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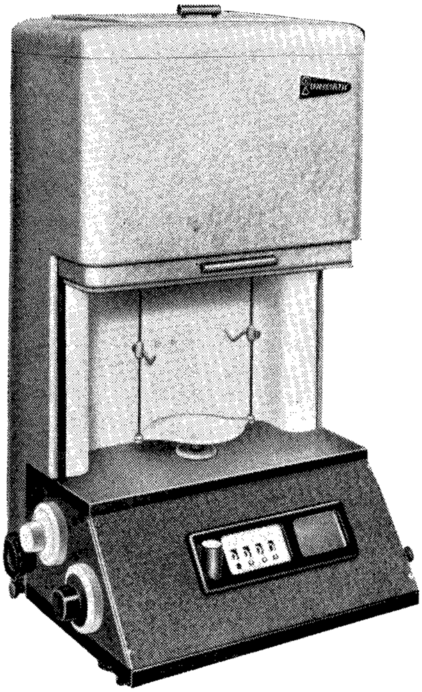

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SUMMARIES FOR CARD INDEXES

The accuracy of gas chromatography: A. F. WILLIAMS and W. J. MURRAY, *Talanta*, 1963, **10**, 937. (Research and Development Department, Imperial Chemical Industries Ltd., Nobel Division, Stevenston, Ayrshire, Scotland.)

Summary—It is considered that insufficient reliable information is available concerning the accuracy of gas chromatographic methods for quantitative analysis employing packed columns. Aspects which appeared to require further investigation were sample transfer, particularly in relation to the effect of size of sample, and calculation of the result. A study of these factors has been made, employing first the katharometer, then the flame-ionisation detector. Different chemical systems have been examined and the results show that, with the katharometer as detector, much more control of sample size is necessary for some systems than is required for others if accurate results are to be obtained. With the flame-ionisation detector, in addition to control of sample size, more detailed attention to the spacing of the electrodes is necessary for some types of samples than for others. It is shown that under the conditions described, measurement of peak heights can lead to highly accurate results and there is no advantage in measuring peak areas.

The infrared spectra of chelate compounds—II: A study of some bivalent metal chelate compounds of 8-hydroxyquinoline in the region 625 to 250 cm^{-1}: R. J. MAGEE and LOUIS GORDON, *Talanta*, 1963, **10**, 961. (Department of Chemistry, Case Institute of Technology, Cleveland, 6, Ohio, U.S.A.)

Summary—An investigation of the infrared spectra in the region 625–250 cm^{-1} of the complexes of copper, zinc, manganese, magnesium and calcium with 8-hydroxyquinoline has been carried out. The spectra are simple, but, despite their simplicity, they differ from one another, both in the number of peaks and the relative positions of corresponding peaks. Possible analytical applications of the spectra in this region are discussed.

The infrared spectra of chelate compounds—III: A study of some tervalent metal chelate compounds of 8-hydroxyquinoline in the region 5000–250 cm^{-1}: R. J. MAGEE and LOUIS GORDON, *Talanta*, 1963, **10**, 967. (Department of Chemistry, Case Institute of Technology, Cleveland, 6, Ohio, U.S.A.)

Summary—The infrared spectra of 8-hydroxyquinoline and of its complexes with aluminium, gallium and indium have been determined in the region 5000–250 cm^{-1}. The spectra show similarities, but differences between the aluminium complex and the other two occur in the region 625–250 cm^{-1}. A discussion of the spectra and of the structures of the oxinates is presented.

Continuous coulometric titration of various oxidising substances by electrogenerated iron^{II}: TAKEO TAKAHASHI and HIROSHI SAKURAI, *Talanta*, 1963, **10**, 971. (Institute of Industrial Science, University of Tokyo, Azabu-Shinryudocho, Tokyo, Japan.)

Summary—Iron^{II} reacts rapidly and quantitatively with various oxidising substances, such as potassium permanganate, potassium bichromate or free chlorine, in acidic solution. Continuous coulometric titrations of such solutions have been carried out with iron^{II} electrogenerated from iron^{III} at a platinum cathode. The progress of the reaction in the titration cell is followed potentiometrically with a platinum-calomel electrode pair. The potential difference between the detected potential and the end-point potential is amplified with a d.c. amplifier, whose output controls the electrolytic current so that the detected potential becomes equal to the end-point potential. Thus the electrolytic current which generates the iron^{II} is directly proportional to the concentration of oxidising constituent in the sample solution. In order to obtain good results, it is desirable to make a dynamic titration curve empirically in order to locate the optimum for the end-point in the coulometric titration.

A new principle of activation-analysis separations—V: Substoichiometric determination of traces of indium: ADOLF ZEMAN, JIŘÍ STARÝ and JAROMÍR RŮŽIČKA, *Talanta*, 1963, **10**, 981. (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Praha 1, Břehová 7, Czechoslovakia.)

Summary—A substoichiometric determination of traces of indium in germanium dioxide has been developed. It consists of adding indium carrier to the dissolved irradiated sample followed by extraction of indium dithizonate using thiosulphate and cyanide as masking agents. Indium is removed from the organic extract by shaking with dilute sulphuric acid. To the separated aqueous layer a substoichiometric amount of EDTA is added and the indium complex separated from the excess of unreacted indium ions on a cation-exchange column. The content of indium is calculated from the activity of the eluate obtained. The method is very selective, simple and rapid. Using the substoichiometric separation principle the necessity of determining the chemical yield is avoided.

The determination of traces of cobalt in samples of platinum by neutron-activation analysis: D. F. C. MORRIS and R. A. KILLICK, *Talanta*, 1963, **10**, 987. (Department of Chemistry, Brunel College, London, W.3, England.)

Summary—A neutron-activation analysis method for the determination of traces of cobalt in samples of purified platinum is described. Using a pile flux of $1{\cdot}2 \times 10^{12}$ thermal neutrons.cm^{-2}.sec^{-1}, as little as 10^{-9} g of cobalt may be determined. A rapid radiochemical separation procedure coupled with gamma-ray spectrometry permits measurement of 5·26-year cobalt-60 activity. Results of analysis of seven samples of platinum are quoted.

The effect of isotope abundances on the neutron-absorptiometry technique: R. S. BRAMAN, *Talanta*, 1963, **10**, 991. (Callery Chemical Company, Callery, Pa., U.S.A.)

Summary—To obtain accurate analyses by neutron absorptiometry it is essential that the isotope abundance of the element determined be the same as that of the calibration standard. The effect has been used for the comparison and determination of boron−10 isotope abundances in various boron hydrides. Precision is in the ±0·1% relative range.

Determination of nickel in high-purity niobium, tantalum, molybdenum and tungsten metals by chloroform extraction of nickel^{II} dimethylglyoximate: ELSIE M. PENNER and W. R. INMAN, *Talanta*, 1963, **10**, 997. (Department of Mines and Technical Surveys, Ottawa, Ontario, Canada).

Summary—A spectrophotometric method for determining 0·0005–0·10% of nickel in high-purity niobium, tantalum, molybdenum and tungsten metals is described. After sample dissolution and pH adjustment to 6·0, nickel^{II} dimethylglyoximate is extracted with chloroform from an ammonium tartrate-boric acid medium. The chloroform extract is washed with dilute ammonia solution to remove interfering impurities, and nickel is determined spectrophotometrically at 370 mμ directly in the extract.

Thermogravimetric analysis of some interaction products of 1,2,3-benzotriazole hydrochloride with certain negative cyano-complexes of the transition metals: RAY F. WILSON and G. HENRY, JR., *Talanta*, 1963, **10**, 1005. (Department Chemistry, Texas Southern University, Houston, 4, Texas, U.S.A.)

Summary—Thermogravimetric pyrolyses of some interaction products of certain negative cyano-complexes of the transition metals with 1,2,3-benzotriazole hydrochloride and identification of several intermediate products formed during the course of the reactions are reported.

Absorptiometric determination of niobium^V with 4-(2-pyridylazo)-resorcinol as reagent: R. Belcher, T. V. Ramakrishna and T. S. West, *Talanta*, 1963, **10**, 1013. (Chemistry Department, University of Birmingham, Birmingham 15, United Kingdom.

Summary—4-(2-Pyridylazo)-resorcinol forms a 1:1 purple-coloured complex ($\lambda_{max} = 550\ m\mu$) with niobium^V in an acetate-tartrate medium at pH 5·8. This is suitable for the spectrophotometric determination of niobium down to 0·1 ppm. The colour is formed within 45 min, and is stable thereafter for several days; the molecular extinction coefficient, $\epsilon_{550m\mu} = 38,700$, is as high as that reported for the well-known thiocyanate procedure, and the stability is very much superior. The interference of over 40 ions has been examined at the 1000-μg level in the presence of excess of cyanide and EDTA; only uranium^{VI}, vanadium^V and phosphate interfere. Vanadium may be masked by addition of zinc ions, and uranium by ammonium oxalate. 1000 μg of tantalum exhibit weak colour formation with the reagent, but this can be eliminated by the addition of larger amounts of tartrate, with only a slight decrease in the sensitivity of the niobium reaction. This new procedure does not necessitate an extraction, and is easier to operate than the standard methods.

A new reductimetric reagent: Iron^{II} in a strong phosphoric acid medium—IV*: Simultaneous potentiometric determination of vanadium^V and uranium^{VI} (or molybdenum^{VI}) in mixtures: G. Gopala Rao and L. S. A. Dikshitulu, *Talanta*, 1963, **10**, 1023. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—The formal redox potential of the V^V/V^{IV} couple has been determined in a medium of varying phosphoric acid concentration. Potentiometric procedures have been developed for the simultaneous titrimetric determination of vanadium^V and uranium^{VI} (or molybdenum^{VI}) in mixtures, using iron^{II} as a reductimetric reagent in 12M phosphoric acid. Two breaks in potential are obtained, the first corresponding to the complete reduction of vanadium^V to vanadium^{IV} and the second to the simultaneous reduction of vanadium^{IV} to vanadium^{III} and uranium^{VI} to uranium^{IV} (or molybdenum^{VI} to molybdenum^V). Manganese^{II} and tungsten^{VI} do not interfere. These procedures have definite advantages over those involving titanium^{III}, tin^{II} and chromium^{II}.

Semi-automatic determination of calcium and magnesium hardness in water: J. Lacy, *Talanta*, 1963, **10**, 1031. (Imperial Chemical Industries Ltd., Billingham Division, Billingham, Durham, England.)

Summary—A photometric method is described for the determination in a single titration of both calcium and magnesium hardness in waters using only one indicator. The method involves the addition of Eriochrome Black T to the solution containing calcium and magnesium buffered to pH 10, followed by titration with EDTA. The course of the titration is followed on a simple semi-automatic apparatus which is described. The complete titration curve obtained from a potentiometric recorder shows two distinct end-points; this permits the determination of both calcium and magnesium from a single titration.

Use of masking agents in chelatometric titrations—II: β-Aminoethylmercaptan: Koichi Yamaguchi and Keihei Ueno, *Talanta*, 1963, **10,** 1041. (Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka, Japan.)

Summary—The masking properties of *β*-aminoethylmercaptan (AEM) and its possible use in chelatometric titrations have been studied. AEM has been found to mask selectively at pH 10, many bivalent metals such as cobalt, nickel, copper, zinc, cadmium and mercury, resulting in the formation of colourless or slightly coloured soluble complexes. Thus it is possible to titrate the alkaline earth metals at pH 10 with Erio T indicator, where moderate amounts of interfering cations are masked by AEM plus triethanolamine. It is also possible to titrate manganese^{II} in the presence of other heavy metals.

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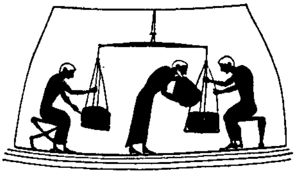

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[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

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Talanta, 1963, Vol. 10. pp. 937 to 959. Pergamon Press Ltd. Printed in Northern Ireland

THE ACCURACY OF GAS CHROMATOGRAPHY*

A. F. WILLIAMS and W. J. MURRAY
Research and Development Department, Imperial Chemical Industries Ltd.
Nobel Division, Stevenston, Ayrshire, Scotland

(*Received* 9 *November* 1962. *Accepted* 30 *April* 1963)

Summary—It is considered that insufficient reliable information is available concerning the accuracy of gas chromatographic methods for quantitative analysis employing packed columns. Aspects which appeared to require further investigation were sample transfer, particularly in relation to the effect of size of sample, and calculation of the result. A study of these factors has been made, employing first the katharometer, then the flame-ionisation detector. Different chemical systems have been examined and the results show that, with the katharometer as detector, much more control of sample size is necessary for some systems than is required for others if accurate results are to be obtained. With the flame-ionisation detector, in addition to control of sample size, more detailed attention to the spacing of the electrodes is necessary for some types of samples than for others. It is shown that under the conditions described, measurement of peak heights can lead to highly accurate results and there is no advantage in measuring peak areas.

GAS chromatography is now at a stage of advanced development and is probably employed more widely in organic analytical and research laboratories than any other general analytical procedure. There is no shortage of published information,[1,2,3] but it must be apparent to many workers that it is by no means easy to select the best conditions for accurate analysis of a given sample. Instructions are often vague and sometimes contradictory and any newcomer to the field is confronted by a confused situation.

Text books[1,2,3] which have been published in recent years tend to devote too little space to the quantitative aspects of gas chromatography and the treatment is similar, much of the approach being based on generalised conclusions taken from insufficient work. It is not uncommon to read statements, the authority for which is often doubtful; for example, it is becoming accepted that the highest accuracy can only be obtained by calculating results from the measurements of peak areas.[3,4] The work described in this paper for a range of different types of analysis has shown that, in many circumstances, measurement of peak heights and their use in calculating results often leads to greater accuracy.

Thermal conductivity cells or katharometers are possibly still the most widely used detectors.[1,2,3,5] Their response to a wide range of various types of compound in different carrier gases has been studied in considerable detail.[6,7] Because it is relatively inexpensive and readily obtained, nitrogen is probably more generally used as carrier

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* This work is an extension of that described at the Feigl Anniversary Symposium, University of Birmingham, England, April, 1962.

gas than other acceptable gases, such as hydrogen and helium. We have examined a number of groups of organic substances in nitrogen and have confirmed the findings of other workers that the response curves of the katharometer may show a considerable departure from linearity.[8] Using sample loads of the order of 1 μl (small loads lead to the highest column efficiencies), it has been concluded that the non-linearity of response, when nitrogen is used as carrier gas, is possibly more serious for some types of mixture than is generally believed. Even relatively small variations in the size of the sample may seriously affect the accuracy obtained for the analysis of an unknown sample, when the response factors obtained on another sample size are used to calculate the results. Contrary to the findings of other workers,[6] we have found that this departure from linearity is also encountered when helium is used as carrier gas, although not to so marked an extent.

Numerous papers have been published on the theoretical aspects of processes which are at work in gas chromatography, both with respect to the column packing itself and to the detector employed.[1,9,10] It seems, however, that the 'simpler' details, such as adding the sample to the column and the recording and use of the data obtained, have tended to receive insufficient attention. Thus, it has been found that with the relatively expensive modern precision syringe ('Hamilton'-type), the volume of sample transferred is dependent on the depth of insertion of the needle into the pre-heated zone of the column, and it may be appreciably different from the volume shown on the graduated scale of the syringe. As is demonstrated later, in some separations this might have a serious effect on the result obtained. On the other hand, some separations may involve constituents for which the katharometer responses are more nearly linear and variations in load are relatively unimportant (see page 947). In such cases the simple, inexpensive, capillary-dipping procedure used by James and Martin[11] may be adequate and it dispenses with the necessity for employing the more expensive syringe.

Many manufacturers are now incorporating the flame-ionisation detector into their apparatus and it is becoming usual for it to be recommended for quantitative work. During the present work we have found, however, that possible variables to be taken into account are probably greater than in the corresponding consideration of the katharometer. There is evidence to show that the few publications which are so far available, in relation to quantitative work, have tended to arrive at conclusions which cannot be accepted as general for all flame-ionisation detectors.[12] Indeed, it may be necessary to establish conditions in a detector which are peculiar to the particular group of compounds under consideration (see pages 955 and 957).

A systematic study has been made to find the conditions required for accurate quantitative analysis using either the katharometer or the flame-ionisation detector in conjunction with orthodox packed columns. These detectors have been chosen because they are readily made and serviced in laboratory workshops and, moreover, there can be considerable latitude in design. Emphasis has been placed on the size and manner of transfer of the sample to the column. In addition, the interpretation of the recorder data for calculating the results has been examined with special reference to peak height and peak area (using an integrator) measurements. It was considered that factors, such as flow rate, and pressures and temperatures contributing to column stability, could be made sufficiently constant to render minor changes in these conditions relatively unimportant and this has been confirmed in practice.

The investigations have been carried out using a number of simple but chemically different systems:—

(a) benzene-toluene-xylene,
(b) methylchlorosilanes,
(c) aliphatic chlorinated hydrocarbons,
(d) organic nitrate esters,
(e) polymethylsiloxanes.

Because errors in the determination of macro components would be more serious than in the determination of minor constituents, only the former have been considered.

I—ACCURACY OF METHODS USING KATHAROMETER DETECTION

Apparatus

The apparatus comprised two vapour-heated glass columns, each 4 ft long (4 mm dia.) and connected to the top of a glass katharometer.[13] The top 9 cm of the column were heated electrically and the "dead space" above the packing was about 2 cm long. Similarly, the "dead space" at the bottom of the column packing leading to the katharometer wire was also kept very small. A 'Hamilton'-type syringe was used during this work because it was considered to have a number of advantages over the older, wider-bore plunger type. Because the inlet pressure to the column was above atmospheric pressure, there was less tendency for back-surge of sample in the 'Hamilton' syringe. Provided the depth of insertion of the syringe needle through the serum cap was kept the same, *e.g.*, 2 cm, it was found that an apparent load of 1 μl put on the column could be reproduced to within $\pm 10\%$ whether it was taken from a 1-μl or a 10-μl syringe. As might be expected, an apparent load of 1 μl taken from the smaller syringe was different in size from the same apparent load taken from the larger syringe. Taking the 1-μl load from the 10-μl syringe gave an amount which was about 20% greater than the 'same' load from the 1-μl syringe (see page 942).

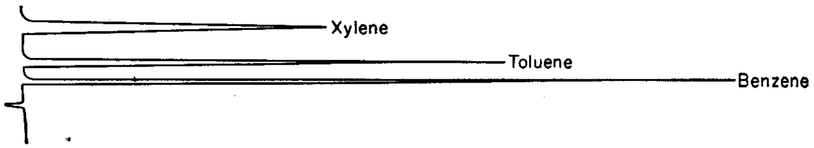

FIG. 1.—Typical chromatogram for benzene-toluene-xylene mixture using katharometer detection.

TABLE I. COMPOSITION OF BENZENE-TOLUENE-XYLENE MIXTURES

Mixture No.	1	2	3	4	5	6	7
Benzene, % *by wt.*	33·7	20·3	10·0	60·1	50·5	80·7	10·0
Toluene, % *by wt.*	33·2	25·0	25·3	20·1	24·4	9·0	9·8
Xylene, % *by wt.*	33·1	54·7	64·7	19·8	25·1	10·3	80·2

Analysis of benzene-toluene-xylene mixtures with nitrogen as carrier gas

Throughout this work the conditions employed both for katharometer and flame-ionisation detection were such that separation into discrete peaks was usually obtained for the particular mixture under investigation. Fig. 1 shows a typical trace obtained for the separation of a benzene-toluene-xylene mixture under the conditions given in Table II using katharometers. A range of mixtures of the aromatic hydrocarbons was prepared as shown in Table I and used for subsequent analyses. Using mixture No. 2 (Table I), the results given in Table II were obtained under the conditions described. Two sets of results are given, the first employing a capillary pipette[11] and the second using the more exact 'Hamilton' syringe for addition of the sample to the column.

It is evident that the factors for benzene and xylene are in reasonable agreement when the syringe is used, but when the capillary pipette is employed there is a wide and random variation in the individual factors. As is confirmed by other experiments (see page 942), this is undoubtedly because of the effect of small variations in load on the factors obtained for the constituents of this particular mixture, showing that it is not possible to easily add a reproducible load by the capillary pipette. The syringe permits a much closer control of the size of the load and with experience and care it has been possible to obtain results for factors which were in even better agreement than those given in Table II (see under *Apparatus*, page 939, and results for "unknowns" Table VII).

TABLE II. FACTORS[a] FOR BENZENE AND XYLENE (TOLUENE = 1) BASED ON PEAK HEIGHTS

[Column: 110°; preheater: 140°; carrier gas: 140°; 10% silicone elastomer (E301) on 'Embacel' (60–100 mesh); nitrogen flow rate: 11 ml/min at inlet to column; column inlet pressure: 103 cm of mercury absolute; katharometer bridge current: 200 mA.]

Capillary pipette[b]				'Hamilton' syringe[c]			
		Deviation from mean, %				Deviation from mean, %	
Benzene	Xylene	Benzene	Xylene	Benzene	Xylene	Benzene	Xylene
0·65	1·53	−10	+2	0·84	1·50	+4	−1
0·75	1·47	+5	−2	0·81	1·49	nil	−2
0.83	1·40	+14	−7	0·80	1·52	−1	+1
0·69	1·55	−3	+3	0·79	1·54	−3	+2
0·70	1·56	−1	+4				
0·68	1·60	−5	+7	Mean 0·81	1·51		
0·69	1·42	−3	−6				
Mean 0·71	1·50						

[a] $$\text{Factor for benzene (toluene} = 1) = \frac{\text{peak height of toluene/unit weight of toluene}}{\text{peak height of benzene/unit weight of benzene}},$$

and similarly for xylene

[b] *Ca.* 1-μl sample.

[c] 1-μl sample from 10-μl syringe

Experiments which led to the results obtained in Table II, employing sample loads of 1 μl added to the column from a 10-μl syringe, were repeated on mixtures Nos. 1–6 (Table I), again using nitrogen as carrier gas. Factors together with the spread of the values obtained for the determinations for each mixture are given in Table III and it is seen that the factors are not in agreement, but change, depending on the composition of the mixture. This clearly indicates that the katharometer response curves for each of the three constituents are not linear and explains the variation in factors obtained by changing the sample load going onto the column (see Table II and results for capillary pipette).

Employing a 1-μl 'Hamilton' syringe, factors were determined on sample loads of 1 and 0·2 μl, employing three of the mixtures given in Table I.

The 1-μl 'Hamilton' syringe differs from the 10-μl syringe (see page 942) in that the plunger of the latter terminates its travel at the top of the needle, but in the 1-μl syringe it terminates at the lower tip of the needle. Thus the whole intake from the 1-μl syringe is ejected in contrast to the 10-μl syringe where the needle remains at least partly filled. Table IV shows the factors obtained based on measurement of peak height and peak area (using an integrator). The marked effect on factors of change in sample load is readily seen for each of the three mixtures; the effects are similar for both peak height and peak area factors. In view of these results it is not surprising that capillary pipette addition for the benzene series of hydrocarbons shows the wide differences in factors given in Table II. It should be borne in mind, however, that this departure from linearity of response may not be exhibited by all classes of compounds to the same degree; thus, as will be seen later, over a wide range of mixtures of methylchlorosilanes it is possible to use the capillary dipping procedure.

TABLE III. FACTORS FOR BENZENE AND XYLENE (TOLUENE = 1) BASED ON PEAK HEIGHTS

Mixture No.		1	2	3	4	5	6
Benzene	Mean	0·82	0·81	0·81	0·90	0·86	0·95
	Spread	0·02	Nil	Nil	0·01	0·01	0·03
Xylene	Mean	1·41	1·54	1·58	1·39	1·40	1·37
	Spread	0·01	0·01	0·02	Nil	Nil	0·04

Column conditions as for Table II but 1-μl sample from 10-μl syringe.

Analysis of benzene-toluene-xylene mixtures with helium as carrier gas: Effects of changes in sampling technique and miscellaneous studies

Helium is often used as carrier gas because, generally, the response curves of a katharometer are more nearly linear than when nitrogen is used. Bayer[8] refers to helium and points to this advantage. He quotes the findings of Messner, Rosie and Argabright[6] that there is a linear relationship between the relative molar response and molecular weight in a chemical series when peak areas are used. These authors imply that with loads up to 30 μl, linearity and quantitative results are obtained. As shown on page 943, we have been unable to confirm their results using loads of the order of 1 μl (*i.e.*, loads in the range of greater column efficiency). Although the response of the detector to the benzene homologues was found to be more nearly linear with helium than was the case with nitrogen, it was found that factors obtained for benzene, toluene and xylene were still influenced by load size and mixture compositions whether peak areas or peak heights were used. Van de Craats[8] has stated that the response of the detector to different substances was proportional neither to weight nor molecular concentration.

TABLE IV. FACTORS FOR BENZENE AND TOLUENE (TOLUENE = 1) BASED ON PEAK HEIGHTS AND PEAK AREAS AT TWO LOAD LEVELS

		Area					
		1 μl			0·2 μl		
Mixture No.		1	3	6	1	3	6
Benzene	Mean	1·17	1·26	1·21	1·25	1·41	1·04
	Spread	0·01	0·09	0·01	0·05	0·09	0·06
Xylene	Mean	0·92	0·89	0·96	0·92	0·80	0·96
	Spread	0·01	0·01	0·06	0·03	0·03	0·04
		Peak height					
Benzene	Mean	0·82	0·82	0·98	0·83	0·93	0·73
	Spread	0·01	Nil	0·01	0·01	Nil	0·02
Xylene	Mean	1·42	1·56	1·34	1·41	1·31	1·39
	Spread	0·01	0·02	0·02	Nil	0·02	0·02

Column conditions as for Table II using 1-μl syringe.

Employing helium as carrier gas, investigations similar to those made with nitrogen have been carried out for benzene-toluene-xylene mixtures, the response of the detector being studied in relation to sample size, composition of sample and molecular weight of hydrocarbon, employing both peak height and peak area measurements.

(*a*) *Effect of load and composition of sample on response factors:* Two series of results were obtained on five of the mixtures given in Table I and the fact that they did not agree emphasised the critical effect of sample load (see Table V). Thus, it was found that when an apparent 1-μl sample was injected from a 1-μl syringe so that the needle only penetrated 2 cm into the rubber closure, the amount of sample entering the column was only about half of that transferred by taking an apparent 1 μl from a 10-μl syringe (with the penetration of the entire needle, namely 5 cm).

TABLE V. FACTORS FOR BENZENE AND XYLENE (TOLUENE = 1) BASED ON PEAK HEIGHTS

Mixture No.		1	2	3	4	7
		1-μl taken from 10-μl syringe (needle full length into packing)				
Benzene	Mean	0·74	0·73	0·72	0·72	0·69
	Spread	Nil	0·01	0·01	Nil	0·02
Xylene	Mean	1·54	1·63	1·65	1·55	1·74
	Spread	Nil	0·01	Nil	0·01	0·01
		1-μl taken from 1-μl syringe (needle injected 2 cm)				
Benzene	Mean	0·75	0·75	0·69	0·75	0·71
	Spread	0·02	0·01	0·01	0·01	0·01
Xylene	Mean	1·55	1·54	1·58	1·53	1·58
	Spread	0·05	0·02	0·03	0·02	0·05

Helium flow rate of 25 ml/min at 103 cm of mercury absolute pressure, otherwise column conditions as for Table II.

Table V shows two sets of results obtained under the conditions used with helium as carrier gas. As is the case with nitrogen carrier gas, these results demonstrate the importance of ensuring that the volume of sample added to the column is closely standardised. The difference between nitrogen and helium, however, is the wider range of concentrations with helium as carrier gas over which it should be possible to work without changing the factor (*cf.* Table IV).

