicated in the following equation:

$$NiD_2 \rightarrow NiD + D$$

where

NiD_2 = nickel-dimethylglyoximate

NiD = nickel-dimethylglyoxime 1:1 complex

D   = dimethylglyoxime

the presence of free dimethylglyoxime should be spectrophotometrically observable in

such solutions. Because dimethylglyoxime was not so detected, 2 molecules of dimethylglyoxime must be associated with each atom of nickel in the complex. Diehl[3] discusses yellow or green-yellow compounds which are 1:1 complexes of nickel and the amphiform of dioximes; obviously, these compounds and the yellow species previously described are not identical.

When aqueous solutions containing the yellow species were "seeded" with nickel dimethylglyoximate crystals, the yellow colour slowly disappeared. Similarly, when aqueous solutions containing the yellow species were shaken vigorously, a red precipitate of nickel dimethylglyoximate was obtained. All of the experimental observations point to the conclusion that it is dissolved nickel dimethylglyoximate which is responsible for the yellow coloured aqueous solutions.

The difference in colour between the yellow solution species (aqueous or organic) and the red crystalline solid may result from the state of aggregation of nickel dimethylglyoximate. In the crystalline solid, the nickel dimethylglyoximate molecules are separated by an interplanar spacing[4] of 3·245 Å. Under these conditions there is the possibility that a particular excited electronic state in the monomer would interact in the crystalline aggregate so as to produce a red shift.[5]

KINETIC STUDIES
PRELIMINARY INVESTIGATIONS

In order to find a method for studying the reactions between biacetyl, hydroxylamine, and nickel[II] in aqueous ammoniacal solution, attempts were made to follow changes in the concentrations of the various components in the reaction solution by spectrophotometric and polarographic techniques. As a first step, aqueous solutions of biacetyl, hydroxylamine, biacetyl monoxime, dimethylglyoxime, nickel dimethylglyoximate, nickel-ammonia complex, and nickel-hydroxylamine complex were each studied individually, in order to determine both their visible and ultraviolet absorption spectra, and their polarographic half-wave potentials. The absorption spectra of aqueous solutions of biacetyl monoxime, dimethylglyoxime, and nickel dimethylglyoximate are shown in Fig. 1.
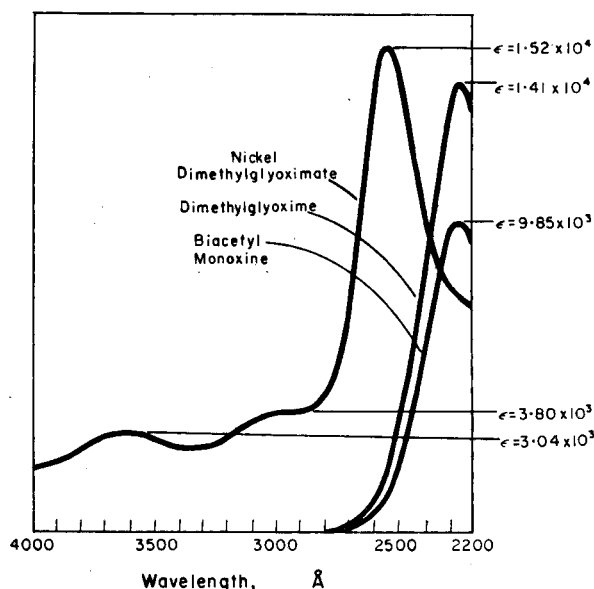

FIG. 1.—The absorption spectra of aqueous solutions of biacetyl monoxime, dimethylglyoxime, and nickel dimethylglyoximate.

It became apparent that it would be extremely difficult to follow the changes in concentration of the various components in the reaction solution by polarographic methods because there was not sufficient separation in the polarographic half-wave potentials. It was also found that it would be difficult to follow the changes in concentration of any component, except that of nickel dimethylglyoximate, by spectrophotometric means because of overlapping spectra, e.g., the absorption maxima for dimethylglyoxime and biacetyl monoxime both occur at 2250 Å.

Because of the difficulties of utilising the spectrophotometric method for a complete kinetic study, a separation technique was then developed capable of determining the individual concentrations of biacetyl monoxime, dimethylglyoxime, and nickel dimethylglyoximate.

SEPARATIONAL PROCEDURE

(a) Experimental

The separation technique was based upon three factors.

First, the nickel dimethylglyoximate precipitate can be filtered from the reaction solution at any time, and subsequently determined colorimetrically.

Secondly, the biacetyl monoxime and dimethylglyoxime can be separated from hydroxylamine by ether extraction. Hydroxylamine is much more soluble in water than it is in ether and, therefore, this operation effectively stops the reaction at the time of the extraction.

Thirdly, because biacetyl monoxime and dimethylglyoxime are acidic, they can be transferred back into aqueous solution by extraction with $1N$ sodium hydroxide, and individually determined polarographically by adjustment of the pH of the alkaline solution to a value which gives a sufficient separation in the polarographic half-wave potentials.

Details of separation

A schematic diagram of the separations involved is shown in Fig. 2; the detailed procedure is as follows:

The hydroxylamine hydrochloride to be used in the kinetic experiment was weighed to the nearest 0·1 mg, transferred to a 150-ml beaker and dissolved in about 50 ml of distilled water; an appropriate aliquot of nickel[II] stock solution was added to it. The solution was diluted to about 100 ml with distilled water, and the pH was adjusted to a desired value with ammonium hydroxide solution.

The solution was quantitatively transferred to a 250-ml volumetric flask and diluted to about 230 ml with distilled water. The volumetric flask was then placed, along with another flask containing biacetyl stock solution, in a constant temperature bath to reach temperature equilibrium.

The experiment was initiated when an aliquot of the biacetyl stock solution was pipetted into the 250-ml volumetric flask and the reaction mixture was diluted to volume with distilled water. The solution in the flask was carefully mixed and the time was noted.

A sample of this reaction solution was placed in a thermostatically controlled spectrophotometric cell in the spectrophotometer, and the supersaturation concentration of nickel dimethylglyoximate was determined spectrophotometrically at 3600 Å.

Ten-ml aliquots of the reaction mixture were also pipetted into test tubes which were then placed in the constant temperature bath. When the concentrations of biacetyl monoxime, dimethylglyoxime, and the amount of nickel dimethylglyoximate precipitated were to be determined, a 10-ml aliquot was quantitatively transferred to a 15-ml medium glass frit crucible.

The solution was quickly filtered through the crucible into a 60-ml separatory funnel, the precipitate was washed with a small amount of distilled water, and the amount of nickel dimethylglyoximate was determined colorimetrically according to the method of Passamaneck.[6]

One ml of $6N$ hydrochloric acid was added to the filtrate contained in the separatory funnel. The biacetyl monoxime and dimethylglyoxime were extracted first with one 20-ml portion of diethyl ether and then with two successive 10-ml portions of the ether. The combined ether extracts were extracted with three successive 20-ml portions of $1N$ sodium hydroxide solution. The combined alkaline extracts were then acidified with $6N$ hydrochloric acid to pH 2·5 ± 0·2 just before polarographic analysis. The solution was quantitatively transferred to a 100-ml volumetric flask, diluted to 100 ml with distilled water, and then subjected to polarographic analysis for the biacetyl monoxime and dimethylglyoxime.

(b) Results and discussion

The aqueous phase reaction of biacetyl with hydroxylamine at various pH values and in the absence of nickel[II] was also studied by use of the separational procedure.

These reactions are indicated below:

$$\begin{matrix} CH_3-C=O \\ | \\ CH_3-C=O \end{matrix} \quad +H_2NOH \quad \rightarrow \quad \begin{matrix} CH_3-C=NOH \\ | \\ CH_3-C=O \end{matrix} \quad +H_2O$$

$$\begin{matrix} CH_3-C=NOH \\ | \\ CH_3-C=O \end{matrix} \quad +H_2NOH \quad \rightarrow \quad \begin{matrix} CH_3-C=NOH \\ | \\ CH_3-C=NOH \end{matrix} \quad +H_2O$$
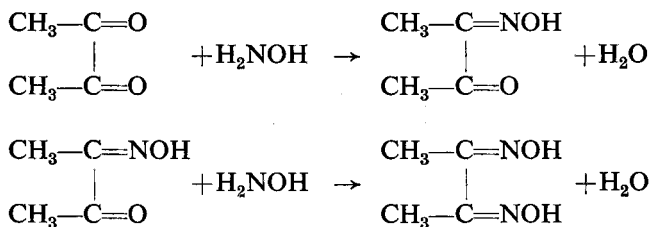
FIG. 2.—Schematic diagram of separations involved in the separational procedure

REACTION MIXTURE

Nickel[II]
Hydroxylamine
Biacetyl
Biacetyl monoxime
Dimethylglyoxime
Nickel dimethylglyoximate

FILTRATION

Filtrate	Precipitate
Nickel[II] Hydroxylamine Biacetyl Biacetyl monoxime Dimethylglyoxime	Nickel dimethylglyoximate *Colorimetric determination*

ETHER EXTRACTION

Ether Phase	Aqueous phase
Biacetyl Biacetyl monoxime Dimethylglyoxime	Nickel[II] Hydroxylamine

ALKALINE EXTRACTION

Ether phase	Alkaline phase
Biacetyl	Biacetyl monoxime Dimethylglyoxime *Polarographic determination*

The equations can be expressed in the following simplified manner:

$$B + H \xrightarrow{k_1} M \tag{1}$$

$$M + H \xrightarrow{k_2} D \tag{2}$$

where
$B =$ solution concentration of biacetyl,
$H =$ solution concentration of hydroxylamine,
$M =$ solution concentration of biacetyl monoxime,
$D =$ solution concentration of dimethylglyoxime,
$k_1 =$ rate constant for reaction (1),
$k_2 =$ rate constant for reaction (2).

If both reactions are first order with respect to each reactant, then

$$-\frac{dB}{dt} = k_1 HB \tag{3}$$

$$\frac{dM}{dt} = k_1 HB - k_2 HM. \tag{4}$$

If the initial hydroxylamine concentration is much larger than the initial biacetyl concentration so that the hydroxylamine concentration can be considered to be constant throughout the course of the reaction, then:

$$-\frac{dB}{dt} = k_1' B \tag{5}$$

$$\frac{dM}{dt} = k_1' B - k_2' M \tag{6}$$

and

$$B = B_0 e^{-k_1' t} \tag{7}$$

$$M = \frac{k_1' B_0}{k_2' - k_1'} (e^{-k_1' t} - e^{-k_2' t}) \tag{8}$$

where
$t =$ time,
$k_1' = k_1 H$,
$k_2' = k_2 H$,
$B_0 =$ initial solution concentration of biacetyl.

If $k_1' > k_2'$, when t is large enough, $e^{-k_2' t} \cong 0$ and,

$$M = -\frac{k_1' B_0}{k_2' - k_1'} e^{-k_2' t} \tag{9}$$

$$\frac{M}{B_0} = -\frac{k_1'}{k_2' - k_1'} e^{-k_1'' t} \tag{10}$$

$$-\ln \frac{B_0}{M} = \ln \left(-\frac{k_1'}{k_2' - k_1'} \right) - k_2' t \tag{11}$$

$$\ln \frac{B_0}{M} + \ln \left(-\frac{k_1'}{k_2' - k_1'} \right) = k_2' t. \tag{12}$$

A plot of ln (B_0/M) versus t should give a straight line with a slope equal to k_2' with intercept $\cong 0$.

Quantitative information about reaction (2) could be obtained. However, it was impossible to gain more than qualitative information about the relatively faster reaction (1) owing to the uncertainties necessarily introduced into the experiments because of the sampling technique, $i.e.$, the successive ether extractions require several minutes to complete, which makes it difficult to know exactly when the reactions were stopped. Also, the reaction solutions are acidified just before extraction. This is necessary to ensure that the oximes are present in the acidic form, so that they can be extracted into the ether phase, but errors are introduced because of the change in pH of the reaction solution.
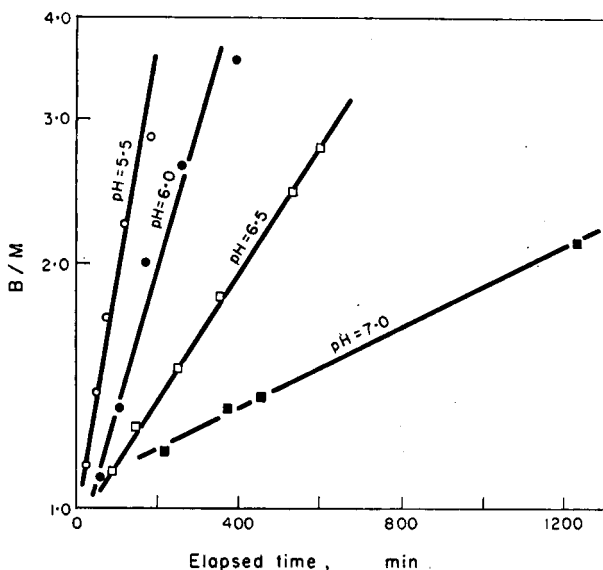
FIG. 3.—Ln (B_0/M) versus time for the reaction of biacetyl with hydroxylamine in the absence of nickel[II] at various pH values
Initial biacetyl concentration: $9 \cdot 2 \times 10^{-4}M$
Initial hydroxylamine concentration: $1 \cdot 0 \times 10^{-1}M$
Temperature: $15 \cdot 0°$

Because the amount of hydroxylamine taken was much greater than that of biacetyl, the hydroxylamine concentration was effectively unchanged throughout the course of the reaction. Reaction (2) was found to be first order with respect to biacetyl monoxime, as is indicated by the straight lines obtained in a plot of ln (B_0/M) versus time. The rate of reaction was found to increase with increased solution acidity (from pH $6 \cdot 0$ to $5 \cdot 5$). These results are summarised in Fig. 3.

As indicated previously, the reaction of biacetyl with hydroxylamine in the presence of nickel[II] was studied at various pH values through the use of the sampling technique. As before, the amount of hydroxylamine taken was much greater than that of biacetyl.

When nickel[II] is present in the reaction solution, reactions (1) and (2) occur; however, the dimethylglyoxime formed reacts with nickel to produce the nickel dimethylglyoximate chelate:
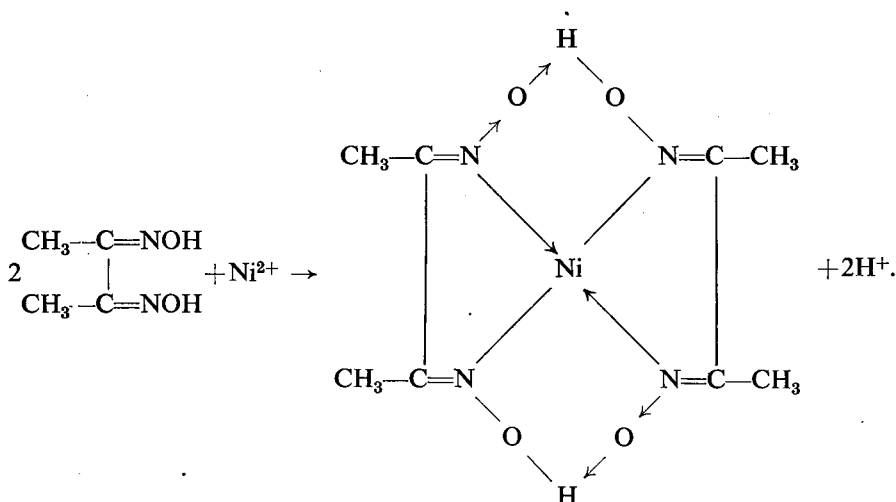
Proceeding as before:

$$2D + N \xrightarrow{k_3} ND_2 \tag{13}$$

where

D = Solution concentration of dimethylglyoxime

Ni = Solution concentration of nickel^{II}

ND_2 = Nickel dimethylglyoximate concentration

k_3 = Rate constant for reaction (13)

A mass balance of the solution at any time yields:

$$B + M + D + 2NiD_2 = \text{constant} = B_0. \tag{14}$$

If $k_3 \gg k_2$, the dimethylglyoxime reacts with nickel^{II} in reaction (13) faster than it is produced in reaction (2), and the concentration of free dimethylglyoxime in the reaction solution at any time is negligible, i.e.,

$$2ND_2 = B_0 - B - M. \tag{15}$$

Thus, the concentration of nickel dimethylglyoximate can be expressed as a function of the biacetyl and the biacetyl monoxime concentration at any time. As assumed by equation (15), it was also found experimentally that free dimethylglyoxime could not be detected in the reaction solution as long as there was enough nickel^{II} to react with the dimethylglyoxime as it is being generated.

The reaction which produces dimethylglyoxime in the presence of nickel appears to be quite complex. It is not first order with respect to biacetyl monoxime as it is in the case when nickel is absent. The production of dimethylglyoxime in the early stages of the reaction is much faster when nickel is present in the reaction solution, but the rate of generation of dimethylglyoxime gradually decreases until, in the later stages of the reaction, the rate is much slower than when nickel is absent from the reaction solution.

SPECTROPHOTOMETRIC PROCEDURE

(a) *Experimental*

Because the preliminary kinetic studies utilising the separational procedure indicated that the concentration of dimethylglyoxime uncombined with nickel was negligibly small, the kinetic study was

simplified to a great extent, *i.e.*, the concentration of biacetyl monoxime in the reaction solution could be determined directly by spectrophotometric methods because of the lack of interference from dimethylglyoxime.

Procedure: Twice the amount of hydroxylamine hydrochloride to be used in the kinetic experiment was weighed to the nearest 0·1 mg and quantitatively transferred to a 100-ml beaker. Twice the required amount of nickel^{II} stock solution was pipetted into the beaker and the solution diluted to about 50 ml with distilled water. The pH was adjusted to the desired value with ammonium hydroxide, and the solution was quantitatively transferred to a 100-ml volumetric flask, and diluted to volume with distilled water. The solution was carefully mixed and then divided into two equal portions, which were transferred to 100-ml volumetric flasks. One solution was diluted to 100 ml with distilled water, carefully mixed, and set aside to be used as a spectrophotometric blank. The other solution was diluted to approximately 80 ml with distilled water and placed in the constant temperature bath.

A biacetyl solution was prepared by pipetting 0.200 ml of redistilled biacetyl into a 100-ml volumetric flask just before it was to be used experimentally. Water was added to dissolve the biacetyl and the solution diluted to volume. A 10-ml aliquot of this solution was pipetted into a second 100-ml volumetric flask. This solution was brought up to volume with distilled water, carefully mixed, and placed in the constant temperature bath. The biacetyl concentration of this solution was $2.16 \times 10^{-3}M$.

The solutions were allowed to remain in the constant temperature bath until they reached the desired temperature. The experiment was started when an aliquot of the biacetyl solution was pipetted into the flask containing the nickel and hydroxylamine, and the volume brought up to 100 ml with distilled water. The solution was carefully mixed, and a sample of it was placed in a thermostatically controlled spectrophotometric cell in the spectrophotometer. At intervals the supersaturation concentration of nickel dimethylglyoximate was determined at 3600 Å, the concentration of biacetyl monoxime at 2250 Å, and the component of each of these spectra produced by light scattering from the precipitate at 5600 Å.