(*b*) *Variations in the same apparent load from variations in the addition procedure related to manipulation of the syringe:* Further experiments were carried out in order to emphasise the change which may occur in the factor obtained for one particular hydrocarbon mixture if rigid adherence is not made to the procedure for adding a known volume of sample from a syringe. Employing mixture No. 7 (Table I), a sample load of 1 μl was added in different ways from both the 1-μl and 10-μl syringes. In addition, in some cases, the effect of increasing the load up to about 3 μl was examined. Factors for benzene and xylene were determined under these conditions. Results obtained with helium as carrier gas showed that it is important to ensure that the syringe is operated in exactly the same way if reproducible results are to be obtained. Thus, when an apparent 1 μl of sample was added from a 10-μl syringe, the xylene factor changed from 1·65 for a 2·0-cm immersion of the needle to 1·69 for a 5-cm immersion. However, when the amount of sample was increased to an apparent 2 μl, the corresponding change was from 1·72 to 1·91. When an apparent 3 μl sample was used the change was from 1·97 to 2·05. The corresponding changes in the benzene factors were smaller, the factors only varying from 0·68 to 0·71.

(*c*) *Molar responses for benzene, toluene and xylene based on peak areas:* In contrast to the findings of Messner *et al.*[6] with sample loads of the order of 30 μl, the relationship between the molar responses of the various compounds in a homologous series, at a 1-μl level of sample load, showed that the responses, based on peak area measurement (using an integrator of the disc type connected to a Honeywell Brown recorder), were not constant over the range of mixtures studied. The results obtained on five of the mixtures given in Table I are reported in Table VI. In this table the response for benzene is taken as 100 units. The factors were calculated as shown on page 940, except, of course, that integrator counts (equivalent to peak areas) were used in place of peak heights.

TABLE VI. FACTORS (TOLUENE = 1) AND MOLAR RESPONSES BASED ON INTEGRATOR COUNTS FOR BENZENE-TOLUENE-XYLENE MIXTURES

Mixture No.	Factors			Molar Responses		
	Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
1	1·05	1·00	0·98	100	124	146
2	1·07	1·00	1·01	100	126	144
3	0·97	1·00	1·04	100	114	127
4	1·06	1·00	1·01	100	125	140
7	1·01	1·00	1·03	100	120	134

Column conditions as for Table V.

Analysis (using mainly peak heights) of various samples of benzene, toluene and xylene of compositions unknown to the operator

The experiments previously described have shown that with nitrogen or helium as carrier gas it is only possible to obtain a high degree of accuracy for the analysis of a completely unknown mixture of benzene, toluene and xylene, by using factors determined from a mixture whose composition approximates to the mixture under test. From the work already described it is seen, however, that less stringent control of the composition of the mixture used for determination of factors is required for helium than is the case for nitrogen.

Table VII shows in detail the stages involved and the results obtained for the analysis of four benzene-toluene-xylene mixtures, using nitrogen as carrier gas, and a further mixture containing a relatively large percentage of a foreign material which in this case was methylene chloride. The analyses were carried out by a scientific assistant to whom the compositions were completely unknown.

Column 2 of Table VII shows the reproducibility obtained for peak heights for replicate determinations; the values are all within ±10%, which for routine operation using a 10-μl 'Hamilton' syringe under standard conditions (1-μl sample taken), is considered to be satisfactory. The factors given in column 4 are the average of those obtained from Table III and were used to calculate the preliminary results shown in columns 5 and 6. The results based on toluene as a marker are given because they demonstrate the gross errors which tend to be masked by normalising. Those factors given in column 8 were obtained from the mixtures shown in column 7, the compositions of which resemble the compositions found in column 5, and the factors were used to calculate the true compositions of the mixtures using the peak height figures given in column 2. The high order of accuracy obtained is shown from the results in columns 9 and 10. Column 11 shows some results obtained based on peak area measurement. The area factors given in column 12 were obtained on the mixtures given in column 7, using a tachogenerator integrator.

The last mixture, containing 30·2% of methylene chloride, is interesting because it might be considered as an industrial crude hydrocarbon mixture containing 30·2% of unknown material, only the benzene, toluene and xylene contents being required. It is obvious that the normalisation method cannot be used and a known amount of marker is therefore required. In this case it is assumed that 19·2% of toluene (see column 1) have been added as marker and an analysis for benzene and xylene is to be made. The analytical stages to be adopted are then as used for the previous mixtures. It should be borne in mind, of course, when determining the final factor, that the true load is only about 0·7 μl. The final result given in column 10 is considered to be very satisfactory.

In Table VIII results are shown for the analysis of three of the mixtures given in Table VII using helium as carrier gas. It is seen from column 3 that the normalised results calculated from the over-all mean factors taken from Table V are more accurate than the corresponding results obtained when nitrogen was used as carrier gas and this is as would be expected. Column 6 shows a very high order of accuracy obtained when a second factor determination is used to calculate the results.

TABLE VII. ANALYSIS OF BENZENE-TOLUENE-XYLENE MIXTURES WITH NITROGEN AS CARRIER GAS

	1	2	3	4	5	6	7	8	9	10	11	12
					Results using factor in previous column				Final Result			
	Composition of "unknown" SAMPLE, %	Peak heights, *mm*	Mean and corrected for attenuation	Factors (average of No. of mixtures)	Normalised, %	Toluene underlined & % present taken as value for "marker"	Mixture made up for final factors, %	Final factors	Normalised, %	Toluene underlined & % present taken as value for "marker"	Normalised, areas, %	Factor used
Benzene	70·1	216, 202	836	0·86	69·1	66	69·2	0·92	70·3	70·5		
Toluene	27·5	155·5, 144	300	1·00	28·5	27·5	26·9	1·00	27·4	27·5		
Xylene	2·4	56, 50·5	17·5	1·46	2·5	2·4	3·9	1·39	2·3	2·3		
	100·0				100·1	95·9	100·0		100·0	100·3		
Benzene	9·7	158, 151, 163	157	0·86	12·7	11·0	10·0	0·76	9·7	9·7	9·6	1·13
Toluene	10·1	124, 119, 129	124	1·00	11·6	10·1	9·8	1·00	10·1	10·1	9·6	1·00
Xylene	80·2	550, 540, 576	555	1·46	75·7	66·0	80·2	1·77	80·2	79·3	80·8	0·93
	100·0				100·0	87·1	100·0		100·0	99·1	100·0	
Benzene	39·3	327, 300, 315	628	0·86	40·0	39·0	39·8	0·86	39·2	39·0	40·0	1·13
Toluene	20·8	150, 139, 143	288	1·00	21·3	20·8	20·0	1·00	21·0	20·8	20·3	1·00
Xylene	39·9	186, 170, 181	356	1·46	38·7	37·6	40·2	1·53	39·8	39·5	39·7	0·93
	100·0				100·0	97·4	100·0		100·0	99·3	100·0	
Benzene	6·8	110, 119, 112	114	0·86	9·0	7·7	10·0	0·76	6·8	6·8	6·6	1·13
Toluene	7·2	88, 94, 5, 90	91	1·00	8·4	7·2	9·8	1·00	7·2	7·2	6·6	1·00
Xylene	86·0	600, 630, 609	612	1·46	82·6	70·7	80·2	1·77	86·0	85·7	86·8	0·93
	100·0				100·0	85·6	100·0		100·0	99·7	100·0	
								1 µl 0·8 µl		1 µl 0·8 µl		
Benzene	48·9 } 69·8		2489	0·86		44·5	69·2	0·96 0·93		49·7 48·1		
Toluene	19·2 }		922	1·00		19·2	26·9	1·00 1·00		19·2 19·2		
Xylene	1·7		57	1·46		1·7	3·9	1·40 1·41		1·7 1·7		
							100·0					
Methylene chloride	30·2											

1-µl sample taken from 10-µl syringe; column conditions as for Table III.

TABLE VIII. ANALYSIS OF BENZENE-TOLUENE-XYLENE MIXTURES WITH HELIUM AS CARRIER GAS

1		2	3	4	5	6
Composition of "unknown" sample, %		Factors (average of No. of mixtures)	Results using factor in previous column (normalised), %	Mixture made up for final factors, %	Final factors	Final results (normalised), %
Benzene	9·7	0·71	10·6	10·0	0·68	9·9
Toluene	10·1	1·00	10·6	9·8	1·00	10·2
Xylene	80·2	1·63	78·8	80·2	1·72	79·9
Benzene	39·3	0·71	40·1	39·8	0·69	39·4
Toluene	20·8	1·00	20·5	19·9	1·00	20·8
Xylene	39·9	1·63	39·4	40·2	1·63	39·8
Benzene	6·8	0·71	7·6	10·0	0·68	7·0
Toluene	7·2	1·00	7·7	9·8	1·00	7·4
Xylene	86·0	1·63	84·7	80·6	1·72	85·6

1-μl sample; column conditions as for Table V.

Analysis of chlorinated hydrocarbon mixtures, methylchlorosilane mixtures and organic nitrate esters

(a) *Effect of composition of methylene chloride-chloroform-carbon tetrachloride mixtures on response factors:* The methylene chloride-chloroform-carbon tetrachloride system was examined with nitrogen as carrier gas, then with helium. Table IX shows the results obtained employing a range of sample mixtures with nitrogen as carrier gas. The column itself contained the same stationary phase as used for the benzene hydrocarbon mixture. Peak heights were used for the calculation of factors which varied according to the composition of the mixture. It is apparent that with nitrogen as carrier gas the same technique would need to be adopted for the analysis of unknown mixtures as was used for benzene-toluene-xylene mixtures (see Table VII).

TABLE IX. FACTORS FOR CHLOROFORM AND CARBON TETRACHLORIDE (METHYLENE CHLORIDE = 1) BASED ON PEAK HEIGHTS

Mixture		Composition of samples, % *by wt.*				
		1	2	3	4	5
Methylene chloride		38·0	40·0	40·4	41·2	40·3
Chloroform		53·4	40·6	30·6	18·0	8·9
Carbon tetrachloride		8·6	19·4	29·0	40·8	50·8
		Factors				
Chloroform	Mean	1·98	1·85	1·88	1·82	1·80
	Spread	0·03	0·07	0·01	0·01	Nil
Carbon tetrachloride	Mean	2·84	2·86	3·04	3·08	3·19
	Spread	0·04	0·15	0·04	0·03	0·06

Column: 40°; preheater: 100°; carrier gas: 100°; nitrogen flow rate: 13 ml/min at inlet to column; column inlet pressure: 98 cm of mercury absolute; katharometer bridge current: 200 mA; 0·4-μl sample added from 10-μl syringe.

TABLE X. FACTORS FOR CHLOROFORM AND CARBON TETRACHLORIDE (METHYLENE CHLORIDE = 1) BASED ON PEAK HEIGHTS

		Composition of samples, % *by wt.*					
Mixture		1	2	3	4	5	6
Methylene chloride		26·1	83·1	6·5	79·6	10·0	39·4
Chloroform		39·5	9·3	76·2	10·3	10·3	39·5
Carbon tetrachloride		34·4	7·6	17·3	10·1	79·7	21·1
		Factors					
	Mean	2·13	2·08	2·27	2·06	2·08	2·13
	Spread	Nil	Nil	Nil	0·04	Nil	Nil
Carbon tetrachloride	Mean	3·60	3·51	3·71	3·50	3·87	3·60
	Spread	Nil	0·06	0·05	0·07	0·03	0·05

(Column conditions as for Table IX, except for the following changes:— katharometer bridge current: 150 mA; 1-μl sample added from 10-μl syringe; helium flow rate: 25 ml/min at inlet to column; column inlet pressure: 104 cm of mercury absolute.)

Another series of experiments was carried out in which helium was used as carrier gas and factors were then determined on a new range of mixtures. The factors obtained showed no better agreement than when nitrogen was used as carrier gas (see Table X) using a similar range of mixtures.

Table XI shows the accuracy obtained for the analysis of three mixtures of the chlorinated hydrocarbons, examined in the same manner as the mixtures of benzene, toluene and xylene (see Tables VII and VIII); helium was used as carrier gas. When the results were worked out using an average factor, only in the case of the third mixture was a comparatively large error obtained; in this case the determination of a final factor gave a result in very close agreement with the original compositions.

TABLE XI. ANALYSIS OF METHYLENE CHLORIDE-CHLOROFORM-CARBON TETRACHLORIDE MIXTURES

			Results using factors in previous column				Final results	
Composition of unknown samples, %		Factors (average of number of mixtures)	Normalised, %	CH_2Cl_2 taken as marker, %	Mixtures made up for final factors, %	Final factors	Normalised, %	CH_2Cl_2 taken as marker, %
Methylene chloride	21·0	1·00	21·1	21·0	26·1	1·00	21·0	21·0
Chloroform	39·2	2·12	39·1	39·2	39·5	2·13	39·3	39·2
Carbon tetrachloride	39·8	3·60	39·8	39·8	34·4	3·60	39·7	39·6
Methylene chloride	80·7	1·00	80·2	80·7	83·1	1·00	80·4	80·7
Chloroform	10·0	2·12	10·4	10·4	9·3	2·08	10·4	10·5
Carbon tetrachloride	9·3	3·60	9·4	9·5	7·6	3·51	9·2	9·3
Methylene chloride	4·9	1·00	5·1	4·9	6·5	1·00	4·8	4·9
Chloroform	78·7	2·12	77·3	74·0	76·2	2·27	78·6	79·6
Carbon tetrachloride	16·4	3·60	17·6	16·8	17·3	3·71	16·6	16·9

Column conditions as for Table X.

TABLE XII. FACTORS FOR MONOMETHYLTRICHLOROSILANE AND DIMETHYLDICHLOROSILANE IN MIXTURES WITH PHENYLCHLOROSILANES (ETHYL IODIDE AS MARKER = 1) BASED ON PEAK HEIGHTS WITH NITROGEN AS CARRIER GAS

Mixture No.	1	2	3	4	5	6	7
Monomethyltrichlorosilane:							
%	16	—	91	25	—	46	8
Mean factor	0·59	—	0·59	0·59	0·59	0·59	0·59
Over-all mean				0·59			
Dimethyldichlorosilane:							
%	14	22	9	15	37	16	27
Mean factor	0·62	0·64	0·42*	0·63	0·64	0·59	0·64
Over-all mean[a]				0·63			
Phenylchlorosilanes:							
% ($PhSiCl_3 + Ph_2SiCl_2$)	70	78	Nil	60	63	38	65

[a] Excluding*

[Column: 40°; preheater: 100°; stationary phase: 2-nitrodiphenyl (20% on 'Embacel'); nitrogen flow rate: 19 ml/min inlet to column; column inlet pressure: 105 cm of mercury absolute; katharometer bridge current: 150 mA; about 1-μl sample (from capillary pipette)]

(b) *Analysis of mixtures of methylchlorosilanes:* The analysis of mono-, di- and trimethylchlorosilane has been carried out satisfactorily for a number of years in our laboratory using 2-nitrodiphenyl as stationary phase and nitrogen as carrier gas; the simple capillary pipette procedure is used as the method for adding the sample to the column. Ethyl iodide is added as marker; in any case, it is not possible to normalise because of the presence of unidentified impurities. Because it has been possible to apply the same factors over a very wide range of concentrations, it follows that the katharometer response curves for these silanes must be more nearly linear than is the case for the separations previously described. Hence, for a sample load of about 1 μl there is no need for the close control required in the analysis of benzene-toluene-xylene mixtures. In the examination of commercial blends of monomethyltrichlorosilane and dimethyldichlorosilane with phenylchlorosilanes, it is seen from Table XII that there is excellent agreement between all of the factors (based on peak height measurement) obtained for monomethyltrichlorosilane; however, in the case of dimethyldichlorosilane the factor does show some change when the ratio of monomethyltrichlorosilane: dimethyldichlorosilane is greater than about 3 : 1. In the analysis the relatively high-boiling phenylchlorosilanes were back-flushed from the column by having a short zone of packing at the top of the column which could be heated to a temperature of about 250° between successive analyses.

Table XIII shows mean factors obtained on three determinations made on each of three of the methylchlorosilane blends given in Table XII. In addition, the over-all spread on each set of determinations is given. Because a capillary pipette was employed for addition of the sample the remarkably good agreement of the results for each mixture shows that the katharometer response curves approach linearity over a wide range of mixtures.

(c) *Analysis of organic nitrate mixtures:* The final study in this investigation of accuracy employing katharometer detection was concerned with the determination of ethylene glycol dinitrate in nitroglycerine. Nitrobenzene was employed as a marker. A 10% solution of its mixture with the nitrate

TABLE XIII. TEST OF REPLICABILITY FOR SILANE FACTORS (ETHYL IODIDE AS MARKER = 1)

	Monomethyltrichlorosilane		Dimethyldichlorosilane		
	Mixture No.		Mixture No.		
Factor	1	6	1	2	6
Mean	0·59	0·59	0·62	0·64	0·59
Spread	0·01	0·03	0·01	0·03	0·03

esters was prepared in toluene and a 10-μl sample of the resulting solution added to the column from a syringe. The column again contained E301 silicone elastomer as stationary phase, at a temperature of 140° (preheater: 165°), and a nitrogen flow rate of 25 ml/min (measured at the inlet to the column), was used. Employing mixtures of 2, 5, 10, 15 and 20% of ethylene glycol dinitrate in nitroglycerine with 25% of nitrobenzene as marker, the factors obtained (nitrobenzene = 1) were 1·12, 1·08, 0·98, 0·96 and 0·93. This indicated a considerable departure from linearity. The method of employing a second factor prepared from a knowledge derived from a preliminary analysis did not seem particularly attractive because of the hazardous nature of the materials and because the method was required for routine work. As will be seen later (see page 955), satisfactory conditions have been found by using a flame-ionisation detector.

Conclusions regarding the use of katharometers

Investigations have been carried out with a katharometer detector using small amounts of sample (1 μl or less), namely, quantities which are in the range recommended for highest efficiency of separation, and the results have shown that requirements for accurate analysis of a particular group of substances must be examined separately. This applied whether nitrogen or helium is used as carrier gas. It is possible that the load employed will need to be fairly closely controlled, in which case a syringe must be used and care must be taken to use the syringe in the same way. In some cases, such as that quoted for the methylchlorosilanes, the inexpensive capillary pipette may be used for transfer of sample because calibration is hardly affected by size of sample (carrier gas: nitrogen). Although the katharometer response curves are usually more nearly linear when helium is employed as carrier gas than is the case when nitrogen is used, for accurate results the procedure for nitrogen (two factors with close control of load) may often be required.

Evidence has been obtained to show that no advantage is to be gained by using an integrator.

II—APPLICATIONS OF THE FLAME-IONISATION DETECTOR

Because of the relative ease of operation and maintenance, in addition to its high sensitivity, the application of the flame-ionisation detector to the analysis of some of the mixtures used in the investigation of the katharometer has been studied. Orthodox packed columns were again used and sample loads in the range of a few μg to about 1 mg were examined. When the small loads were used, particular attention was given to avoid disproportionation of the sample.

There are now a number of references to the use of the flame-ionisation detector, particularly concerning its geometry, size of jet, and hydrogen and air flow rates.[9,14,15] Nowhere does there appear to be a detailed account of the degree of accuracy which can be obtained under standard conditions with packed columns. Although we have studied the use of a flame-ionisation detector constructed in glass for the determination of trimethyleneglycol in glycerol,[16] for the present investigations we decided to use a detector constructed in metal because of the increased sensitivity and stability.

Apparatus

The detector employed for this work is shown in Fig. 2 and it is constructed entirely in metal; it is based on McWilliam's design,[17] except for a few minor modifications. The output from the detector led to a Brown recorder through a Perkin Elmer amplifier and when necessary an integrator was used in conjunction with the Brown recorder.

Two techniques for adding the very small samples to the column have been investigated. In the first method the sample to be analysed (*e.g.*, benzene-toluene-xylene mixture) was made up as a dilute solution in carbon disulphide (to which the detector is relatively insensitive) and in the other a splitting arrangement was used without prior dilution of the sample.

All of the equipment required was built into an electrically heated oven (Griffin & George Ltd., England). This housed the columns which were made of Bundy tubing (tinned iron: $\frac{1}{4}$ inch o.d., $\frac{3}{16}$ inch i.d.). The vaporising and stream splitting unit and the detector, both made in metal, were housed at the top of the oven and partly projected inside the heated zone of the oven so that the columns were readily connected. Flow meters (Fisher & Porter) were housed on the sides of the oven. Like the detector, the vaporiser and splitting unit (see Fig. 3) was made in metal and resembled McWilliam's design[17] apart from minor modifications.

Procedure

The sample was injected through a Neoprene serum cap using a 'Hamilton' syringe, touching the top of the needle onto glass fibre placed above the metal gauze packing situated in the vaporising tube (see Fig. 3). The sample immediately vaporised into a stream of dry nitrogen which had been preheated in a copper coil prior to passing up the annular space surrounding the vaporising tube. On reaching the bottom of the tube (about 0·3-ml capacity), the sample either passed directly onto the column in the stream of nitrogen (by-pass needle valve is shut) or the sample was split into two parts, the major portion passing to waste (by-pass needle valve is open). With a splitting ratio of the order of 400 : 1 for a 1-μl sample, about 2-μg would go onto the column. After a brief period of time the needle valve could be closed, or alternatively, the valve could be kept open, but this involved a heavy wastage of carrier gas. In recent vaporising units the cylinder has been replaced by a metal coil (Tecalemit tubing: 11 inch long, $\frac{1}{8}$ inch o.d. and $\frac{3}{64}$ inch i.d.) with a funnel shaped top into which the tip of the needle is inserted. Pressure controllers were fitted to the filtered nitrogen, hydrogen and air streams.

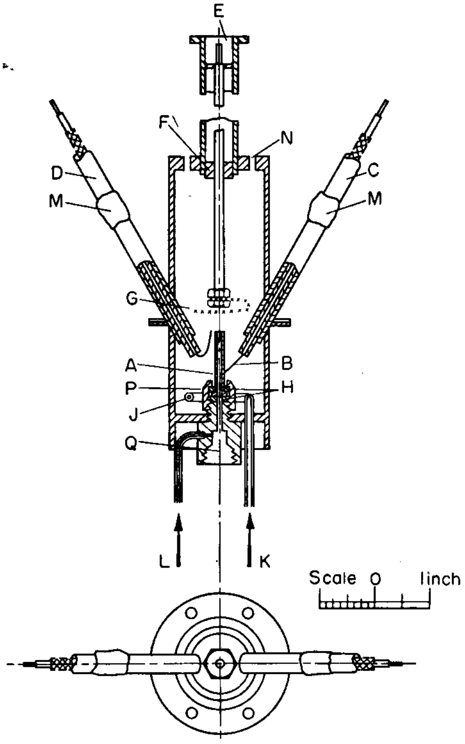

FIG. 2.—Flame-ionisation detector:

A Stainless steel hypodermic needle (0·020 inch i.d.) or platinum/rhodium jet (0·010 inch i.d.) both at negative potential
B Coaxial connection to jet
C Coaxial cable to high tension supply
D Coaxial cable to flame igniter
E Coaxial socket to collector electrode
F Polytetrafluoroethylene
G Gauze electrode (platinum or brass)
H Jet insulating rings (Pyrophillite)
J Air distribution ring
K Air inlet
L Hydrogen inlet
M Araldite seals
N Air vent
P Jet retaining nut
Q Column connecting point

Direct sample addition in dilute solution

(a) *Analysis of benzene-toluene-xylene mixtures in carbon disulphide solution:* In these experiments the sample was diluted with carbon disulphide prior to its transfer to the column. Carbon disulphide was chosen because of its relatively low response in the hydrogen flame. One μl of carbon disulphide solution containing 0·3% (*i.e.*, 3 μg) was added directly to the column. The conditions for the detector were finally chosen after an examination of the literature and after making a number of preliminary experiments in which the gas flow rates were investigated. As will be seen later, the effect of variations in the electrode gap could be important.

Table XIV shows mean factors and the spread of the individual determinations on each mixture for xylene (toluene = 1) obtained on five of the mixtures given in Table I; factors for benzene are not given because they showed wide variations from interference by the large excess of carbon disulphide

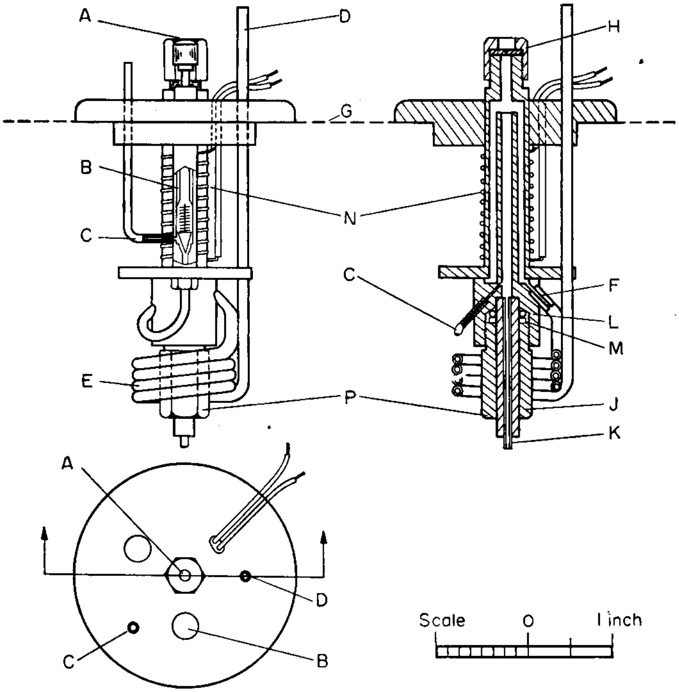

FIG. 3.—Sample vaporiser and stream splitter:

A Injection point
B By-pass needle valve;
valve: brass,
seating: stainless steel
C By-pass outlet
D Nitrogen inlet
E Nitrogen preheater coil
F Nitrogen inlet to vaporiser
G Top of oven
H Neoprene disc
J $\frac{1}{4}$ inch Ferrule, required when capillary column is used.
K Capillary column (or $\frac{1}{4}$ inch dia. conventional packed column)
L Silicone "O" ring
M Compression ring
N Preheater windings (22G Brightray C) 12-V supply
P Column retaining nut
Q Vaporiser tube (replaced in later models by a coil of Tecalemit tubing, 11 inch long, $\frac{1}{8}$ inch o.d. and $\frac{3}{64}$ inch i.d.)

TABLE XIV. FACTORS FOR XYLENE (TOLUENE = 1) USING CARBON DISULPHIDE SOLUTION

Mixture No.	Factors (peak areas)		Factors (peak heights)	
	Mean	Spread	Mean	Spread
1	1·00	0·04	1·45	0·01
2	1·02	0·04	1·52	0·03
3	1·02	0·02	1·53	0·03
5	1·00	0·01	1·47	nil
6	0·95	0·01	1·53	0·03

[Column: 3·5 ft of Bundy tubing; Silicone elastomer E. 301 (10%) on 'Embacel'; column temperature: 110°; preheater: 170°; nitrogen carrier gas: 33 ml/min; hydrogen to flame: 36 ml/min; air to flame: 1750 ml/min; electrode potential: 300 V; electrode gap: 2 cm.]

which was present (the flame-ionisation detector is not completely insensitive to carbon disulphide and the interference with benzene can to some extent be seen on the recorder trace shown in Fig. 4).

It will be seen from Table XIV that in spite of the lack of complete agreement between mean factors for various mixtures, if an over-all average factor is taken, both for peak areas (1·00) and peak heights (1·50), the maximum error is only about ±3%. The technique of using a second factor derived from a first preliminary result, as with the katharometer, would only be necessary for high accuracy. There appears to be no advantage in using peak area determinations derived from an integrated value. Results for the analysis of benzene-toluene-xylene mixtures employing a splitting procedure are given later. The carbon disulphide dilution technique, such as the one just described, is limited to products which are miscible with carbon disulphide and it is not entirely satisfactory for routine use.