(b) Results and discussion

If the absorbances of the biacetyl monoxime and dimethylglyoxime in the reaction solution are each quantitatively related to their respective concentrations, and if the solutions are sufficiently dilute, so that Beer's law holds, then:

$$M = \frac{A_M}{b\varepsilon_M} \tag{16}$$

$$D = \frac{A_D}{b\varepsilon_D} \tag{17}$$

and,

$$A = A_M + A_D \tag{18}$$

where   M = solution concentration of biacetyl monoxime,
      D = solution concentration of dimethylglyoxime,
      b = length of spectrophotometric cell in cm,
      ε_M = molecular extinction coefficient for biacetyl monoxime,
      ε_D = molecular extinction coefficient for dimethylglyoxime,
      A_M = absorbance due to biacetyl monoxime,
      A_D = absorbance due to dimethylglyoxime,
      A = total absorbance of the solution,

because the absorption maxima for both biacetyl monoxime and dimethylglyoxime occur at the same wavelength (2250 Å). Substitution of equations (16) and (17) into equation (18) yields:

$$A = b\varepsilon_M M + b\varepsilon_D D. \tag{19}$$

If the cell path length is always 1 cm

$$A = M\varepsilon_M + D\varepsilon_D. \tag{20}$$

A mass balance of the reaction solution yields

$$B + M + D = \text{constant} = B_0.\tag{21}$$

Substitution of equations (7) and (8) into equation (21) yields

$$D = B_0 - B_0 e^{-k_1't} - \frac{k_1'B_0}{k_2' - k_1'}(e^{-k_1't} - e^{-k_2't}),\tag{22}$$

and substitution of equations (8) and (22) into equation (19) yields

$$A = B_0\left[\frac{(\varepsilon_M - \varepsilon_D)k_1'}{k_2' - k_1'}(e^{-k_1't} - e^{-k_2't}) + \varepsilon_D(1 - e^{-k_1't})\right].\tag{23}$$

If $k_1 \gg k_2$, $\dfrac{k_1'}{k_2' - k_1'} \cong -1$, and when t is large, $e^{-k_1't} \cong 0$. Equation (23) then becomes

$$A = B_0(\varepsilon_M - \varepsilon_D)e^{-k_2't} + B_0\varepsilon_D.\tag{24}$$

When t is small, $e^{-k_2't} \cong 1$ and equation (23) becomes

$$A = B_0[\varepsilon_D(1 - e^{-k_1't}) - (\varepsilon_M - \varepsilon_D)(e^{-k_1't} - 1)].\tag{25}$$
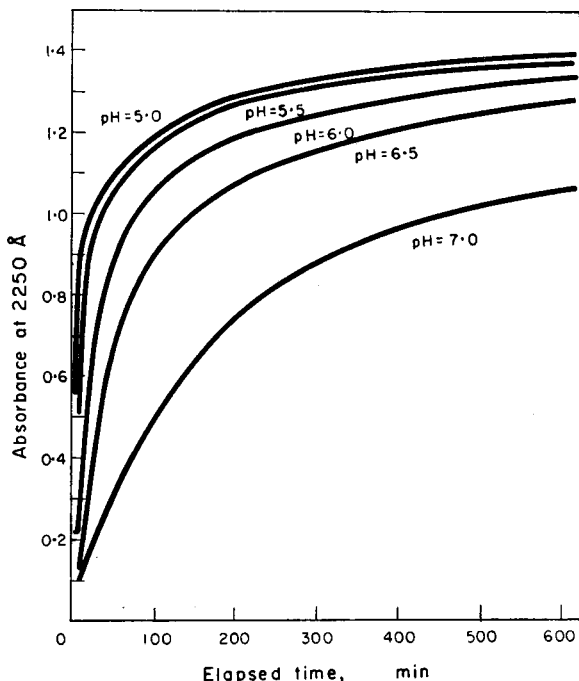
FIG. 4.—Absorbance versus time for the continuous spectrophotometric determination
of biacetyl monoxime and dimethylglyoxime
Initial biacetyl concentration: $1 \cdot 08 \times 10^{-4}M$
Initial hydroxylamine concentration: $7 \cdot 20 \times 10^{-2}M$
Temperature: $15 \cdot 0°$

Equations (24) and (25) indicate that quantitative information about reactions (1) and (2) can be obtained through the use of spectrophotometric techniques, because the total absorbance of the reaction solution at 2250 Å is functionally related to the rate constants of both reactions.

Equations (24) and (25) were used to evaluate the spectrophotometric results (obtained directly from the recording spectrophotometer as absorbance versus time graphs, cf. Fig. 4). When t was large, $e^{-k_1't} \cong 0$, and equation (24) was solved for k_2'. When t was small, $e^{-k_2't} \cong 1$, and equation (25) was solved for k_1'. The two constants were then adjusted when necessary by trial and error methods so that equation (23) was true at all times. The result of the experiments are summarised in Figs. 5 and 6.

The experimental results obtained from the spectrophotometric kinetic study of the reactions between biacetyl and hydroxylamine in the presence of nickel^{II} are summarised in Figs. 7 and 8. These results substantiate the information obtained from the separational procedure. The same characteristic reactivity of biacetyl monoxime was
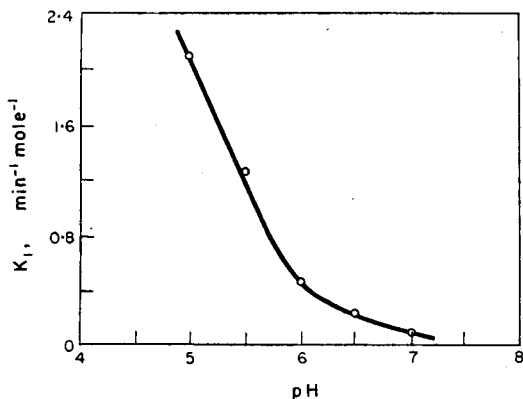
FIG. 5.—Rate constant, k_1, versus pH for the generation of biacetyl monoxime from
biacetyl and hydroxylamine in the absence of nickel^{II}
Initial biacetyl concentration: $1·08 \times 10^{-4}M$
Initial hydroxylamine concentration: $7·20 \times 10^{-2}M$
Temperature: $15·0°$
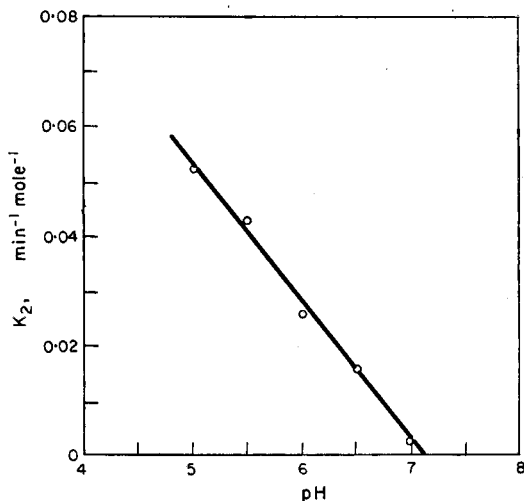
FIG. 6.—Rate constant, k_2, versus pH for the generation of dimethylglyoxime from
biacetyl monoxime and hydroxylamine in the absence of nickel^{II}
Initial biacetyl concentration: $1·08 \times 10^{-4}M$
Initial hydroxylamine concentration: $7·20 \times 10^{-2}M$
Temperature: $15·0°$
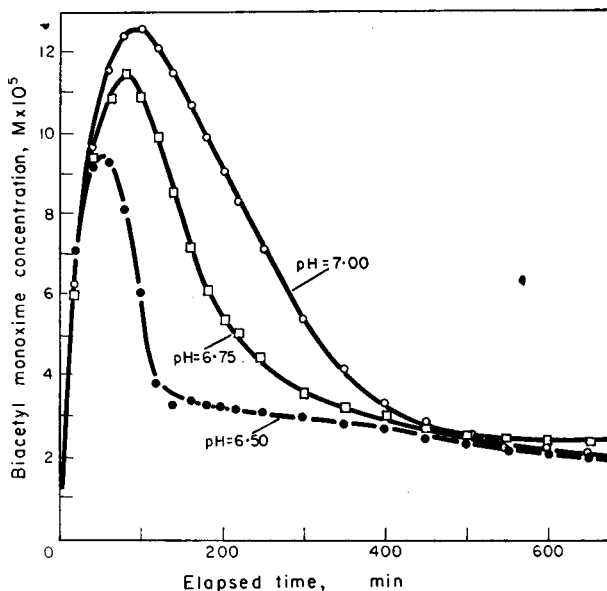
Fig. 7.—Biacetyl monoxime concentration versus time for the reaction between biacetyl
and hydroxylamine in the presence of nickel^{II} (three typical experiments)
Initial biacetyl concentration: $2\cdot16 \times 10^{-4}M$
Initial hydroxylamine concentration: $7\cdot20 \times 10^{-2}M$
Initial nickel^{II} concentration: $3\cdot36 \times 10^{-3}M$
Temperature: $15\cdot0°$
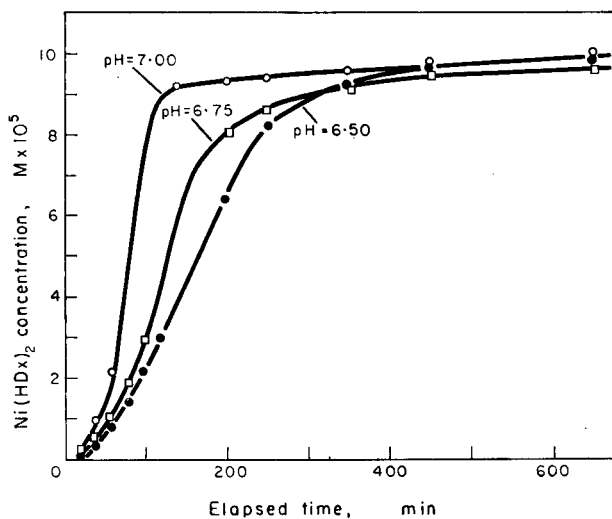
Fig. 8.—Total nickel dimethylglyoximate (precipitated and in solution) versus time for
the reaction between biacetyl and hydroxylamine in the presence of nickel^{II} (three
typical experiments)
Initial biacetyl concentration: $2\cdot16 \times 10^{-4}M$
Initial hydroxylamine concentration: $7\cdot20 \times 10^{-2}M$
Initial nickel^{II} concentration: $3\cdot36 \times 10^{-3}M$
Temperature: $15\cdot0°$

observed, *i.e.*, the reactivity of biacetyl monoxime in the early stages of the reaction is much greater when nickel is present, but the reactivity gradually decreases until, in the later stages of the reaction, the rate is slower than when nickel is absent from the reaction solution. As was observed in experiments utilising the separational procedure this effect became more pronounced with decreased solution acidity from pH 6·5 to 7·0.

The complicated reactivity of biacetyl monoxime under these circumstances can possibly be partially explained by the formation of a relatively stable intermediate complex between biacetyl monoxime and nickel[II]. Evidence for such complex formation was obtained from experiments in which the individual spectra of separate ammoniacal solutions of biacetyl monoxime and nickel[II] were compared with the spectrum of a mixture of biacetyl monoxime and nickel[II] in ammoniacal solution. The spectrum of the mixture was not a simple combination of the spectra of the two individual components of the mixture. A definite absorption maximum was observed at 3020 Å which was not observed in either of the other individual spectra, and if the mixture is concentrated enough the solution appears brown coloured. This intermediate complex could be formed at a rate comparable to the rate of the reaction between uncomplexed biacetyl monoxime and hydroxylamine, so the total process might be as follows:

$$
\begin{array}{c}
CH_3-C=NOH \\
| \\
CH_3-C=O
\end{array}
+ H_2NOH \xrightarrow{\text{fast}}
\begin{array}{c}
CH_3-C=NOH \\
| \\
CH_3-C=NOH
\end{array}
+ H_2O
$$

$$
2\begin{array}{c}
CH_3-C=NOH \\
| \\
CH_3-C=O
\end{array}
+ Ni^{2+} \xrightarrow{\text{fast}}
\quad + 2H^+
$$

$$
+ 2H_2NOH + 2H^+
$$

$$
\xrightarrow{\text{slow}} 2\begin{array}{c}
CH_3-C=NOH \\
| \\
CH_3-C=NOH
\end{array}
+ 2H_2O
$$
$$
+ Ni^{2+}
$$
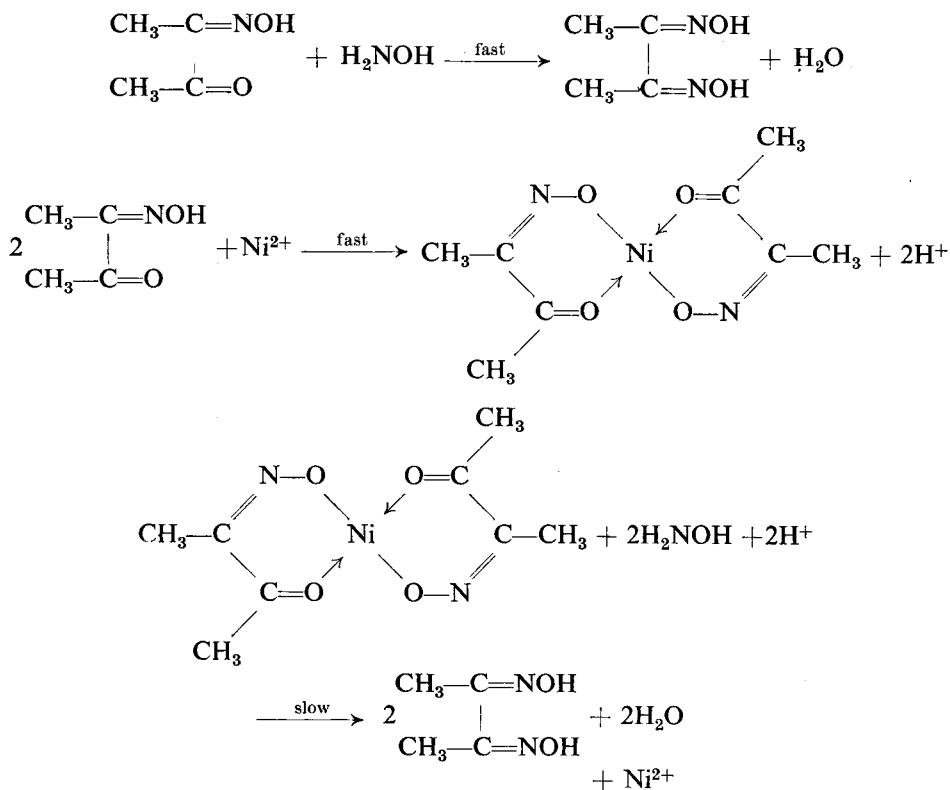
Because the first and second reactions could both occur, the total net result would be a more rapid decrease in the biacetyl monoxime concentration in the early stages of

6

the kinetic run than in the case when nickel[II] is absent from the reaction solution. As the free biacetyl monoxime concentration is reduced to zero, the only remaining species capable of reaction with hydroxylamine is the relatively unreactive nickel complex. It is reasonable to assume that all of the biacetyl would, therefore, not be converted to nickel dimethylglyoximate under these conditions. This could account for the consistently low results obtained by Barnicoat[7] in his attempts to determine quantitatively biacetyl at room temperature.

Adding to the complexity of the reaction of biacetyl monoxime with hydroxylamine in the presence of nickel[II] is the fact[8,9] that hydroxylamine also forms co-ordination compounds with nickel[II]. The reactivity of each one of these compounds probably differs from those of the others and from the reactivity of free hydroxylamine.

These complexes and the complex between biacetyl monoxime and nickel[II] become increasingly disassociated in increasingly acidic solutions. It should be expected, then, that as the reaction solution acidity is increased, the reactivity of biacetyl monoxime in nickel[II] solution should approach the reactivity of biacetyl monoxime in nickel[II] free solutions. This was experimentally observed (cf. Fig. 7).

NUCLEATION STUDIES

(a) Experimental

The generation and solution supersaturation of nickel dimethylglyoximate was followed spectrophotometrically during each experimental run. The absorbance-time curves were obtained with the
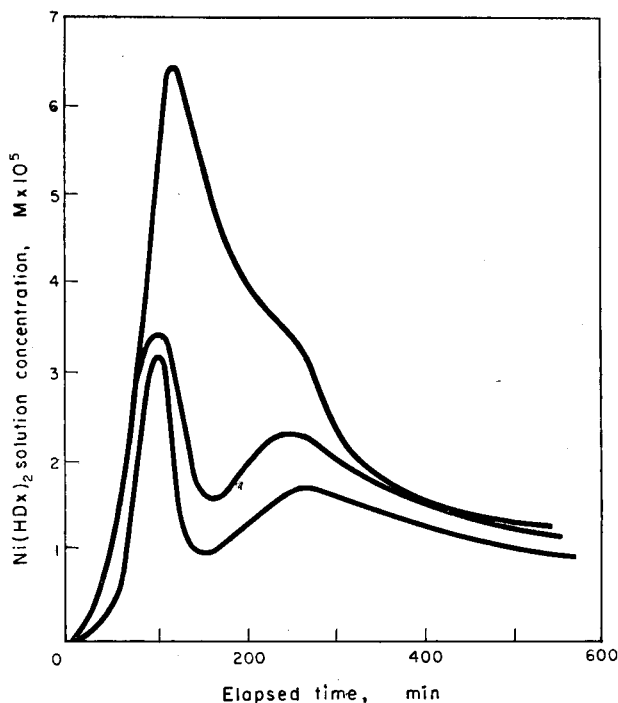

FIG. 9.—Degree of supersaturation versus time for the precipitation of nickel dimethylglyoximate from homogeneous solution (three typical experiments)
Equilibrium solubility of Ni(HDx)$_2$ in aqueous salt solution[8] $= 2 \times 10^{-7} M$

recording spectrophotometer. The component of the total absorbance caused by light scattering from the precipitate was determined at 5600 Å and subtracted from the absorbance observed at 3600 Å in order to obtain the true solution concentration of nickel dimethylglyoxime at any time.

(b) Results and discussion

Typical results of these experiments are given as the supersaturation-time curves of Fig. 9. The solution concentration of nickel dimethylglyoxime increased to a point well beyond the equilibrium solubility concentration, as determined by Christopherson and Sandell;[10] supersaturation concentrations of several hundred times the equilibrium solubility of nickel dimethylglyoxime were attained.

Another unusual phenomenon which occurred in certain experiments was an increase in the supersaturation (cf. Fig. 9) of the solution well after the initial decrease in the supersaturation was observed. This could be caused by settling of the precipitate particles which nucleate in the first "burst" so that subsequent growth on them does not occur at a rate which is rapid enough to relieve the solution of all of the nickel dimethylglyoxime which is being generated in the solution. The supersaturation of the solution would then increase again until another "burst" of precipitate particles occurs.

An attempt was made to apply the method of Klein, Gordon, and Walnut[11] to determine the precipitation nucleus of nickel dimethylglyoxime. No apparent correlation between the area under the supersaturation-time curve and the number of precipitate particles obtained from an arbitrary volume of reaction solution for this system was found. It is possible that the multiple precipitation "bursts" are responsible for this lack of correlation, and that not only the area under the curve but the shape of the curve is important in any determination of the nucleus size for the nickel dimethylglyoxime system.

The persistent supersaturation of the solutions containing nickel dimethylglyoxime serves to explain some previous anomalous experimental observations. One of these is the observation of Jones,[12] who found that amounts of nickel in steel as high as 0·1 % were frequently reported as "traces". When the amount of nickel was less than 0·06 %, some nickel was quite certainly not precipitated even on prolonged standing. To check these results, Jones took various amounts of nickel and carried out the precipitation, as usual in slightly ammoniacal solution, in a volume of 100 ml. After the solutions were allowed to stand overnight, the precipitate was filtered but was not washed, and the nickel in the filtrate was determined colorimetrically. The results of these experiments are given in Table I.

TABLE I

Weight of nickel taken, g	Nickel found in filtrate, %
0·0001	35·0
0·0002	7·5
0·0003	5·0
0·00075	2·0
0·0010	2·25
0·0015	1·0
0·0020	0·25
0·0025	negligible

Equilibrium solubility could not account for such large amounts of nickel in the filtrate.

Finally, Komarek[13] observed in freshly precipitated nickel dimethylglyoximate solutions a polarographic wave which disappeared after a few minutes. It is reasonable to suspect that this is the same wave observed in the previously described preliminary polarographic experiments, and which can be attributed to the supersaturation of nickel dimethylglyoximate.

Zusammenfassung—Die Reaktion zwischen Diacetyl und Hydroxylamin (Bildung von Dimethylglyoxim) nimmt in Abwesenheit von Nickel einen einfachen Verlauf. In Gegenwart von Nickel jedoch zeigen kinetische Studien, dass Komplexbildung zwischen Diacetyl, Monoxim und Nickel auftritt. Dieser Komplex und andere Komplexe, die in der Mischung auftreten, bestimmen die Geschwindigkeit der Bildung von Nickeldimethylglyoxim. Übersättigungskonzentrationen hundert und mehrmals grösser als die Gleichgewichtskonzentration für die Löslichkeit von Nickeldimethylglyoxim wurden während der Durchführung von Nukleationexperimenten erhalten. Das Studium der Raktionkinetik und Keimbildung erlaubt nun die Erklärung für verschiedene in früheren Experimenten beobachtete Abnormalitäten. Die starke Tendenz zu Übersättigung erklärt, warum kleine Nickelmengen nicht vollständig gefällt werden können. Die gelbe Färbung der Lösung, die man am Beginn der Nickelfällung aus homogener Lösung beobachtet, wird durch gelöstes Nickeldimethylglyoxim verursacht.

Résumé—Les auteurs ont trouvé que la réaction entre le biacétyle et l'hydroxylamine pour former la diméthyl-glyoxime suivait une cinétique simple en l'absence de nickel. Cependant, en présence de nickel(II), l'étude cinétique montre nettement la formation d'un complexe entre biacétyle, monoxime et nickel. Ce complexe et les autres formés avec le nickel dans le mélange réactionnel déterminent la vitesse globale de formation du diméthylglyoximate de nickel. Des concentrations de sursaturation de plusieurs centaines de fois la solubilité à l'équilibre du diméthylglyoximate de nickel sont atteintes dans les expériences d'amorçage. Les études de cinétique et d'amorçage fournissent les explications de quelques observations expérimentales considérées comme anormales, par exemple: la sursaturation persistante dans ce système explique l'inaptitude à précipiter complètement de faibles quantités de nickel(II) par la diméthylglyoxime. La couleur jaune observée au stade initial de précipitation du nickel en solution homogène est due au diméthylglyoximate de nickel dissous.

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A NEW REDUCTIMETRIC REAGENT: IRON^{II} IN A STRONG PHOSPHORIC ACID MEDIUM

TITRATION OF URANIUM^{VI} WITH IRON^{II} AT ROOM TEMPERATURE

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Summary—The formal redox potential of the Fe^{III}/Fe^{II} couple has been determined in media of varying phosphoric acid concentration, and found to decrease steeply with increasing phosphoric acid concentration. Above a certain concentration of phosphoric acid, the difference between the formal potentials of the U^{VI}/U^{IV} and Fe^{III}/Fe^{II} couples becomes sufficiently great to enable iron^{II} to reduce uranium^{VI} even at room temperature. This is the reversal of the normal redox reaction—oxidation of uranium^{IV} by iron^{III}. A careful study of the various factors involved has enabled us to develop a new reductimetric titration of uranium^{VI} with iron^{II} in strong phosphoric acid medium (11.0 to 13.5M) at room temperature using either a potentiometric end-point or a visual end-point with methylene blue or thionine as an internal redox indicator. Because the new procedure enables the titration to be carried out at room temperature, it is more convenient than procedures involving titanium^{III} and chromium^{II} which require temperatures ranging from 60 to 90°. The new procedure has a further advantage in that it can be used for the determination of uranium^{VI} even in the presence of iron^{III} and tungsten^{IV}, using an electrometric end-point. Also, the new procedure does not require the elaborate precautions which are necessary for the preparation and storage of titanium^{III} or chromium^{II} solutions.

IN 1955 Canning and Dixon[1] made the interesting observation that uranium^{VI} can be reduced to uranium^{IV} by heating to the boiling point with an excess of iron^{II} in a medium containing 40% (by volume) of orthophosphoric acid. They showed that the reaction can be employed for the spectrophotometric determination of uranium^{VI}. It is obvious that the reaction discovered by Canning and Dixon is the reversal of the normal redox reaction, in which uranium^{IV} is oxidised by iron^{III}. Because the new reaction appeared to offer interesting possibilities for the use of iron^{II} in a concentrated phosphoric acid medium as a powerful reductometric reagent, a systematic investigation of this reagent has been planned by Gopala Rao since 1955.

Linga Murty[14] determined the formal potentials of the Fe^{III}/Fe^{II} and U^{VI}/U^{IV} couples in media of varying phosphoric acid concentration. These determinations have afforded an explanation for the reversal of the normal redox reaction. The data presented in Tables I and II and the curves given in Fig. 1 show that the redox potential of the Fe^{III}/Fe^{II} couple decreases steeply on increasing the phosphoric acid concentration, while the redox potential of the U^{VI}/U^{IV} couple increases with increasing phosphoric acid concentration. It will be noted further that above a certain phosphoric acid concentration, the formal potential of the Fe^{III}/Fe^{II} couple attains a value lower than that of the U^{VI}/U^{IV} couple, the difference in the two potentials being sufficient to enable the reduction of uranium^{VI} by iron^{II}. The potential values

reported by Baes[2] and Marcus[3] are in general agreement with the values given here.

We have been able to establish conditions under which uranium[VI] can be deter-mined in concentrated phosphoric acid medium at room temperature by titration with a solution of iron[II] sulphate, using either a potentiometric end-point or a visual end-point with methylene blue or thionine as an internal redox indicator. Although the actual reductant is a complex of iron[II] and phosphoric acid, the complex need not be pre-formed and used as such. According to our procedure an iron[II] sulphate solution is run from a burette into an uranium[VI] solution containing 90% of syrupy phosphoric acid (volume by volume), the specific gravity of the syrupy phosphoric acid being 1·75 (89% by weight). Our method has the obvious advantage that the reagent is more stable than the usual reductometric reagents available for the titration of uranium[VI], namely titanium[III] and chromium[II], which require special storage conditions. Furthermore, our reagent has the advantage that it enables the titrimetric determination of uranium[VI] to be carried out at room temperature, whereas the titra-tions of uranium[VI] with titanium[III] or chromium[II] have been recommended to be made at higher temperatures with consequential disadvantages.

Kolthoff and Tomicek[4] carried out the titration of uranium[VI] with titanium[III] chloride at 55–60°, employing a potentiometric end-point. Steur[5] considered this procedure unsatisfactory and improved it by the addition of tartrate to the uranyl salt solution. Minczewski, Przytycka and Kohman[6] carried out the titration of uranyl fluoride at 70° (in an atmosphere of carbon dioxide) with titanium[III] chloride in the presence of Rochelle salt. Lingane and Iwamoto[7] prescribed the coulometric titration of uranium[VI] to be carried out in a citrate medium (at pH 0·5 to 1·5) at 85° with titanium[III], electrogenerated by the reduction of titanium[IV] at a mercury cathode. Flatt and Sommer[8] employed chromium[II] for the titrimetric determination of uranium[VI] in a hot acid medium (2·0 to 6·0N hydrochloric acid or 1·0 to 6·0N sul-phuric acid). Investigating the same titration, Elshamy and Ed-Din Zayan[9] stated that the best titration of uranium[VI] with chromium[II] is possible in 8·0N hydrochloric acid at 90°. A further disadvantage of titanium[III] and chromium[II] is that they react with iron[III], with the result that they cannot be used for the titrimetric determination or uranium[VI] in the presence of iron[III]. The reagent now proposed by us is free from this defect.

EXPERIMENTAL

Determination of Formal Redox Potentials of Fe^{III}/Fe^{II} and U^{VI}/U^{IV} Couples in a Concentrated Phosphoric Acid Medium

Reagents

Uranium[VI] solution: An approximately 0·025M solution in 1·0N sulphuric acid is prepared from Analytical Reagent Grade uranyl acetate supplied by Mallinkrodt Chemical Co., New York, U.S.A. The solution is standardised by reduction in a Jones reductor according to the customary procedure, followed by titration with a standard solution of cerium[IV] sulphate according to the procedure pre-scribed by Gopala Rao and coworkers.[10]

Uranium[IV] solution: A known volume of the uranium[IV] solution is reduced electrolytically using a small platinum wire electrode as anode and a clean bright platinum gauze as cathode. The reduction is carried out for 10 hr at 4V. The resultant uranium[IV] solution is standardised by the method already mentioned.

Iron[II] solution: Prepared by dissolving a known weight of Analytical Reagent Grade iron wire in Analytical Grade sulphuric acid and diluting the resulting solution to a known volume. The solution is standardised by titration with a standard solution of sodium vanadate, using N-phenylanthranilic acid as indicator

Iron^{III} solution: Prepared by oxidising the iron^{II} solution with hydrogen peroxide.

Phosphoric acid: Syrupy phosphoric acid (89%, E. Merck) has been employed in these investigations.

Procedure

The free acid in the salt solutions prepared as described above has been determined according to the procedure of Schumb, Scherill and Sweetser.[11] Solutions of equimolar mixtures of iron^{III} and

TABLE I

Concentration of phosphoric acid, *moles per litre*	Formal redox potential (N.H.E.) of Fe^{III}/Fe^{II} couple, V	
	0·5M H$_2$SO$_4$	0·25M H$_2$SO$_4$
nil	0·684	0·680
0·177	0·626	0·594
0·355	0·594	0·566
0·532	0·577	0·552
0·886	0·558	0·532
1·770	0·521	0·500
2·660	0·503	0·481
3·550	0·491	0·472
5·320	0·468	0·440
7·090	0·448	0·429
7·980	0·438	0·425
8·920	0·429	0·415
9·810	0·420	0·409
10·690	0·411	0·400
11·58	0·400	0·388

iron^{II} are prepared by mixing solutions of these two salts in appropriate amounts to give a 0·01N solution with respect to total iron when diluted to 100 ml, sufficient sulphuric acid and phosphoric acid being added to give the desired concentrations. The solutions are allowed to attain the temperature of the thermostat (28° ± 0·1°) before measuring the potentials. It is observed that a bright platinum electrode (freshly heated) placed in the above solution readily acquires a stable potential. All the

TABLE II

Concentration of phosphoric acid, *moles per litre.*	Formal redox potential (N.H.E) of U^{VI}/U^{IV} couple, V	
	0.5M H$_2$SO$_4$	0.25M H$_2$SO$_4$
0.000	0·549	0·494
0·177	0·559	0·518
0·355	0·560	0·519
0·532	0·561	0·521
0·709	0·558	0·520
0·886	0·558	0·519
1·770	0·557	0·522
2·660	0·561	0·545
3·550	0·569	0·565
5·320	0·595	0·583
7·080	0·595	0·584
8·920	0·596	0·585
10·690	0·600	0·585

potentials have been measured using a saturated calomel electrode as a reference electrode and a saturated potassium chloride agar as the salt bridge. During the measurements, the iron salt solution is maintained under an atmosphere of nitrogen free from oxygen. The results are summarised in Table I.

From the results in Table I, it is evident that the formal redox potential of the Fe^{III}/Fe^{II} couple decreases with increasing concentration of phosphoric acid.

The formal redox potential of the U^{VI}/U^{IV} couple has also been measured in a phosphoric acid medium at a total uranium concentration of $0.01M$ and a temperature of $28° \pm 0.1°$. Considerable difficulty has been experienced in the attainment of steady potentials for this system. However, fairly reproducible values have been observed after waiting for 7-8 min, when the precaution is taken to ignite the bright platinum electrode several times. The results are summarised in Table II.

From the results in Table II, it is seen that the redox potential of the U^{VI}/U^{IV} couple very slowly increases with increasing phosphoric acid concentration, even when the solution contains $0.25-0.5M$ sulphuric acid.
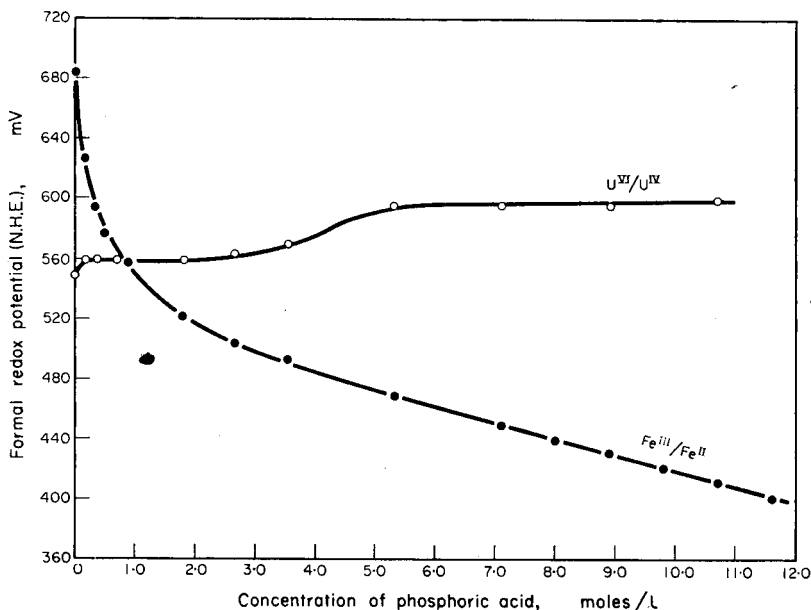
FIG. 1—Formal redox potentials of U^{VI}/U^{IV} and Fe^{III}/Fe^{II} couples in a phosphoric acid medium.

Fig. 1 gives the curves showing the variation of the formal redox potential with change in phosphoric acid concentration in each case. Besides phosphoric acid the mixture contains sulphuric acid at $0.5M$ concentration. It will be noted from the curves that the formal redox potential of the Fe^{III}/Fe^{II} couple has a value lower than that of the U^{VI}/U^{IV} couple when the concentration of phosphoric acid is $0.886M$ or higher. The difference between the formal potentials of the two systems is about 0.18 V at a concentration of phosphoric acid of $9.8M$ and this difference increases as the phosphoric acid concentration is increased further. There is thus a possibility that iron^{II} may reduce uranium^{VI} even in the cold when the phosphoric acid concentration is greater than $9.8M$.

Photometric investigation of the reduction of uranium^{VI} by iron^{II} at varying phosphoric acid concentration

In order to ascertain the concentration of phosphoric acid at which a speedy reduction of uranium^{VI} occurs, we have carried out a photometric study of a mixture of uranium^{VI} with a slight excess of iron^{II} at varying concentrations of phosphoric acid; the optical density of the mixture is noted at a wavelength of 660 mμ at varying times in a Klett-Summerson photoelectric colorimeter using optically matched tubes. Preliminary work has shown that this is the region at which uranium^{IV} has a high absorption, while iron^{III}, iron^{II} and uranium^{VI} have negligible absorption in phosphoric acid solution. The results are presented in Table III.

The limiting value of the optical density for each system is obtained from a carefully prepared artificial mixture of uranium^{IV}, iron^{II} and iron^{III} sulphates and phosphoric acid at the corresponding concentrations. It is interesting to note that there is a slight change in the optical density of the uranium^{IV} solution with changing phosphoric acid concentration, as revealed by the slight changes in the limiting values given in Table III. Similar observations have been made by Andrews, Schaap and Gates.[12] From the observations recorded in Table III, it is evident that the speed of reduction of uranium^{VI} by iron^{II} increases with increasing concentration of phosphoric acid. Under the conditions

of the experiments, the reaction is complete in less than 30 sec in media containing phosphoric acid at an overall concentration of $11.6M$ and above. Hence, we carried out electrometric titration of uranium[VI] with iron[II] at room temperature at two concentrations of phosphoric acid, *viz.* $11.6M$ and $13.1M$.

Electrometric titration of uranium[VI] with iron[II] in concentrated phosphoric acid medium

Reagents

$0.025M$ *uranyl acetate solution:* Prepared in $0.5M$ sulphuric acid and standardised according to the procedure already described.

TABLE III

Time, min	Photometer dial reading Phosphoric acid concentration, M					
	5.7	7.3	8.7	10.2	11.6	13.1
0.5	—	—	—	34	36.5	37.0
2	5.0	15.0	29.0	34.5	36.5	37.0
10	13.0	27.0	34.0	34.5	36.5	37.0
15	17.0	30.5	34.0	34.5	36.5	37.0
30	24.5	33.0	34.0	34.5	36.5	37.0
60	28.0	33.5	34.0	34.5	36.5	37.0
120	30.0	33.5	34.0	34.5	36.5	37.0
300	33.0	33.5	—	—	—	—
600	33.0	33.5	—	—	—	—
Limiting value	33.0	33.5	34.0	34.5	36.5	37.0

5.0 ml of uranium[VI] ($0.02738m$) + 1.2 ml of iron[II] ($0.5130m$) + X ml of syrupy phosphoric acid + water to make up to 50 ml.

$0.25M$ *iron[II] solution:* Prepared from Mohr's salt in $0.5M$ sulphuric acid and standardised according to the procedure already described. The concentration of iron[II] is kept high to keep the titre low so that the concentration of phosphoric acid in the mixture does not fall appreciably.

Syrupy phosphoric acid: For the bulk of the electrometric titrations syrupy phosphoric acid of B.P. grade supplied by Albright and Wilson Ltd., Birmingham, England, has been used. Control experiments with Merck's syrupy phosphoric acid have shown that phosphoric acid obtained from Albright and Wilson is quite satisfactory.

TABLE IV

Uranium[VI] taken, millimoles	Uranium[VI] found, millimoles
0.0725	0.0725
0.0925	0.0936
0.1050	0.1040
0.1125	0.1113
0.1250	0.1245
0.1507	0.1522
0.1758	0.1740

Procedure

About 4 to 8 ml of $0.025M$ uranyl salt solution is transferred to a titration vessel fitted with a five-holed stopper. These holes accommodate the inlet and outlet tubes for carbon dioxide, the platinum indicator electrode, the nozzle of the microburette containing the iron[II] solution and one limb of the saturated potassium chloride bridge. The other limb of the bridge dips into a beaker containing saturated potassium chloride solution and this is connected to a saturated calomel electrode. From 30 to 65 ml of syrupy phosphoric acid is added to the titration vessel. The mixture is stirred by means of a Baird and Tatlock Ltd. magnetic stirrer, while the iron[II] solution is run in from the burette. The e.m.f. of the cell is measured with the help of a Cambridge potentiometer and a Pye galvanometer. Electrometric titrations have been made using both a platinum wire electrode and a platinum gauze electrode. We have observed that the potentials attained stable values more easily with the platinum

wire electrode than with the platinum gauze electrode. Potential measurements were made 3 min after the addition of each instalment of titrant. Typical curves are given in Fig. 2. Some typical results from a large number of titrations are presented in Table IV.

Ferrometric Determination of Uranium^{VI} Using Methylene Blue and Thionine as Indicators

From the potentiometric titration curves the formal redox potentials of the U^{VI}/U^{IV} couple and the Fe^{III}/Fe^{II} couple can be computed to be 0·742 V* and 0·298 V*, respectively, in a medium containing phosphoric acid at a concentration of 13·1M. When the concentration of phosphoric acid is
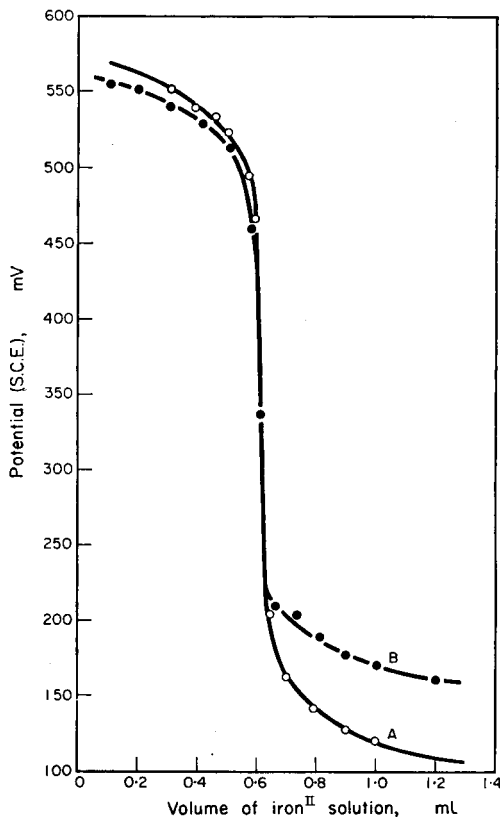
FIG. 2—Potentiometric titration of uranium^{VI} with iron^{II}
A—13·1M phosphoric acid,
B—11·6M phosphoric acid.

11·6M, the formal redox potentials of the two couples will be 0·73 V* and 0·35 V*, respectively. The difference in the potentials is sufficient for a direct titration to be made in media containing phosphoric acid at a concentration lying between 13·1 and 11·6M. Any redox indicator having a transition potential of about 0·5 to 0·6 V may work satisfactorily in the above titration. Hence, we have attempted to use methylene blue and thionine as redox indicators in this titration. The transition potentials of methylene blue and thionine have been found by the authors to be 0·550 V and 0·560 V in a medium containing phosphoric acid at 11·0–13·5M. The normal redox potentials for these indicators have been reported[13] to be 0·53 V and 0·56 V, respectively.

* These values may not correspond to the true equilibrium redox potentials of the U^{VI}/U^{IV} couple in view of the fact that the potentials have been taken after waiting for an arbitrary time interval of 3 min. Moreover, the potentials obtained during the titration are likely to be influenced by the presence of extraneous ions, *viz.* Fe^{3+} and Fe^{2+}. Similar considerations may also apply to the Fe^{III}/Fe^{II} couple.

Experiments made by us have shown that methylene blue and thionine are rapidly reduced by iron^{II} in an atmosphere free from oxygen in a concentrated phosphoric acid medium, even at concentrations of reactants obtaining near the close of a titration of uranium^{VI} with iron^{II}. We have also noticed that the oxidation of the leuco dye by uranium^{VI} is rather slow. Hence the two reactions important for the satisfactory functioning of the indicator can be represented as follows:

$$D + 2H^+ + 2Fe^{2+} \xrightarrow{H_3PO_4} DH_2 + 2Fe^{3+} \tag{1}$$
$$\text{(Dye)} \qquad\qquad \text{(Leuco dye)}$$

$$DH_2 + UO_2^{2+} + 2H^+ \xrightarrow{H_3PO_4} D + U^{4+} + 2H_2O \tag{2}$$
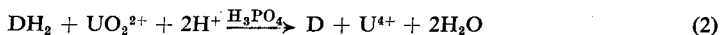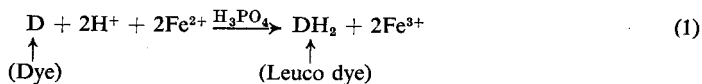
The fact that reaction (2) is slow and 'reaction (1) is fast' may make us believe that these dyes may not function satisfactorily as redox indicators in the reductimetric titration of uranium^{VI} with iron^{II} in a phosphoric acid medium. However, we made the interesting observation that the oxidation of leuco methylene blue by uranium^{VI} is induced by the fast reaction between iron^{II} and uranium^{VI}, so that the dyes can work satisfactorily as redox indicators.