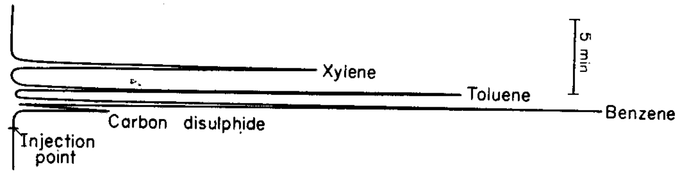

FIG. 4.—Chromatogram showing separation of benzene, toluene and xylene in carbon disulphide solution.

(b) *Determination of maximum load in carbon disulphide solution:* The next experiments were carried out in order to find the maximum load of the benzene hydrocarbons which could be tolerated. A constant load of 1 μl of the dilute carbon disulphide-hydrocarb onmixture was employed for one particular blend of hydrocarbons. Results obtained for mixture No. 1 (Table I) are shown in Table XV

TABLE XV. EFFECT ON XYLENE FACTOR (TOLUENE = 1) OF INCREASING HYDROCARBON CONCENTRATION IN CARBON DISULPHIDE

Sample, μg		Factor
Carbon disulphide	Mixture	
Nil	900	0·76
600	450	0·76
700	225	0·77
960	112	0·87
1080	56	1·00
1140	28	0·99
1170	14	0·99
1190	7	1·00
1200	3·5	0·98

where it will be seen that a load which is somewhere near 56 μg of the benzene-toluene-xylene mixture can be tolerated, namely about 20 μg of each constituent. Only the results based on peak area measurement are recorded. This aspect of loading has been studied in greater detail in the alternative method of adding the sample to the column, namely by the splitting procedure described below. It is evident, however, that there is considerable latitude for load size although the amount is of a different order from that used for the katharometer technique.

Addition of sample using splitting procedure

(a) *Analysis of benzene-toluene-xylene mixtures:* The analysis of benzene-toluene-xylene mixtures was examined by the method involving the splitting of a sample of 1 μl or so after vaporisation in the nitrogen carrier-gas stream. All relevant conditions are described in Table XVI. Factors (means of 3 determinations) obtained for mixtures Nos. 1 to 6 (see Table I) are given in Table XVI, together with the spread of the individual determinations on each mixture. Although there are small differences in the value of the factors for the various mixtures, the final mixture, namely, No. 7 also given in Table XVI, is seen to give a factor (peak heights only are given) which is considerably greater than those for the earlier mixtures. This indicates that although the use of an over-all mean factor might be reasonably satisfactory for a wide range of samples, those which have a very high xylene content may require the application of a second factor derived from information obtained from the first preliminary analysis (as with katharometer detection). A more recent investigation (see page 955) has shown that the size of the electrode gap has an important effect on the value of the factors obtained from the different mixtures.

TABLE XVI. FACTORS OBTAINED FOR TOLUENE AND XYLENE (BENZENE = 1) USING A SPLITTING PROCEDURE

Mixture (see Table I)	Factors (peak areas)				Factors (peak heights)			
	Mean		Spread		Mean		Spread	
	Toluene	Xylene	Toluene	Xylene	Toluene	Xylene	Toluene	Xylene
1	0·99	1·00	0·04	0·04	1·50	2·42	0·04	0·15
2	0·98	0·98	0·02	0·04	1·49	2·44	nil	nil
3	0·98	0·99	0·02	0·03	1·49	2·39	0·04	0·06
4	1·04	1·07	0·03	0·10	1·54	2·47	0·02	0·03
5	1·00	1·02	0·03	0·02	1·52	2·44	0·01	0·05
6	1·06	1·03	0·10	0·05	1·48	2·41	0·01	0·05
Over-all mean of mixtures Nos. 1–6	1·01	1·01			1·50	2·43		
Mixture No. 7					1·60	2·88	0·06	0·10

(Nitrogen carrier gas: 13·5 ml/min; by-pass: 2500 ml/min; vaporiser load: 0·8-μl; load on column: 4 μg; other column conditions as for Table XIV.)

Comparison of the factors derived from the peak height measurements with those obtained by integration show that no advantage is to be gained by using an integrator. Using the results in Table XVI, the calculated over-all mean factor using mixtures Nos. 1–6 for xylene (toluene = 1) is found to be 1·61. The corresponding factor, shown in Table XIV, derived from the sample prepared in carbon disulphide solution is lower.

(b) *Determination of the maximum load using the splitting procedure: Varying load with constant nitrogen by-pass:* In these experiments the conditions employed were the same as those given in Table XVI, except that a by-pass flow of 1500 ml of nitrogen/min was used with a column flow rate of 40 ml/min. The total load of sample was varied in the range 0·8 to 3·0 μl, for mixture No. 2 (Table I) the actual column loading being in the range 25 to 200 μg. Results obtained are given in Table XVII;

TABLE XVII. EFFECT ON FACTORS (BENZENE = 1) OF INCREASING LOAD WITH CONSTANT BY-PASS

Vaporiser load, μl	Column load (approx), μg	Mean factors (peak areas)		Mean factors (peak heights)	
		Toluene	Xylene	Toluene	Xylene
0·8	25	0·94	0·93	1·50	2·46
1·5	50	0·94	0·95	1·52	2·45
2·0	100	1·01	0·97	1·62	2·50
2·5	150	0·98	0·94	1·57	2·55
3·0	200	0·97	0·98	1·43	2·65

comparison of the peak height factors with the over-all mean factors given in Table XVI indicates that departure from these factors probably occurs in the range of about 50 μg, which is near to the limit obtained by the direct addition of diluted sample (see Table XV). A point of interest concerning these results is that in spite of the marked change in carrier gas flow rate compared with that used for the results obtained in Table XVI, the factors given in Table XVII (up to 50 μg of sample) are quite near to those obtained previously (see Table XVI).

Constant total load with varying nitrogen by-pass: Again employing mixture No. 2 (Table I), another series of experiments was carried out in which the actual column loading was changed by altering the by-pass flow rate progressively from 2500 ml/min to 500 ml/min, thus gradually increasing the amount of sample going onto the column from 4 to 90 μg derived from a total loading of 0·8 μl. Other conditions were as given in Table XVI. The progressive decrease in by-pass flow rate meant, of course, that there was a corresponding decrease in retention times for the various hydrocarbons. Thus, the retention time of benzene decreased from 156 to 39 sec when the by-pass flow rate was changed from 2500 to 500 ml/min.

The results given in Table XVIII show, as in the previous experiments, that under the conditions employed there is a limiting load which is of the order of about 50 μg, above which the factors (particularly for xylene by peak heights) tend to change.

TABLE XVIII. EFFECT ON FACTORS (BENZENE = 1) OF INCREASING LOAD WITH VARYING NITROGEN BY-PASS

By-pass flow, *ml/min*	Column load (approx), μg	Mean factors (peak areas)		Mean factors (peak heights)	
		Toluene	Xylene	Toluene	Xylene
2500	4	0·97	0·98	1·49	2·43
2000	12	0·95	0·96	1·46	2·47
1000	45	0·95	0·94	1·47	2·46
700	64	0·94	0·95	1·49	2·63
500	90	0·91	0·93	1·46	2·65

(c) *Effect of closing by-pass after fixed period of time:* Some experiments were carried out with a view to economy in nitrogen carrier gas usage, because with the by-pass open throughout an analysis a considerable wastage occurs. In these experiments, the by-pass was allowed to remain open for a period of 2 min.

It appeared that when the column was operated in this manner disproportionation of the sample could occur; nevertheless, with a standard time of 2 min before closing the by-pass, consistent results were obtained. This was demonstrated by the results given in Table XIX which gives mean values for the factors for each of three mixtures (see Table I). By comparison with Table XVI it will be seen that the factors by peak heights for example, are appreciably different, but comparison of the two Tables for the calculated factors for xylene based on toluene = 1 shows better agreement, which indicates a preferential loss of benzene under the conditions for Table XIX.

TABLE XIX. FACTORS (BENZENE = 1) OBTAINED WITH BY-PASS OPEN FOR 2 MIN

Mixture	Column load assuming 400 : 1 splitting ratio, μg	Mean factors (peak areas)		Mean factors (peak heights)	
		Toluene	Xylene	Toluene	Xylene
1	2·25	1·03	1·03	1·41	2·19
2	2·25	1·03	1·04	1·44	2·24
3	2·25	1·00	1·03	1·40	2·17

Fig. 5 shows recorder traces obtained when (a) the by-pass is closed for 2 min, and (b) with the by-pass continuously open. Note the almost instantaneous return to the baseline after closing the by-pass.

Effect of changes in jet design and in electrode gap

Various mixtures were next analysed with modified detectors, otherwise the same general conditions as previously described in Table XVI were employed; the hypodermic needle which had so far been used as the jet was replaced by a platinum-rhodium jet. In two series of experiments the electrode gap was maintained at 20 mm and 5–6 mm, respectively. A series of new mixtures, each containing in turn high and low concentrations of the various hydrocarbons, was used for analysis. Table XX shows the mean values obtained for the various factors based on peak height measurements.

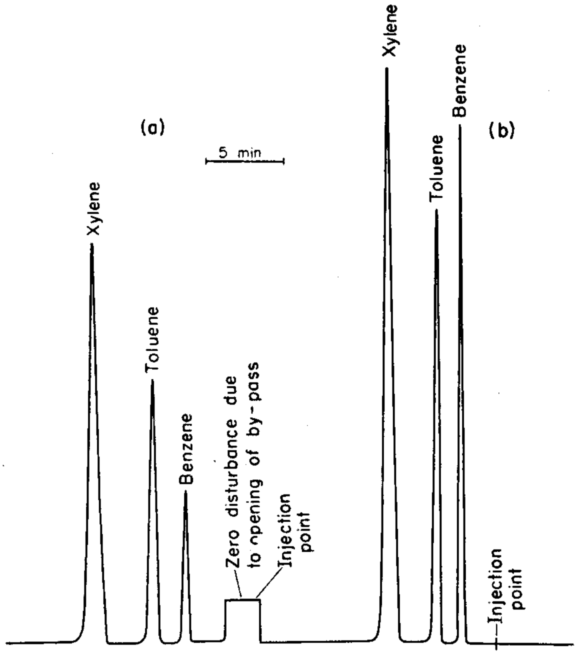

Fig. 5.—Chromatogram showing separation of benzene, toluene and xylene with flame ionisation detection:
(a) by-pass closed after 2 min,
(b) by-pass open for duration of test.

In spite of the difference in size of the electrode gap for the two detectors it is seen that the factors for each mixture are in reasonably close agreement. It will be seen, however, that as in the case of earlier experiments (see Table XVI) there are small differences between the levels of factors depending on the composition of the mixture. The over-all mean factors for the two electrode gaps shown in Table XX are in close agreement with one another and also with those obtained with the standard hypodermic jet (see Table XVI), except for the second mixture of Table XX which resembles in composition mixture No. 7 of Table XVI. In view of the behaviour of the two types of jet towards this particular mixture it is evident that further investigations are required, particularly as not only the material of the jets was different but also their lengths.

Conclusions concerning conditions for accuracy with flame-ionisation detection

It has been shown, using packed columns in conjunction with the flame-ionisation detector, that in so far as a simple mixture (benzene-toluene-xylene) is concerned accurate analyses can be accomplished from peak height measurements. With a splitting procedure for sample addition, a column loading of a few μg or in any case no more than about 50 μg should be employed and preferably the column by-pass should remain open. Satisfactory results may be obtained under carefully standardised conditions by closing the by-pass after allowing a short standard period of time (2 min) which is in excess of the time required to sweep the vaporised sample from the heated vapour cylinder (or coil).

For high accuracy it may be necessary to carry out a second factor determination using a mixture prepared on the basis of the first result because there are small differences between factor levels for various mixtures.

High column loadings are unsatisfactory for quantitative analysis. When the direct procedure (without dividing the sample at a by-pass) for adding the sample to the column is employed the large amount of diluent, *e.g.*, carbon disulphide, does not interfere so long as any peak derived from the relatively large amount of diluent is sufficiently removed from the peaks from the substances being measured. Thus, carbon disulphide interferes with benzene but not with toluene and xylene (see Fig. 4). As with the splitting procedure, amounts of sample up to about 50 μg can be tolerated.

TABLE XX. EFFECT OF CHANGE IN ELECTRODE GAP WITH FACTORS (BENZENE = 1) BASED ON PEAK HEIGHTS

% by wt. in mixture			Electrode gap			
			20 mm		5–6 mm	
Benzene	Toluene	Xylene	Toluene	Xylene	Toluene	Xylene
10·0	25·0	65·0	1·52	2·46	1·50	2·42
10·5	10·1	79·4	1·49	2·44	1·50	2·45
34·3	33·0	32·7	1·51	2·36	1·51	2·37
79·1	10·9	10·0	1·42	2·30	1·45	2·38
10·3	79·6	10·1	1·56	2·48	1·56	2·47
Over-all mean factor			1·50	2·41	1·50	2·42

It has been shown, however, that if the hypodermic jet is replaced by a platinum-rhodium jet the range of mixtures giving reasonably similar factors can be extended (compare Tables XVI and XX). In the analysis of benzene-toluene-xylene mixtures both the 20- and 5 to 6-mm electrode gaps were satisfactory when using the platinum-rhodium jet (0·010 inch dia.). There may, of course, be other satisfactory collector electrode and jet assemblies.

III—APPLICATION OF THE FLAME-IONISATION DETECTOR TO THE ANALYSIS OF CHEMICAL GROUPS OTHER THAN BENZENE HOMOLOGUES

The stages of investigation followed and the studies made in order to attain an accurate analysis of benzene-toluene-xylene mixtures have been described and the results form the basis for preliminary investigations into other chemical mixtures. The accuracy of flame-ionisation detection for the analysis of mixtures of ethylene glycol dinitrate and nitroglycerine, mixtures of chlorinated hydrocarbons and mixtures of polysiloxanes was next investigated.

Ethylene glycol dinitrate-nitroglycerine mixtures

It was shown (see page 948) that accurate analyses of ethylene glycol dinitrate-nitroglycerine mixtures could not be readily obtained by using a system based on the katharometer as detector. This mixture has been examined in conjunction with flame-ionisation detection. The detector had a platinum-rhodium jet (0·010-inch bore) with a platinum gauze collector electrode and 2-cm gap. Because of possible hazards involved, a procedure was worked out in which the sample was added directly to the column in a solution of methylene chloride rather than employing a splitting procedure. Nitrobenzene was added as a marker. Table XXI shows results obtained for four different mixtures. On the basis of these results it is considered that the procedure could be readily applied as a quantitative method for the determination of ethylene glycol dinitrate in nitroglycerine. A method has now been evolved for the determination of ethylene glycol dinitrate in blasting explosives. Fig. 6 shows a typical trace.

TABLE XXI.—FACTORS FOR ETHYLENE GLYCOL DINITRATE (NITROBENZENE = 1) OBTAINED WITH FLAME IONISATION

Sample	Ethylene glycol dinitrate, %	Nitrobenzene, *M*%	Nitroglycerine, %	Factor calculated from peak height
1	22·8	0·74	76·4	38·4, 36·0, 37·7, 37·7, 37·3, 39·8 Mean 37·7
2	17·2	0·79	81·9	37·7, 37·5, 36·3, 36·3, Mean 37·0
3	11·2	0·85	87·9	36·2, 36·3, 36·1, Mean 36·2
4	4·0	0·91	95·1	36·3, 35·7, 37·7, 36·3, Mean 36·6

(1-μl of methylene chloride solution containing 10% of the prepared sample was added to the column; column: 130°; preheater: 170°; hydrogen to flame: 36 ml/min; nitrogen: 40 ml/min; air: 1200 ml/min.)

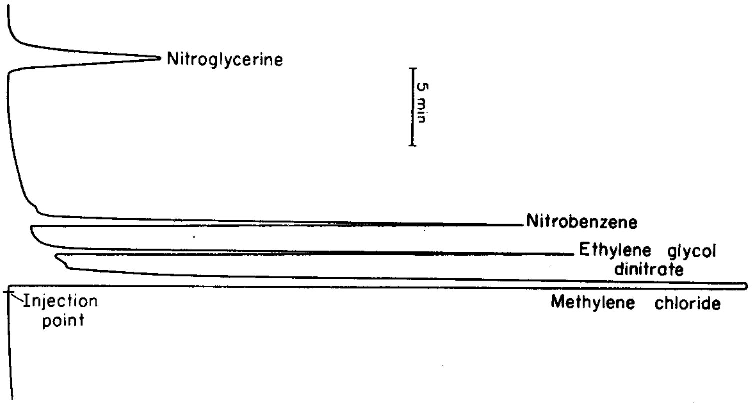

FIG. 6.—Chromatogram showing separation of ethylene glycol dinitrate in nitroglycerine with nitrobenzene as internal standard.

Polysiloxanes

Mixtures of the three polysiloxanes, $(Me_2SiO)_n$, namely, the trimer, tetramer and pentamer (see Table XXII), have been successfully analysed with a detector comprising the usual hypodermic needle as the jet electrode and a brass collector electrode with a 5–6-mm electrode gap instead of platinum gauze as used in the work previously described. Table XXIII shows a comparison of factors obtained with the standard detector conditions (hypodermic needle as jet with 2-cm gap and platinum gauze collecting electrode).

TABLE XXII.—COMPOSITION OF THE MIXTURES OF TRIMER, TETRAMER AND PENTAMER

Polysiloxane, % *by wt.*	A	B	C
Trimer	81·5	10·8	10·6
Tetramer	9·7	79·8	11·0
Pentamer	8·8	9·4	78·4

Mixture A was diluted with an equal volume of benzene in order to keep the large amount of trimer in solution and the true column loading was therefore 8 μg, compared with 16 μg for samples B and C.

The results given in Table XXIII show that the improvement brought about by changing from the standard jet conditions with a 20-mm gap to the other conditions with the 6-mm gap is very marked.

TABLE XXIII.—FACTORS FOR TRIMER, TETRAMER AND PENTAMER MIXTURES (TRIMER = 1)

Mixture	Electrode gap					
	20 mm				6 mm	
	Mean factors (peak areas)		Mean factors (peak heights)		Mean factors (peak heights)	
	Tetramer	Pentamer	Tetramer	Pentamer	Tetramer	Pentamer
A	0·92	0·99	1·93	4·78	2·25	5·82
B	1·07	1·05	2·43	5·37	2·38	5·85
C	0·97	1·04	2·14	5·61	2·25	5·83

(E. 301 silicone elastomer as stationary phase; column: 137°; preheater: 190°; nitrogen carrier gas: 12 ml/min; by-pass: 2000 ml/min; hydrogen to flame: 36 ml/min; air to flame: 1750 ml/min; vaporiser load: 1 μl; load to column: 8 or 16 μg added by splitting procedure with by-pass open continuously.)

There is reasonably good agreement between the factors obtained under the latter conditions for the various mixtures, whereas the differences with the former electrode conditions are too great to permit the use of an average factor for the analysis of these mixtures. The effect of change in electrode conditions is much more noticeable in the case of these siloxanes than for benzene-toluene-xylene mixtures. Further work is needed to study electrode conditions for the polysiloxanes.

TABLE XXIV.—COMPOSITION OF METHYLENE CHLORIDE-CHLOROFORM-CARBON TETRACHLORIDE MIXTURES

Chlorinated hydrocarbon, *% by wt.*	A	B	C
Methylene chloride	78·2	9·9	9·0
Chloroform	10·6	80·8	9·7
Carbon tetrachloride	11·2	9·3	81·3

Chlorinated aliphatic hydrocarbons

The behaviour of the flame ionisation detector in relation to its application to the analysis of mixtures of methylene chloride, chloroform and carbon tetrachloride (see Table XXIV) was next investigated. The two sets of electrode conditions used for the polysiloxanes were again employed. Table XXV shows the results obtained; again, as for the polysiloxanes, there is a marked improvement by employing the smaller electrode gap. However, the agreement between factors for the three different compositions is not sufficiently good to preclude a second determination for an unknown mixture submitted for analysis.

For both the chlorinated bodies and the polysiloxanes no advantage is obtained by using integrated peak area measurements.

The study of the four types of mixtures, namely, hydrocarbons, nitrate esters, polysiloxanes and chlorinated hydrocarbons, has shown that without making any far reaching changes in a particular apparatus with flame-ionisation detection it may be possible to adjust the conditions of the detector to

TABLE XXV. FACTORS FOR CHLORINATED ALIPHATIC HYDROCARBONS (METHYLENE CHLORIDE = 1)

Mixture	Electrode gap 20 mm, Mean factors (peak areas), Chloroform	Electrode gap 20 mm, Mean factors (peak areas), Carbon tetrachloride	Electrode gap 20 mm, Mean factors (peak heights), Chloroform	Electrode gap 20 mm, Mean factors (peak heights), Carbon tetrachloride	Electrode gap 6 mm, Mean factors (peak heights), Chloroform	Electrode gap 6 mm, Mean factors (peak heights), Carbon tetrachloride
A	1·03	1·38	1·54	2·73	2·26	3·67
B	1·83	1·95	2·54	3·52	2·11	3·59
C	1·34	1·98	1·86	3·87	2·04	3·34

(E. 301 nitrogen used as stationary phase: column: 70°; preheater: 110°; carrier gas: 20 ml/min; by-pass: 2500 ml/min; hydrogen to flame: 36 ml/min; vaporiser load: 0·8 μl; load to column: 10 μg added by splitting procedure with by-pass open continuously.)

those required to enable the method to be used for the accurate analysis of unknown mixtures. It may often be necessary, however, to make a second factor determination based on the results of a preliminary analysis.

Zusammenfassung—Der Ausgangspunkt der Arbeit liegt darin, dass die Informationen über die Genauigkeit von Gaschromatographie mit geackten Säulen unzureichend sind. Besonders schienen Probeneinführung, Probengrösse und Berechnung der Resultate weiterer Untersuchungen zu bedürfen. Die Faktoren wurden studiert unter Anwendung eines Katharometers und eines Flammenionisationsdetektors. Eine Reihe verschiedener, chemischer Systeme wurde untersucht und es wurde gefunden, dass bei der Katharometermethode die Probenmenge viel genauer kontrolliert werden muss als bei anderen Methoden um gute Ergebnisse zu erhalten. Für den Flammdetektor ist bei manchen Proben der Elktrodenabstand von hoher Bedeutung. Es wurde gezeigt, dass Messung der Spitzenhöhe zu sehr genauen Resultaten führen kann und Planimetrieren der Fläche keinen Vorteil hat.

Résumé—On considère qu'il n'y a pas assez des informations sûrs à propos de la précision des méthodes de chromatographie gazeuse pour l'analyse quantitative utilisant les colonnes garnies. Les facteurs demandant d'autres précisions résultent du transport de l'échantillon, en relation directe avec sa dimension, et le calcul des résultats. Une étude de ces facteurs a été faite en utilisant successivement un catharomètre et un détecteur à flamme d'ionisation. Quelques systèmes chimiques ont pu être étudiés et les résultats montrent que l'emploi d'un catharomètre comme détecteur impose un contrôle très soigneux de la dimension de l'échantillon dans le cas de certains systèmes si l'on désire une précision suffisante. A cette précaution s'ajoute, dans le cas d'un détecteur à flamme d'ionisation, un soin particulier à l'écartement des électrodes, certains échantillons y étant plus sensibles que d'autres. Dans ces conditions, la mesure de la hauteur des pics conduit à des résultats d'une précision suffisamment élevée pour qu'il ne soit pas nécessaire de mesurer les surfaces.

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THE INFRARED SPECTRA OF CHELATE COMPOUNDS—II*

A STUDY OF SOME BIVALENT METAL CHELATE COMPOUNDS OF 8-HYDROXYQUINOLINE IN THE REGION 625 TO 250 cm^{-1}

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Summary—An investigation of the infrared spectra in the region 625–250 cm^{-1} of the complexes of copper, zinc, manganese, magnesium and calcium with 8-hydroxyquinoline has been carried out. The spectra are simple, but, despite their simplicity, they differ from one another, both in the number of peaks and the relative positions of corresponding peaks. Possible analytical applications of the spectra in this region are discussed.

THE infrared spectra in the region 5000–625 cm^{-1} of some metal chelates of 8-hydroxyquinoline have already been reported.[1]

Investigations of metal chelates in the region 625–250 cm^{-1} are few in number. Dismukes *et al.*[2] have recorded the infrared spectra of some metal-acetylacetonate complexes between 700 and 350 cm^{-1}, and Lane *et al.*[3] have recently obtained the infrared spectra of 2-(2-pyridyl)-imidazoline, 2-(2-pyridyl)-benzimidazole, 2-(*o*-hydroxyphenyl)-imidazoline, 2-(*o*-hydroxyphenyl)-benzimidazole, and their metal chelates in the region between 5000 and 300 cm^{-1}. However, no investigation of 8-hydroxyquinoline and its metal chelates in this low frequency range has been reported.

EXPERIMENTAL

Materials

The metal oxinates used in the investigation were prepared, as far as possible, by the method of precipitation from homogeneous solution;[4,5] these were copper,[6] zinc,[7] manganese,[5] magnesium[5] and calcium.[5]

Potassium bromide discs were prepared using a Perkin Elmer die in conjunction with an "Elmes" hydraulic press capable of delivering 23,000 pounds total load on a ram 3 inches in diameter. Before use, the KBr, which was of spectroscopic grade, was dried at 150° for 24 hr, and was ground to pass 100 mesh.

Measurement of the infrared spectra

All spectra were recorded on a Perkin-Elmer, Model 21, Spectrophotometer with a CsBr prism; resolution was 1000, response 12, and speed 32.

The spectra obtained for 8-hydroxyquinoline and the five metal chelates are shown in Figs. 1–6.

RESULTS AND DISCUSSION

The principal absorption peaks observed in the spectra of 8-hydroxyquinoline and the metal oxinates (Figs. 1–6), recorded in μ except where stated, are given below:

8-*Hydroxyquinoline*

15·71, 17·40, 18·39, 20·40, 21·3, 21·52, 23·62, 33·00.

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* Part I—see ref. 1.

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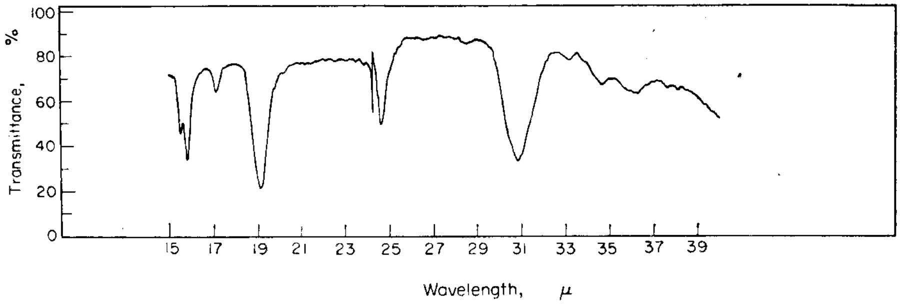

FIG. 1.—The infrared spectrum of copper oxinate in the region 15–40 μ. (2 mg of copper oxinate in 400 mg of KBr.)

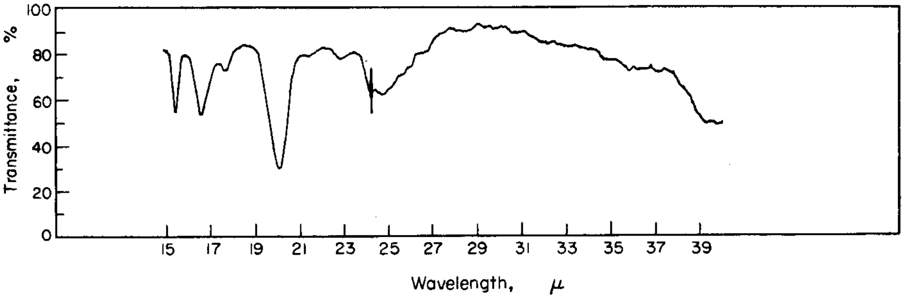

FIG. 2.—The infrared spectrum of zinc oxinate in the region 15–40 μ. (2 mg of zinc oxinate in 400 mg of KBr.)