In view of the above findings the authors have carried out the reductimetric titration of uranium^{VI} with iron^{II} using methylene blue as indicator in a medium containing phosphoric acid at a concentration not less than 11·6M. During such experiments it has been observed by the authors that in titrations containing small quantities of uranium (0·025 millimole of uranium per 50 ml), the colour change at the end-point is from blue to pale green or light green, this being the colour of uranium^{IV}. If the amount of uranium present in the solution is greater than 0·15 millimole for a final volume of 50 ml, the colour transition at the end-point is difficult to notice.

Reagents

Uranium^{VI} and iron^{II} solutions: Prepared and standardised as described above.

Methylene blue: A 0·1% aqueous solution of methylene blue prepared from the substance obtained from Dr. G. Grubler & Co., Leipzig, Germany.

When 0·5 ml of 0·1% methylene blue is used as indicator in titrations with 0·1N iron^{II} solution, the indicator correction has been found to be 0·02 ml. Hence this volume has to be deducted from the experimentally observed titres in order to get the correct values.

Thionine: A 0·1% aqueous solution of thionine prepared from a sample supplied by G. T. Gurr & Co., London, England.

Because leuco dyes are oxidised by air, the authors recommend that the titration of uranium^{VI} with iron^{II} using methylene blue and thionine as indicators be carried out in an atmosphere of carbon dioxide.

Procedure

An aliquot of uranium^{VI} containing less than 0·15 millimole of uranium and less than 5·0 ml in volume is transferred to a 100-ml beaker with the necessary arrangements already described. Forty-five ml of syrupy phosphoric acid and 0·5 ml of the dye solution are added and the mixture is kept well stirred with the magnetic paddle placed inside the mixture. Carbon dioxide is allowed to pass through the mixture. After 10 min, iron^{II} solution is added from a micro burette until the pale green or light green colour appearing at the end-point does not change to blue within 1 to 2 min. The amount of uranium present in the mixture is calculated after applying the necessary indicator correction. Some typical results obtained by the authors are given in Table V.

TABLE V

Methylene blue as redox indicator		Thionine as redox indicator	
Uranium^{VI} taken, *millimoles*	Uranium^{VI} found, *millimoles*	Uranium^{VI} taken, *millimoles*	Uranium^{VI} found, *millimoles*
0·0265	0·0267	0·0500	0·0503
0·0530	0·0533	0·0875	0·0870
0·0795	0·0790	0·1000	0·1005
0·1060	0·1060	0·1100	0·1100
0·1325	0·1320	0·1238	0·1231
0·1458	0·1450	0·1350	0·1353

Interferences

Iron[III] and tungsten[VI] have been found not to interfere with the accuracy of the determination of uranium[VI] when the titration is carried out electrometrically. The presence of tungsten[VI] is indeed beneficial as it helps a rapid attainment of stable potentials. This is the case even with higher amounts of tungstate although it gives a turbidity.

Vanadium[V], molybdenum[VI] and chromium[VI] interfere in the titration of uranium[VI] with iron[II] in a strong phosphoric acid medium. Further work is in progress.

Zusammenfassung—Die Formalpotentiale von Ferri/Ferro-Lösungen wurden in Gegenwart wechselnder Mengen von Phosphorsäure bestimmt; das Potential zeigt einen scharfen Abfall mit ansteigender Phosphatkonzentration. Oberhalb einer bestimmten Phosphorsäure-konzentration wird der Unterschied in den Formalpotentialen von U(VI)/U(IV) und Fe(III)/Fe(II) genügend gross, sodass Eisen(II) imstande is Uran(VI) selbst bei Zimmertemperatur zu reduzieren. Dies ist die Umkehr der üblichen Reaktion in der Uran(IV) durch Eisen(III) oxydiert wird. Eine Methode wurde ausgearbeitet um Uran(VI) in stark phosphorsaurem Medium (11–13·5 m) mit Eisen(II)-lösung zu titrieren. Die Endpunktsanzeige erfolgt entweder potentio-metrisch oder visuell mittels Methylenblau oder Thionin. Die Methode is vorteilhaft, weil bei Raumtemperatur titriert wird und Uran(VI) in Gegenwart von Eisen(III) und Wolfram(VI) potentiometrisch bestimmt werden kann. Ein weiterer Vorteil ist, dass keine besonderen Vor-kehrungen zur Lagerung der sonst üblicherweise verwendeten Titan(III) oder Chrom(II)-lösungen nötig sind.

Résumé—Les auteurs ont déterminé le potentiel normal apparent du couple fer(II)/fer(III) en milieu acide phosphorique de concentrations variées; ce potentiel décroît rapidement quand la concentration de l'acide phosphorique augmente. Au-dessus d'une certaine concentra-tion d'acide phosphorique, la différence entre les potentiels normaux apparents des couples U(VI)/U(IV) et Fe(III)/Fe(II) devient suffisam-ment grande pour permettre la réduction de l'uranium (VI) par le fer(II) même à la température ambiante; cette réaction est l'inverse de la réction d'oxydo-réduction normale qui consiste en l'oxydation de l'uranium (IV) par le fer(III). Une étude soignée des différents facteurs mis en jeu a permis de mettre au point un nouveau titrage de l'uranium (VI) par le fer(II) en milieu acide phosphorique concentré (11,0 à 13,5 M) à la température ambiante; le point équivalent est déterminé par potentiométrie ou par colorimétrie en utilisant le-bleu de méthylène ou la thionine comme indicateur interne. Le nouveau procédé, permettant de réaliser le titrage à la température ambiante, est plus commode que les méthodes qui mettent en jeu le titane(III) et le chrome(II) et qui nécessitent des températures de 60 à 90°. Il possède un avantage supplémentaire: il peut être utilisé pour le dosage de l'uranium(VI) même en présence de fer (III) et de tungstène(VI) en déterminant le point équivalent par électrométrie. Enfin, il ne demande pas les précautions spéciales nécessaires pour la préparation et la conservation des solutions de titane(III) et de chrome(II).

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PRELIMINARY COMMUNICATION

The hydrolysis of 8-acetoxyquinoline

8-HYDROXYQUINOLINE has been widely used as a precipitant for certain metallic ions and its *in situ* generation by the hydrolysis of its acetate ester in buffered media has been employed for precipitation from homogeneous solution.[1,2,3,4,5,6] Because the rate of this hydrolysis is an important factor in the success of this technique, a study of some of the factors which affect the rate has been undertaken. The data obtained might also suggest a possible mechanism for the hydrolysis of this compound in which the structural relationship of the ester group and the basic ring nitrogen is rather unique. The rate of hydrolysis of 7-acetoxyquinoline had been determined under similar conditions in order to provide a basis for comparisons.

The hydrolysis of these esters at 35° in buffered solutions over a pH range of from 0 to 10 has been followed by means of spectrophotometric measurements in the ultraviolet region. The reaction was found to be first order with respect to the ester in this range and the rates, as calculated from the first order plots, found to be highly pH sensitive. The results of these measurements are summarised in Fig. 1.

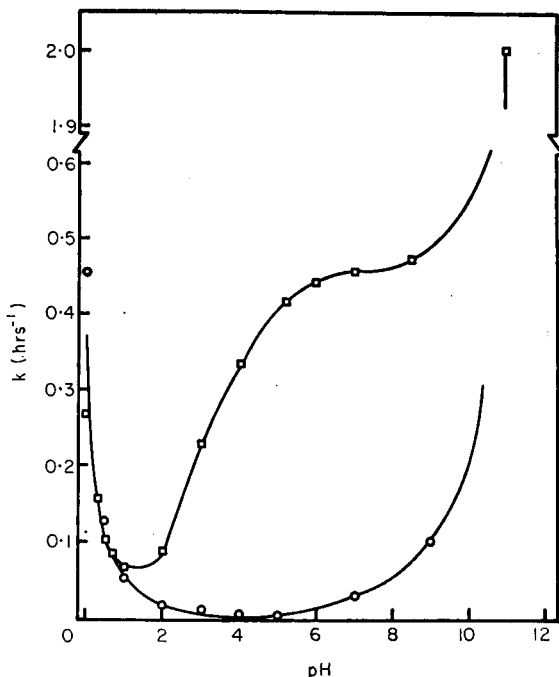FIG. 1. Effect of pH on the first order rate constant: □—8-acetoxyquinoline, ○—7-acetoxyquinoline. Note the discontinuity in the ordinate.

From these data it is readily apparent that the selection of the correct pH is an important factor in evolving an effective procedure for precipitation from homogeneous solution. Although the effect of temperature upon this reaction has not been investigated, a first approximation would be that

increased temperature would not appreciably alter the shape of the rate *vs.* pH curve. With this assumption it is possible to estimate the effect that changes in acidity will have on rates of precipitation at the higher temperatures employed in such procedures.

A difference in the behaviour of the two esters in the pH range between 2 and 10 is quite evident, and it is suggested that this difference is probably caused by the formation of an intramolecular hydrogen bond between the nitrogen and the ester group in the case of the 8-acetoxyquinoline. This chelation, which is impossible with the 7-isomer, may catalyse the hydrolysis of the 8-acetoxyquinoline by stabilising the intermediate whose formation is the rate-limiting step. Further investigation is under way to confirm or refute the postulated mechanism, to study the effects of the presence of metallic cations, and to determine the changes induced by changing temperatures. A report of this current work and a more thorough description of the experimental techniques will be made at a later date.

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Summary—The rates of hydrolysis of 7-acetoxyquinoline and 8-acetoxyquinoline at 35° have been measured and are reported for the pH region from 0 to 10.

Zusammenfassung—Die Hydrolysegeschwindigkeiten von 7-acetoxychinolin und 8-acetoxychinolin wurden bei 35°C gemessen und werden für den pH-Bereich 0–10 mitgeteilt.

Résumé—Les auteurs ont mesuré les vitesses d'hydrolyse de la 7-acétoxyquinoléine et de la 8-acétoxyquinoléine à 35° et donné les valeurs obtenues pour le domaine de pH: 0–10.

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SHORT COMMUNICATIONS

## Spot test for bivalent sulphur based on pyrolysis with mercuric cyanide*

STUDIES of pyrolysis reactions of mercuric cyanide with inorganic and organic compounds at temperatures up to 180° included an investigation of the behaviour of elementary sulphur. Because of the marked affinity between sulphur and mercury, and also because of the ease with which mercuric cyanide breaks down when heated, according to the reaction:

$$Hg(CN)_2 \rightarrow Hg° + (CN)_2,$$
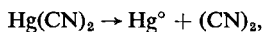
it was only natural to expect the occurrence of the reaction

$$S° + Hg(CN)_2 \rightarrow HgS + (CN)_2.$$
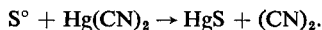
Trials showed that black mercuric sulphide did in fact appear very quickly, but dicyanogen was not produced since no response was given for this volatile compound when the extremely sensitive test with alkali cyanide and 8-hydroxyquinoline (red colour[1]) was applied. In contrast, when a disc of filter paper moistened with copper acetate-benzidine acetate was held above the heated reaction mixture, the paper turned blue, a reaction characteristic of hydrogen cyanide.[2] Because the formation of mercuric sulphide and hydrogen cyanide is known to occur even during the dry heating of mercuric thiocyanate, the pyrolysis of mercuric cyanide with sulphur may involve the formation and thermal decomposition of mercuric thiocyanate. The formation doubtless occurs through the addition reaction:

$$2S + Hg(CN)_2 \rightarrow Hg(CNS)_2.$$
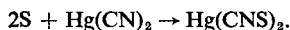
The formation of mercuric sulphide points to fission of mercuric thiocyanate by thermal decomposition, leading to dicyanogen sulphide:

$$Hg(CNS)_2 \rightarrow HgS + (CN)_2S \tag{1}$$
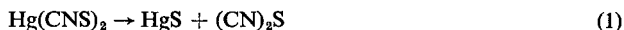
Dicyanogen sulphide has been prepared by other procedures and has been described[3] as a compound which sublimes appreciably at 30°-40° and melts at 60°. Furthermore, when dissolved in water it decomposes with formation of hydrogen cyanide. Therefore we assume that the positive response to the hydrogen cyanide colour reaction, when the $(CN)_2S$ vapours come into contact with the moist reagent paper, results from a hydrolysis leading to hydrogen cyanide, with participation of atmospheric oxygen. The following reactions may be involved:

$$(CN)_2S + H_2O \rightarrow HCN + HCNSO \tag{2}$$

$$(CN)_2S + H_2O + O \rightarrow 2\,HCN + SO_2 \tag{2a}$$
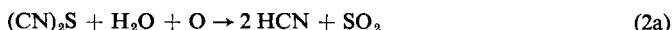
Evidence for the occurrence of reaction (2a) is furnished by the fact that the vapours evolved during the dry heating of mercuric thiocyanate, or a mixture of mercury cyanide and sulphur, give the colour reaction characteristic of sulphur dioxide (blue colour on Congo paper moistened with H_2O_2 or on filter paper moistened with $Fe[Fe(CN)_6]$ solution.[4]

It has now been found that alkali thiocyanates and organic thiocyanates behave in the same manner as elementary sulphur when pyrolysed with mercuric cyanide. Obviously, these compounds break down thus:

$$2\,KCNS + Hg(CN)_2 \rightarrow Hg(CNS)_2 + 2\,KCN$$

$$2\,R(Ar)CNS + Hg(CN)_2 \rightarrow Hg(CNS)_2 + 2\,R(Ar)CN$$
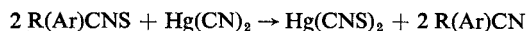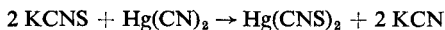
and reactions 1, 2, and 2a may then occur.

The removal of sulphur from organic thiocyanates is readily detected by the hydrogen cyanide colour reaction. Since these compounds contain bivalent sulphur in the SCN group, it could be

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* Translated by Ralph E. Oesper, University of Cincinnati, U.S.A.

expected[5] that other organic compounds containing bivalent sulphur would react in an analogous fashion. This expectation is confirmed in the case of open and cyclic thioethers, aliphatic and aromatic disulphides, and thioketones. We suggest that the following 'pyrolytic reactions lead to the formation of mercuric thiocyanate:

$$2 \,{>}C - S - C{<} + Hg(CN)_2 \rightarrow Hg(CNS)_2 + 2 \,{>}C - C{<}$$

$$\,{>}C = S - S - C{<} + Hg(CN)_2 \rightarrow Hg(CNS)_2 + \,{-}{>}C - C{<}{-}$$

$$2 \,{>}C = S + Hg(CN)_2 \rightarrow Hg(CNS)_2 + \,{>}C = C{<}$$

The above desulphurisations, which patently are a consequence of the marked tendency of mercuric thiocyanate to form, make possible (in combination with reactions 1, 2, and 2a), the detection of compounds of these types; they may also be of interest from the viewpoint of preparative organic chemistry in cases where the course of the reactions postulated here applies.

Organic compounds containing bivalent sulphur include not only sulphides, disulphides and thioketones but also thiols. This last group reacts (in the wet way) with mercuric cyanide through the acidic SH group, with formation of hydrogen cyanide:

$$2 \, R(Ar)SH + Hg(CN)_2 \rightarrow [R(Ar)S]_2Hg + 2 \, HCN$$

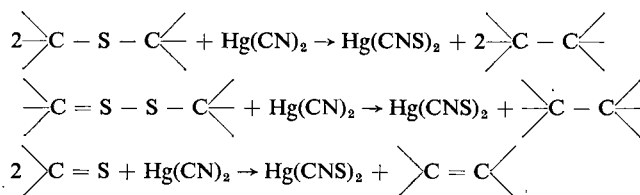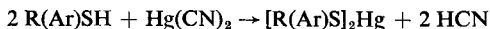Accordingly, the production of hydrogen cyanide during the pyrolytic action with mercuric cyanide may be utilised as a preliminary test for bivalent sulphur in organic compounds. A necessary condition is the absence of acidic compounds which likewise yield hydrogen cyanide when dry-heated with mercuric cyanide.* However, in the majority of instances, sulphides, disulphides and thioketones can be separated from acidic compounds (including thiols) by shaking the sample in alkaline medium with chloroform or ether. The alkali salts of the acidic compounds remain in the water layer.

Neutral compounds containing quadrivalent sulphur do not react with mercuric cyanide. For instance, alkali salts of sulphinic acids were tested, with negative results.

Trials were made to learn how elementary selenium and organic compounds containing bivalent selenium behave when pyrolysed with mercuric cyanide. Since black mercuric selenide results, the likelihood is that the initial product is mercuric selenocyanide, which then thermally decomposes to yield dicyanoselenide. The latter also produces hydrogen cyanide on hydrolysis. Therefore the test for bivalent sulphur as described here, by pyrolysis with mercuric cyanide, is reliable only in the absence of organic compounds containing bivalent selenium. The presence or absence of selenium can be recognised simply by means of a recently described spot test.[6]

Procedure: A micro test-tube is used. A small amount of the solid test material, or of the evaporation residue from 1 drop of a benzene solution, is stirred with several cg of mercuric cyanide using a dry glass rod. A drop of acetone is added and volatilised. The test-tube is immersed to a depth of about 0·5 cm in a glycerol bath preheated to 120°, and the open end is covered with a piece of filter paper moistened with hydrogen cyanide reagent. The temperature is raised to 180°. Development of a blue stain on the reagent paper indicates a positive test.

Hydrogen cyanide reagent (copper acetate-benzidine acetate solution). The preparation of this reagent solution is described in detail elsewhere, ref 5, p. 366.

Limits of identification:
10 μg o-carboxyphenylthiourea, ethyl ester,
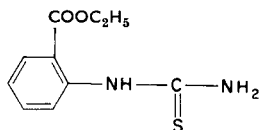
10 μg N,N'-dichlorothiourea, $SC{<}^{NH—Cl}_{HN—Cl}$

$$C_{10}H_7—NH—C—NH_2.$$
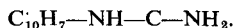
* It has been found that a test for such materials can be based on this reaction.

10 μg naphthylthiourea,

5 μg 4,4'-bis(dimethylamino)thiobenzophenone, $[(CH_3)_2NC_6H_4]_2$ CS.

50 μg thiocarbanilide C_6H_5NH—CS—NHC_6H_5.
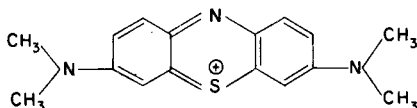
10 μg methylene blue,

5 μg l-cystine, $[—SCH_2CH(NH_2)COOH]_2$.

5 μg phthalylsulphathiazole,

5 μg dithio-oxamide, $NH_2CSCSNH_2$.
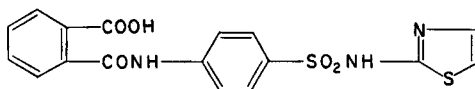
Summary—The test described for bivalent sulphur in organic compounds is based on the finding that hydrogen cyanide c an be detected in the gas phase if the sample is heated with mercuric c yanide to 180°. The identification limits range from 5 to 50 μg. An explanation is advanced for the chemistry of the pyrolytic reaction.

Zusammenfassung—Es wird ein Nachweis von 2-wertige m Schwefel in organischen Verbindungen beschrieben, der darauf ve ruht dass bei trockener Erhitzung (180° C.) mit Quecksilberzyanid in der Gasphase Cyanwasserstoff nachzuweisen ist. In der Arbeitsweis e der Tüpfelanalyse werden Erfassungsgrenzen von 5-50 μg erhalt en. Für den Chemismus der pyrolytischen Umsetzung kann eine plaus ible Erklärung gegeben werden.

Résumé—Les auteurs décrivent une recherche du soufre au degré d'oxydation + 2 dans les composés organiques; cette recherche est basée sur le fait qu'on peut décéler de l'acide cyanhydrique en phase gazeuse si l'échantillon est chauffé à 180° C avec du cyanure mercurique. Les limites d'identification vont de 5 à 50 μg. Une explication plausible peut être suggérée pour la chimie de la réaction pyrolytique.

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Contribution to the analytical use of a standard solution of iodine trichloride

THE analytical use of hydrochloric acid solutions of iodine monochloride and of iodine trichloride as standard solutions—"iodine-chlorometry"—was first suggested by Gengrinovich and coworkers.[1,2]

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A $0.1N$ standard solution of iodine trichloride was prepared from equivalent amounts of potassium iodide and potassium iodate with the use of hydrochloric acid, according to the equation:

$$KI + 2KIO_3 + 12HCl \rightarrow 3ICl_3 + 3KCl + 6H_2O \qquad (1)$$

The resulting solution, about $0.5N$ with respect to hydrochloric acid, was found to be suitable for solving a number of analytical problems.[3,4,5,6,7,8,9]

According to the above authors,[2] the following equilibria exist in the solution of iodine trichloride:

$$ICl_3 + HCl \rightleftharpoons HICl_4 \qquad (2a)$$

$$HICl_4 \rightleftharpoons H^+ + ICl_4^- \qquad (2b)$$

$$ICl_4^- \rightleftharpoons ICl_2^- + Cl_2 \qquad (2c)$$

The different types of reaction of iodine trichloride were interpreted by these authors on the basis of (2a), (2b) and (2c).

However, on considering the results of our experiments conducted with hydrochloric acid solutions of iodine trichloride from quite different aspects,[10] the existence of equilibria of the type shown does not seem probable. In order to clarify the situation, the following experiments were carried out.

The absorption curves of a $0.01N$ standard solution of "iodine trichloride"* (prepared from $0.1N$ iodine trichloride standard solution by dilution with $0.5N$ hydrochloric acid) and of a $0.01N$ standard solution of iodine monochloride (prepared from $0.1N$ iodine monochloride standard solution by dilution with $0.5N$ hydrochloric acid) were established.

In both cases regular curves, characteristic of the chloride complex of iodine monochloride, were obtained. However, differences appeared in the values of the extinctions measured at the site of the maximum ($343 \, m\mu$). Namely, the extinction value of the $0.01N$ solution of iodine monochloride was exactly the quadruple of that of the $0.01N$ solution of "iodine trichloride". This points to the fact that 25% of the full oxidation power of the "iodine trichloride" actually originates from iodine monochloride. According to its spectrum the solution contains no elementary iodine, so that the residual 75% of the oxidation power might be ascribed to elementary chlorine or iodate or eventually to both of them.

The accurate composition of the standard solution of "iodine trichloride" was established in the following manner.

1. In order to determine the chlorine content of the solution, an aliquot was treated with potassium cyanide solution which had been previously neutralised with hydrochloric acid. The oxidising power of the mixture was then determined iodometrically. The value agreed with the "full" oxidising power.†

From (2c), the full oxidising power is given by:

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-.$$

$$ICl_2^- + I^- \rightarrow I_2 + 2Cl^-.$$

However, if potassium cyanide is added first:

$$Cl_2 + CN^- \rightarrow ClCN + Cl^- \text{ (see reference 11)}$$

$$ICl_2^- + CN^- \rightarrow ICN + 2Cl^- \text{ (see reference 12)}$$

which is followed by:

$$ICN + I^- + H^+ \rightarrow I_2 + HCN$$
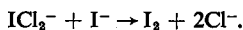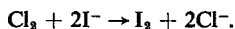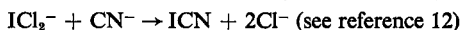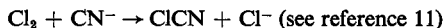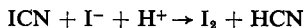
since cyanogen chloride is inactive iodometrically. The fact that no decrease in the oxidation power occurs after treatment with potassium cyanide [a 50% decrease would be expected on the basis of (2c)] proves that the solution contains no elementary chlorine. Because iodate does not react with cyanide ion, the effect on the oxidation power of any iodate present in solution would be unchanged after adding potassium cyanide.

2. In order to determine the iodate content of the solution, an aliquot was treated with potassium cyanide and sodium hydroxide, then warmed. The oxidising power of this solution was determined iodometrically and found to be 75% of the "full "oxidising power.

Assuming the chloride complex of iodine monochloride and iodate to be present in the original solution, the full oxidising power is given by:

$$ICl_2^- + I^- \rightarrow I_2 + 2Cl^-$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O.$$
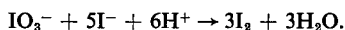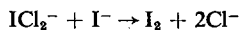
* Quotation marks are used because, as will be proved later, no iodine trichloride or only traces of it are actually present in the standard solution.

† The oxidising power determined without adding potassium cyanide.

However, if potassium cyanide is added first (iodate does not react with cyanide ion) and warmed with sodium hydroxide:

$$ICl_2^- + CN^- \rightarrow ICN + 2Cl^-$$

$$ICN + OH^- \rightarrow I^- + CNO^- + H^+$$

which is followed by:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O.$$
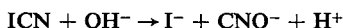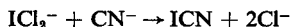
Consequently, from the aspect of oxidation power, a standard solution of "iodine trichloride" presumably contains equimolecular amounts of iodate and iodine monochloride.

The experiments described above under 1 and 2 were repeated with a $0 \cdot 1N$ solution of tetrachloro-hydriodic acid (pure crystalline $HICl_4 \cdot 4H_2O$ was prepared and dissolved in $0 \cdot 5N$ hydrochloric acid). The absorption curve of this solution diluted to $0 \cdot 01N$ with $0 \cdot 5N$ hydrochloric acid was also established. The data obtained from these experiments supported the conclusion that "iodine trichloride" solution contains equal amounts of iodate and iodine monochloride.

On the basis of our results, the following overall conversion presumably takes place in a standard solution of iodine trichloride which is about $0 \cdot 5N$ with respect to hydrochloric acid, immediately after its preparation:

$$2ICl_3 + 3H_2O \rightleftharpoons ICl + HIO_3 + 5HCl \qquad (3)$$

Our investigations with respect to the mechanism of this reaction will be published elsewhere.[10]

In terms of the above knowledge of a $0 \cdot 1N$ standard solution of iodine trichloride in hydrochloric acid it is readily possible to interpret both the oxidation and the addition and halogen substitution reactions of the solution. It appears unnecessary to interpret oxidation reactions separately. In substitution and addition reactions, iodine monochloride participates by saturating the olefinic bond and substituting the aromatic ring, respectively. The residual iodate, together with the excess of standard solution is measured iodometrically. (According to Gengrinovich[1] one actually measures excess standard solution and chlorine on back titration.)

Obviously there is no objection against the further use of analytical methods connected with a standard solution of "iodine trichloride" or of the conventional equivalent weights [cf. (2c) and (3)]. It is, however, preferable to use standard solutions of bromine chloride and iodine monochloride, respectively, in oxidation, in addition or in halogen substitution reactions.

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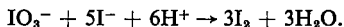Institute of Inorganic and Analytical Chemistry
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Hungary

Summary—In order to establish its accurate composition, the $0 \cdot 1N$ standard solution of iodine trichloride suggested by Gengrinovich has been subjected to re-investigation. It was found that iodate is responsible for 75% and iodine monochloride for 25% of the total oxidation power of the solution. The presence of iodine trichloride could not be detected. In terms of this knowledge of the exact composition of the solution it is possible to consider in an entirely new way the chemical reactions occurring during its use.

Zusammenfassung—Um die richtige Zusammensetzung der von Gengrinovich als Massflüssigkeit empfohlenen 0,1N Jodtrichloridlösung haben die Verfasser Versuche ausgeführt. Es wurde festgestellt, dass 75% des totalen Oxidierungswertes der Masslösung dem infolge Hydrolyse des Jodtrichlorids entstandenen Jodat-Ion und 25% des Oxidierungswertes dem Jodmonochlorid ($2JCl_3 + 3H_2O \rightarrow FCl + HJO_3 + 5HCl$) zuzuschreiben ist. Die Anwesenheit von JCl_3 konnte weder auf fotometrischem Wege (u.v.), noch mit chemischen Methoden nachgewiesen werden

Résumé—Les auteurs ont étudié la solution standard 0,1N de trichlorure d'iode suggérée par Gengrinovich, afin d'établir sa composition précise. Ils trouvèrent que l'iodate est responsable de 75% des propriétés oxydantes de la solution et le monochlorure d'iode de 25%. La présence de trichlorure d'iode n'a pas pu être décelée dans la solution. Pour connaître la composition exacte de la solution, les auteurs ont pu considérer d'une manière tout à fait nouvelle les réactions chimiques qui se produisaient pendant son utilisation.

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Chelating action of thioglycollic acid with silver and some common bivalent cations

THIOGLYCOLLIC acid has been much used as a colorimetric agent for the spectrophotometric determination of iron^{III} with which it forms a soluble red product in ammoniacal solution. The constitution of this complex has been reported variously as $Fe(OH) \cdot (SCH_2COO)_2{}^{2-}$,[1] $Fe(SCH_2COO)_2{}^{1-}$,[2] and $[Fe(SCH_2COO)_2]_2KFe$.[3] Thioglycollic acid forms precipitates or soluble coloured compounds with many ions, *e.g.*, bismuth, cobalt, nickel, lead, mercury^I, uranium^{VI}, manganese and gold, but has been said not to react with aluminium, barium, calcium, strontium, chromium and zinc.[4] More recently, however, it has been shown that in alkaline solution the soluble colourless complexes of thioglycollic acid with lead, bismuth, cadmium, silver, mercury^{II}, zinc, thallium^{III}, indium and tin, are stronger than the EDTA complexes of these metals.[5] Thioglycollic acid therefore serves as a useful masking agent in complexometric titrations with EDTA and can be used in place of potassium cyanide in many determinations. Thioglycollic acid has also been used in the extractive determination of molybdenum.[6]

Leussing[7] has reported that some bivalent metals, namely manganese, iron, cobalt, nickel and zinc, form complexes of the type $M(SCH_2COO)_2{}^{2-}$. From the evidence of potentiometric titrations he concluded that no complex formation occurred on replacing the first (carboxylic) proton, but that it did occur on replacement of the second (thiol) proton. No evidence was found for the formation of higher complexes. The following overall formation constants were reported:—manganese^{II} $3 \cdot 6 \times 10^7$: iron^{II}; $1 \cdot 7 \times 10^{10}$: cobalt^{II}; $1 \cdot 4 \times 10^{12}$: nickel; $3 \cdot 4 \times 10^{13}$: zinc; $1 \cdot 1 \times 10^{15}$. In an earlier paper Li and Manning[8] reported on the lead, cadmium and zinc complexes of thioglycollic acid. In their study they reported $\log_{10} k_1$ for the lead complex as $8 \cdot 5$ and $\log_{10} k_1 \times k_2$ for the zinc complex as $14 \cdot 41$; the cadmium complex was not investigated. The mercury^{II} complex has been reported as $Hg(SCH_2COO)_2{}^{2-}$ with $\log_{10} K = 43 \cdot 82$ and the formation of a slightly soluble complex $Hg_2(SCH_2COO)_2$ was also noted.[9]

In this communication we report a brief examination of the reaction between thioglycollic acid (TGA) and several metal ions, namely silver, lead, zinc, mercury^{II} and cadmium, with a view to assessing the potentialities of TGA as a complexometric titrant. The reactions were examined (a) by direct titration using metallochromic indicators, and (b) by a process of back-titration in which an excess of the metal ion was added to the buffered TGA solution and determined by complexometric titration with EDTA.

Zinc. Zinc was titrated directly with TGA at the $0 \cdot 1M$ level with Solochrome Black T as indicator at pH 10 in an ammonia buffer. The quality of the end-point was poor because of attack by TGA on the indicator. Optimum conditions were obtained by adding the indicator only near the end-point. Clear indication of a highly soluble $Zn(SCH_2COO)_3{}^{4-}$ complex was obtained. A very precise end-point was obtained by the back-titration process with EDTA and the same indicator-buffer system. Once more, clear evidence was obtained of a 1:3 complex. Such a complex could presumably be formed readily at pH by addition of another TGA molecule to the $Zn(SCH_2COO)_2{}^{2-}$ complex previously reported by others. In fact Leussing comments that the remaining co-ordination sites on the

zinc ion in the 1:2 complex are probably occupied by water molecules. However, under our conditions at least, there is very precise definition of the 1:3 complex and we find no stereochemical reason for non-formation of such a complex.

Mercury[II]. Mercury was titrated with TGA at pH 6 in a pyridine acetate buffer. A precipitate was formed initially, then dissolved sharply near the end-point. Xylenol Orange was used as indicator, but the disappearance of the colloidal precipitate at equivalence gave a clear indication of the nearness of the end-point. The mechanism of this particular reaction is of considerable interest. The $Hg_2(SCH_2COO)_2$ insoluble compound postulated by earlier workers may well account for the initial formation of the precipitate observed by us in the initial stages of the titration where an excess of mercury[II] ions would further repress its solubility. Furthermore, the removal of free mercury[II] ions by TGA at equivalence (1:1) would account for the disappearance of turbidity and the near simultaneous colour change of the indicator is to be expected because the 1:1 complex may be assumed to be sufficiently associated not to affect visibly the Xylenol Orange indicator. Thus the existence of the $Hg(SCH_2COO)_2^{2-}$ complex reported by Kolthoff and his coworkers would not be in evidence here for the reasons noted above.

A 1:1 complex was also found in the second series of experiments when an excess of mercury[II] was added to TGA and the excess back-titrated with EDTA using the Xylenol Orange indicator and pyridine buffer system. Here once more we would not expect experimental evidence for the formation of anything other than the 1:1 complex because the latter is obviously more stable than the mercury[II]-EDTA complex under these conditions. Both procedures therefore confirm the existence of the 1:1 complex which was previously reported by Kolthoff *et al.*[9] and assigned a binuclear structure by them.

Cadmium. Cadmium was titrated directly with TGA in an ammonia buffer at pH 10 with Solochrome Black 6B as indicator. Solochrome Black T and Catechol Violet were also examined as indicators, but the first mentioned was preferred. As with zinc, difficulties were once more experienced because of attack on the indicator. Despite this, however, consistently reproducible results were obtained which indicated the formation of a highly soluble $Cd_2(SCH_2COO)_3^{2-}$ complex. Similarly, when an excess of cadmium[II] ions was added to TGA and the excess was back-titrated with EDTA using the same indicator-buffer system once more, a clear indication of a 2:3 complex was obtained. Other workers have avoided definition of the cadmium complex probably because similar results obtained by them did not fit in with the usual 1:2 ratio pattern for all other ions which had been examined previously.

Lead. Lead was titrated directly with TGA in a manner similar to zinc and cadmium. As before, a rather poor end-point was obtained, but in this instance the evidence pointed to the formation of a $Pb(SCH_2COO)_2^{2-}$ complex. A back titration process with EDTA as above also gave a reaction ratio Pb:TGA = 1:2. This result agrees well with the 1:2 complexes previously reported for nickel[II], iron[II], cobalt[II] and manganese[II].

Silver. There is a lack of metallochromic indicators for silver ion, but it was found possible to detect the end-point with *p*-dimethylaminobenzalrhodanine. The end-point was quite sharply defined though the colour contrast was poor. The addition of Xylene Cyanol F.F. improved the colour change in ammoniacal solution and the direct titration was readily effected with precise indication of an $Ag(SCH_2COO)^-$ complex. It was not possible to carry out a back-titration in this instance because of the low stability constant of the silver-EDTA chelate. However, potentiometric titration with a silver-metal indicator electrode was performed successfully. This also gave unequivocal evidence of a 1:1 complex. The silver complex does not appear to have been formulated previously.

Homologues of thioglycollic acid and allied reagents

As a matter of general interest some additional titrations of silver were carried out potentiometrically with β-mercaptopropionic acid, β-mercaptosuccinic acid and thiodiglycol. Since we were not concerned with quantitative data here, the technical acids, which were the only materials available to us, were used for the preparation of these reagents and no purification or standardisation was attempted. The potentiometric curves obtained with these reagents are compared with that of thioglycollic acid in Fig. 1. As expected, β-mercaptopropionic acid behaved in a manner similar to thioglycollic acid whilst thiodiglycol, which contains no active mercapto-group, showed no complexing action. The β-mercaptosuccinic acid curve shows fairly definite evidence of a 2:1 as well as a 1:1 silver: reagent complex. This work was not pursued further, however, because these reagents offer no particular advantages for analytical purposes, which was the aspect of this study of immediate interest to us at the time.

DISCUSSION

The foregoing study has established the empirical formulae of some complexes of bivalent metal ions with thioglycollic acid, mainly in an ammoniacal medium where it was proposed to use the complexing action of TGA for complexometric titration purposes. In no case, however, has the reagent
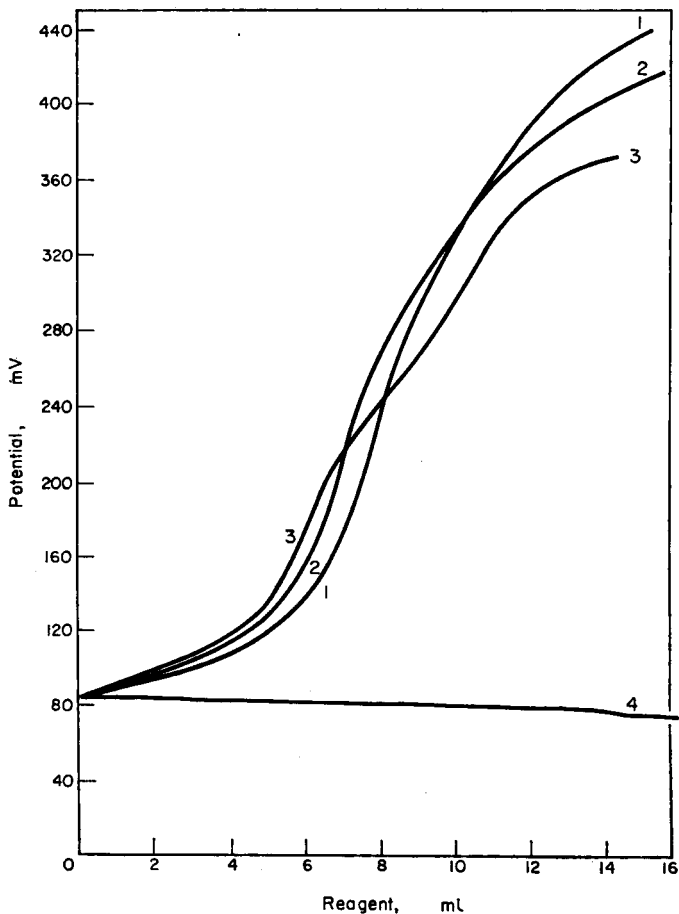
FIG. 1—Potentiometric titration of 10 ml of 0·1 M silver nitrate in ammoniacal solution
(silver-metal/calomel electrode system):
1—1 % β-mercaptopropionic acid,
2—1 % thioglycollic acid,
3—1·5 % β-mercaptosuccinic acid,
4—1·2 % thiodiglycol.

been found to possess sufficient advantage over conventional methods with ethylenediaminetetra-acetic acid except that a direct complexometric titration of silver may be possible though with a poorly defined visual end-point. The potentiometric end-point for silver is fairly well defined, but in this respect it may be stated that the end-points obtained when cyanide ion or chloride ion are used are probably superior.

We have obtained good results for the analysis of chlorides, bromides and iodides by dissolving these halide precipitates of silver in an excess of ammoniacal TGA and back-titration to a potentio-metric or p-dimethylaminobenzalrhodanine end-point, but once more the lack of a more suitable visual indicator militates against the adoption of such a procedure.

An aqueous 1 % solution of TGA stored in a well-stoppered brown bottle is not markedly un-stable, and our evidence is that after 14 days, during which time the bottle was opened *ca.* once per 2 days, the equivalence of the solution was still 90 % of its original value, when freshly prepared. No perceptible decrease in strength of the reagent solution was observed over the first 24 hr, though it is possible that considerable differences for stability could be obtained depending on the manner of storage and frequency of opening the vessel, *etc.*

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Summary—The reactions between thioglycollic acid and some bivalent cations, *viz.* zinc, mercury, cadmium, lead and more particularly with silver, are studied by direct and indirect complexometric titration. New complexes are reported with zinc, cadmium and lead, and the silver complex is also formulated. The potential use of the reagent as a complexometric titrant for silver ion is hindered by the lack of suitable metallochromic indicators.

Zusammenfassung—Die Reaktion zwischen Thioglycolsäure und einigen zweiwertigen Ionen (Zn, Hg, Cd, Pb) und im besonderen Silber wurde mittels direkter und indirekter komplexometrischer Titration studiert. Neue Komplexe mit Zn, Cd und Pb wurden nachgewiesen und der Silberkomplex wurde formuliert. Die Verwendung des Reagenses als komplexometrisches Titrationsmittel für Silber ist theoretisch möglich, scheitert aber in Praxis am Fehlen eines geeigneten metallochromen Indicators.

Résumé—Les auteurs ont étudié, par titrage complexométrique direct et indirect, les réactions entre l'acide thioglycollique et quelques cations divalents: Zn, Hg, Cd, Pb et plus particulièrement Ag. De nouveaux complexes sont décrits dans le cas de Zn, Cd et Pb et une formule du complexe de Ag est donnée. L'utilisation du réactif comme agent de titrage complexométrique pour l'ion Ag est gênée par le manque de réactifs métallochromes convenables.