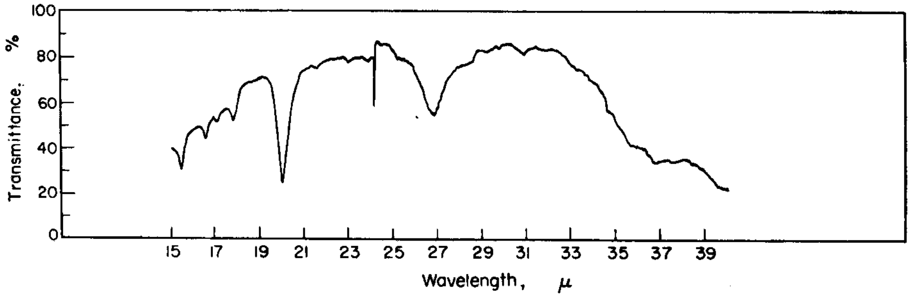

FIG. 3.—The infrared spectrum of manganese oxinate in the region 15–40 μ. (2 mg of manganese oxinate in 400 mg of KBr.)

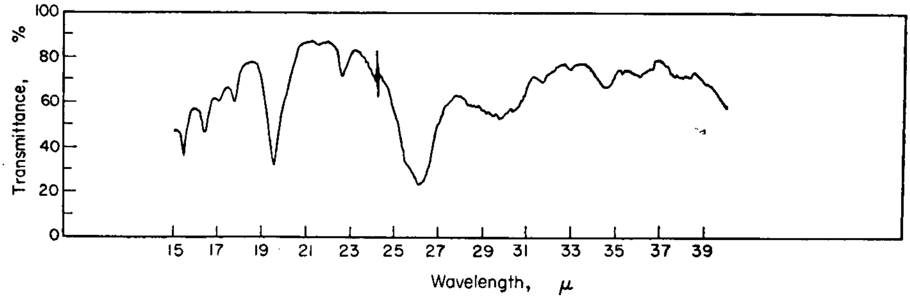

FIG. 4.—The infrared spectrum of magnesium oxinate in the region 15–40 μ. (2 mg of magnesium oxinate in 400 mg of KBr.)

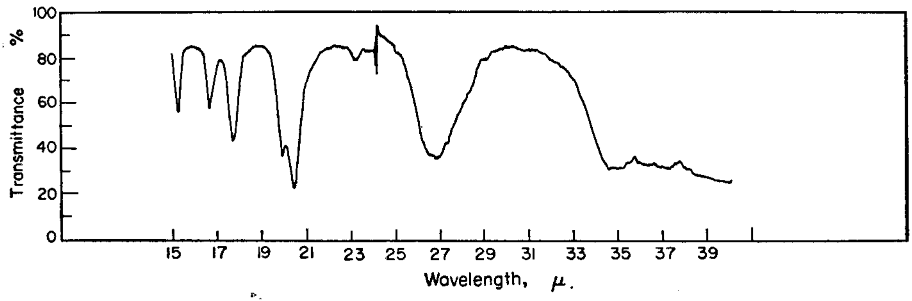

FIG. 5.—The infrared spectrum of calcium oxinate in the region 15–40 μ. (2 mg of calcium oxinate in 400 mg of KBr.)

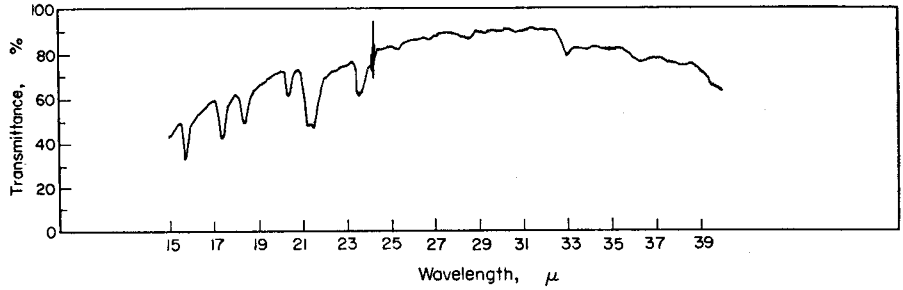

FIG. 6.—The infrared spectrum of 8-hydroxyquinoline in the region 15–40 μ. (2 mg of 8-hydroxyquinoline in 400 mg of KBr.)

Copper oxinate

15·53, 15·82, 17·15, 19·15 (522·19 cm^{-1}), 24·64 (405·84 cm^{-1}), 30·82.

Zinc oxinate

15·41, 16·60, 17·68, 20·11 (497·26 cm^{-1}), 24·70 (404·86 cm^{-1}).

Manganese oxinate

15·49, 16·62, 17·10, 17·80, 20·05 (498·75 cm^{-1}), 26·86 (372·30 cm^{-1}), 30·88.

Magnesium oxinate

15·47, 16·40, 17·05, 17·76, 19·55 (511·51 cm^{-1}), 20·65 (484·26 cm^{-1}), 26·12 (382·85 cm^{-1}), 31·68, 32·99, 34·50.

Calcium oxinate

15·30, 16·74, 17·75, 19·95 (501·25 cm^{-1}), 20·47 (488·52 cm^{-1}), 23·25, 26·78 (373·41 cm^{-1}).

The spectra (of 8-hydroxyquinoline and the metal chelates) in the region examined are quite simple, in contrast to those taken at higher frequency.[1]

In the caesium bromide region, *i.e.*, the region of the investigation, absorption may be caused by internal vibrations, torsional oscillations[8] of water in the sample, or lattice vibrations, although these last are not likely above 300 cm^{-1}. Miller *et al.*[8] point out that where water of crystallisation exists in a sample, rotations become hindered and are better described as torsional oscillations. These oscillations produce absorption in the caesium bromide region. Water can, however, cause difficulty in this region and often produces peaks which are broad.

The spectra of the metal chelates, despite their simplicity, differ markedly from one another, both in the number of peaks and the relative positions of corresponding peaks. They also differ from 8-hydroxyquinoline itself. Perhaps the most interesting peak is that which occurs in the region around 19–20 μ, or more specifically, copper (19·15 μ; 522·19 cm^{-1}); zinc (20·11 μ; 497·26 cm^{-1});[5] manganese (20·05 μ; 498·75 cm^{-1}); magnesium (19·55 μ; 511·51 cm^{-1}), and calcium (19·95 μ; 501·25 cm^{-1} or 20·47 μ; 488·52 cm^{-1}). The peak in this region occurs in all of the metal chelates but not in the spectrum of 8-hydroxyquinoline.

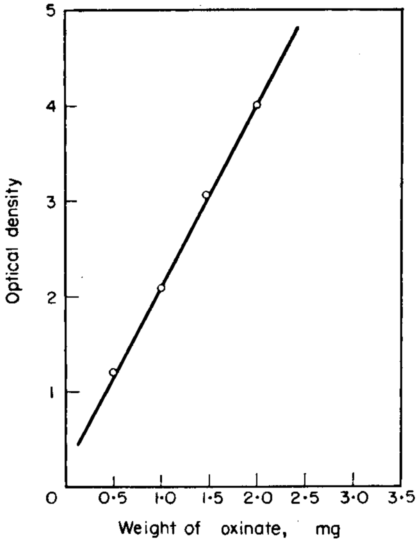

FIG. 7.—Optical densities plotted against weight of copper oxinate.

The peaks for calcium at 26·78 μ (373·41 cm^{-1}), for magnesium at 26·12 μ (382·85 cm^{-1}) and for manganese at 26·86 μ (372·30 cm^{-1}) are broad. They do not occur in the spectra of copper and zinc. These peaks possibly represent water of crystallisation.

Analytical applications

The infrared spectra in the region under investigation are much simpler than those obtained in the region 5000–625 cm^{-1}.[1] Despite their simplicity, however, considerable differences occur between the spectra of the individual metal oxinates (Fig. 1–6). These differences are such that qualitative analysis for the metals may be carried out using the spectra as a basis. To investigate the quantitative significance of the technique the peak at 19·15 μ or 522·19 cm^{-1} in the copper oxinate spectrum was examined. Potassium bromide discs were prepared by the procedure outlined elsewhere,[1] and the optical densities for different amounts of copper oxinates were determined. In Fig. 7 the optical densities obtained are plotted against the weights of oxinate taken. It can be seen that the points lie on a straight line. The actual peaks for three different amounts, 0·5, 1·0 and 2·0 mg of copper oxinate are shown in Fig. 8.

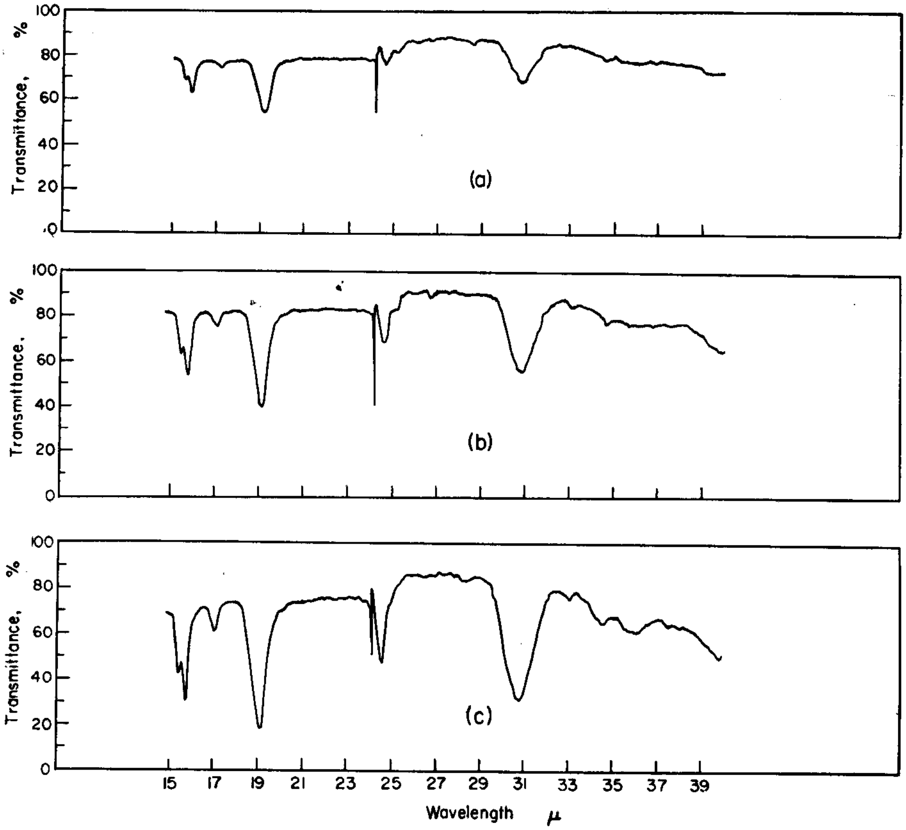

FIG. 8.—The peaks for three different amounts of copper oxinate, in 400 mg of KBr: (*a*) 0·5 mg; (*b*) 1·0 mg; (*c*) 2·0 mg.

It is clear that the infrared technique in the range 625–250 cm^{-1} has potentialities for the quantitative determination of elements by means of their oxinates. In this work detailed analytical investigations were not carried out, but a quantitative analytical study is considered to be worthwhile. It is proposed to carry out such a study and the results will be reported later.

Acknowledgements—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under Contract AT(11-1)-582. Thanks are also due to the Research Department of the Union Carbide Co., Parma, Ohio, U.S.A., for use of the Model 21 spectrophotometer.

Zusammenfassung—Eine Untersuchung der Oxinate von Cu, Zn, Mn, Mg und Ca im IR-Bereich (625–250 cm^{-1}) wurde durchgeführt. Die Spektren sind einfach, unterscheiden sich aber trotzdem voneinander. Sowohl die Anzahl als auch die Lage der Spitzen ist verschieden. Die Möglichkeiten einer analytischen Anwendung der Methode wurden diskutiert.

Résumé—Une recherche sur les spectres infra-rouges des chélates de l'hydroxy-8-quinoléine et des métaux suivants (cuivre, zinc, manganèse, magnésium, calcium) a été effectuée dans les régions 250–625 cm^{-1}. Les spectres obtenus sont simples, mais malgré leur simplicité, ils diffèrent sensiblement à la fois par le nombre des pics et la position relative de ces pics. On presente une discussion des possibilités d'application de ces spectres à l'analyse.

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THE INFRARED SPECTRA OF CHELATE COMPOUNDS—III*

A STUDY OF SOME TERVALENT METAL CHELATE COMPOUNDS OF 8-HYDROXYQUINOLINE IN THE REGION 5000–250 cm^{-1}

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Summary—The infrared spectra of 8-hydroxyquinoline and of its complexes with aluminium, gallium and indium have been determined in the region 5000–250 cm^{-1}. The spectra show similarities, but differences between the aluminium complex and the other two occur in the region 625–250 cm^{-1}. A discussion of the spectra and of the structures of the oxinates is presented.

THE infrared spectra in the region 5000–250 cm^{-1} of a number of bivalent metal chelates of 8-hydroxyquinoline have already been recorded.[1,2] In the present paper the spectra in the ranges 5000–625 and 625–250 cm^{-1} of the complexes with aluminium, gallium and indium are described. The only other report on the infrared spectra of the tervalent metal chelates of 8-hydroxyquinoline is that by Charles *et al.*,[3] who studied the infrared spectra of 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline, 4-methyl-8-hydroxyquinoline, and a number of metal chelates derived from these reagents, including those of aluminium and indium in the range 3000–625 cm^{-1}.

EXPERIMENTAL

Materials

The metal oxinates used in the investigation were all prepared by the method of precipitation from homogeneous solution;[4] these were aluminium,[5] gallium,[6] and indium.[7] Potassium bromide discs were prepared using a Perkin-Elmer die in conjunction with an "Elmes" hydraulic press capable of delivering 23,000 pounds total load on a ram 3 inches in diameter. Before use, the spectroscopic grade potassium bromide was dried at 150° for 24 hr, and was ground to pass 100 mesh.

Measurement of the infrared spectra

All spectra were recorded on Perkin-Elmer Model 21, and Beckman IR-5A spectrophotometers. The spectra obtained for hydroxyquinoline and the three metal chelates in the region 625–250 cm^{-1} are shown in Figs. 1–3. That for 8-hydroxyquinoline in the same region has already been recorded.[2]

RESULTS AND DISCUSSION

The principal absorption peaks observed in the spectra of 8-hydroxyquinoline and the metal oxinates in the region 5000–250 cm^{-1} (Figs. 1–3), measured in μ, are recorded below, the significance of those peaks marked by an asterisk being discussed later:

8-*Hydroxyquinoline*

33·00, 23·62, 21·52, 21·3, 20·40, 18·39, 17·40, 15·71, 14·08, 13·5, 12·8, 12·38, 12·2,

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* Part II—See ref. 2.

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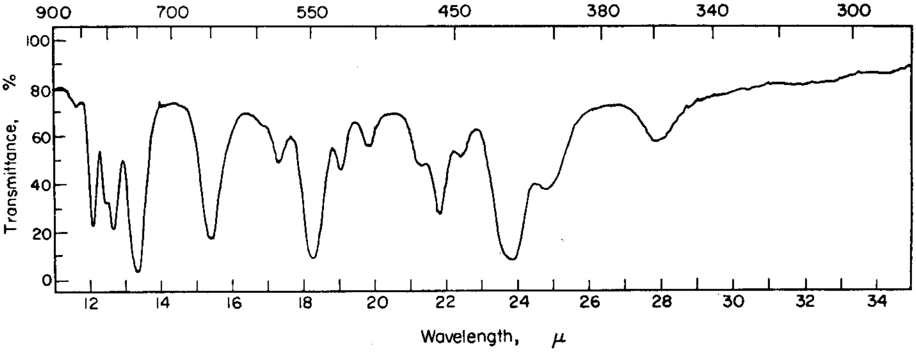

FIG. 1.—The infrared spectrum of aluminium oxinate in the region 15–35 μ. (1·6 mg of aluminium oxinate in 300 mg of KBr.)

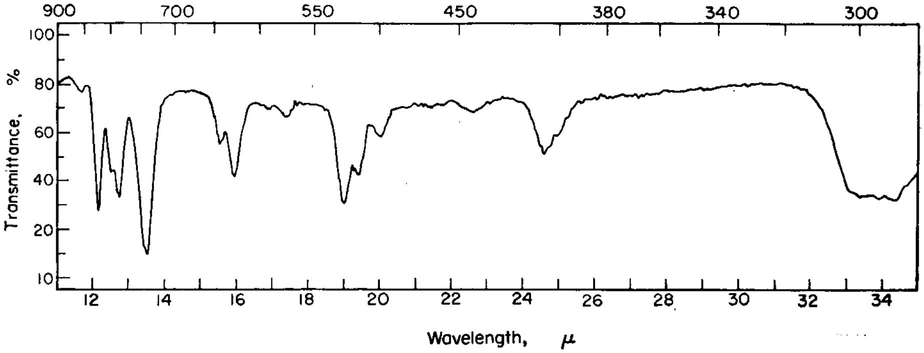

FIG. 2.—The infrared spectrum of gallium oxinate in the region 15–35 μ. (1·6 mg of gallium oxinate in 300 mg of KBr.)

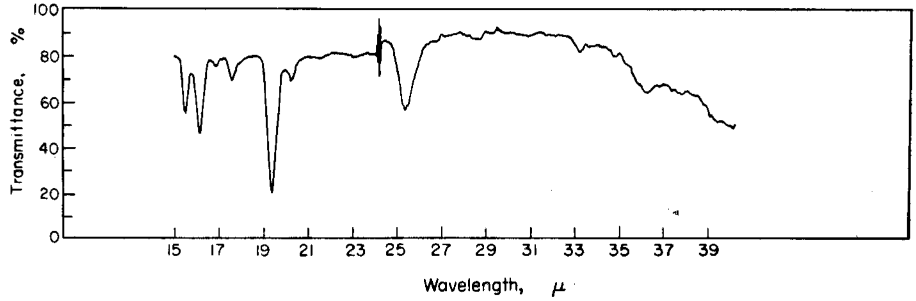

FIG. 3.—The infrared spectrum of indium oxinate in the region 15–35 μ. (1·6 mg of indium oxinate in 300 mg of KBr.)

11·54, 11·15, 10·24, 9·7, 9·43, 8·75, 8·55, 8·28, 8·16, 7·8, 7·23, 7·06, 6·96, 6·78, 6·65, 6·31, 5·25, 3·3 (a broad peak).

Aluminium oxinate

27·9, 24·75, 23·81, 22·4, 21·81, 21·3, 19·82, 19·02, 18·22 (547 cm^{-1})*, 17·29, 15·4, 13·35, 12·68, 12·45, 12·17, 11·65, 10·94, 10·48, 10·22, 9·7, 9·5, 8·98, 8·52, 8·14, 7·8, 7·52, 7·24, 7·02, 6·82, 6·68, 6·33, 6·22, 5·8, 5·23, 3·84, 3·76, 3·28, 2·93.

Gallium oxinate

24·55, 22·55, 20·01, 19·47, 19·26, 19·00 (525 cm^{-1})*, 17·35, 16·86, 15·95, 15·52, 13·5, 12·75, 12·5, 12·18, 11·66, 10·98, 10·48, 9·7, 9·5, 9·0, 8·84, 8·52, 8·17, 7·81, 7·53, 7·25, 7·02, 6·84, 6·69, 6·34, 6·25, 5·83, 5·25, 3·28, 2·92.

Indium oxinate

25·17, 19·65, 19·19 (517 cm^{-1})*, 17·3, 15·95, 15·58, 15·25, 13·61, 13·43, 13·3, 12·69, 12·45, 12·16, 11·55, 11·0, 9·67, 9·38, 9·02, 8·80, 8·52, 8·08, 7·8, 7·55, 7·24, 7·0, 6·83, 6·67, 6·32, 6·24, 5·9, 5·77, 5·2, 3·28, 2·93.

Spectra and structure of aluminium, gallium and indium oxinates

Differences exist between the spectra of these metal chelates and that of 8-hydroxyquinoline. In general, the spectra of the metal chelates, as might be expected, are similar, with one outstanding exception. In the wavelength region 650–250 cm^{-1} the spectrum of the aluminium complex is different from those of the gallium and indium complexes. Possible reasons for this are discussed below.

In the region 5000–625 cm^{-1} the spectra of all these oxinates are very similar, but indium oxinate shows bands at 13·3 and 13·45 μ which are not present in the spectra of the other complexes.

In the region 650–250 cm^{-1} the principal differences between gallium and indium are shifts in the peaks. For example, the band at 525 cm^{-1} (19·00 μ) in the gallium complex is found at 517 cm^{-1} (19·19 μ) in indium oxinate and 547 cm^{-1} (18·22 μ) in aluminium oxinate.

Because of the availability of *d* orbitals, the elements aluminium, gallium and indium can form semicovalent octahedral complexes.[8] The electronic configuration of aluminium is $1s^2$; $2s^2$, $2p^6$; $3s^2$, $3p^1$. By the loss of electrons from the $3s$ and $3p$ orbitals, these, together with the empty $3d$ orbitals, become available for bonding. By this arrangement the 12 electrons from the ligands can be accommodated by hybridisation of the type sp^3d^2 which gives rise to an octahedral structure. The co-ordinating ligands can be accommodated on the $d_{x^2-y^2}$, d_{z^2} orbitals, without involving the d_ε orbitals. Such a structure is undoubtedly octahedral,[9] and the hybridisation is therefore $sp^3d_{z^2}$.

In the case of gallium and indium the same reasoning applies, except that for gallium the orbitals involved are the $4p$, $4s$ and $4d$ orbitals, and for indium the orbitals involved are the $5s$, $5p$ and $5d$. In all cases the predicted picture of the structure of these three complexes is octahedral. If, however, consideration is taken into account of the size of the ions involved, because the ionic radius ranges from 0·50 Å for aluminium to 0·81 Å for indium, *i.e.*, a 60% increase, then distortion of the octahedral structure will occur, which will be reflected in the infrared spectra.

Acknowledgment—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under Contract AT(11-1)-582.

Zusammenfassung—Die Infrarotspektren von 8-Hydroxychinolin und einigen seiner Chelate mit dreiwertigen Metallen (Al, Ga und In) wurden von 625–250 cm^{-1} gemessen. Die Spektren sind ähnlich, aber zwischen Aluminium und den anderen beiden Metallen treten Unterschiede auf. Die Spektren werden diskutiert und Strukturvorschläge für die Oxinate gemacht.

Résumé—On présente une étude des spectres infra-rouges de l'hydroxy-8-quinoléïne et de ses chélates formés avec des métaux trivalents (aluminium, gallium, et indium), dans la région des 250–625 cm^{-1}. Les spectres sont similaires mais il existe des diffèrences entre celui de l'aluminium et les deux autres dans la région des 250–625 cm^{-1}. On discutre les spectres et la structure des oxinates.

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CONTINUOUS COULOMETRIC TITRATION OF VARIOUS OXIDISING SUBSTANCES BY ELECTROGENERATED IRON^{II}

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Summary—Iron^{II} reacts rapidly and quantitatively with various oxidising substances, such as potassium permanganate, potassium bichromate or free chlorine, in acidic solution. Continuous coulometric titrations of such solutions have been carried out with iron^{II} electrogenerated from iron^{III} at a platinum cathode. The progress of the reaction in the titration cell is followed potentiometrically with a platinum-calomel electrode pair. The potential difference between the detected potential and the end-point potential is amplified with a d.c. amplifier, whose output controls the electrolytic current so that the detected potential becomes equal to the end-point potential. Thus the electrolytic current which generates the iron^{II} is directly proportional to the concentration of oxidising constituent in the sample solution. In order to obtain good results, it is desirable to make a dynamic titration curve empirically in order to locate the optimum for the end-point in the coulometric titration.

INTRODUCTION

POTASSIUM permanganate, potassium bichromate, cerium^{IV} sulphate and other oxidising substances can be determined by coulometric titration with electrogenerated iron^{II}. This method is free from the trouble of atmospheric oxidation of iron^{II} which occurs in a conventional titration with an iron^{II} solution.

Oelsen and Göbbels[1] proposed a determination of vanadate and permanganate by coulometric titration with iron^{II} electrogenerated at constant current. This method was subsequently applied to the determination of vanadium and chromium in steel.[2] Cooke, Reilley and Furman used the coulometric titration with electrogenerated iron^{II} for determination of cerium^{IV} and bichromate,[3] vanadium in uranium[4] and a minute amount of permanganate.[5] Futhermore, Meites[6] determined cerium^{IV}, vanadium^{V}, chromium^{VI} and manganese^{VII}.

Takahashi, Kimoto and Sakurai[7] developed a back-titration coulometric method which consisted of electrogeneration of cerium^{IV} from cerium^{III} in the presence of iron^{III}, reaction of cerium with the components to be determined in the sample and coulometric titration of the excess cerium^{IV}. This back-titration method was comfirmed by Fenton and Furman[8] to be an excellent method because of the almost 100% current efficiency during the coulometric titration.

The present authors[9,10] have constructed a continuous titration apparatus using coulometry and used it, for example, to carry out a continuous titration of arsenous acid with bromine electrogenerated from potassium bromide; the principle of such a continuous coulometric titration apparatus and its manipulating conditions have also been discussed.

Furthermore, the authors have investigated the continuous determination of micro quantities of iron dissolved in water by coulometric titration with electrogenerated bromine[11] and confirmed the applicability of the continuous coulometric titration method.

In the present paper the authors have studied the continuous coulometric titration of potassium permanganate, bichromate and chlorine in dilute solutions using iron^{III} as the electrolyte solution.

EXPERIMENTAL

Reagents

Electrolyte solution (about 0·1N in ammonium iron^{III} sulphate and 2N in sulphuric acid): Prepared by dissolving 100 g of extra-purified sulphuric acid and 48 g of extra-purified ammonium iron^{III} sulphate in 1 litre of water.

0·1N Potassium permanganate and bichromate solutions: Prepared by dissolution of extra-purified reagents in water and suitable dilution.

Chlorine water: Prepared by absorption of chlorine gas evolved from 1:1 hydrochloric acid and bleaching powder in 1N hydrochloric acid and subsequent dilution with water. The concentration of free chlorine was determined by iodometric titration.

Apparatus

The apparatus used in the present experiments (Fig. 2) is as in previous reports.[9,10] The electrolyte solution (ammonium iron^{III} sulphate solution) is introduced into the titration cell at a definite rate, iron^{II} being generated electrolytically at the cathode surface; the solution then reaches the titration cell where it is mixed with the stream of sample solution. The titration cell is provided with a platinum indicating electrode and a saturated calomel electrode, between which is applied a d.c. constant voltage, slightly more negative than the potential corresponding to the end-point. The solution in the titration cell is always automatically controlled so as to contain a small excess of iron^{II}. The electrogenerated iron^{II} reacts with the oxidising substance in the sample solution and the remaining iron^{II} changes the potential at the indicating electrode; the potential difference between the indicator and reference electrodes is fed into the d.c. amplifier and its output supplied as electrolytic current for the electrogeneration of iron^{II}.

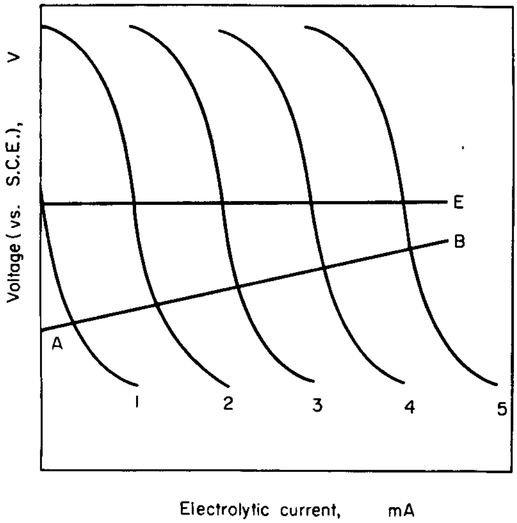

FIG. 1.—Dynamic titration curves for determination of an oxidising substance with iron^{II}.