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Phase titrations—I: Binary systems involving carbon tetrachloride and binary systems involving carbon disulphide

THE technique of phase titration is not new. Siggia[1,2] mentions two component phase titrations, Bogin[3] and Spiridonova[4,5,6] have reported phase titrations and, recently, Caley and Habboush[7] reported the phase titration of 14 binary systems involving alcohols and aromatics, using water as the titrant. They give a discussion of errors which may arise and take detailed precautions to avoid them. In the present work, calibration curves were set up by titrating known solutions under the same conditions as unknowns, stressing, not the avoidance of error, but its cancellation. The result is a very

rapid technique allowing as many as 15 to 20 titrations to be carried out in 1 hr, using the simplest apparatus and chemicals and sacrificing only a small degree of the accuracy inherent in phase titrations.

THEORY

When water is added to a homogeneous solution of two organic liquids, one of which is immiscible with water, a phase separation takes place and the solution becomes turbid. The amount of water which must be added to cause phase separation depends on the temperature of the system, the nature of the organic liquids and their relative amounts. A common method of determining the phase diagrams for systems of water and two organic liquids is phase titration with water to a turbidimetric end-point.[8] If the composition of several solutions is known, the phase diagram can be determined. Conversely, if the phase diagram is known, the composition of the original binary solution can be determined.

Phase diagrams

Ternary phase diagrams have been represented by equilateral triangles for many years.[9] Fig. 1 shows the phase diagram of a common type of ternary system, in which one pair of liquids is immiscible in all proportions and the other two are miscible in all proportions. The phase diagram for carbon
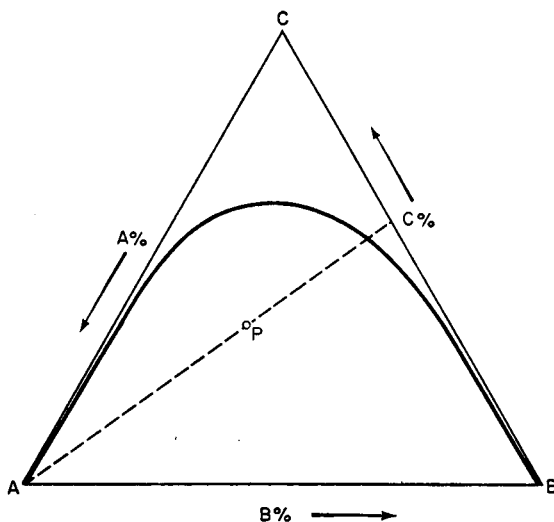
FIG. 1.—Representation of a three component system using an equilateral triangle. The dotted line represents the titration of a 40:60 binary solution of B to C with A. Point P represents the ternary solution with the composition 40% of A, 24% of B and 36% of C.

tetrachloride, ethanol and water[10] is one of many like Fig. 1. Systems represented by a point below the solubility curve (curved line within triangle) are heterogeneous and turbid.

A straight line from one apex, say A, to the opposite side is the locus of points representing a constant ratio of B to C and varying amounts of A. Such a line represents the titration of a binary mixture of B and C using A as the titrant. The intersection of the dotted titration line with the solubility curve is the composition at which the second phase separates and turbidity appears.

Phase Titrations

The phase titration of a 90:10 mixture of C to B with A follows line 1 in Fig. 2(a). Titrations of 80:20, 70:30, 60:40 and 50:50 mixtures of C to B follow lines 2 to 5. As the concentration of the immiscible component, B, becomes greater, the amount of A necessary to cause phase separation rapidly becomes smaller. The titre approaches infinity (complete miscibility with the titrant) as the original solution composition approaches pure C and zero (complete immiscibility) as the original solution composition approaches pure B.

If the volume (ml) of A necessary to cause turbidity is plotted as a function of the percentage of B, a calibration curve is obtained, Fig. 2(b), in which each point corresponds to the titration line with the corresponding number in Fig. 2(a). A solution of unknown composition can be titrated, and its composition determined directly from the calibration curve.
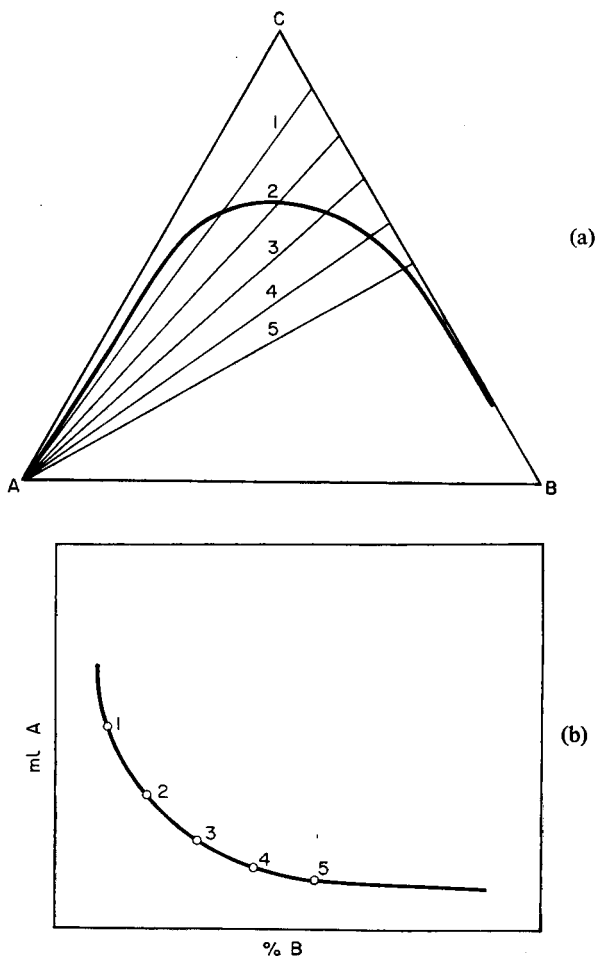
FIG. 2a–b.—The relationship between a three component phase diagram and a calibration curve. Each point on the calibration curve represents the intersection of the corresponding titration line with the solubility curve.

Not only can binary solutions of B and C be determined by titrating with A but homogeneous binary solutions of A and C can be titrated with B to a turbidimetric end-point. In either case, there will be an optimum concentration range of the mixture to be titrated which is dependent on the shape of the phase diagram. Finally, it is possible to determine the ratio of immiscible components of a two phase system, A and B, by titrating with C to the disappearance of turbidity.

Potential sources of error are: (1) variation in temperature caused by ambient fluctuations and heat of mixing, (2) false turbidity caused by air bubbles from too vigorous stirring, and (3) slow attainment of phase equilibrium.

In order to avoid these errors, the reaction flask can be fitted with a constant temperature jacket or the titration can be carried out in a constant temperature bath with a suitable arrangement for observing the phase change through the bath water. Gentle stirring can be maintained and additions of titrant be made very slowly to assure temperature and phase equilibrium throughout the course of

the titration. In addition, an indicator soluble in one component but not in the other can be used to make the appearance of opalescence easier to observe. Large samples can be used to increase the titre.

Taking all of these precautions, very accurate results have been obtained but the method becomes so slow and complicated that its usefulness is questionable.

In the procedure given below, none of these precautions were taken; it was only necessary to run known samples along with the unknown so that the calibration curve was obtained under conditions identical to the titration of unknowns. The technique is so rapid that a calibration curve can be run every day if ambient fluctuations make it necessary to do so.

There are a number of general advantages of phase titrations: (1) In many systems, water is the titrant, eliminating all standardisation, cost and storage problems. (2) There is no indicator, hence no indicator error. (3) The turbidimetric end-point should be well adapted to automatic titrators. (4) Sample size has no effect on the end-point. (5) Ternary mixtures can be analysed by a combination of phase titration and a standard determination of one of the components.[2] (6) There is a vast number of systems to which phase titrations might be applied. One need only think of 10 solvents miscible with water and 10 immiscible with it to have a list of three hundred systems suitable for investigation. (7) A large number of phase diagrams are already in the literature[10,11,12] to serve as a guide for setting up new systems.

EXPERIMENTAL

Reagents

Reagent grade methanol, isopropanol and dioxan were used. Technical grade ethanol, carbon disulphide, carbon tetrachloride and acetone were used. Distilled water was the titrant except as otherwise indicated.

Procedure

The phase diagram, if it is in the literature, may be converted to a rough calibration curve. Guided by the rough curve, five or six binary mixtures were made up and titrated. Their titre was plotted against the volume percentage of the insoluble component. Titrations were carried out using 10 ml of sample in a 25-ml Erlenmeyer flask. Water was added from a 5-ml pump microburette. The solution was stirred vigorously by means of a magnetic stirrer. Splashing was prevented and vaporisation retarded by closing the flask with a one-hole rubber stopper through which the tip of the burette protruded. Water was added rapidly to the appearance of a definite, permanent turbidity. The observance of turbidity was facilitated by strong cross illumination and a black background.

Unknown solutions were determined by comparison with the calibration curve, titrating under identical conditions. If a sample is outside the optimum titration range (a titre of 1 to 10 ml), a known quantity may be diluted with one or the other of its pure components to bring it into the optimum range.

RESULTS AND DISCUSSION

Table I shows the results for a number of binary systems to which phase titrations have been applied. Calibration curves and unknowns were determined on the same day. In each case the calibration curve resembled that shown in Fig. 2(b), the main difference being a displacement away from the x-axis as the water miscible component became less polar. For example, methanol and carbon tetrachloride require less water to cause turbidity than isopropanol and carbon tetrachloride of the same volume composition.

Turbidity, which depends on the difference in refractive index between the two phases, was clearly visible in all cases. The end-point change was rapid in each case except the carbon disulphide-ethanol system which exhibited slow attainment of phase equilibrium and required about a 0·5-min pause between additions of titrant near the end-point. Partial miscibility was observed between carbon disulphide and methyl and ethyl alcohol but this was not encountered between concentrations listed in Table I as the optimum titration concentrations. A considerable heat of mixing effect was observed during the titration of binary solutions containing methanol. Apparently this has not decreased the precision.

Table II shows the results of titration carried out on 5 different days under widely different atmospheric conditions. The results indicate a considerable decrease in reproducibility.

Table III shows, first, the titration of solutions of acetone and water using carbon tetrachloride as the titrant and second, the titration of some heterogeneous mixtures of carbon tetrachloride and water using the principle that binary solutions represented by any of the three sides of a ternary phase diagram can be titrated with the component represented by the opposite apex. The titration of the homogeneous binary systems of acetone and water is in all respects similar to those given in Table I. Titrations of the heterogeneous binary mixtures of carbon tetrachloride and water give a very different

TABLE I. RESULTS FOR THE TITRATION OF 10 HOMOGENEOUS BINARY SYSTEMS WITH WATER. THE END-POINT WAS INDICATED BY THE APPEARANCE OF A DISTINCT PERMANENT TURBIDITY. TITRATIONS AND DETERMINATION OF THE CALIBRATION CURVE WERE CARRIED OUT ON THE SAME DAY

Sample	Optimum range, %	Number of titrations	Standard deviation
CCl_4-methanol	2–30	12	0·16
CCl_4-ethanol	3–50	10	0·31
CCl_4-isopropanol	10–50	15	0·47
CCl_4-dioxane	2–20	8	0·16
CCl_4-acetone	3–25	12	0·26
CS_2-methanol	2–20	17	0·16
CS_2-ethanol	3–20	10	0·12
CS_2-isopropanol	20–40	11	0·14
CS_2-dioxane	3–20	10	0·08
CS_2-acetone	3–25	10	0·11

TABLE II. TITRATIONS OF BINARY SOLUTIONS CARRIED OUT ON 5 DIFFERENT DAYS. ALL SAMPLES WERE COMPARED TO THE SAME CALIBRATION CURVE AND NO CORRECTIONS WERE MADE FOR AMBIENT FLUCTUATIONS

Sample	Optimum range, %	Number of titrations	Standard deviation
CCl_4-isopropanol	20–40	15	1·39
CCl_4-acetone	5–25	15	0·81

TABLE III. TITRATIONS USING TITRANTS OTHER THAN WATER. THE SYSTEM ACETONE-WATER IS HOMOGENEOUS. THE SYSTEM CARBON TETRACHLORIDE-WATER IS HETEROGENEOUS; THE END-POINT IS INDICATED BY THE DISAPPEARANCE OF TURBIDITY

Sample	Titrant	Optimum range, %	Number of titrations	Standard deviation
Acetone–water	CCl_4	4–20	9	0·10
CCl_4–water	Acetone	3–10	9	0·04

calibration curve from Fig. 2(b) because the solubility curve is being approached from the opposite side. Indeed, the more polar titrant, acetone was tried and found to be unsuitable at reasonable proportions of carbon tetrachloride (3%), because the titre was too large; the solubility curve approaches the apex representing acetone too closely.

The titration of heterogeneous mixtures of water and carbon tetrachloride showed an increase in turbidity as the end-point was approached and the emulsion of carbon tetrachloride in the water–acetone system became more stable. Just at the end-point turbidity disappeared and, with very little time lag to establish phase equilibrium, the ternary solution became homogeneous.

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Summary—The theoretical basis of phase titrations is discussed, a simple, rapid titration method is described and its errors and advantages are evaluated. Typical calibration curves are shown and related to the corresponding three component phase diagram. Data are included for the analysis of carbon tetrachloride and carbon disulphide

in binary solutions with methanol, ethanol, isopropanol, dioxan and acetone, using water as the titrant. Titrations of heterogeneous systems and titrations using carbon tetrachloride as the titrant are briefly discussed and a few representative results are presented.

Zusammenfassung—Die theoretischen Grundlagen von Phasentitrationen werden diskutiert, eine einfache und rasche Titrationsmethode wird beschrieben und ihre Fehlerquellen und Vorteile werden bewertet. Typische Eichkurven werden gezeigt und mit den dazugehörigen Phasendiagrammen von Dreikomponentensystemen in Beziehung gebracht. Daten für die Analyse von Tetrachlorkohlenstoff und Kohlenstoffdisulfid in binärer Lösung in Methanol, Äthanol, Isopropanol, Dioxan und Aceton unter Verwendung von Wasser als Titrationsmittel werden mitgeteilt. Die Titration heterogener Systeme und Titrationen mit Tetrachlorkohlenstoff werden kurz diskutiert und einige repräsentative Daten gegeben.

Résumé—Les auteurs discutent la base théorique des titrages de phase, décrivent une méthode de titrage simple et rapide et évaluent ses erreurs et ses avantages. Les courbes d'étalonnage caractéristiques sont données et rapportées au diagramme correspondant à trois composés. Les auteurs donnent les résultats d'analyse du tétrachlorure de carbone et du sulfure de carbone en solutions binaires avec le méthanol, l'éthanol, l'isopropanol, le dioxanne et l'acétone, utilisant l'eau comme agent titrant. Les titrages de systèmes hétérogènes, ainsi que ceux qui utilisent le tétrachlorure de carbone comme agent titrant sont brièvement discutés et quelques résultats caractéristiques sont donnés.

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LETTERS TO THE EDITOR

Photometric determination of uranium in calcium fluoride with 1-(2-pyridylazo)-2-naphthol (PAN) using 1,2-diaminocyclohexanetetra-acetic acid as masking agent

SIR:

CALCIUM fluoride doped with small amounts of uranium^{III} is one of the important optical masers.[*][1] A sensitive and accurate method of determining its uranium content is needed. Cheng and Bray[2] reported that small amounts of alkaline earth metals do not give any colour reaction with PAN. It was found, however, that large amounts (for instance, 1 mmole) of alkaline earth metals (also manganese^{II}) give colour reactions with PAN at pH above 9. For the same quantity of the metal, the colour intensities of the complexes follow the order: Mn > Ca > Mg > Ba > Sr. Although addition of EDTA eliminates the interference of calcium, its presence affects slightly the formation of coloured uranium-PAN complex unless its quantity added can be carefully controlled.[3] It was found that 1,2-diaminocyclohexanetetra-acetic acid (DCTA) not only effectively masks the PAN complexes of the interfering metals (including the alkaline earth metals), but also that the presence of its free form does not affect the colour development of the uranium-PAN complex at pH 10. In general, the DCTA complexes are more stable than EDTA complexes. Here it seems that the stability of the uranium complexes is an exception, in that the uranium^{VI}-EDTA complex is more stable than the uranium^{VI}-DCTA complex. At present one cannot compare their stability directly, because their stability constants are not available in the literature. It was also found that DCTA can be successfully used as a masking agent in the determination of uranium with 4-(2-pyridylazo)-resorcinol (PAR),[4] or 1,3-diphenyl-1,3-propanedione,[5] where large amounts of calcium and EDTA also interfere.

The red PAN complexes of alkaline earth metals are presumed to be co-ordinated with molecular water, since they are not extractable by non-polar solvents such as benzene, chloroform, carbon tetrachloride, etc.; however, they are extractable by higher alcohols. Large amounts of calcium do not give high results in the determination of uranium because the calcium-PAN complex is not extractable by dichlorobenzene; on the contrary they give low results because of their competition with uranium for PAN. The maximum colour development for the uranium-PAN complex requires at least 5 min of standing.

Calcium fluoride is not decomposed by hydrochloric acid, nitric acid, sulphuric acid, or *aqua regia*. It was found that fuming perchloric acid dissolves it readily.

Procedure: To a finely-ground calcium fluoride sample (approximately 0·2 g) in a 100-ml beaker add 2 ml of 60% perchloric acid, and heat on a hot plate until it is fumed to approximately 1 ml. Cool, transfer to a 100-ml volumetric flask, and make to the mark with water. Take a suitable aliquot (containing not more than 100 μg of uranium) into a small beaker, add a slight excess of DCTA, a few ml of NH_4OH-NH_4Cl pH 10 buffer solution, 1 drop of 2% KCN solution, and 2 ml of 0·1% PAN solution in methanol. Dilute to approximately 20 ml with water, and adjust the pH to 10·0 ± 0·1 with NH_4OH or HCl, if necessary. Transfer to a 60-ml separatory funnel and let stand for 10–15 min or longer. Add exactly 10 ml of o-dichlorobenzene, and shake vigorously for 30–60 sec. Filter the extract through glass wool. Measure the absorbance at 570 mμ against a reagent blank. Assess concentration of uranium from a calibration curve, which has been prepared from known amounts of uranium.

By using the above procedure, excellent results were obtained for synthetic solutions containing 10–100 μg of uranium and 0·1 g of calcium fluoride.

<div align="right">K. L. CHENG</div>

RCA Laboratories,
Princeton, N.J., U.S.A.
  1 *April* 1962

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* *Maser* is an acronym for *m*icrowave *a*mplification by the *s*timulated *e*mission of *r*adiation. An optical maser (also called "laser") is a device for light waves amplification and control to provide a beam which is highly directional, coherent, intense, and nearly monochromatic.

Source of error in arsenic determinations

SIR:

I WONDER whether a source of serious analytical errors which I recently had occasion to encounter, is generally known. If not, it might be of interest to bring it to the attention of your readers. I have not found it clearly mentioned in the literature at my disposal.

When trying to test certain materials for traces of arsenic, the results were positive to a quite improbable degree and also, not reproducible.

The technique used consisted in heating the material in Kjeldahl flasks (adding a few glass balls to prevent bumping) with nitric and sulphuric acids (all of AsT grade) and submitting the residue, after the expulsion of nitrate and chloride, to a modified Gutzeit test with polarographic finish.[1] Many "blanks" on the reagents were negative. Known amounts of arsenic standard solution added to "blanks" were duly recovered, but not only were the results on the material under test improbably high and erratic—also attempts at recovering known quantities of arsenic added to this material had equally unsatisfactory results.

The material under test contained a substantial quantity of fluorides and so, after many frustrating experiments, the suspicion arose that their presence, together with the nitric and sulphuric acids, would lead to attack on the glass and liberation of arsenic should the glass contain arsenic.

This was confirmed by the following experiments.

AnalaR sodium fluoride, when treated with the acid mixture in large platinum crucibles, was found to be practically free from arsenic, and added arsenic was again satisfactorily recovered within the limitations of the method (q.v.). When, however, the same test on the sodium fluoride was repeated (also in platinum vessels) with the addition of glass balls of the same batch which had been added to the Kjeldahl flasks in the actual tests to prevent bumping, several hundred μg of arsenic were readily found, the quantity depending upon the number and size of the glass balls added and the quantity of fluoride present.

Porcelain Raschig rings added to the same quantities of sodium fluoride and acids in large platinum crucibles did not yield any arsenic; and these can serve the same purpose as the glass balls. Carborundum chips extracted with *aqua regia* were also very efficient in preventing bumping and did not yield any arsenic.