Fig. 1 shows the characteristics obtained when using the continuous coulometric titrator for the determination of an oxidising substance with iron^{II}. The curves represent the titration of sample solutions containing increasing amounts of the reacting component. A is the applied voltage, E is the theoretical potential at the end-point, and the line AB represents the working characteristic of the d.c. amplifier, *i.e.*, the relationship between the input (the potential difference between the indicator and reference voltages) and the output current (the electrolytic current).

In the present work the iron^{II} was generated coulometrically, so that the titration curve had a sigmoid shape as shown in Fig. 1, and the end-point indication circuit as shown in Fig. 2 was inverse compared with that in the coulometric titration with electrogenerated bromine. The positive side of the applied voltage was connected to earth, while the negative side was connected to the platinum indicator electrode. The above applied voltage (A in Fig. 1) was less than that at the equivalence point. The potential difference between the applied voltage and the changing potential during the titration was fed into the d.c. amplifier, whose output was applied to the electrogenerating electrodes (platinum cathode and anode in electrolysis cell).

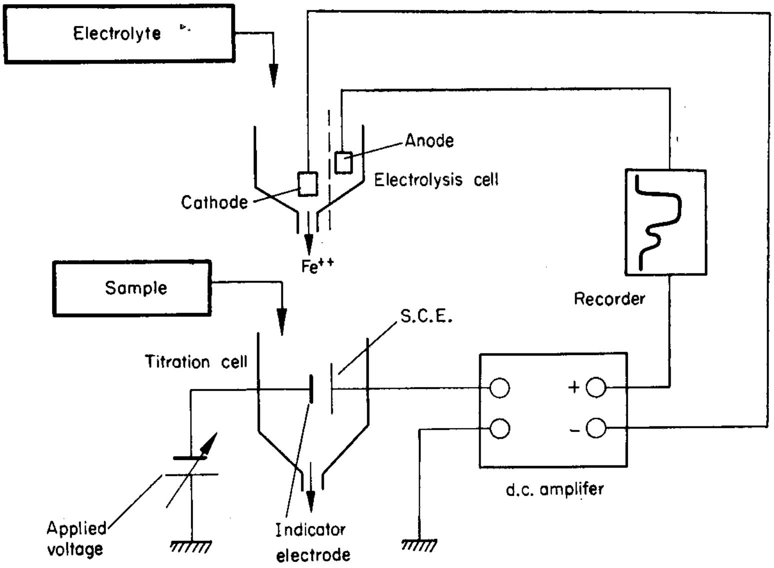

FIG. 2.—Schematic diagram of automatic continuous coulometric titrator.

Current efficiency of electrogeneration of iron^{II}

To find the effect of the concentration of electrolyte solution and electrolytic current intensity on the current efficiency, three electrolytic solutions (0·1*N*, 0·03*N* and 0·01*N* ammonium iron^{III} sulphate in 2*N* sulphuric acid) were supplied to the electrolysis cell, whose effluent containing electrogenerated iron^{II} was taken into the titration cell. The flow rate of the electrolyte solution was held at 0·1–0·15 ml/sec. The effluent was gathered during the electrolysis for 600 sec and analysed for electrogenerated iron^{II} by a conventional potentiometric titration with 0·005*N* potassium permanganate standard solution. The results are shown in Table I.

From Table I the concentration of the ammonium iron^{III} sulphate must be at least 0·1*N*, even if the generating current was less than 3 mA, and this concentration was employed for the electrolyte solution in the subsequent experiments.

Continuous coulometric titration of potassium permanganate

Potassium permanganate is conventionally titrated with iron^{II} in acidic solution. In the present experiment, however, a minute amount of potassium permanganate was determined by continuous coulometric titration with electrogenerated iron^{II}. Dynamic curves of the titration of potassium permanganate with ammonium iron^{II} sulphate are given in Fig. 3, which indicate that the electrolytic current balancing the applied voltage changes in accordance with the applied voltage when potassium permanganate solution is fed in at a constant flow-rate of 0·16 ml/sec. The dynamic curve corresponds to the lower part of the titration curve. The titration proceeded slightly through the end-point and only a continuous coulometric titration could be carried out, because the equivalence potential frequently fluctuated with the large oscillation, although it was very sensitive at the equivalence.

The relationship between the applied potential and amplitude of fluctuation (the vibrating distance) of the writing pen in the recorder is shown in Table II. The optimum applied voltage can be found from Fig. 3 and Table II, and is about 0·62 V.

TABLE I.—CURRENT EFFICIENCY IN ELECTROGENERATION OF IRON^{II}

No.	Electrolytic current, *mA*	Iron^{III} electrolyte solution, *N*	0·005*N* $KMnO_4$, *ml*	Current efficiency, %
1	0·95	0·1	1·250	98·9
2	1·00	0·1	1·333	100·1
3	2·13	0·1	2·650	96·8
4	2·16	0·1	2·657	95·7
5	2·97	0·1	3·624	95·9
6	2·95	0·1	3·610	97·8
7	0	0·1	0·080	
8	0	0·1	0·080	
9	1·09	0·03	1·344	95·4
10	1·09	0·03	1·348	95·7
11	2·16	0·03	2·134	77·5
12	2·23	0·03	2·255	79·4
13	3·34	0·03	2·523	59·5
14	3·33	0·03	2·568	60·7
15	0	0·03	0·049	
16	1·03	0·01	0·794	56·7
17	1·03	0·01	0·885	63·8
18	2·12	0·01	1·064	37·6
19	2·10	0·01	1·063	38·1
20	3·19	0·01	1·095	25·8
21	3·18	0·01	1·132	26·9
22	0	0·01	0·070	
23	0	0·01	0·064	

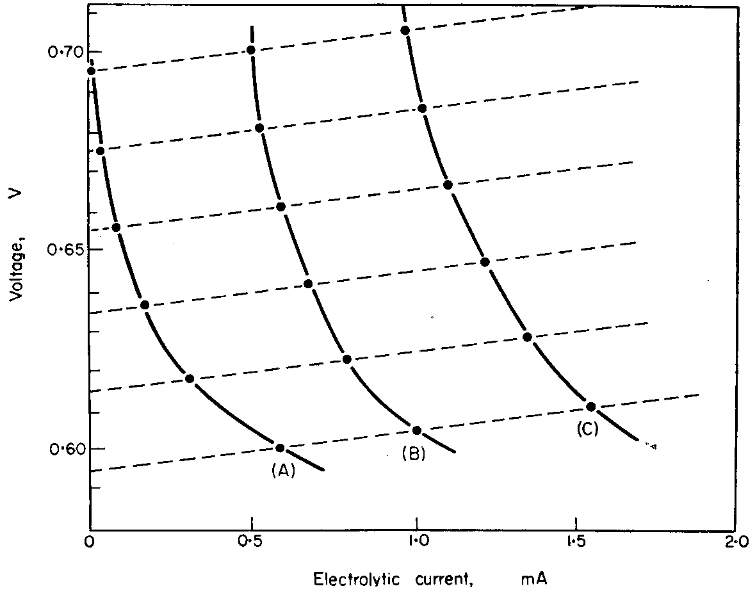

FIG. 3.—Dynamic curves for titration of potassium permanganate with iron^{II}: (A) H_2O, (B) 0·5 × $10^{-4}N$ $KMnO_4$, (C) 1 × $10^{-4}N$ $KMnO_4$.

The relationship between the concentration of potassium permanganate and the electrolytic current intensity is shown in Table III. In these experiments the sample solutions ($0{\cdot}5 \times 10^{-4}$, $1{\cdot}0 \times 10^{-4}$, $1{\cdot}5 \times 10^{-4}$ and $2{\cdot}0 \times 10^{-4}N$ potassium permanganate solutions) were fed successively, but alternately with water, into the titration cell for 10 min and the electrolytic currents recorded. The applied voltage was set at 0·61 V; the feed rate of sample solutions was 0·16 ml/sec and that of the electrolyte solution 0·15 ml/sec. This series of experiments with the 4 sample solutions was repeated seven times and the electrolytic currents recorded in Table III have the background current (the electrolytic current for water alone in the titration cell) deducted.

TABLE II.—RELATIONSHIP BETWEEN APPLIED VOLTAGE AND AMPLITUDE OF FLUCTUATION

$KMnO_4$, N	Applied voltage, V								
	0·60	0·62	0·64	0·66	0·68	0·70	0·90	1·00	1·05
H_2O	0 (mA)	0	0	0	0	0	0	0	0
5×10^{-5}	0	0·01	0·05	0·45	0·70	0·95	0·75	—	—
1×10^{-4}	0·02	0·04	0·45	0·75	0·95	—	1·20	0·45	0·03

TABLE III.—RELATIONSHIP BETWEEN CONCENTRATION OF POTASSIUM PERMANGANATE AND ELECTROLYTIC CURRENT

No.	$KMnO_4$, N			
	5×10^{-5}	1×10^{-4}	$1{\cdot}5 \times 10^{-4}$	2×10^{-4}
1	0·80 (mA)	1·53 (mA)	2·30 (mA)	3·00 (mA)
2	0·78	1·54	2·30	2·98
3	0·88	1·63	2·35	3·12
4	0·93	1·63	2·48	3·12
5	0·86	1·66	2·44	3·12
6	0·88	1·62	2·37	3·08
7	0·82	1·58	2·38	3·09
Av.	0·85	1·60	2·37	3·07
Std. dev.	0·049	0·046	0·062	0·060
Theoretical current	0·772	1·544	2·316	3·088

The results show that the theoretical and measured values coincide very well and the relationship between the concentration and electrolytic current is almost linearly proportional. It may be said more exactly that the ratio electrolytic current/concentration diminishes slightly with increase of concentration. This can be explained by the decrease of the excess concentration of iron^{II} at the equivalence point with increase of the concentration of potassium permanganate.

The stability of the recording was examined by the following procedure. Distilled water and $5 \times 10^{-5}N$ potassium permanganate were used as sample solutions flowing for 2 hr and the electrolytic current was measured every 4 min. The experimental results showed that it was almost constant (the average current for 30 measurements was 0·345 mA with a standard deviation of 0·005 mA in the case of distilled water, and 1·194 mA with a standard deviation of 0·039 mA in the case of $5 \times 10^{-5}N$ potassium permanganate).

Continuous coulometric titration of potassium bichromate

Potassium bichromate can be easily titrated by the conventional potentiometric method with iron^{II} in acidic solution. The dynamic titration curves are shown in Fig. 4 and they were taken in the same manner as for potassium permanganate. These curves differ from those of potassium permanganate, however, in that they run smoothly, this resulting from the indistinctness of the equivalence potential. This difference is considered to be caused not only by the smaller potential change for potassium bichromate-iron^{II} than that for potassium permanganate-iron^{II}, but also to a slow electrode reaction rate or to a slow following of the indicator electrodes near the equivalence point. The oscillation could not be seen when the applied voltage increased to 0·7 V.

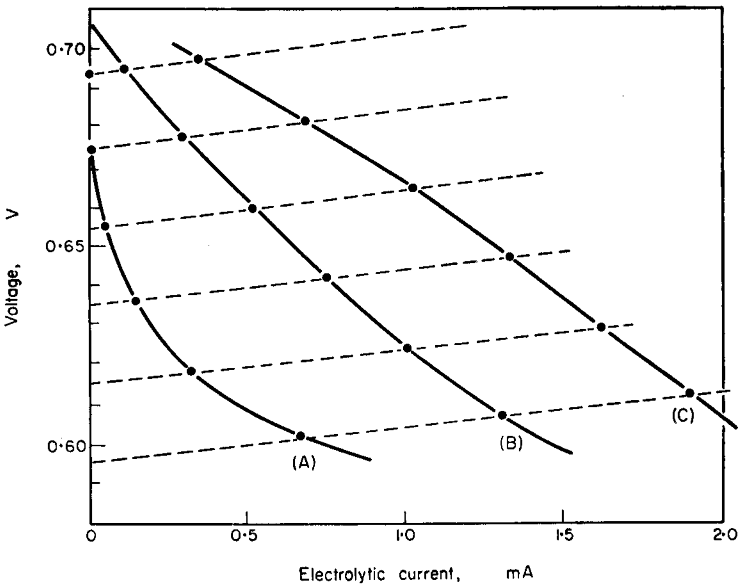

FIG. 4.—Dynamic curves for titration of potassium bichromate with iron^{II}: (A) H_2O, (B) 0·5 × $10^{-4}N$ $K_2Cr_2O_7$, (C) 1 × $10^{-4}N$ $K_2Cr_2O_7$.

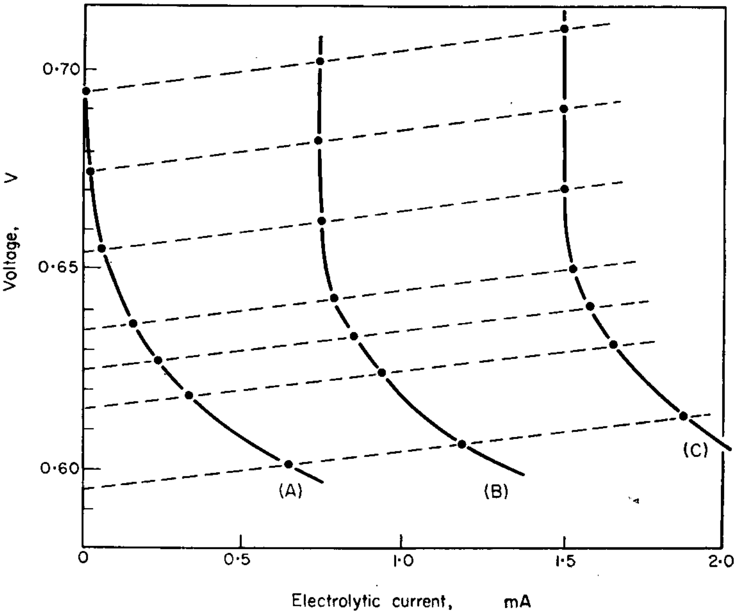

FIG. 5.—Dynamic curves for titration of free chlorine in water: (A) H_2O, (B) 4·5 × $10^{-5}N$ Cl_2, (C) 9 × $10^{-5}N$ Cl_2.

TABLE IV.—RELATIONSHIP BETWEEN CONCENTRATION OF POTASSIUM BICHROMATE AND ELECTROLYTIC CURRENT

No.	$K_2Cr_2O_7,N$			
	5×10^{-5}	1×10^{-4}	$1{\cdot}5 \times 10^{-4}$	2×10^{-4}
1	0·63 (mA)	1·31 (mA)	1·97 (mA)	2·62 (mA)
2	0·65	1·33	1·98	2·59
3	0·65	1·32	1·98	2·61
4	0·64	1·31	1·96	2·59
5	0·63	1·29	1·96	2·58
Av.	0·64	1·31	1·97	2·58
Std. dev.	0·009	0·013	0·009	0·023
Theoretical current	0·772	1·544	2·316	3·088

The relationship between the concentration of potassium bichromate and electrolytic current intensity is shown in Table IV (the current intensity has the background current deducted). The applied voltage was set at 0·64 V. The results show a linear proportionality between the concentration of potassium bichromate and the electrolytic current, but the electrolytic current is lower than the theoretical value by about 16%. This may be caused by the large deviation between the dynamic and the static titration curves at the equivalence point. The deviation increases with increase of applied voltage.

Continuous coulometric titration of free chlorine in water

Free chlorine dissolved in water has been determined by the titration of liberated iodine or bromine from potassium iodide or potassium bromide. A very low concentration of free chlorine can be determined colorimetrically or spectrophotometrically using *o*-tolidine, benzidine hydrochloride or dimethyl-*p*-phenylendiamine as reagents. In the present case the free chlorine content in water was determined potentiometrically by titration with electrogenerated iron^{II} using the continuous coulometric titrator.

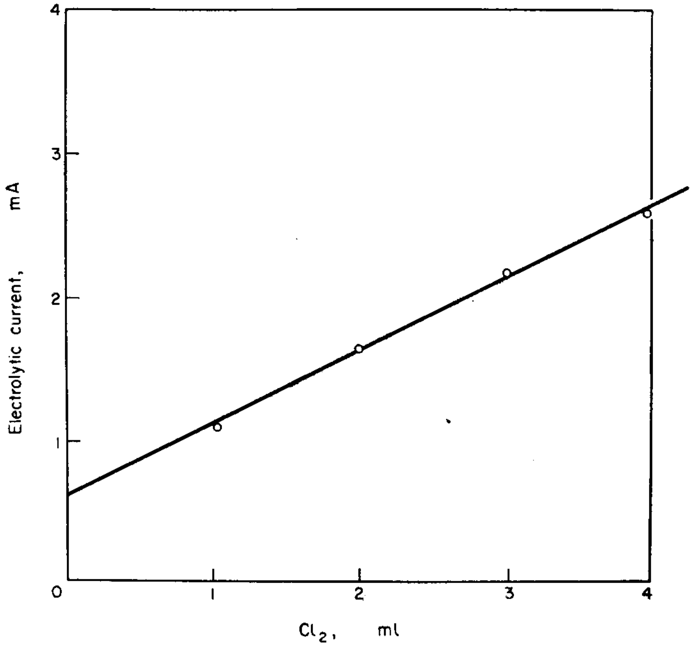

FIG. 6.—Relationship between concentration of chlorine in sample and electrolytic current.

The dynamic titration curves are shown in Fig. 5. The equivalence potential is about 0·82 V (*vs*. S.C.E.), where the oscillation occurs when the applied voltage is set near the equivalence point, because the potential sensibility is fairly large at the equivalence point. The relationship between applied voltage and amplitude of fluctuation is shown in Table V.

TABLE V.—RELATIONSHIP BETWEEN APPLIED VOLTAGE AND AMPLITUDE OF FLUCTUATION

Cl_2, *N*	Applied voltage, *V*									
	0·60	0·62	0·64	0·66	0·68	0·70	0·80	0·90	1·00	1·10
4·5 × 10^{-5}	0 (mA)	0	0·005	0·01	0·25	0·35	0·50	0·45	0·25	0·05
9 × 10^{-5}	0·01	0·01	0·020	0·05	0·35	0·45	0·80	0·75	0·60	0·20

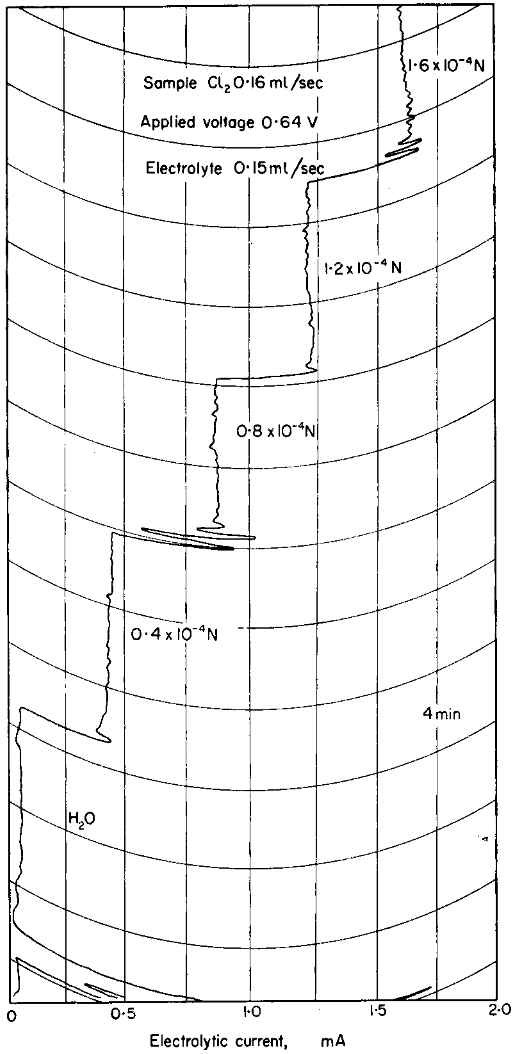

FIG. 7.—A typical chart recording in the continuous titration of chlorine.

The relationship between the concentration of chlorine in the sample solution and the electrolytic current is given in Fig. 6. The sample solutions were prepared from the original chlorine solution (0·045*N*) by dilution of 1, 2, 3, or 4 ml to 1 litre with water. The abscissa in Fig. 6 shows the volume of the original solution taken. The ordinate is the average measured value of six electrolytic currents (standard deviations are 0·033, 0·020, 0·014 and 0·020 mA in order of increasing chlorine concentration).

Fig. 7 is a typical chart recording for the continuous coulometric analysis of chlorine, in which the applied voltage was set at 0·64 V and the flow rate of the electrolytic solution was 0·15 ml/sec.

Zusammenfassung—Eisen(II) reagiert in saurer Lösung rasch und quantitativ mit verschiedenen Oxydationsmitteln wie Permanganat, Dichromat oder freiem Chlor. Kontinuierliche coulometrische Titrationen solchêr Lösungen wurden mit an einer Platinkathode aus Eisen(III) erzeugtem Eisen(II) durchgeführt; der Reaktionsverlauf in der Titrationszelle wurde mit Hilfe eines Platin-Kalomel-Elektrodenpaares potentiometrisch verfolgt. Die Potentialdifferenz zwischen gemessenem und Endpunktspotential wurde mit einem Gleichstromverstärker verstärkt; dessen Ausgang steuerte den Elektrolysestrom, sodaß das gemessene Potential gleich dem Endpunktspotential wurde. So war der das Eisen(II) liefernde Elektrolysestrom der Konzentration des Oxydationsmittels direkt proportional. Um gute Ergebnisse zu erzielen, ist vorher die Aufnahme einer dynamischen Titrationskurve empfehlenswert, um das Optimum für den Endpunkt der coulometrischen Titration festzulegen.

Résumé—L'ion ferreux réagit rapidement et quantitativement avec des oxydants variés comme le permanganate de potassium, le bichromate de potassium et le chlore libre en solution acide. Les dosages coulométriques de telles solutions ont été éffectués par l'ion ferreux formé par galvanoplastie à partir de l'ion ferrique sur électrode de platine. La marche de la réaction dans la cellule de dosage est recueillie potentiométriquement par un couple d'électrodes platine/calomel. La diffèrence de potentiel entre le potentiel détecté et le potentiel du point équivalent est amplifié par un amplificateur d.c. dont le courant de sortie est contrôlé de telle manière que le potentiel détecté devienne égal à celui du point équivalent. Ainsi, le courant électrolytique qui fournit l'ion ferreux est alors directement proportionnel à la concentration de l'agent oxydant dans la solution étudiée. Pour obtenir de bons résultats, il est nécessaire d'éffectuer une courbe de dosage empirique en vue de localiser au mieux le point équivalent du dosage coulométrique.

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A NEW PRINCIPLE OF ACTIVATION-ANALYSIS SEPARATIONS—V*

SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF INDIUM

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Summary—A substoichiometric determination of traces of indium in germanium dioxide has been developed. It consists of adding indium carrier to the dissolved irradiated sample followed by extraction of indium dithizonate using thiosulphate and cyanide as masking agents. Indium is removed from the organic extract by shaking with dilute sulphuric acid. To the separated aqueous layer a substoichiometric amount of EDTA is added and the indium complex separated from the excess of unreacted indium ions on a cation-exchange column. The content of indium is calculated from the activity of the eluate obtained. The method is very selective, simple and rapid. Using the substoichiometric separation principle the necessity of determining the chemical yield is avoided.

INTRODUCTION

SUBSTOICHIOMETRIC determination, the theory of which was given in the first paper of this series,[1] has been used for the determination of traces of zinc,[2] copper,[2] molybdenum[3] and silver.[4] This method of analysis may be carried out using three types of substoichiometric procedure: solvent extraction, formation of chelates combined with ion exchange, and precipitation reactions. The outstanding advantages of the first type of procedure have already been demonstrated.[2–4] In the present paper substoichiometric determination using ion exchange is experimentally verified by the determination of traces of indium in germanium dioxide.

Classical radiochemical procedures for separation of indium are mostly based on precipitation reactions. These procedures are complicated and time consuming. Thus, the method proposed by Cali and coworkers[5,6] may be briefly summarised as follows: indium is precipitated as trisulphide at pH 3 to 4 and then dissolved. The resulting solution is scavenged several times with arsenic trisulphide, bismuth trisulphide and antimony trisulphide, indium is precipitated several times as trisulphide, extracted by 8-hydroxyquinoline in chloroform, then re-extracted into hydrochloric acid by boiling off the chloroform. Subsequently the indium is precipitated, filtered, washed, dried, weighed and mounted for counting as indium 8-hydroxyquinolinate. Another procedure, proposed by Irving and coworkers,[7–9] includes extraction of indium into ethyl ether from hydrobromic acid, but does not differ substantially from the scheme outlined above and consists of approximately 11 steps, some of which are several times repeated. The separation scheme based predominantly on

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* Part IV: see reference 4.

solvent extraction has recently been simplified,[10] but an excess of reagents is used and the chemical yield must still be determined.

Using solvent extraction of indium dithizonate into carbon tetrachloride for the separation of indium from an irradiated test sample followed by substoichiometric separation as indium-EDTA complex, the time of analysis is substantially reduced and the necessity of determining the chemical yield avoided.

EXPERIMENTAL

Apparatus

Scintillation counter: Well-type with NaI(Tl) crystal.

Ion-exchange columns: A set of 6 columns, each 10 cm high and 0·7 cm in diameter.

Reagents

All reagents used were of AnalaR purity.

Indium carrier solution: $4 \times 10^{-3}M$ $InCl_3$ in $0{\cdot}01M$ hydrochloric acid.

Buffer-masking solution: A solution 5% in potassium cyanide, 20% in sodium thiosulphate and $1M$ in ammonium acetate, prepared freshly before use.

Dithizone solution: $10^{-3}M$ in carbon tetrachloride.

EDTA solution: $10^{-3}M$, disodium salt.

Ion-exchange resin: Dowex 50 (Na-form), 50–100 mesh, total capacity 5·2 ± 0·3 mequiv/g of dry weight.

pH 4·6 *Buffer solution:* $0{\cdot}1M$ sodium acetate-acetic acid.

Irradiation

Samples of germanium dioxide and a comparative standard of indium nitrate were sealed in quartz ampoules and simultaneously irradiated in a nuclear reactor at a neutron flux of 5×10^{12} neutrons.cm^{-2}.sec^{-1} for 3 days. The radiochemical procedure was started after allowing 2 weeks for cooling of the irradiated samples.

Development of the method

The amount (y) of the element to be determined may be calculated from the equation:

$$y = y_s \frac{a}{a_s} \qquad (1)$$

where y_s = the amount of the element to be determined present in an irradiated standard sample, and a and a_s = the activities isolated from the test and standard samples, respectively.

This basic equation of substoichiometric determination is valid only if the following two conditions are fulfilled:[1]

(1) The amounts of carrier added to the analysed and standard samples are exactly equal.

(2) The amounts of element to be determined isolated from the standard and test samples are equal.

The second condition may be fulfilled substoichiometrically and its verification was carried out as follows: The volume of EDTA solution which corresponds to 1 ml of indium carrier solution was determined. The titration was carried out complexometrically with Xylenol Orange as indicator at pH 4·6. The volume of EDTA required was approximately 4 ml.

The reproducibility of the substoichiometric separation was investigated by the following experiments: A series of solutions containing 1–4 ml of indium carrier solution labelled with ^{114m}In was prepared. To these solutions an identical but substoichiometric amount of EDTA solution (1·00 ml) was added and the acidity of all solutions adjusted to about pH 2. The solutions were simultaneously passed through a set of ion-exchange columns containing Dowex-50 in the Na-form. The negatively charged indium-EDTA chelate is thus separated from the excess of unreacted indium ions. The reproducibility of the separation may be seen from the activities of identical volumes of eluate (see Table I). A second series of solutions containing equal amounts (2·00 ml) of labelled indium carrier solution was prepared. To these solutions 1·00–6·00 ml of EDTA solution were added and the pH adjusted to approximately 2. After passing these solutions through a set of ion-exchange columns the activities of the eluates were measured (see Table II).