The writer wonders how generally it is known among analysts how frequently arsenic is added deliberately to glass, both to soft and special glasses, as an oxidising and refining agent. Of two large chemical encyclopedias, one[2] gives, under the heading "Chemical, general scientific and heat resisting glasses" in the specification of Pyrex glass 0·7% As_2O_3, in that of various "British present day types" 0–0·5% As_2O_3.

The other[3] states that mineral acids can dissolve from the glass the As_2O_3 added to the glass melt for decolorising purposes, and that this has to be taken into consideration in the determination of very small amounts of arsenic. The 2nd edition of the same encyclopedia (Vol. 5, 756) quotes Fresenius (without specified reference) as emphasising the importance of this arsenic content of glass for forensic work. This is not in agreement with the negative "blanks" obtained by the writer with nitric and sulphuric acids only, in absence of fluorides. The possible importance of the presence of fluorides is not mentioned; if they are present, their effect is obviously much greater; and in any case these remarks do not seem to have found general attention.

The writer consulted Messrs. Jobling, the makers of the British Pyrex glass, and they wrote that before 1950, Pyrex brand laboratory glassware contained approximately 0·3% of arsenic as As_2O_3, but that now Pyrex is refined by other means and the arsenic level controlled to be less than 5 ppm. Similar information was also received from Messrs. Wood Bros., who also emphasise that in the soft glasses the addition of As_2O_3 is still fairly common practice, and that one would expect to find up to 0·5% of arsenic in glasses of this type.*

It seems noteworthy, however, that the writer also found arsenic (although in very much smaller quantity than in the presence of glass balls) when treating fluorides in Kjeldahl flasks with nitric and sulphuric acids, using either porcelain Raschig rings or platinum gauze instead of glass balls, although there was hardly a visible attack of the flask, and its loss in weight was only of the order of 0·1–0·2 g. The quantity of arsenic found in the reaction product varied from flask to flask and was of the order of 1 to 10 μg, hence enough to be troublesome in certain cases.

The material under test contains, apart from fluoride, also large amounts of chloride, and thus cannot be treated with nitric acid in platinum vessels; silica vessels did not yield arsenic but were badly attacked, much more than borosilicate glass. Large porcelain crucibles (Royal Worcester) were eventually used, which suffered only slight attack during the analysis and did not yield any arsenic, although they lost their glaze after one or two tests, which did not seem to make them unserviceable.

* The information received from both firms is acknowledged with thanks.

It may be said that this source of error will not often come into play in the practice of arsenic determination. It would, however, operate if one were to test minerals like cryolite or fluorspar or other fluorides for arsenic, but it might even become important in (admittedly rare) forensic cases, *e.g.* a test for arsenic might be called for if for some reason the suspicion of arsenical poisoning arose in a case which in fact was one of fluoride poisoning. If the wrong type of glass (be it glass balls or vessels) were used, ordinary "reagent blanks" would *not* offer any protection against the error described, as normally no fluoride would be added to a control.

Greenland cryolite and fluorspar also came within the scope of the writer's test series, and there these spurious findings of arsenic seemed to fall in line with a remark in the literature (which in this case acted as a kind of "red herring") that arsenopyrite is one of the minerals found associated in small amounts with the cryolite. In fact, however, the specimen of cryolite tested was practically free from arsenic.

These experiments were carried out in the laboratory of International Alloys Ltd., Haydon Hill, Aylesbury, Bucks., England, and the permission of the Management to publish them is acknowledged with thanks.

I am, Sir,

International Alloys Ltd   Yours faithfully,
Haydon Hill,   (Dr.) W. STROSS
Aylesbury, Bucks., England   *Chief Chemist*
28 *June* 1962

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BOOK REVIEWS

Dosages Colorimétriques des Éléments Minéraux. G. CHARLOT. Masson et Cie, Paris, 1961. 2nd Edition. Pp. 379.

THERE are several comprehensive works on colorimetric methods of analysis, and serviceable as such books may be, they are frequently top-heavy in some respects, with a mass of somewhat superfluous detail and out-of-date material. There is most certainly room for a new book on this topic which is cut on cleaner lines, and which has a newer and less cumbered approach. No one can disagree that the modern trend has been away from the classical techniques of gravimetric and titrimetric analysis towards something which requires less manipulation by an operator. In recent years many of the more exotic physical methods of analysis have held sway, but some of these are, in perspective, now realised to be rather expensive and troublesome in the demands they make on the operator's time and knowledge of electronics and physics as well as of chemistry. The advent of automatic methods of analysis has considerably redressed the balance, with the results that simpler and more rugged methods are again more widely used. Absorptiometry, or spectrophotometry, is such a technique. Based on simple pH adjustment, standard reagent addition and simple one-parameter measurement, it can be automated readily to determine a wide variety of metals, non-metals, organic compounds, *etc.* on a single automatic instrument. As a result, there is little doubt that the technique will largely replace gravimetry and titrimetry as the standard routine method of analysis. The range of modern spectrophotometers has removed the difficulty of dealing with large amounts of materials since these can now be resolved satisfactorily by a differential technique with the sensitive detecting devices of modern instruments.

The present book has a comprehensive outlook, yet it maintains a reasonable size by virtue of its arrangement and planning. Part I, sub-titled *Généralités*, deals with the fundamental laws of light absorption and methods of measurement, with technique and attainable precision, and with the choice of conditions for applying a spectrophotometric method. It also discusses less-frequently used techniques such as fluorimetry, turbidimetry, nephelometry and photometric titration. Extensive coverage is given to modern separation/concentration methods such as solvent extraction, chromatography, ion-exchange, electrodeposition, adsorption on carriers and distillation.

Part II details the determination of the elements from aluminium through to zirconium, and includes some non-metals in their more common ionic forms, *e.g.* sulphur, nitrogen, oxygen, phosphorus, fluorine, silicon, *etc.* With commendable economy it also covers very fully less common elements such as rhenium, iridium, osmium, germanium, *etc.* Each element is treated in brief monograph form, with an account of the appropriate separation methods noted above; and the principles and working details of the experimental procedure for the more important methods are clearly outlined. Admirable coverage is given to the influence of foreign ions and the elimination of interferences. In each case a fairly extensive bibliography is appended, and "off-beat" methods are by no means ignored.

Taken all over, this book is well balanced, up-to-date, delightfully critical, well informed in its approach and altogether the best book on spectrophotometry I have so far met.

T. S. WEST

Anodic Oxide Films. L. YOUNG. Academic Press Inc., New York: Academic Press Ltd., London, 1961. pp. 377. 70s.

DR. Lawrence Young has been an active researcher in the field of anodic oxidation for the last decade. On seeing a pre-publication notice of this book the reviewer anticipated that it would be comprehensive, argumentative and stimulating. These anticipations have been fully realised.

It will be undoubtedly of great value to those active in this field of research, as well as collecting much of the recent data which is invaluable for persons who either require up-to-date information, but are not themselves active in research, or are engaged on allied topics (*e.g.* solid state chemistry, metallic corrosion).

The author has divided the book into two main sections: first a general section dealing with fundamental principles and experimental techniques used in anodic oxidation studies, and then a more specific section occupying more than half the book. This latter section deals in detail with a large number of metals and semiconductors in turn, probably covering all the systems worthy of discussion. The author has attempted to follow critically the development of thought in each case and the reviewer found this particularly stimulating.

There is a short appendix which is meant to give the non-specialist an insight into the subject. Each chapter has copious up-to-date references to original papers.

M. W. ROBERTS

Photometric Titrations. J. B. HEADRIDGE. Pergamon Press, London, 1961. pp. x + 131. 45s.

THIS monograph on photometric titration is the first of its kind, yet it approaches the topic with a sureness of purpose and treatment which is characteristic of an experienced author writing on a subject already well documented and one where pitfalls and inadequacy of treatment are already well known.

The text begins with the historical background of the method, then reviews various types of titration, sources of error peculiar to this technique and theoretical curves with and without added indicator substances. This introductory section ends with a useful account of end-point indices. The ensuing section reviews apparatus, and the remainder of the text details methods for acid-base, oxidation-reduction, complexometric and precipitation titrations. The last two chapters are concerned with coulometric titrations which make use of photometric end-points and with miscellaneous methods, *e.g.* the titration of water in glacial acetic acid, micelle concentration in soap solutions, photonometric titrations, *etc.*

This little book gives a really first-class account of this relatively new technique, and does not suffer from the all too frequent over-enthusiasm and over-emphasis which is prevalent in so many monographs on new techniques of analysis. Thus, on the very first page the author warns that there is little point in carrying out a photometric titration if a satisfactory visual indicator is already available. While the reviewer is not convinced of the logical necessity of bolstering up a troublesome titration by having resource to photometric detection of the end-point when frequently a non-titrimetric method might be applied, he fully recognises that this is a matter of policy to be decided by the individual analyst. For those who prefer to apply a titrimetric method under such circumstances, Dr. Headridge has performed an invaluable service. The topic is presented very clearly in an attractive manner and with full working details for all the more important procedures.

T. S. WEST

Dissociation Constants of Organic Acids in Aqueous Solution. Compiled by G. KORTÜM, W. VOGEL and K. ANDRUSSOW, for the International Union of Pure and Applied Chemistry, Section of Analytical Chemistry, Commission on Electrochemical Data. Butterworths, London, 1961. pp. xxii + 357, 50s.

THIS is a very useful compilation of data. The tables are preceded by an excellent critical survey of methods of measurement (printed in both English and German) which explains the theoretical basis of the available methods and assesses their relative accuracy. The tables themselves are extensive, listing dissociation constants for 1056 organic acids, together with an indication of the method of determination and the probable reliability of the results for each acid. There are over 400 references to the literature. The tables are clearly laid out and the volume is well printed and produced.

J. E. B. RANDLES

Quimica Analytica Cualitativa. J. RAMIREZ-MUNOZ and G. SALCEDO-ESCOBAR. Ediciones UIS, Universidad Industrial de Santander, Bucaramanga, Colombia, 1961. pp. 347.

A MORE appropriate title for the book would be *Laboratory Manual for Qualitative Analysis*. This would indicate that the impressive 347 pages actually boil down to about 100 filled with text, the rest consisting of sheets with some lines and check squares to be filled in by the student in order to report his analysis. The 100 pages, containing instructions on how to handle laboratory ware and schedules for analysis are, however, extremely good. The book is based on the conventional hydrogen sulphide procedure

for the cations usually treated in a beginner's course, and includes procedures for the systematic investigation of anions. The procedures are extremely well written, and are clearly organised by the use of decimal classification, which greatly facilitates cross-referencing. It is very commendable that, contrary to the usual custom, in every case more than one identification reaction is given. The flow sheets contain instructions for macro as well as for micro scale procedures. The best part of the book, in the reviewer's opinion, is the second one dealing with laboratory operations. This part contains a quite complete description of operations (filtering, precipitation, stirring, spot plate handling, etc.), from the macro scale to microscopic slide technique. It is very clearly written and contains a very great number of clear figures. If an equally adequate theoretical approach is used in the courses for which the present book is intended, the training of the student should be on a high level.

H. FLASCHKA

Atomic Absorption Spectrophotometry. W. T. ELWELL and J. A. F. GIDLEY, Pergamon Press, London, Paris and New York 1961. pp 102, 30s.

SINCE the introduction, by Walsh, of the technique of atomic absorption, workers in the field have used equipment ranging from simple filter photometers to spectrographs. It is therefore difficult for the prospective user to assess the value of the technique; and the authors, who have been in the forefront of development in this country, have, in this very readable book, endeavoured to collate available information and present it in due perspective.

Approximately half the book is devoted to a discussion of the basic information necessary for a modest understanding of the technique, including consideration of the various instruments which have been employed. These chapters are written in a very lucid manner and with considerable economy of expression. The statement that the effective band width of the monochromator used would be of the order of 0·01 Å in absorption measurement as against 5 Å in emission cannot, however, be left unchallenged. The implication that the resolution of the system is enhanced to this extent is contradicted by the authors themselves when they report interference in the determination of zinc, when using a brass hollow cathode source, by copper which absorbs copper radiation "in the vicinity of" the zinc line, which is also to some extent transmitted by the monochromator. Despite this minor quibble these chapters should be required reading for all those who propose to use the technique.

It is the second half of the book, devoted to consideration of specific elements, whose value may be debated. Presumably the authors intend this to indicate whether or not a particular problem can be solved by atomic absorption. To this end they have included all available information published up to the end of 1960, including practical details of procedures used in their own laboratory. It is unfortunate, however, that it is not possible to deduce, from the information given, the performance of commercial equipment in any particular case and that the table of comparative sensitivities published by Gatehouse and Willis appeared too late for inclusion in place of the almost useless values given in Table 14.

Such criticisms, however, are dealt with disarmingly by the authors who state in their introduction that they appreciate that their then current information will soon become out-dated.

The book is well produced, remarkably free from misprints and presents a clear picture of the position of atomic absorption in 1960. It can be recommended to all those who are interested in modern analytical technique; and, for those engaged, or about to engage, in atomic absorption spectrophotometry, it presents a unique condensation of the relevant literature.

T. R. ANDREW

Chemistry of Organic Fluorine Compounds. M. HUDLICKÝ. Pergamon Press Limited, 1961. pp. 536, 60s.

ORGANIC fluorine compounds came of age with the publication of Bockemüller's *Organische Fluorverbindungen* in 1936. From that date, the fundamental nature of the differences between organofluorine compounds and other organohalogen compounds came to be generally appreciated, and the right of the former to special treatment recognised. In spite of their great theoretical interest, and enormous and increasing technical importance, carbon-fluorine compounds have not, however, been well served by text-books. This seems to be the first major work on the subject by a single author since Bockemüller's classic came out.

The present English edition is a revised version of the Czech edition of 1958. The occasional flaws in the English do not obscure the sense, nor mar the clear and lively style in which it is written. It is a pleasant book to read. In general plan, it is a guide for the practising organofluorine chemist, rather than a descriptive monograph. Most of the space is devoted to methods of synthesis for organo-fluorine compounds, and the types of reaction they undergo; the emphasis, in fact, is on methods of all kinds. Nevertheless, the abundant illustrative examples, the selective bibliography of 1105 references, and the formula index combine to make the book also an outstandingly fine first source of factual information. Forty-four practical procedures for syntheses and reactions of organofluorine compounds are described in detail. There are sections on the preparation and handling of inorganic fluorinating agents, and the analysis of organic fluorine compounds. The text ends with a chapter on the practical applications of the organic compounds of fluorine. The author does not claim to treat the theoretical side of the subject thoroughly, but a good sense of theoretical relationships pervades the organisation of the material, and adequate explanatory passages are included at appropriate points. The book is up to date; for example, the very recently developed reagents sulphur tetrafluoride and perchloryl fluoride are dealt with. It is not without faults—the production of elementary fluorine, for instance, has been better described elsewhere—but the faults are much less in evidence than the virtues.

This is the sort of book that gets worn out by constant use before it is overtaken by the development of the subject. It is well worth the price.

H. G. HEAL

Ore Microscopy. EUGENE N. CAMERON. John Wiley and Sons, Inc., New York, London, 1961. Pp. xii + 293. 79s.

THIS work has been developed from the author's course in Ore Microscopy at the University of Wisconsin, but he has restricted its scope to the theory and practice of mineral identification and to the mineralogical and textural analysis of ores. It covers both the qualitative and quantitative approaches. By its nature, microscopy has a subjective bias, but the variety of equipment now available on the market for quantitative measurement of optical properties is beginning to enable such measurement to be adopted as a routine.

The author takes the view that the student should begin the use and manipulation of the microscope as soon as possible in order to obtain the maximum amount of practice in the teaching course. To this end the consideration of theoretical principles are deferred till chapter Six and presented graphically where possible. The balance of the book emphasises this approach as the chapter headings show: 1. Introduction, 2. The Ore Microscope, 3. The Preparation of Polished Surfaces, 4. The Physical Properties of Ore Minerals in Polished Sections, 5. The Optical Properties of Ore Minerals, 6. Theory of Reflected Light, 7. Microchemical Techniques, 8. Systems of Mineral Identification, 9. Applications of Ore Microscopy and an Appendix with tables of practical data concerning the properties of ore minerals.

Attention to the practical details of microscope manipulations characterise the text. The language is lively with flashes of homely imagery, and the author's enthusiasm for his subject is very evident. The illustrations and photomicrographs are well produced (Fig. 4.18.b is reversed) and are usually present in the text which refers to them, thus making for economy in reading.

The theory of reflected light presented in the book with the minimum of mathematics makes the assimilation of information absorbing reading. Taken with mouth-watering photographs of the new ore microscopes, the book is calculated to make any student eager to take up the study of ore microscopy. The subject is economically useful, and a wide field exists for the application of new instruments; yet, because the investigator remains the final judge of what he sees, he can never become a slave of his machine, the microscope.

R. G. H. B. BODDY

The Use of Organometallic Compounds in Purification of Magnesium, Calcium, Mercury, Gallium, Rhenium and Nickel. A. R. GATTI and W. A. G. GRAHAM. Arthur D. Little, Inc., 1961. pp. 68.

EVERY chemist has heard stories of commercial chemicals alleged to be "chemically pure", which turned out on investigation to contain only twenty or thirty per cent of the substance named on the label. Most chemists have also had the disappointing experience of finding that a chemical of "analytical reagent" grade contained some impurity not mentioned on the label in far greater quantity than

any of the impurities there listed. In the last decade, however, a quiet revolution has been taking place in the standards of purity of commercial chemicals, and many elements and compounds can now be obtained with a total impurity content of only a few parts per million. The demand for these, arising from industry, universities and government departments, has been met by means of new techniques of purification (zone melting, ion exchange, *etc.*), with the help of new and extremely refined methods of purity control (such as vapour phase chromatography).

This report describes what happened when attempts were made to prepare very pure metals by the decomposition of organometallic compounds. These were thought to offer some promise because their volatility allows them to be purified by physical methods not suitable for most of the inorganic compounds of the metals. The standard of purity aimed at was a content of less than 0·001 ppm of any impurity. Full success was achieved only with mercury, which was formed in a state of absolute spectroscopic purity by the photolysis of diethyl mercury. The pyrolysis of rhenium and nickel carbonyls gave metal samples of good purity, but not nearly approaching the 0·001-ppm standard. Impure magnesium was obtained by the electrolysis of ethyl magnesium hydride. No results of any value were obtained with organocalcium and organogallium compounds. The whole report is of an exploratory character; none of the investigations described could be regarded as exhaustive or final; and much of its value lies in the guidance it will give to future experimenters.

H. G. HEAL

Statistical Mechanics. NORMAN DAVIDSON. McGraw-Hill Publishing Co. Ltd., London: McGraw-Hill Book Company, Inc., New York, 1962. pp. ix + 540. £5.12.6.

STATISTICAL mechanics are concerned with the derivation of the macroscopic properties of materials, such as pressure, heat capacity, entropy, magnetic susceptibility, *etc.* from a knowledge of the quantum state accessible to the atoms or molecules making up the material. Often the calculation of the macroscopic property by the methods of statistical mechanics is easier than direct measurements: in all cases statistical mechanics provide the theoretical link between the two types of knowledge and thus indicates what are the important atomic or molecular factors that determine the macroscopic property. Applications of methods of statistical mechanics to problems in analytical chemistry are as yet few: one such is the application to the equilibria of isotope fractionation reactions.

By their nature, statistical mechanics are mathematical and depend upon the logically prior subjects of classical mechanics and quantum mechanics. At the same time the subject has many and diverse applications in physics and chemistry. To write a successful book on statistical mechanics for chemists is, therefore, not easy. Professor Davidson, in his book, presents the fundamentals and main applications of the subject lucidly and thoroughly. The book will be valuable to the chemist who wishes to understand the mathematical and theoretical basis of the subject and who is prepared to read the text carefully and to work through at least those of the problems which are interspersed in the main text. Mathematics of approximately university subsidiary standard is required.

Professor Davidson devotes quite a large part of the book to concise accounts of subjects which are either logically prior to statistical mechanics, such as classical mechanics and quantum mechanics, or subjects like spectroscopy and the activity coefficients of ions in solution, of which a knowledge is needed for the application of statistical mechanics in the system considered. Generally these accounts are good, though the reviewer feels that many topics are discussed so concisely that the reader who is not previously acquainted with (to take a few examples) Lagrange's and Hamilton's equations of motion, quantum mechanical operators or the calculation of the vibration frequencies of polyatomic molecules, will find the going difficult.

In a few cases the presentation could be improved. The reader might well spend considerable time puzzling over equation (3-6d) without reading the further half page necessary to discover that the rule he or she had been trying to apply, given on the previous page, did not hold in this case. Omission of ". . ." made several equations (from a pedantic viewpoint) not true.

In places it seemed to this reviewer that the treatment tended to be unnecessarily austere, and that the mathematical bare bones were not sufficiently covered with chemical fact: perhaps an example of this tendency is the single seventeen-year-old reference given on p. 194 to (presumably) data on characteristic vibration frequencies.

These are, however, minor criticisms of a well-written, useful and thorough book: the fact that it is written as a standard classroom textbook for graduate students in America is food for thought for those who teach students elsewhere.

A. D. E. PULLIN

Bevezetés a komplex vegyületek kémiájába (Introduction to the Chemistry of Complex Compounds).
    A. A. GRINBERG. Akadémiai Kiadó, Budapest, 1958. pp. 408. 95 Hungarian forints. In
    Hungarian.

THIS book is a translation of the second Russian edition published in 1951. This date itself determines
that the book cannot account for the enormous progress of co-ordination chemistry during the last
decade. Apart from this disadvantage the book is a valuable contribution to the literature of complex
chemistry, since it treats thoroughly the results of "classical" complex chemistry. The author
is a distinguished member of the Soviet school of complex chemistry and so the book gives an
authentic review of the subject, especially of the results achieved between the two World Wars.
    The book consists of an Introduction and eleven Chapters. Chapter 1 gives a survey of some
simple types of co-ordination compound. Chapter 2 deals with Werner's theory and also touches on its
predecessors. Chapter 3 deals with the stereochemical consequences of the octahedral configuration,
while Chapter 4 continues the review of the complexes of co-ordination number six. Chapter 5
treats the complexes of co-ordination number four, especially the complexes of platinum.
Chapter 6 summarises the different types of isomerism, while Chapter 7 deals with the nature of
chemical bonding in complexes. The complete lack of a review of modern theories is regrettable.
Chapter 8, which treats the mutual effects of co-ordinated groups, especially the problems of *trans*
effect, is particularly interesting. Chapter 9 gives a too short account of the solution chemistry of
complexes, while Chapter 10 touches on some special types of co-ordination compound. In the last
chapter one finds an interesting attempt to relate the complex forming ability of elements with their
position in the periodic system.
    As can be seen from the above list, the contents of the book comprise almost the whole field of
complex chemistry. In some respects, especially in the stereochemistry of complex compounds, it is
much more than an introduction for a beginner. Nevertheless, as a whole, it does not give a satisfac-
tory picture even for a novice because of the lack of the newer achievements which have not only
widened enormously our knowledge, but have also modified our view of inorganic chemistry.
    The reviewer understands that the author is working on a new revised edition. Knowing the
valuable features of the present book this new version is eagerly awaited.
    The translation is in general fairly good, the text is very readable, but some superficialities in the
double transcription of the non-Russian names has resulted in puzzles for the reader.

                                                                        M. T. BECK

NOTICES

(Material for this section should be sent directly to the Associate Editor)

ARGENTINA

Sunday–Saturday 16–22 *September* 1962: **Eighth Latin-American Congress of Chemistry.** Buenos Aires (see *Talanta*, 1962, **9**, 184).

CANADA

Monday–Wednesday 17–19 *September* 1962: **Ninth Ottawa Symposium on Applied Spectroscopy:** *Canadian Association for Applied Spectroscopy.* Ottawa (see *Talanta*, 1962, **9**, 399).

FRANCE

Lundi–Vendredi 1–5 *Octobre* 1962: **XIIIèmes Journées Pharmaceutiques Françaises:** organisées par *la Société de Technique Pharmaceutique.* Paris.

Sunday 26 *May–Saturday* 1 *June* 1963: **Sixth International Mineral Processing Congress:** *Société de l'Industrie Minérale.* Cannes (see also *Talanta*, 1961, **8**, 764).

The provisional programme is now available from the Secrétariat Général du 6e Congrès International de la Préparation des Minerais, 28, Rue Arthur-Rozier, Paris XIXe, France.

JAPAN

Monday–Saturday 10–15 *September* 1962: **International Symposium on Molecular Structure and Spectroscopy:** *I.U.P.A.C.* and *Science Council of Japan.* Tokyo (see *Talanta*, 1962, **9**, 401).

UNITED KINGDOM

Sunday–Saturday 9–15 *September* 1962: **Fifth Triennial Summer School in Analytical Chemistry:** *Royal Institute of Chemistry* with the participation of *Society for Analytical Chemistry.* Manchester College of Science and Technology (see *Talanta*, 1961, **8**, 913).

Monday–Wednesday 17–19 *September* 1962: General Discussion on **High Resolution Nuclear Magnetic Resonance:** *Faraday Society.* University of Oxford, Laboratory of Physiology, South Parks Road, Oxford.

The papers will be presented and discussed under the following headings:
1. Nuclear Magnetic Resonance in Diamagnetic Materials.
2. Nuclear Magnetic Resonance in Paramagnetic Materials.
3. Applications to the Determination of Molecular Structure.
4. Applications to the Study of Kinetic Processes.

Further details may be obtained from The Secretary, The Faraday Society, 6 Gray's Inn Square, London, W.C.1.

Tuesday–Friday 18–21 *September* 1962: **First International Congress of Food Science and Technology.** Imperial College of Science and Technology, South Kensington, London, S.W.7 (see *Talanta*, 1962, **9**, 403).

Friday–Saturday 21–22 *September* 1962: **Modern Trends in Small-Scale Inorganic Analysis:** *Society for Analytical Chemistry, Microchemistry Group and Royal Institute of Chemistry, Dublin and District Section.* Dublin.

The **National Lending Library for Science and Technology** announces the following changes of procedure:
1. All loan requests which hitherto would have been sent to the Science Museum Library should now be sent to the NLL at Boston Spa, Yorkshire, addressed to the Loans Department.
2. Requests for borrowing facilities or for the supply of loan forms should be sent to the NLL at Boston Spa, addressed to the Director.

To facilitate the smooth development of the NLL's loan service:—
(a) requests for the supply of photocopying forms and
(b) individual photocopy requests
should continue to be sent to the Science Museum Library, South Kensington, London, S.W.7, except where it is known that the publications are not likely to be available there.

The following information is intended for those wishing to obtain *translations of foreign scientific literature* from **Aslib** or the **National Lending Library for Science and Technology**. The services provided are available to all individuals and organisations in the United Kingdom, whether or not they are members of Aslib.

Aslib (3, Belgrave Square, London, S.W.1) maintains the U.K. copy of the British Commonwealth Index of Scientific Translations. This is a location index for translations, mostly unpublished, made in the principal countries of the Commonwealth *from all languages* into English. It also includes details of translations collected since January 1959 under the American O.T.S./S.L.A. scheme and now listed in *Technical Translations*. The U.K. copy is intended to be the central checkpoint for the U.K. at which persons or organisations can ascertain whether a given article has been translated and, if so, from which, and conditions on which, it can be borrowed.

The National Lending Library for Science and Technology (Boston Spa, Yorkshire) collects and lends translations *from the Russian*. Details of these translations are incorporated in the Aslib index, with the exception of a few made before 1959.

British Standards Institution announces the following **New British Standards**:

B.S. 1428: *Microchemical apparatus: Group E general accessory apparatus: Part E* 4: 1962: *Crucible Holder, microburner, spatulas and forceps.*
This specifies the following items of apparatus for use in microchemical analysis:
 (i) Crucible holder suitable for use in the ignition of crucibles of top diameter up to about 60 mm including all types of crucibles specified in B.S. 1428 Part E 1.
 (ii) Microburner jet for use with coal gas, giving a non-luminous flame up to about 5 cm in height.
 (iii) Three types of spatula; heavy stainless steel, light stainless steel and light platinum-tipped with hollow stainless steel shaft.
 (iv) Reverse action and normal action forceps.
The specification also recommends a suitable micro burner and includes fully dimensioned drawings (Price 5s.).
B.S. 3473: 1962: *Methods for testing the chemical resistance of glass used in the production of laboratory glassware.* This describes methods for determining the resistance of types of glass used in the production of laboratory glassware towards attack by
 (i) A boiling aqueous solution of mixed alkali.
 (ii) Water at 100°.
 (iii) Water at 121° in an autoclave.
The test procedures are based on two German standards and one United States standard (Price 5s.).
B.S. 3517: 1962: *Methods for thermal shock tests on laboratory glassware.* This describes three methods for determining the resistance to thermal shock of the types of glass used in the production of laboratory glassware, *i.e.* for testing whole articles at temperature differences less than 100°, for testing whole articles at temperature differences of 100° or more and for testing the rims of articles (Price 3s.).
B.S. 3513: 1962: *Gamma-radiography sealed sources.* This specifies general constructional requirements, tolerances on source activity and radiation output, and dimensions, both of the radioactive material and the outer capsule for gamma-ray sources of activity up to *ca.* 100 curies for cobalt-60 or 300 curies for caesium-137 or iridium-192. Test requirements with regard to freedom from surface radioactive contamination and leak freedom are given, with details of the test methods, and requirements are also laid down concerning the marking of the sources and the provision of certain certificates. The specification replaces B.S. 2783 which specified source capsules only (Price 5s.).

The following *Revised British Standards* are also announced:
B.S. 700: 1962: *Graduated pipettes.* This specifies three types of graduated pipette: Type 1 calibrated for delivery from zero line to graduation line, Type 2 calibrated for delivery down to jet, Type 3 calibrated for content, and 1-, 2-, 5-, 10- and 25-ml sizes for each type of pipette. It gives full dimensions, but lists only the essential ones as mandatory, the remainder being given for the guidance of manufacturers. It includes standard methods for the determination of capacity and delivery time, and tolerances for both, as well as requirements for material, construction, graduation and marking (Price 5s.).
B.S. 1428: *Microchemical apparatus: Group C apparatus for determination of organic groups: Part C* 1: 1962: *Alkoxyl and alkylimino group determination apparatus.* This specifies components for use in the micro determination of alkoxyl groups by the Zeisel method and of alkylimino groups by the Friedrich method. It describes Zeisel apparatus with ground glass joints and Friedrich apparatus and also a glass weighing spoon for use with the former. It includes fully dimensioned drawings for all components (Price 5s.).

The following *Amendment Slips* are also announced:

B.S. 769: 1961: *Chemical analysis of butter. Amendment No.* 1: *PD* 4556.
B.S. 812: 1960: *Methods for sampling and testing mineral aggregates, sands and fillers. Amendment No.* 1: *PD* 4563.
B.S. 1647: 1961: *pH Scale. Amendment No.* 1: *YD* 4565.

UNITED STATES OF AMERICA

Wednesday–Friday 5–7 September 1962: **Symposium on Measurement of Thermal Radiation Properties of Solids:** *Aeronautical Systems Division, U.S.A.F., National Bureau of Standards and National Aeronautical and Space Administration.* Biltmore Hotel, Dayton, Ohio.

Sunday–Friday 9–14 September 1962: **142nd National Meeting of American Chemical Society.** Atlantic City, N.J.

Sunday–Thursday 16–20 September 1962: **Second Annual Conference on Pharmaceutical Analysis.** King's Gateway, Land O'Lakes, Wisconsin (see *Talanta*, 1962, **9**, 406).

Wednesday–Friday 26–28 September 1962: **Practice of Gas Chromatography:** *A.S.T.M. Committee E-19 and Michigan State University.* Michigan State University.

Wednesday–Friday 14–16 November 1962: **1962 Eastern Analytical Symposium and Instrument Exhibit:** *Analytical Chemistry Groups of American Chemical Society* of New York and North Jersey Sections, and New York, Delaware Valley, New England and Baltimore-Washington Sections of Society for Applied Spectroscopy, and Metropolitan Microchemical Society. Statler Hilton Hotel, New York.

The meeting will consist of a series of 3-hr symposia of invited papers of extended length by experts in a number of fields of interest to analysts. The emphasis will be on recent developments in these specialities. The exhibition will consist of 85 manufacturers of scientific apparatus and supplies.

The detailed programme of symposia is as follows:

Wednesday 14 November: 9.00 a.m.

Thermal Analysis

Thermometric Titrations.	J. JORDAN
Cryoscopic Evaluation of Purity.	R. J. BEST
Thermogravimetry and DTA.	S. GORDON

Gas Chromatography in Medical Research

Analyses of Urinary Steroids by Gas Chromatography.	R. ROSENFELD
Use of Gas Chromatography in the Study of Hypocholesterolemic Agents.	W. HOLMES
A Study of the Fatty Acids and Aldehydes of Human Platelet Phosphatides by Gas Chromatography.	A. MARCUS

Wednesday 14 November: 2.00 p.m.

Preparative Gas Chromatography

Preparative Gas Chromatography.	H. FELTON
Preparative Gas Chromatography in Academic Research.	J. AMY
New Approaches to Preparative Gas Chromatography.	H. SZYSMANSKI
Panel Discussion of Gas Chromatography.	

Analytical Applications of NMR

The Realm of NMR—High Resolution, Broad Line and Relaxation Phenomena.	L. N. MULAY
NMR Relaxations in Polymer Melts and Solutions.	D. McCALL
NMR Applied to Polymer Research.	J. A. SAUER
Quantitative Aspects of NMR.	H. FOSTER

Thermal Analysis of High Polymers

DTA of High Polymers.	J. R. KNOX
DTA Instrumentation for High Polymer Studies.	J. CHIU
Thermogravimetry in Polymer Research.	C. D. DOYLE
Effluent Analyses in Thermal Studies.	P. A. GARN

Advances in Instrumentation Clinic

Analytical Instrumentation in the Medical Sciences—S. NATELSON

Thursday 15 November: 9.00 a.m.

New Developments in Excitation Sources

Excitation of Various Elements by Radio Frequency Excitation: Potential R. MAVRODINEANU
  Analytical Applications. and R. C. HUGHES
Optical Microemission Stimulated by a Ruby Laser. F. BRECH
Plasma Jets and Gas-Stabilised Arc Sources. M. MARGOSHES

Quantitative Micro Analysis

Use of X-rays in Quantitative Clinical Chemistry. S. NATELSON
Determination of Fluorine and Oxygen by Neutron Activation. R. STEELE
Quantitation in Inorganic Microchemistry. K. CHENG

X-rays in Polymer Analysis

Use of Pole Figure Analysis in the Study of Polymers. P. H. LINDENMEYER
Studies of Partially Ordered Crystalline Polymers. H. W. WYCKOFF
Studies of Low Angle X-ray Scattering from Polymers. W. O. STATTON
  Thursday 15 November: 2.00 p.m.

Recent Applications of Electron Probe Microanalysis

Geological and Mineralogical Applications of the Microprobe. I. ADLER
Analytical Procedures in Microprobe Analysis. T. ZIEBOLD
Metallurgical Applications of the Scanning Beam Microprobe. R. M. FISHER

Chromatography

Thin Layer Chromatography. E. WOLLISH
Electrophoresis. P. PLAISTED
Paper Chromatography. H. STRAIN

Molecular Weight Measurements

Number Average Molecular Weights Osmometry. W. R. KRIGBAUM
Ebulliometry. M. EZRIN
Weight Average Molecular Weights Light Scattering. D. McINTYRE
Equilibrium Ultracentrifugation. D. A. YPHANTIS
Nonequilibrium or Transport Numbers. W. H. STOCKMAYER
Fractionation. N. S. SCHNEIDER

Advances in Instrumentation Clinic

Gas Analysis (Gas Chromatography-Absorption Spectroscopy-Mass
Spectroscopy)—R. GOHLKE
  Friday 16 November: 9.00 a.m.

Symposium on Evaluation of Spectrophotometric Performance

Instrumental Parameters in Spectrophotometry. R. C. HAWES
  W. KAYE
  W. SLAVIN

Trace Analysis

Modern Techniques of Trace Element Analysis. G. H. MORRISON
Activation Analysis with Portable Neutron Generators. E. L. STEELE
Analysis of Solid State Materials. S. J. ADLER
Meaning of Trace Metal Analysis to the Biological Sciences. B. L. VALLEE

Chemical Microscopy

Introduction and General Applications. F. W. FARWELL
Theory and Principle of Measurement. P. BARTELS
Specialised Applications including Pleochromism. M. WILLARD
  Friday 16 November: 2.00 p.m.

Symposium on Evaluation of Spectrophotometric Performance

Wavelength and Photometric Standards in Infrared Spectrophotometry. M. K. WILSON
Photometric Standards in Visible and Ultraviolet Spectrophotometry. J. M. VANDENBELT
Panel Discussion: Speakers from both sessions.

Qualitative Organic Microchemistry

Techniques and Applications in Organic Qualitative Analysis.	N. CHERONIS
Crime and Crystallography.	L. DALCORTIVO
Identification of Unsaturation.	J. SHARESKIN

Advances in Instrumentation Clinic: 2.00 p.m.

Quality Control in Emission Spectroscopy—Automation.	R. J. CARLS
Sample Preparation Techniques in X-ray Spectroscopy.	G. CRUMRINE

Further information may be obtained from P. LUBLIN, General Telephone and Electronics Laboratories Inc., Bayside Laboratories, Bayside 60, N.Y.

In co-operation with National Bureau of Standards, the Atomic Energy Commission has prepared a chemical standard sample of plutonium for use by educational and research institutions in the United States and abroad. Having a purity of 99·97%, the plutonium sample (NBS Standard Sample No. 949) can be utilised as a comparison standard for all plutonium chemical analyses. Each sample consists of about 0·5 g of plutonium metal sealed in a glass ampoule under reduced argon atmosphere.

A new radioactivity standard sample, cobalt-57, and three reissues of previously available standards, zinc-65 and two concentrations of sodium-22, are now being distributed by the Bureau. All are in solution form except the zinc standard, which is prepared as a point source deposited on a mylar film.

The Bureau has recently issued *Standard Materials*, Miscellaneous Publication 241, a catalogue which lists the standard materials—over 600 different standards of metals, ores, ceramics, chemicals and hydrocarbons—available from the Bureau with their prices, shipping weights and directions for ordering. Summarised tables of analyses are also presented to indicate the types of standards of composition presently available. The publication may be obtained for 30 cents from the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C.

ERRATA — VOLUME 9

Page 381, line 5: for *stimulate* read *simulate*.

Page 384, the heading on the last column of Table III should refer to the footnote by reading *Corrected*[a].

Page 387, *Introduction, line* 8: this should read *complex fluoride ions. All of the fluoride, both free and in the form of tantalum complex, complexes with boron.*

Page 449, *Preliminary Communication by F. Vydra and V. Marková: Received* 13 *February* 1962. *Accepted* 22 *February* 1962.

PAPERS RECEIVED

Detection and quantitative estimation of some polynuclear hydrocarbons by electron spin resonance: B. D. FLOCKHART and R. C. PINK. (28 *May* 1962).

Amperometrische Bestimmung der Metalle unter der Anwendung von Thioacetamid—IV: Untersuchungen über Tl_2S-Bildungsgeschwindigkeit in ammoniakalischen Tl^+-Ionenlösungen mittels Thioacetamid (TAA): MARIA PRYSZCZEWSKA. (30 *May* 1962).

Spectrophotometric determination of iron in high-purity niobium, tantalum, molybdenum and tungsten metals: ELSIE M. PENNER and W. R. INMAN. (1 *June* 1962).

Studies of the absorptiometric determination of soluble phosphorus in textiles: J. T. MCALOREN and G. F. REYNOLDS. (1 *June* 1962).

Photometric determination of aluminium with xylenol orange: EVA PAVLÍKOVÁ and JOSEF JANKOVSKÝ. (1 *June* 1962).

Contribution to the basic problems of complexometry—X: Determination of nickel and cobalt in the presence of iron, copper and some other metals: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (11 *June* 1962).

Mitteilung über quantitative organische Analyse—XXXIV: Beitrag zum Studium der Methode zur Bestimmung von Sauerstoff in organischen Substanzen: M. VEČERA, J. LAKOMY and L. LEHAR. (13 *June* 1962).

Quantitative treatment of exchange equilibria involving complexans—III: Chelatometric determination of calcium in the presence of magnesium with EGTA: GENKICHI NAKAGAWA, MOTOHARU TANAKA and HIROKA WADA. (18 *June* 1962).

Sur une réaction colorée des carbamates non substitués a l'azote: Applications analytiques et pharmaceutiques: G. DEVAUX, P. MESNARD et MADAME J. CREN. (18 *June* 1962).

Thermoanalytical investigations on high temperature fusion reactions: L. ERDEY and S. GAL. (19 *June* 1962).

Indirect polarographic determination of silver: M. KOPANICA and R. PŘIBIL. (20 *June* 1962).

Precipitation from mixed solvents—I: Aluminium 8-hydroxyquinolate: LESTER C. HOWICK and JERRY L. JONES. (25 *June* 1962).

Application of the radioactive ionisation detector for the analysis of permanent gases by gas chromatography, and some uses in studies of chemical kinetics: A. K. GALWEY. (25 *June* 1962).