From the results summarised in Tables I and II it follows that the reproducibility of the proposed substoichiometric separation is fully satisfactory.

TABLE I

Amount of indium solution labelled with ^{114m}In, *ml*	1	2	3	4
Activity of indium isolated, *cpm*	1582	1577	1613	1570

TABLE II

Amount of EDTA solution, *ml*	1·00	2·00	3·00	4·00	6·00
Activity of indium isolated, *cpm*	1160	2404	3108	4756	6844
Activity corresponding to 1 ml of EDTA used, *cpm*	1160	1202	1036	1189	1141

Procedure

The irradiated sample of germanium dioxide was dissolved in 3 ml of 8*M* sodium hydroxide solution and 4*M* sulphuric acid added until a white precipitate appeared. This precipitate was redissolved with a few drops of the sulphuric acid and 1·00 ml of indium carrier solution added. After adding 5 ml of buffer-masking solution and adjusting the pH to 5–7, the extraction was carried out with successive portions of dithizone solution. The extraction of indium need not be quantitative. From the combined organic extracts the indium was re-extracted into 2–3 ml of 0·03*M* sulphuric acid. To the separated aqueous layer 2·00 ml of EDTA solution were added. The indium-EDTA chelate formed was separated from the excess of indium ions on a Dowex-50 column in the Na-form. The same procedure was carried out simultaneously with an irradiated standard sample containing a known amount of indium (y_S). From the activities of the eluates obtained from the test (a) and standard (a_S) samples, the amount of indium (y) originally present in the test sample is calculated from equation (1). The decay curve of ^{114m}In isolated from the irradiated germanium dioxide sample is given in Fig. 1.

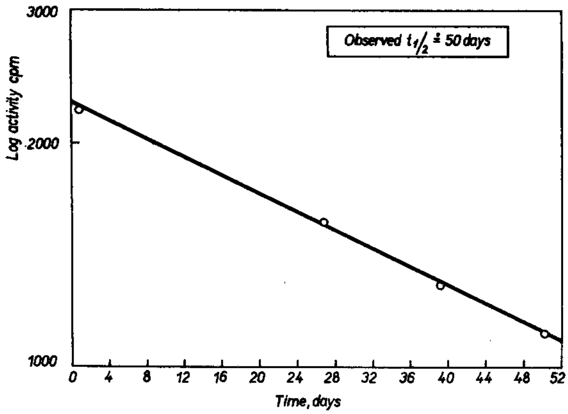

FIG. 1

TABLE III.—THE SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF INDIUM IN GERMANIUM DIOXIDE

GeO_2 analysed, *g*	0·1	0·1	0·1
Amount of irradiated In standard added to irradiated GeO_2 sample, *μg*	—	2·75	5·50
Amount of In in irradiated standard sample (y_S), *μg*	2·75	8·25	5·50
Activity* obtained from the analysed sample (a)	170	4430	8500
Activity* obtained from standard sample (a_S)	4202	13352	8276
Amount of In found, *μg*	0·11 ($1 \times 10^{-4}\%$)	2·74	5·65

* All activities are expressed in cpm and are the mean values of 5 measurements corrected for background.

RESULTS AND DISCUSSION

The results of analyses carried out by the procedure described above are summarised in Table III. From this table it follows that the proposed method can be successfully used and that the analysed germanium dioxide sample contains less than $10^{-4}\%$ of indium.

The selectivity of the method is very high. Under the conditions described only indium, thallium, lead, tin and bismuth can be extracted as dithizonates.[11] From the known stability constants of EDTA complexes it is evident that thallium, lead and tin will not interfere in the substoichiometric determination of indium. Furthermore, bismuth will not interfere because of its nuclear properties.

CONCLUSION

The substoichiometric separation principle has been successfully used for the determination of traces of indium in germanium dioxide. The number of separation steps currently used in radiochemical procedures for indium has been substantially reduced and the necessity of determining the chemical yield avoided. This simple procedure for the analysis of indium in germanium dioxide may be adapted without serious difficulties to the determination of traces of indium in other materials.

Acknowledgement—The authors thank Dr. V. Majer and Dr. M. Williams for their interest in this work and for critical discussion.

Zusammenfassung—Das radiochemische Verfahren zur Bestimmung von In-Spuren in GeO_2 wurde durch Abtrennung mit Reagens-Unterschuß verbessert. Es besteht im Zusatz des Indiumträgers zur gelösten bestrahlten Probe und der Extraktion von Indiumdithizonat unter Maskierung mit Thiosulfat und Cyanid. Indium wird durch Ausschütteln mit verdünnter Schwefelsäure aus dem organischen Extrakt entfernt. Der abgetrennten wäßrigen Phase wird ein Unterschuß EDTA zugesetzt und das gebildete Indiumkomplexonat von nicht umgesetztem Indium am Kationenaustauscher getrennt. Der Indiumgehalt wird aus der Aktivität des Eluats berechnet. Die Methode ist sehr selektiv, einfach und schnell. Durch das Unterschußprinzip entfällt die Notwendigkeit, die chemische Ausbeute zu bestimmen.

Résumé—On décrit un procédé de dosage radiochimique de traces d'indium dans GeO_2, utilisant la méthode de séparation substoéchiométrique. Ce procédé consiste en l'addition d'un traceur de l'indium à l'échantillon dissous et irradié, suivie de l'extraction du dithizonate d'indium en présence de thiosulfate et de cyanure comme agents masquants. L'indium est extrait de la phase organique par agitation avec de l'acide sulfurique dilué. On ajoute à la couche aqueuse des quantités substoéchiométriques d'EDTA et le sel complexé d'indium formé est séparé de l'excès des ions indium n'ayant pas réagi par passage sur une colonne contenant un échangeur de cations. La teneur en indium est calculée à partir de l'activité de l'éluat obtenu. Cette méthode est très sélective, simple et rapide. L'emploi de quantités substoéchiométriques supprime la nécessité de déterminer le rendement chimique.

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THE DETERMINATION OF TRACES OF COBALT IN SAMPLES OF PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A neutron-activation analysis method for the determination of traces of cobalt in samples of purified platinum is described. Using a pile flux of $1{\cdot}2 \times 10^{12}$ thermal neutrons . cm^{-2} . sec^{-1}, as little as 10^{-9} g of cobalt may be determined. A rapid radiochemical separation procedure coupled with gamma-ray spectrometry permits measurement of 5·26-year cobalt-60 activity. Results of analysis of seven samples of platinum are quoted.

NEUTRON-ACTIVATION has been extensively used for the determination of traces of cobalt in various materials.[1–5] This paper describes a procedure utilising a simple radiochemical separation and designed to make use of gamma-ray spectrometry. The method has been applied to the determination of ultramicro amounts of cobalt in samples of purified platinum.

Natural cobalt consists of one isotope of mass number 59. On irradiation with thermal neutrons the nuclide gives rise to the following nuclear reactions and decay sequences:

$$\begin{tikzcd}
{}^{59}\mathrm{Co}(n,\gamma){}^{60m}\mathrm{Co}\ (t_{1/2},\ 10{\cdot}5\ \mathrm{m}) \arrow[dd, "\mathrm{IT}(99+\%)"] \arrow[dr, "\beta^-\ (0{\cdot}28\%)"] & \\
 & {}^{60}\mathrm{Ni}\ (\mathrm{stable}) \\
{}^{59}\mathrm{Co}(n,\gamma){}^{60}\mathrm{Co}\ (t_{1/2},\ 5{\cdot}26\ \mathrm{y}) \arrow[ur, "\beta^-"'] &
\end{tikzcd}$$

The thermal neutron activation cross section for ^{59}Co is large,[6] 36·3 barns (10·5 m + 5·28 y), so that high sensitivity activation analysis of cobalt is possible. Moreover, since ^{60}Co emits high-energy γ-rays, 1·17 (100%) and 1·33 (100%) MeV, it is ideal for gamma-ray spectrometric measurements.

To avoid self-shielding differences between samples and standards, in the present work standards were prepared by the addition of small known quantities of cobalt to analytical samples.

EXPERIMENTAL

Irradiation

About 0·1-g samples of platinum, in the form of powdered sponge, were sealed in silica containers. Comparators were prepared by the addition of weighed portions (*ca.* 0·05 g) of a standard solution of cobalt (50 mg of cobalt per litre as Co^{II} in very dilute nitric acid) to 0·1-g samples of platinum in similar silica containers. The liquid was allowed to soak into the metal powder and then was carefully evaporated to dryness.

Samples, together with comparators containing added cobalt, were sent to the Atomic Energy Research Establishment, Harwell, for activation in a nuclear reactor. Irradiations were for a period of 1 month in a thermal neutron flux of $1{\cdot}2 \times 10^{12}$ neutrons.cm^{-2}.sec^{-1}.

Radiochemical separation

After irradiation the samples and comparators were put through a simple radiochemical procedure to decontaminate the radiocobalt from several other elements.

The irradiated platinum was dissolved in *aqua regia* in the presence of cobalt carrier. Cobalt was then separated by precipitation as the hydroxide in the presence of nitrite which serves to complex platinum metals. After an iron^{III} hydroxide scavenge step, the cobalt was further purified by anion exchange[7,8] and was finally precipitated and mounted for counting as potassium hexanitritocobaltate(III).[9]

Full details of the procedure are as follows:

Transfer irradiated samples and comparators to 150-ml beakers each containing 10 mg of cobalt^{II} carrier and 3 ml of 12*M* hydrochloric acid. To each, add 1 ml of 16*M* nitric acid, and dissolve the platinum by warming on a water-bath. When dissolution is complete, evaporate the solution to dryness on a hot-plate. Moisten the residue with 4 drops of 6*M* hydrochloric acid and dissolve in 25 ml of water. Cautiously add 3 g of sodium nitrite in small portions, boil until brown fumes cease to be evolved and then treat the solution with 2% sodium hydroxide until the pH is 8. Transfer to a 50-ml centrifuge tube, centrifuge and discard the supernate. Wash the precipitate twice with hot water. Dissolve the precipitate by warming with 2 ml of 12*M* hydrochloric acid. Dilute to an acid concentration ~3*M* and add 2 mg of iron^{III} carrier. Warm on a water-bath and precipitate hydrous iron^{III} oxide by the addition of 3*M* ammonia. Centrifuge, and discard the precipitate. Evaporate the supernate almost to dryness and then add 3 ml of 9*M* hydrochloric acid. Pour the solution on to a Deacidite FF (100–200 mesh, pre-equilibrated with 12*M* hydrochloric acid) anion-exchange column 5 cm in length and 1 cm in diameter. Pass 2 ml of 12*M* hydrochloric acid through the column and then elute cobalt with 4*M* hydrochloric acid. Evaporate the eluate to dryness and dissolve the residue in 3 ml of 3*M* acetic acid. Dilute to a volume of 10 ml with water and transfer the solution to a 50-ml centrifuge tube. Cautiously add 3 g of potassium nitrite in small portions. When the initial reaction has subsided, digest on a water-bath for 10 min and then cool in ice for 10 min. Centrifuge and discard the supernate. Wash the precipitate twice with 20-ml portions of 5% potassium nitrite solution acidified with 1 drop of 6*M* acetic acid and then with a little water and ethanol. Finally, transfer the potassium hexanitritocobaltate(III) with ethanol to a weighed aluminium counting tray, dry at 110° for 5 min and determine the chemical yield.

Measurements of radioactivity

Geiger-Müller and gamma-spectral measurements on the separated precipitates of potassium hexanitritocobaltate indicated that they contained, in addition to ^{60}Co, some other radionuclides, such as ^{199}Au. However, gamma-spectrometric and decay studies showed that by application of a sufficient bias voltage the ^{60}Co γ-rays of 1·17 and 1·33 MeV could be counted without interference. In the present work, final precipitates were assayed using a 1·5-inch diam. × 1-inch NaI(Tl) crystal scintillation counter, the discriminator bias being set at such a value that γ-rays of energy $< 0{\cdot}7$ MeV were not recorded (see Fig. 1). The observed counting rates were corrected for background and chemical yield.

RESULTS

In Table I are shown results of analyses of purified samples of platinum.

TABLE I.—COBALT CONTENTS OF SAMPLES OF PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample	Cobalt content, *ppm*
Pt 1	0·012, 0·012
Pt 2	0·104, 0·105, 0·131, 0·131
Pt 3	0·034, 0·032, 0·026, 0·023, 0·035, 0·035
Pt 4	0·050, 0·048, 0·040, 0·039
Pt 5	0·012, 0·013, 0·019, 0·020
Pt 6	0·068, 0·061
Pt 8	0·070, 0·068

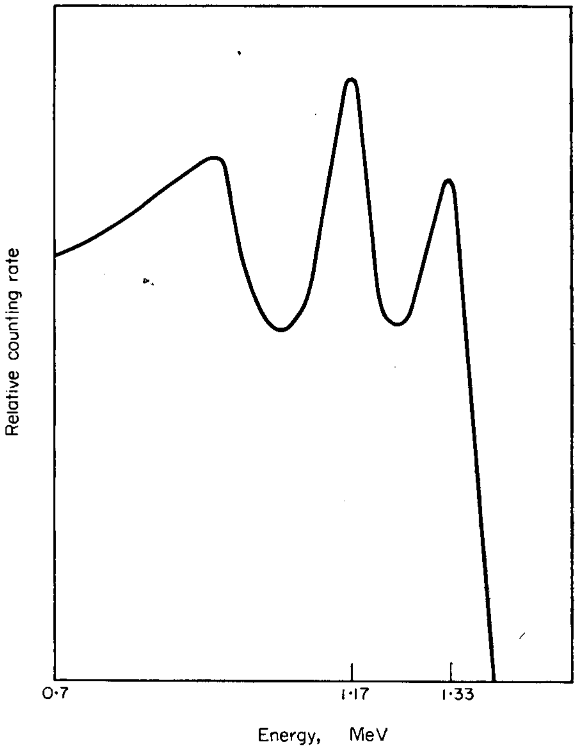

FIG. 1.—Gamma-ray spectrum of a finally separated precipitate for energies > 0·7 MeV.

DISCUSSION

The importance of competing nuclear reactions, such as ^{60}Ni(n, p)^{60}Co, which could give rise to interference with the neutron-activation analysis of cobalt, has been discussed by Smales *et al.*,[10] Miller,[11] and Koch.[3] Such reactions could not give rise to any significant error in the case of samples analysed in the present study.

Acknowledgement—We are grateful to the International Nickel Company (Mond) Ltd., for supplying samples of platinum, for financial support, and for a Research Fellowship to one of us (R. A. K.).

Zusammenfassung—Eine neutronenaktivierungsanalytische Bestimmungs-methode für Kobaltspuren in gereinigtem Platin wird beschrieben. Mit einem Neutronenfluß von 1,2 × 10^{12} thermischen Neutronen pro Sekunde und Quadratzentimeter lassen sich 10^{-9} g Kobalt bestimmen. Eine schnell verlaufende radiochemische Trennmethode mit nachfolgender Gamma-Spectrometrie erlaubt Messung der Kobalt-60-Aktivität (Halbwertszeit 5,26 Jahre). Analysenergebnisse von sieben Platinproben werden aufgeführt.

Résumé—On décrit une méthode d'analyse par activation de neutrons pour la détermination de traces de cobalt dans des échantillons de platine purifié. L'emploi d'un flux de 1,2 × 10^{12} neutron-thermique. $\text{cm}^{-2}.\text{sec}^{-1}$ permet de déceler des quantités de cobalt aussi faibles que 10^{-9} g. Un procédé rapide de séparation radio-chimique couplée avec une analyse spectrométrique aux rayons γ permet de mesurer une activité de 5,26 ans pour le cobalt-60. On donne des resultats concernants 7 échantillons de platine.

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THE EFFECT OF ISOTOPE ABUNDANCES ON THE NEUTRON-ABSORPTIOMETRY TECHNIQUE

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Summary—To obtain accurate analyses by neutron absorptiometry it is essential that the isotope abundance of the element determined be the same as that of the calibration standard. The effect has been used for the comparison and determination of boron-10 isotope abundances in various boron hydrides. Precision is in the ±0·1% relative range.

INTRODUCTION

THE theory and practice of neutron absorptiometry was presented in detail by DeFord and Braman,[1,2] who developed it as a general method for the determination of boron. This technique has been employed at Callery Chemical Company for several years for the routine analysis of organoboron-containing samples. Coincident with the early application of this technique, however, discrepancies between boron analyses by a chemical method and by the neutron-absorption method were noted. The neutron-absorption method gave results from approximately 1% to 8% higher in boron, depending upon the sample source. This systematic error was eventually attributed to isotope-abundance differences between the samples and the standard of the neutron-absorption technique.

Boron-10 and boron-11 are the only two stable isotopes of boron. Essentially, all of the thermal neutron-absorption capacity is inherent in the boron-10 isotope; the cross section for thermal neutron absorption is 4000 barns/atom for boron-10 and 0.05 barns/atom for boron-11.[3] The neutron-absorption method is, therefore, quite sensitive to differences in isotope abundances, because a 1% increase in the boron-10 isotope abundance will appear as a 5% increase in total boron content.

The isotope-abundance effect is a disadvantage somewhat complicating the use of neutron absorptiometry for purposes of general analysis. However, it also points to the possibility of using the technique for determining isotope abundances of neutron-absorbing elements.

To determine the boron-10 content it is necessary to prepare a calibration curve with a known boron-10 compound. Unknown samples can then be analysed directly. To determine the isotope abundance this result is compared with a chemical determination of total boron. This last analysis is not affected by isotope-abundance effects. In the absence of reliable boron-10 standards it is possible to perform isotope-abundance comparisons by choosing a standard material, assuming the best published value for boron-10 isotope abundance, and relating all unknowns to this figure.

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Several other methods have been reported for the determination of boron isotope abundances. Hamlin and Koski[4] applied a somewhat different neutron-absorption technique for the determination of boron-10. Gaseous hydride samples were employed in an alpha-particle-detecting scintillator tube. Scintillations from the $^{10}B\,(n, \alpha)^{7}Li$ reaction were counted. Comparisons were made of the counting rate with known and unknown boron-10-containing samples. Accuracies of ±1% were claimed, but pressure regulation was critical. Mass spectrometry has long been the most convenient method for determining isotope abundances because of the small sample requirement. However, difficulties in work with boron arise from a memory effect. Boron trifluoride, the usual compound employed, adsorbs on the walls of the ionisation chamber and the surface of the glass apparatus. Desorption is slow and it contaminates subsequent samples through exchange. Melton, Gilpatrick, Baldock and Healy[5] have reported a method to minimise the effect. Accuracies of ±0.03% absolute can apparently be obtained.

EXPERIMENTAL

Procedure

A standardisation curve was prepared utilising samples of reagent-grade boric acid dissolved in 100 ml of water. The unused boric acid was set aside and specially marked for retention as an artificial standard for future comparisons. Aliquots of boric acid solutions were taken for analysis by the standard mannitol-borate titration procedure. A pH meter was employed; standard deviations of multiple determinations were in the range of 1 to 2 parts per thousand.

Samples of organoboron compounds, decaborane and boron hydride polymers were oxidised to boric acid by reaction with chlorine in a 1:1 methanol-water solvent. Methanol was allowed to evaporate, and boric acid was crystallised out by cooling the solution. The boric acid recovered was filtered, washed with a small amount of water and then acetone, and dried. The dried product was essentially pure boric acid with only faint traces of chloride in a few cases.

Diborane and sodium borohydride were converted to boric acid by hydrolysis in hot water. Boron trifluoride was converted to boric acid by reacting it with water:

$$4\ BF_3 + 3\ H_2O \rightarrow H_3BO_3 + 3\ HBF_4.$$

Sodium fluoborate was heated in a solution containing calcium chloride. Calcium fluoride precipitated as a gelatinous mass; it was then centrifuged and filtered. The filtrate was evaporated, cooled and filtered. The boric acid which precipitated was further purified by recrystallisation.

Samples of boric acid of approximately 1 g were dissolved in water and analysed for boron content by the neutron-absorption method utilising the assumed standard curve. Aliquot samples of the solution were also analysed for boron by the mannitol-borate titration procedure. At least two aliquots were titrated in each case to obtain an accurate chemical analysis figure for boron; 2 or 3 counting periods were registered for each sample in the neutron-absorption analysis. The neutron-absorption data obtained were in the form of time required to obtain a fixed number of counts. This is directly proportional to the concentration of boron present and was plotted in this manner for graphical presentation.

Calculations

Results of the neutron-absorption analysis are in mg atoms of boron/100 ml of solution. The mg atoms (mat) of boron-10 isotopes are obtained from the known or assumed fraction of boron-10 in the standard:

$$\text{mat boron/100 ml} \times \text{atom \% boron-10} = \text{mat boron-10/ml}.$$

The isotope abundance is obtained from:

$$100 \times \frac{\text{mat boron-10 isotope}}{\text{total mat boron (by titration)}} = \text{\%boron-10} \qquad (1)$$

Standard deviations derived from statistical counting errors can be estimated from experimental data by use of a log C (concentration of boron) versus log T (counting period) plot and the equation:

$$\sigma_C(\%) = \pm \frac{100}{N^{1/2}m} \tag{2}$$

where $\sigma_C(\%)$ is the standard deviation in percentage units, N is the total number of counts recorded and m is the slope of the plot at N counts.

Regression lines were calculated from four different concentrations of boron standards with at least 10^6 counts taken for each standard.

Apparatus

The apparatus employed for measuring the boron content by neutron absorptiometry is shown in Fig. 1. This is the same arrangement as described previously,[2] except for the sample size, 60 ml, and the use of stainless steel sample cells. A Nuclear Chicago Model scaler, an N. Wood Company 45-cm Hg-BF_3 neutron detector and a 20 mc neutron source complete the apparatus employed.

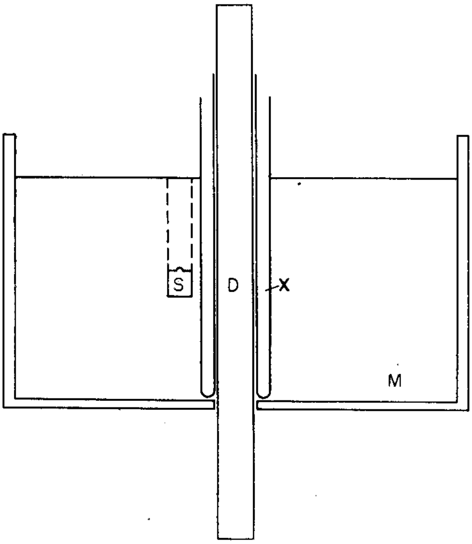

FIG. 1. Typical arrangement of apparatus for neutron absorptiometry M–moderator, S–source, D–detector, X—sample cell (annular).

RESULTS AND DISCUSSION

Table I gives the results of isotope-abundance determinations made on a number of boron compounds or mixtures. The values given for the compounds indicated are compared with the standard, assumed to be 19·98 atom% of boron-10 isotope. Standard deviations shown for the individual analyses were calculated on the basis of the log C versus log T plot and equation (2). Note that the isotope enrichment determined on the alkylated decaborane mixture before and after oxidation is nearly the same. This indicates that the oxidation procedure does not alter the isotope abundance of the oxidised sample.

It is evident that a boron-10 isotope enrichment is present in all of the hydride materials but sodium borohydride, and that the boron-10-enriched materials have approximately the same isotope abundance, 20·74% ± 0·29. This observation supported the use of a single calibration curve for determining boron in boron hydrides or derivative compounds. Sodium borohydride, the exception, is prepared from methyl borate and sodium hydride.

TABLE I.—BORON-10 ISOTOPE ABUNDANCE FOR VARIOUS MATERIALS

Sample	Boron-10, *atom* %^{a}	Remarks
Boric acid (commercial)	19·98	Assumed standard
Trimethoxyboroxine	19·98	Hydrolysis to boric acid in water
Boric acid from commercial boron trifluoride	19.87 ± 0·02	
	19·98 ± 0·03	
	19·98 ± 0·04	
	Average 19·94 ± 0·06	
Boric acid from sodium borohydride	19·71 ± 0·01	
	19·93 ± 0·03	
	19·36 ± 0·02	
	19·95 ± 0·02	
	Average 19·74 ± 0·20	
Boric acid from decaborane	20·40 ± 0·01	
	20·53 ± 0·03	
	Average 20·47 ± 0·06	
Boric acid from B-H polymer	21·48 ± 0·03	Before recrystallisation
	20·98 ± 0·02	After recrystallisation
	Average 21·23 ± 0·25	
Boric acid from alkylated dioborane mixture	21·36 ± 0·03	Before recrystallisation
	20·70 ± 0·03	After recrystallisation
	Average 21·03 ± 0·33	
Boric acid from diborane	20·77 ± 0·03	
	20·80 ± 0·01	
	Average 20·78 ± 0·03	
Boric acid from alkylated decaborane mixture	20·80 ± 0·02	
	20·56 ± 0·03	
	Average 20·68 ± 0·12	
Alkylated decaborane mixture	20·75 ± 0·04	Analysed by Carius method
	20·24 ± 0·02	
	20·98 ± 0·01	
	Average 20·94 ± 0·31	
Boric acid from sodium tetra-fluoborate	19·76 ± 0·01	
	19·97 ± 0·01	
	19·95 ± 0·01	
	Average 19·83 ± 0·08	
Average of enriched samples:	20·7 ± 0·3% boron-10	

[a] Standard deviations shown for individual data are based on statistical counting errors.

The other hydrides are derived from diborane, which is prepared from sodium borohydride:

$$3\,\mathrm{NaBH_4} + 4\,\mathrm{BF_3} \rightarrow 3\,\mathrm{NaBF_4} + 2\,\mathrm{B_2H_6}.$$

This process must result in some discrimination for boron-10 isotope, because diborane and all of its derivative hydrides are enriched. The method for preparation of sodium borohydride apparently does not inhibit the isotope abundance effect.

A sample of 92·0% boron-10 isotope material as elemental boron was obtained after the comparisons of Table I were run. A regression line for this material was calculated from the calibration data and is as follows:

$$y = 0{\cdot}59804x + 17{\cdot}882$$

where y is the time required to register 10^6 counts in min and x is the concentration of boron expressed in mg atoms/100 ml of solution. A similar regression line was calculated for normal boron from data obtained on the same apparatus. It is as follows:

$$y = 0{\cdot}12863x \times 17{\cdot}869$$

where x and y have the same significance as above, except for boron with 92·0% boron-10 isotope present.

If it is assumed that the 92·0% boron-10 figure (supplied by the manufacturer) is correct, then the boron isotope abundance of the standard is 19·75% for boron-10 and the average abundance of the enriched sample is 20·50%. Regardless of the exactness of the isotope-abundance value of the standard, isotope differences can be determined with precision, which is the main point to be demonstrated.

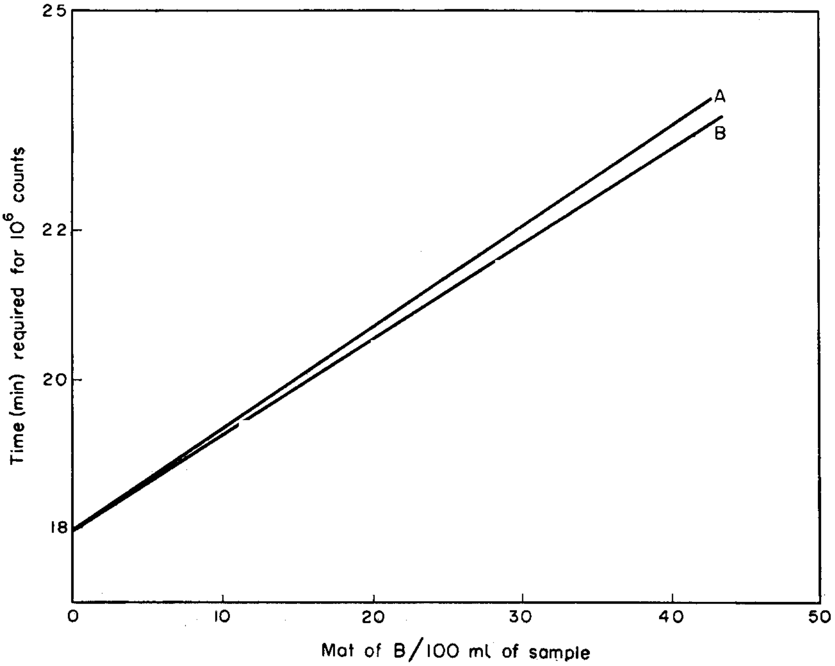

FIG. 2.—Standard analysis curve:
(A)—enriched samples,
(B)—normal boron isotope samples.

To correct for isotope-abundance differences in the development of a routine total boron procedure, a calibration curve (Fig. 2) was prepared utilising boron compounds of the same type as those being analysed. A Carius oxidation procedure (multiple samples) was employed to give the correct total boron content of the standard material. Subsequent analysis checks indicated that the calibration curve prepared with the enriched boron-10 standard was giving precise and accurate results. This observation also indicated that the boron-10-enriched hydrides were uniform in their isotope abundance.

CONCLUSIONS

It is apparent that isotope-abundance effects must be investigated prior to the routine application of the neutron-absorption technique. This can readily be done by comparing results by neutron absorption with an independent chemical analysis. Sufficiently accurate analyses can be made provided the isotope enrichments are uniform from sample to sample.

The neutron-absorption technique can also be employed for comparing boron-10 isotope abundances; total isotope abundances can be determined provided an accurate standard is available. The technique has been employed to indicate a significant enrichment of boron-10 obtained in the preparation of certain boron hydrides. Precision is in the 0·1% relative range, limited by the precision of the titrimetric method for boron. Sample sizes required for the neutron-absorption method are comparatively large. For the most precise work, 20–100 mg of boron-10 isotope per sample should be availabe. Smaller sample sizes can be employed, but decreasing precision will result because of non-optimum sample size.

The application of the neutron-absorption method for the comparison of chlorine-isotope abundances should also be possible if large samples are available. This application is under investigation.

Zusammenfassung—Um mit der Messung der Neutronenabsorption genaue Analysenergebnisse zu erhalten, ist es wesentlich, daß die Isotopenhäufigkeit des zu bestimmenden Elements mit der der Eichsubstanz übereinstimmt. Der Effekt wurde zur Bestimmung und zum Vergleich der ^{10}B-Häufigkeit in verschiedenen Borhydriden verwendet. Die Genauigkeit beträgt etwa ±0,1% relativ.

Résumé—Pour obtenir des analyses précises par absorptiométrie de neutron il est essentiel que l'abondance isotopique de l'élément considéré soit la même que celle de l'échantillon standard de calibration. Cet effet a été utilisé pour la comparaison et la détermination de l'abondance isotopique du bore-10 dans des hydrures de bore variés. La précision est de l'ordre de ±0,1%.

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DETERMINATION OF NICKEL IN HIGH-PURITY NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN METALS BY CHLOROFORM EXTRACTION OF NICKEL^{II} DIMETHYLGLYOXIMATE*

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Summary—A spectrophotometric method for determining 0·0005–0·10% of nickel in high-purity niobium, tantalum, molybdenum and tungsten metals is described. After sample dissolution and pH adjustment to 6·0, nickel^{II} dimethylglyoximate is extracted with chloroform from an ammonium tartrate-boric acid medium. The chloroform extract is washed with dilute ammonia solution to remove interfering impurities, and nickel is determined spectrophotometrically at 370 mμ directly in the extract.

INTRODUCTION

PUBLISHED information pertaining to the determination of small amounts of nickel in niobium, tantalum, molybdenum and tungsten matrices is sparse. Several spectrophotometric procedures have previously been applied to the determination of nickel in niobium and its alloys[1,2] and in tungsten powder,[3] but none of these methods is directly applicable to all four of the above metals without some modifications. Therefore, the present investigation was undertaken to develop a single procedure suitable for determining trace amounts of nickel in high-purity samples of these metals.

Dimethylglyoxime is the best known and most widely used of the various "dioxime" nickel reagents. It reacts with nickel^{II} in weakly acid, neutral or ammoniacal solution to form a red, insoluble complex, but another complex, containing nickel in a higher valency state, may also be formed by alkaline oxidation of a nickel^{II} salt in the presence of dimethylglyoxime.[4] The course of this second reaction has not been fully established. Previous investigators have shown that the nickel^{II} complex can be extracted with chloroform,[5] and nickel then determined by measuring the absorbance of the extract.[6,7] It was decided to investigate the possible application of this procedure in the present work. Rohrer,[3] in determining nickel in tungsten powder, employed this extraction procedure for a preliminary separation of the nickel, but then determined it indirectly by extraction and photometric measurement of the yellow-green diethyldithiocarbamate complex, after stripping it from the chloroform phase. It was considered that a simpler and more expedient procedure would result if absorbance measurements were made directly on the chloroform extract of the nickel^{II} dimethylglyoximate.

The procedure used for dissolution and solution preparation is essentially that previously reported in methods for determining iron[8] and copper.[9]

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EXPERIMENTAL

Apparatus

Spectrophotometer: Beckman Model DU.

pH meter: Leeds and Northrup.

Teflon (tetrafluoroethylene) beakers: 250 ml; Dynalab Corp., Rochester, N.Y., U.S.A.

Reagents

Standard nickel solution: Dissolve 3·3647 g of ammonium nickel sulphate hexahydrate $[Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O]$ in water and dilute to 1 litre. Dilute 5 ml of this stock solution to 250 ml with water. Prepare fresh as needed (1 ml of this diluted solution = 10 μg of nickel).

1% *Dimethylglyoxime solution:* Dissolve 5 g of dimethylglyoxime (British Drug Houses Ltd., England) in ethyl alcohol and dilute to 500 ml with ethyl alcohol.

25% *Ammonium tartrate solution:* Dissolve 125 g of ammonium tartrate in water and dilute to 500 ml.

5% *Boric acid solution:* Dissolve 50 g of boric acid in approximately 800 ml of hot water, cool and dilute to 1 litre.

Chloroform: Analytical reagent grade, obtained from Mallinckrodt Chemical Works, U.S.A.

Ethyl alcohol: Cologne spirits, 95%.

Calibration curve

Add 2 ml of 25% ammonium tartrate solution to each of five 125-ml separatory funnels, then, by burette, add to the last four funnels 2·5, 5, 7·5 and 10 ml, respectively, of standard nickel solution (*i.e.*, 1 ml = 10 μg of nickel). Dilute the contents of each funnel to approximately 100 ml with water. The first funnel contains the blank. Add to each funnel 5 ml of chloroform (graduated pipette) and 5 ml of dimethylglyoxime solution, stopper and shake for 2 min. Allow 5 min for the layers to separate, then drain the chloroform extract into a 60-ml separatory funnel containing 10 ml of 2:98 ammonia solution. (The stem of the 60-ml funnel is first rinsed with ethyl alcohol to remove water droplets). Re-extract the solution by shaking for 1 min with 3 ml of chloroform and then for 30 sec with 1 ml of chloroform. Combine these extracts with the first one. The last extraction serves to wash the aqueous layer and also the stem of the funnel. Shake the combined extracts in the 60-ml separatory funnel for 30 sec with the dilute ammonia solution, allow the layers to separate, then drain the chloroform layer into a dry 25-ml volumetric flask. Finally, wash the ammonia layer by shaking for 30 sec with 1 ml of chloroform and add this to the combined extracts in the 25-ml flask. Dilute to the mark with ethyl alcohol and mix. Determine the absorbance of each of the resulting chloroform-ethyl alcohol solutions of the nickel^{II} dimethylglyoximate against the blank as the reference solution, using 5-cm cells, at a wavelength of 370 mμ. Plot micrograms of nickel *vs.* absorbance.

Procedure for niobium, tantalum, molybdenum and tungsten metals

In the following procedure a reagent blank is carried along with the samples.

Transfer a 0·5000-g sample of the powdered metal to a 250-ml Teflon beaker, add 2 ml of hydrofluoric acid (plastic pipette) and cover the beaker with a Teflon watch glass. Through the lip of the beaker add concentrated nitric acid slowly, approximately 10 drops at a time, until all of the metal is in solution. Usually 1 or 2 ml is sufficient. If a small portion of the sample remains undissolved at this stage, heat gently on the hot plate until in solution. Remove the Teflon cover and wash down the sides of the beaker with a small amount of water. (For molybdenum metal and a separate reagent blank, add at this point 2 ml of concentrated hydrochloric acid and heat until the dark brown colouration disappears and the solution becomes pale yellow). Add 10 ml of 25% ammonium tartrate solution and heat gently without boiling for 5–10 min, at which point the solution should be clear, then add 20 ml of 5% boric acid solution and allow to stand for 20 min. (If the nickel determination cannot be completed the same day, allow to stand overnight at this point).

For samples containing 100 μg of nickel or less (*i.e.*, 0·02% or less) proceed as follows: Using a pH meter, adjust the pH of both sample and blank solutions to 6·0 with concentrated ammonia solution. Transfer both solutions to 125-ml separatory funnels, dilute to approximately 100 ml with water and proceed with the nickel extraction as described for the calibration curve.

For samples containing 100–500 μg of nickel (*i.e.*, 0·02–0·10%) proceed as follows: Transfer both sample and blank solutions to 100-ml volumetric flasks and dilute to volume with water, then transfer either a 50 or 20-ml aliquot of both solutions, depending on the nickel content of the sample, to 100-ml beakers. If a 50-ml aliquot is taken, adjust the pH to 6·0 with concentrated ammonia solution and continue as described in the preceding paragraph. If a 20-ml aliquot is taken, adjust the pH to 6·0 using concentrated ammonia solution together with 1:5 ammonia solution for the final adjustment then dilute to approximately 50 ml with water in the separatory funnel prior to the extraction of the nickel.

Measure the absorbance of the sample against the reagent blank and determine the nickel content of the whole sample or aliquot of the sample by reference to the calibration curve. When the whole sample is taken:

$$1\ \mu g \text{ of nickel} = 0{\cdot}0002\%.$$

RESULTS

Extraction of the coloured complex

Chowdhury and Das Sarma[10] showed that nickel^{II} dimethylglyoximate can also be extracted with a mixture of benzene and n-amyl alcohol, but chloroform was chosen for the present work because it was more readily available and less noxious.

Preliminary experiments carried out over the pH range 4 to 10 with test solutions containing ammonium tartrate and boric acid, showed that up to at least 100 μg of nickel contained in approximately 100 ml of solution could be extracted quantitatively over the pH range 5·35 to 10·0 with two successive extractions with 5 and 3 ml of chloroform. Larger amounts of nickel could also be extracted, depending on the solubility of the nickel^{II} complex in chloroform (*i.e.*, 35 μg of nickel/ml of chloroform[11]), but this was not feasible in the present investigation because of the high optical density of the resulting chloroform-ethyl alcohol solution of the extract when 5-cm cells were used for the spectrophotometric measurement.

Effect of pH

Preliminary experiments to determine the applicability of the nickel^{II} dimethylglyoximate-chloroform extraction procedure to the extraction and subsequent determination of nickel in solutions of the four high-purity metals were carried out at pH 7 on a synthetic sample of each metal prepared according to the described procedure. The results of these tests showed that complete recovery of the added nickel was obtained from the tantalum, molybdenum and tungsten solutions, but not from the niobium solution. Further tests conducted with tantalum, molybdenum and tungsten solutions showed that nickel could be completely extracted from these solutions over the same pH range (5·35 to 10·0) described above for test solutions.

To determine whether the formation of the nickel^{II} complex in niobium solutions is affected by pH, tests were performed with a series of synthetic niobium samples containing 90 μg of added nickel and prepared as described under *Procedure*. The pH of the resulting solutions together with corresponding blank solutions was varied over the pH range 5 to 8. After dilution of each solution and its related blank to 100 ml with water in 125-ml separatory funnels, the nickel was extracted and determined spectrophotometrically according to the procedure described previously.

Because the dilution of the niobium solutions to 100 ml with water prior to extraction of the nickel complex is accompanied by a small change in pH, the initial pH adjustment of these solutions was, therefore, only approximate, and the actual pH at which the complex was formed in these solutions was determined by measuring the pH of the aqueous phase after the complex was extracted. The results of these tests showed that the effect of pH on the formation of nickel^{II} dimethylglyoximate in niobium solutions was critical, and that complete colour development, indicated by total recovery of the added nickel, was obtained over the pH range 5·35 to 6·15.

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Because the dilution of the niobium solutions to 100 ml with water prior to extraction of the nickel complex is accompanied by a small change in pH, the initial pH adjustment of these solutions was, therefore, only approximate, and the actual pH at which the complex was formed in these solutions was determined by measuring the pH of the aqueous phase after the complex was extracted. The results of these tests showed that the effect of pH on the formation of nickel^{II} dimethylglyoximate in niobium solutions was critical, and that complete colour development, indicated by total recovery of the added nickel, was obtained over the pH range 5·35 to 6·15.

During the above tests it was observed that when the pH of the aqueous phase exceeded 6·05, less nickel was extracted into the first extract, indicating that the rate of formation of the nickel^{II} complex in niobium solutions is slower at the higher pH values. This effect could be remedied by adding the dimethylglyoxime solution before the pH adjustment, but this change in the order of addition of the complexing reagent had no remedial effect on the over-all extraction of the nickel because low results were still obtained at the higher pH values.

Therefore it was decided to adjust the pH of the sample solutions to 6·0 prior to the extraction step. The pH does not remain constant throughout the course of the procedure, but decreases slightly when the sample solution or aliquot thereof is washed into the separatory funnel and diluted with water before extraction of the nickel. However, the final pH of the aqueous phase remains within the desired range 5·35 to 6·15.

Effect of diverse metal ions

Bismuth, iron^{II}, cobalt^{II}, copper^{II}, palladium^{II}, platinum^{II} and gold^{III} are known to form complexes with dimethylglyoxime.[4,12] During the chloroform extraction of nickel^{II} dimethylglyoximate from a citrate or tartrate medium, it is known that the iron^{II} complex is not extracted into the chloroform phase,[13] but the cobalt^{II}, copper^{II}, palladium^{II}, platinum^{II} and gold^{III} complexes are extracted to a certain extent and impart colours to the extract.[12] Bismuth, however, does not react with dimethylglyoxime in tartrate solution,[4] and iron^{II} may be prevented from reacting by conversion to iron^{III}. Large amounts of iron^{III} may be present without adverse effect.[12] Oelschläger[13] showed that large amounts of manganese^{II} inhibit the extraction of nickel from a citrate medium, presumably because of oxidation of the complex to the nickel^{IV} form. He also states that some manganese enters the chloroform phase. However, "a few milligrams" of manganese^{II} have been reported not to interfere in the extraction procedure.[12]

With the exception of palladium, platinum and gold, all of the cations mentioned above can be expected to occur in small amounts as impurities in samples of the four high-purity metals. Bismuth and iron do not interfere under the conditions specified in the proposed procedure for sample dissolution and solution preparation, but the possible interference effects of small amounts of manganese, cobalt and copper were considered in the present work. Previous investigators[5,13,14] have shown that these cations may be removed from the extract by shaking it with dilute ammonia solution; consequently, this technique was utilised in the present investigation.

Table I. Effect of diverse metal ions

[Diverse metal ions added: 5 mg each of Mn^{II}, Cu^{II}, Co^{II}, Cr^{III}, V^{V}, Cd and Zn (1·0 μg)]

Test	Ni taken, μg	Total Ni present, μg	Ni found, μg
#1	50·0	51·0	51·0
#2	90·0	91·0	90·5
#3 Nb (nil)	50·0	51·0	50·8
#4 Ta (nil)	50·0	51·0	50·0
#5 Mo (0·5 μg)	50·0	51·5	51·5
#6 W (4·0 μg)	50·0	55·0	55·0

Figures in parentheses show the nickel content of the mixture of diverse ions added and that of 0·5-g samples of the respective high-purity metals as determined by the proposed procedure.

The effects of 5-mg quantities of each of these cations and, in addition, chromium^{III}, vanadium^{V}, cadmium and zinc, which can also occur as impurities in the four metals, were tested separately by the proposed method on test solutions containing 50 μg of nickel. Complete recovery of the added nickel was obtained in each test.

The combined effect of 5-mg quantities of all seven cations together was then tested on known amounts of nickel and on synthetic solutions of the four metals prepared as described under *Procedure*. The results of these tests are given in Table I.

Application to synthetic niobium, tantalum, molybdenum and tungsten samples

To determine the accuracy of the proposed method, it was applied to the analysis of a series of synthetic samples in which the added nickel varied from 0·001 to 0·09%. The standard nickel solution was added directly to the powdered metal samples prior to dissolution with hydrofluoric and nitric acids. The results obtained are given in Table II.

TABLE II. RECOVERY OF NICKEL BY THE PROPOSED METHOD FROM SYNTHETIC NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN SAMPLES

Sample	Total Ni present, %	Ni found, %	Sample	Total Ni present, %	Ni found, %
Nb + 0·0010% Ni	0·0010	0·0010	Ta + 0·0010% Ni	0·0010	0·0010
Nb + 0·0050% Ni	0·0050	0·0050	Ta + 0·0050% Ni	0·0050	0·0050
Nb + 0·0100% Ni	0·0100	0·0099	Ta + 0·0100% Ni	0·0100	0·0099
Nb + 0·0250% Ni	0·0250	0·0247	Ta + 0·0250% Ni	0·0250	0·0248
Nb + 0·0500% Ni	0·0500	0·0500	Ta + 0·0500% Ni	0·0500	0·0500
Nb + 0·0900% Ni	0.0900	0·0905	Ta + 0·0900% Ni	0·0900	0·0904
Mo + 0·0010% Ni	0·0011	0·0012	W + 0.0010% Ni	0·0018	0·0018
Mo + 0·0050% Ni	0·0051	0·0052	W + 0·0050% Ni	0·0058	0·0058
Mo + 0·0100% Ni	0·0101	0·0101	W + 0·0100% Ni	0·0108	0·0108
Mo + 0·0250% Ni	0·0251	0·0248	W + 0·0250% Ni	0·0258	0·0258
Mo + 0·0500% Ni	0·0501	0·0501	W + 0·0500% Ni	0·0508	0·0509
Mo + 0·0900% Ni	0·0901	0·0904	W + 0·0900% Ni	0·0908	0·0905

Duplicate determinations of nickel in the above Nb, Ta, Mo and W metals by the proposed method gave average results of none detected, none detected, 0·0001 and 0·0008%, respectively.

DISCUSSION

Dilution of the combined chloroform extracts to a specified volume with ethyl alcohol prior to spectrophotometric determination of the nickel serves to remove turbidity caused by the retention of small droplets of water in the organic phase. Also, small variations in the amount of chloroform added have no significant effect on the final nickel determination. The chloroform-ethyl alcohol solutions of the extracts were found to be stable for at least 24 hr.

The calibration curve for determining nickel in the four high-purity metals was prepared from data obtained by extracting known amounts of nickel form solutions containing ammonium tartrate. These solutions have a pH of approximately 6·5, which is well within the pH limits specified for extraction of nickel from test solutions; consequently, no preliminary pH adjustment is required.

During the investigation carried out to determine the effect of pH on the formation and subsequent extraction of nickel from niobium solutions, it was observed that, when these solutions were allowed to stand for more than 1 hr after the pH adjustment and prior to extraction of the nickel, low results were obtained. This effect was found to be more pronounced when the pH of the aqueous phase was greater than 6. Below pH 6, the maximum negative error obtained after a solution was allowed to stand for 18 hr was 2 μg at the 90-μg nickel level. This effect occurs with niobium solutions only. The reason for this anomalous behaviour is not known, but by strict regulation of the pH during extraction, and extracting as soon as possible after pH adjustment, accurate nickel results may be obtained for niobium samples by the proposed procedure.

Oelschläger[13] has reported that the chloroform-soluble nickel^{II} dimethylglyoximate may be partially air-oxidised to the chloroform-insoluble nickel^{IV} complex in ammoniacal citrate solutions containing dimethylglyoxime, and that this effect is accelerated with increasing concentrations of ammonia and with large quantities of manganese^{II}. To counteract this effect, he specifies extraction of the nickel complex from solutions containing hydroxylamine hydrochloride. However, because iron is one of the chief impurities in high-purity samples of the four metals, a non-reducing medium was chosen for the present work to keep iron in the tervalent condition and thus prevent its reaction with dimethylglyoxime. Throughout this investigation no adverse effects from air-oxidation of the complex were encountered, and Table I shows that nickel may be effectively extracted from a non-reducing medium in the presence of moderate amounts of the various impurities that could occur in samples of the metals under consideration.

The method presented in this paper is suitable for samples containing 0·0005–0·10% of nickel, but nickel contents below 0·0005% can be determined fairly accurately because the reagent blank contains approximately 2 μg or less of nickel. Materials containing more than 0·10% of nickel can also be successfully analysed by reducing the initial sample weight. The sensitivity of the method is high, the technique required is simple, and results are reproducible under routine conditions.

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Zusammenfassung—Eine spektralphotometrische Methode zur Bestimmung von 0,0005 bis 0,1 % Nickel in hochreinem Niob, Tantal, Molybdän und Wolfram wird beschrieben. Die Probe wird gelöst, der p_H auf 6,0 eingestellt und der Ni^{II}-Dimethylglyoximkomplex mit Chloroform aus einem Ammoniumtartrat-Borsäure-Medium extrahiert. Zur Entfernung störender Verunreinigungen wird der Chloroformextrakt mit verdünntem Ammoniak gewaschen und Nickel direkt im Extrakt bei 370 mμ spektralphotometrisch bestimmt.

Résumé—On décrit une méthode de dosage du nickel en proportion de 0,0005 à 0,10% dans des échantillons très purs de niobium, tantale, molybdène et tungstène. Après dissolution de l'échantillon et réglage du pH à 6,0 le complexe Nickel II-diméthylglyoxime est extrait par le choroforme du milieu acide borique-tartrate d'ammonium. La couche chloroformique est lavée par une solution diluée ammoniacale pour chasser les impuretés gênantes, et le nickel est dosé directement dans l'extrait par spectrophotométrie à 370 mμ.

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THERMOGRAVIMETRIC ANALYSIS OF SOME INTERACTION PRODUCTS OF 1,2,3-BENZOTRIAZOLE HYDROCHLORIDE WITH CERTAIN NEGATIVE CYANO-COMPLEXES OF THE TRANSITION METALS

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Summary—Thermogravimetric pyrolyses of some interaction products of certain negative cyano-complexes of the transition metals with 1,2,3-benzotriazole hydrochloride and identification of several intermediate products formed during the course of the reactions are reported.

THIS paper arises from part of a general study of the interaction products of some of the transition metals with 1,2,3-benzotriazole hydrochloride. Pyrolyses of cyano-complexes of molybdenum, ruthenium, osmium, cobalt, manganese, platinum, palladium and nickel, and of the thiocyano-complex of cobalt have been studied using a thermobalance. It was found that all of the compounds were stable up to at least 45° and that decomposition of the compounds occurred between 45° and 480°. Thermogravimetric analysis of these complex compounds gave support to the proposed formulae of the 1,2,3-benzotriazole hydrochloride interaction products with the aforementioned metal complexes reported by Wilson and James.[2]

The purposes of this study were to use the thermobalance as a means of detecting and following the course of the solid-state reactions of the aforementioned products, and to isolate and attempt to identify some of the intermediate products formed during the course of these reactions.

EXPERIMENTAL

Analyses

Determinations of carbon, nitrogen and hydrogen were provided by commercial analysts. Determinations of the metal content of the compounds were made in this laboratory by decomposing the compounds in air, then reducing the oxides to the pure metal in an atmosphere of hydrogen, employing a Vycor combustion chamber.

Apparatus

The thermobalance and its calibration, operation and use have been reported previously by Wilson and Henry.[3] The furnace temperature was increased at an average rate of 2°/min over a temperature range of room temperature to approximately 600°. A Beckman-IR-5 Spectrophotometer was used for obtaining spectra of various intermediate products, employing the standard potassium bromide-pellet technique in which spectra-grade potassium bromide was used. The intermediate products were obtained according to the procedure reported by Wilson and James.[2]

RESULTS

Thermograms for compounds 1–9 with the respective formulae:

$(C_6H_4N_2NH_2)_4Mo(CN)_8$, $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pt(CN)_6]$,
$(C_6H_4N_2NH)Ni(CN)_2{\cdot}2HCN$, $(C_6H_4N_2NH_2)_2Ru(CN)_6$,
$(C_6H_4N_2NH_2)_3Mn(CN)_6$, $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pd(CN)_6]$,
$(C_6H_4N_2NH_2)_3Co(CN)_6$, $(C_6H_4N_2NH_2)_3Co(SCN)_6$

and

$(C_6H_4N_2NH_2)_2Os(CN)_6$,

were obtained as described by Wilson and Henry.[3] The pyrolysis curves are presented graphically in Figs. 1, 2 and 3; the analysis of these curves is given in Table I and analyses for several of the intermediate products formed during the course of the thermogravimetric analyses are given in Table II. For each of the above compounds

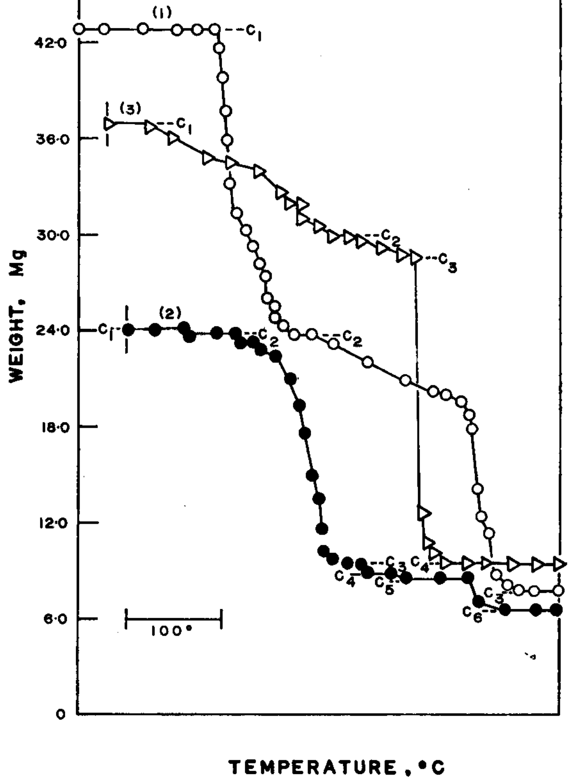

FIG 1.—Thermogravimetric analysis of compounds 1–3:—
(1) $(C_6H_4N_2NH_2)_4$ $Mo(CN)_8$: —○—,
(2) $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pt(CN)_6]$: —●—,
(3) $(C_6H_4N_2NH)Ni(CN)_2 \cdot 2HCN$: —▷—.

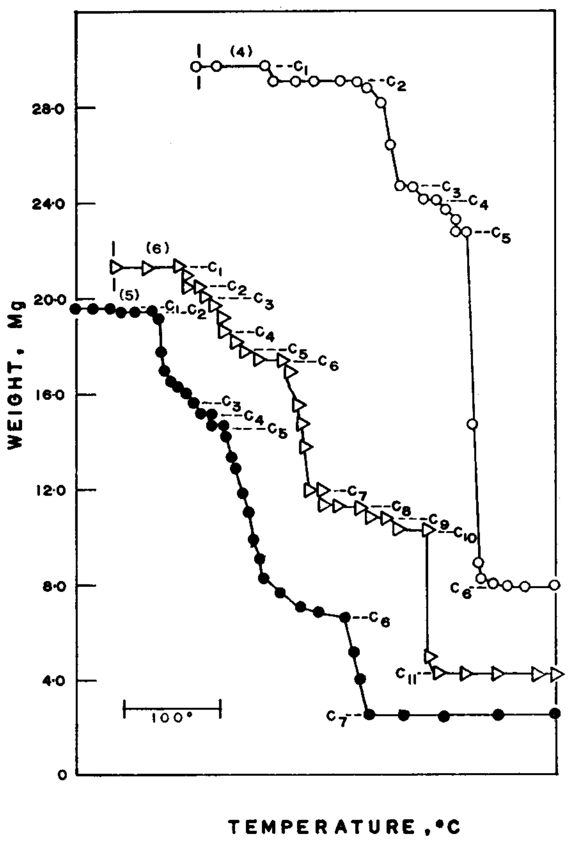

FIG. 2.—Thermogravimetric analysis of compounds 4–6:

(4) $(C_6H_4N_2NH_2)_2Ru(CN)_6$: —○—,
(5) $(C_6H_4N_2NH_2)_3Mn(CN)_6$: —●—,
(6) $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pd(CN)_6]$: —▷—.

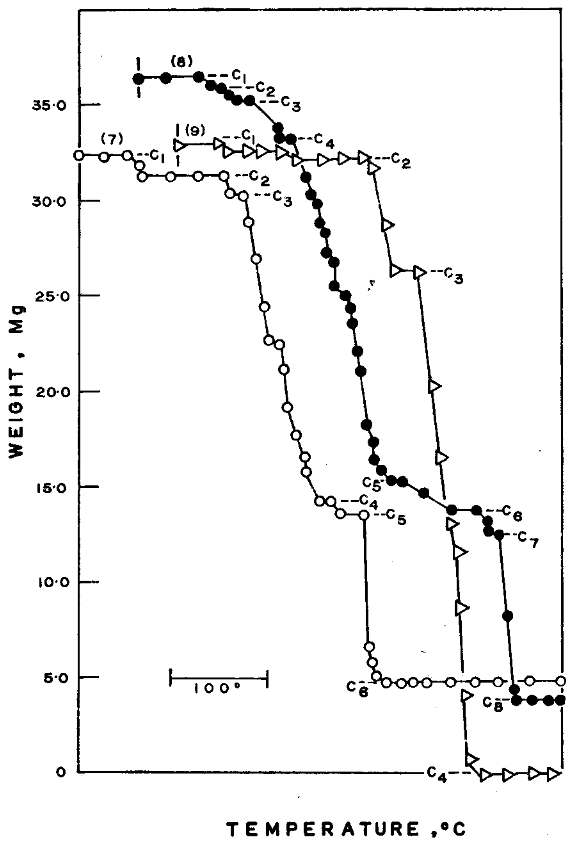

FIG. 3.—Thermogravimetric analysis of compounds 7–9:

(7) $(C_6H_4N_2NH_2)_3Co(CN)_6$: —○—,
(8) $(C_6H_4N_2NH_2)_3Co(SCN)_6$: —●—.
(9) $(C_6H_4N_2NH_2)_2Os(CN)_6$: —▷—.

TABLE I

Compound	C_1			C_2			C_3			C_4		
	Initial weight, *mg*	Weight corrected for moisture, *mg*	Temp range, °*C*	Weight, *mg*		Temp range, °*C*	Weight, *mg*		Temp range, °*C*	Weight, *mg*		Temp range, °*C*
				Calc.	Meas.		Calc.	Meas.		Calc.	Meas.	
1. $(C_6H_4N_2NH_2)_4Mo(CN)_8$	42·9		<140	24·0	23·9	225–240	7·9	7·8	>480			
2. $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pt(CN)_6]$	24·2	24·0	<60									
3. $(C_6H_4N_2NH)Ni(CN)_2{\cdot}2HCN$	37·1		<45	30·0	30·0	45–250				9·5	9·6	>400
4. $(C_6H_4N_2NH_2)_2Ru(CN)_6$	29·7	29·1	<75									
5. $(C_6H_4N_2NH_2)_3Mn(CN)_6$	19·6	19·4	<50									
6. $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pd(CN)_6]$	21·3		<70									
7. $(C_6H_4N_2NH_2)_3Co(CN)_6$	32·4		<50				30·9	30·9	155–165	14·4	14·3	270–295
8. $(C_6H_4N_2NH_2)_3Co(SCN)_6$	36·5		<65									
9. $(C_6H_4N_2NH_2)_2Os(CN)_6$	33·0	32·4	<45				26·4	26·3	220–240	0.0	0·0	>430

TABLE I.—(CONTD.)

Compound	C_5			C_6			C_7			C_8			C_{11}		
	Weight, *mg*		Temp range, °*C*	Weight, *mg*		Temp range, °*C*	Weight, *mg*		Temp range, °*C*	Weight, *mg*		Temp range, °*C*	Weight, *mg*		Temp range, °*C*
	Calc.	Meas.		Calc.	Meas.		Calc.	Meas.		Calc.	Meas.		Calc.	Meas.	
1. $(C_6H_4N_2NH_2)_4Mo(CN)_8$															
2. $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pt(CN)_6]$	8·3	8·4	290–350	6·6	6·7	>375									
3. $(C_6H_4N_2NH)Ni(CN)_2{\cdot}2HCN$															
4. $(C_6H_4N_2NH_2)_2Ru(CN)_6$	22·8	22·7	260–270	8·0	7·9	>280									
5. $(C_6H_6N_2NH_2)_3Mn(CN)_6$	14·9	14·9	130–145				2·7	2·6	>305						
6. $(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pd(CN)_6]$										11·3	11·3	225–260	4·2	4·3	>335
7. $(C_6H_4N_2NH_2)_3Co(CN)_6$				4·7	4·8	>320									
8. $(C_6H_4N_2NH_2)_3Co(SCN)_6$				14·0	13·9	330–350				4·0	3·9	>400			
9. $(C_6H_4N_2NH_2)_2Os(CN)_6$															

TABLE II

Initial compound	Description	Temp. range, °*C*	Intermediate compound	Description	Temp. range, °*C*	Calculated (Found) for % intermediate compounds,			
						Carbon	Nitrogen	Hydrogen	Metal
$(C_6H_4N_2NH_2)_4Mo(CN)_8$	Yellow, crystalline compound	<140	$(C_6H_4N_2NH)_2Mo(CN)_4$	Black, crystalline compound	215–225	43·85 (44·24)	31·96 (31·49)	2·30 (2·54)	21·89 (21·73)
$(C_6H_4N_2NH_2)_2Ru(CN)_6$	Light grey, powdery compound	<160	$(C_6H_4N_2N)_2Ru(CN)_2$	Blue-black, crystalline compound	255–265	43·12 (43·03)	28·73 (28·94)	2·07 (2·24)	26·08 (25·79)
$(C_6H_4N_2NH_2)_3Co(CN)_6$	White, crystalline compound	<55	$(C_6H_4N_2NH)Co(CN)_3$	Black, crystalline compound	275–300	42·21 (42·06)	32·82 (32·75)	1·97 (1·72)	23·01 (23·47)
$(C_6H_4N_2NH_2)_2Os(CN)_6$	Light blue, powdery compound	<190	$(C_6H_4N_2N)_2Os(CN)_2$	Blue-black, crystalline compound	230–250	35·14 (35·02)	23·42 (23·04)	1·69 (1·54)	39·75 (40·40)

the weights for the breaks $C_2, C_3, \ldots, C_n$ were calculated on the basis of the following reactions:

Compound 1

$$C_2\colon\ 2(C_6H_4N_2NH_2)_4Mo(CN)_8 \xrightarrow[\Delta]{(140\text{–}225)^\circ}$$

$$4C_6H_4N_2NH\uparrow + 8HCN\uparrow + 2(C_6H_4N_2NH)_2Mo(CN)_4$$

$$C_3\colon\ 2(C_6H_4N_2NH)_2Mo(CN)_4 + 3O_2 \xrightarrow[\Delta]{(240\text{–}480)^\circ}$$

$$4(CN)_2\uparrow + 4C_6H_4N_2NH\uparrow + 2MoO_3$$

Compound 2

$$C_5\colon\ (C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pt(CN)_6] \xrightarrow[\Delta]{(115\text{–}290)^\circ}$$

$$2HCN\uparrow + 3C_6H_4N_2NH\uparrow + (CN)_2\uparrow + Pt(CN)_2$$

$$C_6\colon\ Pt(CN)_2 \xrightarrow[\Delta]{(350\text{–}375)^\circ} Pt + (CN)_2\uparrow$$

Compound 3

$$C_2\colon\ 2(C_6H_4N_2NH)Ni(CN)_2\cdot 2HCN \xrightarrow[\Delta]{(45\text{–}230)^\circ}$$

$$4HCN\uparrow + 2(C_6H_4N_2NH)Ni(CN)_2$$

$$C_4\colon\ 2(C_6H_4N_2NH)Ni(CN)_2 + O_2 \xrightarrow[\Delta]{(255\text{–}400)^\circ}$$

$$2(CN)_2\uparrow + 2C_6H_4N_2NH\uparrow + 2NiO$$

Compound 4

$$C_5\colon\ (C_6H_4N_2NH_2)_2Ru(CN)_6 \xrightarrow[\Delta]{(260\text{–}270)^\circ} 4HCN\uparrow + (C_6H_4N_2N)_2Ru(CN)_2$$

$$C_6\colon\ (C_6H_4N_2N)_2Ru(CN)_2 + O_2 \xrightarrow[\Delta]{(270\text{–}230)^\circ} G\uparrow + RuO_2$$

where G represents the volatile organic pyrolytic products formed during the course of the chemical process.

Compound 5

$$C_5\colon\ 3(C_6H_4N_2NH_2)_3Mn(CN)_6 \xrightarrow[\Delta]{(130\text{–}145)^\circ}$$

$$15HCN\uparrow + 3(C_6H_4N_2NH)(C_6H_4N_2N)_2Mn(CN)$$

$$C_7\colon\ 3(C_6H_4N_2NH)(C_6H_4N_2N)_2Mn(CN) + 2O_2 \xrightarrow[\Delta]{(150\text{–}305)^\circ}$$

$$3C_6H_4N_2NH\uparrow + G\uparrow + Mn_3O_4$$

Compound 6

$$C_8\colon\ 2(C_6H_4N_2NH_2)_2(C_6H_4N_2NH)[Pd(CN)_6] \xrightarrow[\Delta]{(70\text{–}206)^\circ}$$

$$4HCN\uparrow + 4C_6H_4N_2NH\uparrow + 2(C_6H_4N_2NH)Pd(CN)_4$$

$$C_{11}\colon\ 2(C_6H_4N_2NH)Pd(CN)_4 + O_2 \xrightarrow[\Delta]{(305\text{–}335)^\circ}$$

$$4(CN)_2\uparrow\ 2C_6H_4N_2NH\uparrow + 2PdO$$

Compound 7

$$C_3\colon\ 4(C_6H_4N_2NH_2)_3Co(CN)_6 \xrightarrow[\Delta]{(55\text{–}160)^\circ}$$

$$4HCN\uparrow + 4(C_6H_4N_2NH)(C_6H_4N_2NH_2)_2Co(CN)_5$$

$$C_4\colon\ 4(C_6H_4N_2NH)(C_6H_4N_2NH_2)_2Co(CN)_5 \xrightarrow[\Delta]{(165\text{–}270)^\circ}$$

$$8HCN\uparrow + 8C_6H_4N_2NH\uparrow + 4(C_6H_4N_2NH)Co(CN)_3$$

$$C_6\colon\ 4(C_6H_4N_2NH)Co(CN)_3 + 3O_2 \xrightarrow[\Delta]{(300\text{–}320)^\circ}$$

$$6(CN)_2\uparrow + 4C_6H_4N_2NH\uparrow + 2Co_2O_3$$

Compound 8

$$C_6\text{: } 4(C_6H_4N_2NH_2)_3Co(SCN)_6 \xrightarrow[\Delta]{(60\text{–}330)^\circ} 8H_2\uparrow$$

$$+\ 8(SCN)_2\ 8C_6H_4N_2NH\uparrow + 4(C_6H_4N_2N)Co(SCN)_2$$

$$C_8\text{: } 4(C_6H_4N_2N)Co(SCN)_2 + 3O_2 \xrightarrow[\Delta]{(355\text{–}450)^\circ} G\uparrow + 2Co_2O_3$$

Compound 9

$$C_3\text{: } (C_6H_4N_2NH_2)_2Os(CN)_6 \xrightarrow[\Delta]{(190\text{–}225)^\circ} 4HCN\uparrow + (C_6H_4N_2N)_2Os(CN)_2$$

$$C_4\text{: } (C_6H_4N_2N)_2Os(CN)_2 + 2O_2 \xrightarrow[\Delta]{(250\text{–}420)^\circ} G\uparrow + OsO_4\uparrow$$

Isolation of pyrolysis products

The aforementioned thermogravimetric data, obtained from the pyrolysis of the products resulting from the interaction of certain negative metal ion complexes with the hydrochloride of 1,2,3-benzotriazole, suggested the presence of several decomposition products. To ascertain some further proof of the intermediate products and a qualitative indication of the composition of the volatile organic residue given off over selected temperature ranges, the decomposition vapours resulting from these pyrolyses were trapped and partially analysed. The special all-glass decomposition apparatus, as well as the procedure for isolating the pyrolytic products, have been described previously by Wilson and James.[2] Each of the starting metal-complex compounds was heated separately in the special decomposition apparatus to a temperature slightly above that required to obtain complete decomposition of the compounds. All of the cyano-complex compounds studied, with the exceptions of the ruthenium and osmium compounds, gave decomposition products whose infrared spectra contained all of the principal absorbance bands corresponding to the spectra of pure 1,2,3-benzotriazole in addition to several other absorbance bands which could not be associated directly with 1,2,3-benzotriazole. The presence of 1,2,3-benzotriazole was further verified by dissolving the condensed vapours in water and precipitating the 1,2,3-benzotriazole from an ammoniacal EDTA solution using aqueous silver nitrate, because silver cyanide is highly soluble in such a medium.[1] All of these compounds decomposed to give hydrogen cyanide and/or cyanogen, with the exception of the thiocyanate complex of cobalt, which was precipitated from aqueous silver nitrate solutions as silver cyanide.

For the ruthenium and osmium compounds, the infrared spectra of the volatile organic portion of the residue, after removing any cyanide or cyanogen present, were quite similar and indicated that the residue contained a cyano-compound of 1,2,3-benzotriazole which was not the same, but contained a structure similar to that of *o*-aminobenzonitrile. Similar spectra for the organic portions of the residues of the other seven complex compounds were obtained. These spectra were very similar and indicated that 1,2,3-benzotriazole was the principal organic portion of the residue.

DISCUSSION

These data indicate that complete decomposition of the interaction products of some of the transition metals with 1,2,3-benzotriazole hydrochloride occurs over a temperature range of 45° to 480°. Complete qualitative and quantitative analyses of the organic vapours produced in the thermal decomposition reactions could not readily be obtained because, in most reactions, a small concentration of impurities and/or 1,2,3-benzotriazole derivatives were produced. These could not be easily separated from the 1,2,3-benzotriazole because of the close similarity between these products and 1,2,3-benzotriazole. Decomposition of the complexed compounds gave the metal oxide or mixed metal oxide and in one instance the pure metal, hydrogen cyanide, cyanogen, 1,2,3-benzotriazole, and in one case hydrogen and thiocyanogen.

Zusammenfassung—In dieser Arbeit wird über thermogravimetrische Pyrolysen von Produkten der Reaktion negativer Cyanokomplexe der Übergangsmetalle mit 1,2,3-Benztriazolhydrochlorid berichtet und mehrere Zwischenprodukte identifiziert.

Résumé—On décrit des pyrolyses thermogravimétriques de quelques produits d'interaction de certains complexes négatifs cyanés des métaux de transition avec le chlorhydrate du benzotriazole-1,2,3 et identifie quelques composés intermédiaires produits au cours de cette réaction.

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ABSORPTIOMETRIC DETERMINATION OF NIOBIUM^{V} WITH 4-(2-PYRIDYLAZO)-RESORCINOL AS REAGENT

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Summary—4-(2-Pyridylazo)-resorcinol forms a 1:1 purple-coloured complex (λ_{max} = 550 mμ) with niobium^{V} in an acetate-tartrate medium at pH 5·8. This is suitable for the spectrophotometric determination of niobium down to 0·1 ppm. The colour is formed within 45 min, and is stable thereafter for several days; the molecular extinction coefficient, $\epsilon_{550m\mu}$ = 38,700, is as high as that reported for the well-known thiocyanate procedure, and the stability is very much superior. The interference of over 40 ions has been examined at the 1000-μg level in the presence of excess of cyanide and EDTA; only uranium^{VI}, vanadium^{V} and phosphate interfere. Vanadium may be masked by addition of zinc ions, and uranium by ammonium oxalate. 1000 μg of tantalum exhibit weak colour formation with the reagent, but this can be eliminated by the addition of larger amounts of tartrate, with only a slight decrease in the sensitivity of the niobium reaction. This new procedure does not necessitate an extraction, and is easier to operate than the standard methods.

THE two most widely used methods for the determination of niobium are undoubtedly those based on the formation of its thiocyanate and its 8-hydroxyquinolate. Both procedures require an extractive separation from aqueous solution. Numerous other methods based on the use of molecules containing suitably disposed (*e.g.*, vicinal) hydroxyl groups exist, but none of them is very selective; and frequently the coloured species, or even the reagent itself, is unstable. The thiocyanate procedure works well under carefully controlled conditions, but the colour system must be produced and measured within a fairly narrow time range and it is subject to variations from concentration changes in acidity, reagent, tartrate, tin^{II} chloride, *etc.* The 8-hydroxyquinoline method is somewhat less sensitive and more unselective, but is possessed of a much more stable colour system. There is undoubtedly room for alternative reagents of good sensitivity and selectivity for the determination of small amounts of niobium.

Colour reaction with PAR

In a previous preliminary communication to this journal[1] we reported for the first time on the colour reaction between niobium^{V} and the metallochromic reagent 4-(2-pyridylazo)-resorcinol (PAR). Whereas most of the metal complexes of PAR are readily broken down by the addition of one equivalent of EDTA, the niobium complex remains stable even in the presence of excess. The use of EDTA, therefore, allows a highly selective determination of niobium. Fig. 1 shows the absorption spectra of PAR, and the formation of the purple-coloured complex of niobium when increasing amounts of niobium^{V} in a tartrate medium are added. It will be noted that the absorbance of the reagent, λ_{max} = 410 mμ, is negligible at the wavelength of maximum absorption, λ = 550 mμ, of the niobium complex. The relatively high intensity of the niobium complex may be judged from the fact that a constant amount of 10^{-5} mole of PAR was used in these experiments whilst the amount of niobium was only: (*ii*),

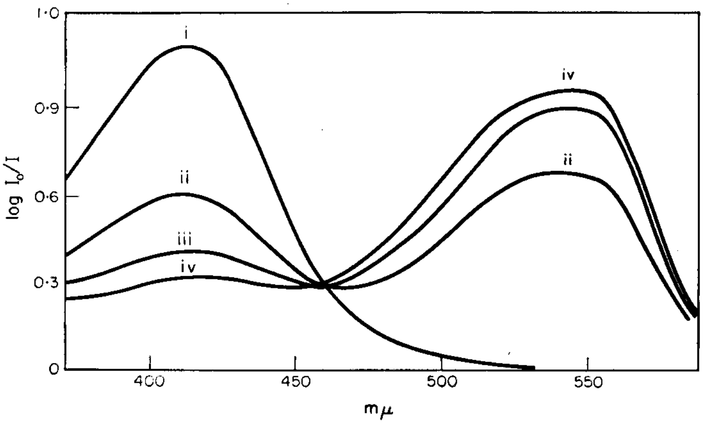


FIG. 1.—Absorption spectra of PAR and its niobium chelate at pH 5·8. (4-cm cuvettes against H_2O.)

(*i*) 10 ml of $10^{-3}M$ PAR + 5 ml buffer/100 ml,
(*ii*) as (*i*) + 5 ml of $10^{-4}M$ Nb solution,
(*iii*) as (*i*) + 10 ml of $10^{-4}M$ Nb solution,
(*iv*) as (*i*) + 20 ml of $10^{-4}M$ Nb solution.

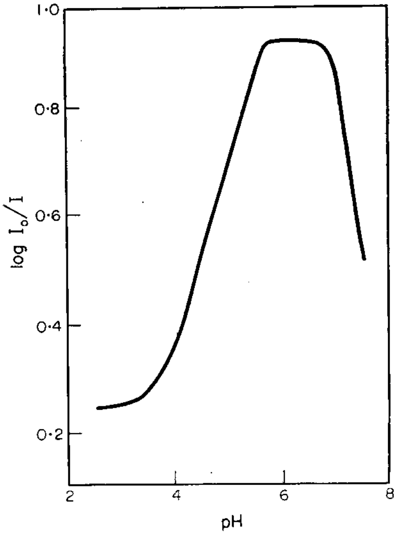


FIG. 2.—Difference in optical density between niobium chelate and PAR blank at various pH values.
(4-cm cuvettes at 550 mμ.)

5×10^{-7}; (*iii*), 10^{-6}; (*iv*), 2×10^{-6} mole. These measurements were made at a pH of 5.8 in a sodium acetate buffer medium with a development time of 1 hour in each instance.

The optimum pH range was established by varying the pH range in a sodium acetate medium whilst maintaining all other conditions unchanged. Fig. 2 shows the plot of the difference in optical density of the niobium complex and the reagent at each pH from 3–8 in the absence of EDTA. This graph shows that the colour system is independent of pH over the range 5·8–6·4. Because the buffer index of a sodium acetate medium is not very high at 5·8, it is better to use ammonium acetate; although in these preliminary experiments we continued to use sodium acetate, and the niobium solutions were roughly neutralised to this pH before use (*cf.* Notes 1 and 2). The time required for the development of maximum colour in the absence of EDTA is 25 minutes, and in the presence of the recommended amount of EDTA it is 40 minutes, no doubt because of the competition of the EDTA and consequent longer time required for equilibrium to be reached. The optical density in both cases remained unchanged after several hours, showed a very slight increase after standing overnight, and then remained unchanged for 5 days. It will be seen that this represents a considerable improvement on the standard absorptiometric methods for niobium. When a fair excess of PAR was used, as noted previously, the colour system was found to obey Beer's law over the range up to 70 μg in the absence or presence of EDTA. In the absence of EDTA the molecular extinction coefficient was $\epsilon_{500\mathrm{m}\mu} = 38{,}700$ and in its presence $\epsilon^{\mathrm{EDTA}}_{500\mathrm{m}\mu} = 35{,}600$. Allowing for the volume of reagents, the most dilute solution used in these experiments was 0·12 ppm and the most concentrated was 9 ppm, but this could obviously be extended up to the neighbourhood of 50–70 ppm where necessary. The sensitivity indices (Log $^{\mathrm{Io}}/_{\mathrm{I}} = 0.001$) were 0·0024 μg.cm^{-2} and 0·0026 μg.cm^{-2} in the absence and presence of EDTA, respectively.

Nature of Nb/PAR *complex*

The nature of the complex formation between PAR and niobium was studied by a variety of optical procedures. Fig. 3 shows a continuous variations plot at three dilutions. This plot, which was carried out in the presence of EDTA, reveals clearly the formation of a 1:1 complex. A Harvey-Manning[2] plot of slope-ratio in a 0·02*M* EDTA medium containing KCl of ionic strength $\mu = 0{\cdot}5$ (Fig. 4*a*), again gives an unequivocal indication of a 1:1 complex. Similar evidence can be seen (Fig. 4*b*) in a Yoe and Jones[3] mole ratio plot. In this last experiment, increasing amounts of PAR were added to a constant (5×10^{-7} mole) amount of niobium$^{\mathrm{V}}$-tartrate complex in the presence of EDTA. Ideally, the plot of optical density (difference from reagent blank) should lie parallel to the abscissa following the break on the curve. However, the competition from tartrate and EDTA are partly responsible for the continued slope of the curve and the absence of a large excess of reagent to promote increased association of the relatively weak complex of PAR with niobium.

Stability of Nb/PAR *complex*

The "apparent" or "conditional" stability constant of the PAR-Nb 1:1 complex formed under the conditions of our experiments was evaluated by two procedures. In the first of these, solutions were formulated containing exactly one proportion each of niobium (as tartrate) and PAR (*cf.* Table I). Under these conditions the complex is appreciably dissociated, as would be expected, and a low optical density, ϵ_s, is obtained. Similar solutions were then prepared containing the same amounts of niobium, but with excess of PAR. In this second instance it may be assumed that the niobium-PAR complex is largely associated and consequently it has a higher optical density, ϵ_m. The difference between the two optical densities represents a measure of the degree of dissociation of the complex:

$$\alpha = \frac{\epsilon_m - \epsilon_s}{\epsilon_m}.$$

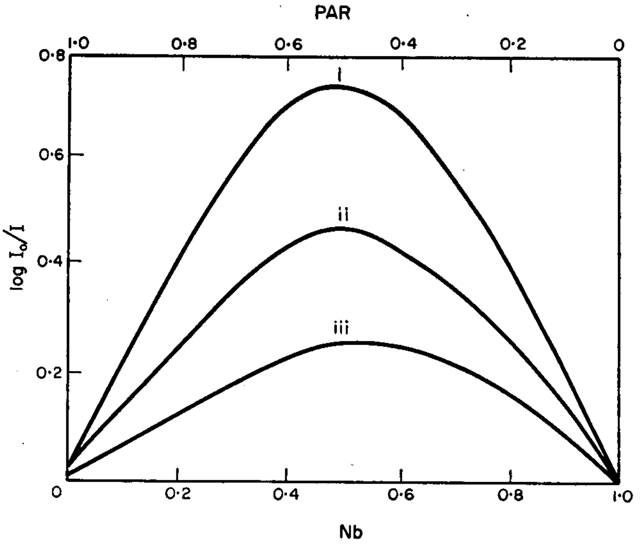


FIG. 3.—Continuous variations curves for niobium PAR chelate.
(pH 5·8 at 550 mμ
4-cm cuvettes.)
$10^{-4}M$ PAR and Nb^V tartrate solutions.
100 ml of solution containing 10 ml of 0·02M EDTA + 5 ml of pH 5·8 buffer:
(*i*) Total concentration of Nb + PAR solutions = 20 ml of $10^{-4}M$/100 ml.
(*ii*) Total concentration of Nb + PAR solutions = 15 ml of $10^{-4}M$/100 ml.
(*iii*) Total concentration of Nb + PAR solutions = 10 ml of $10^{-4}M$/100 ml.
These curves are uncorrected for PAR absorption since this is very slight at 550 mμ.

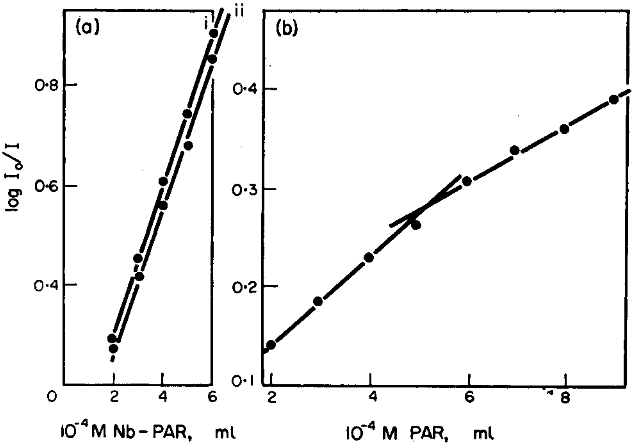
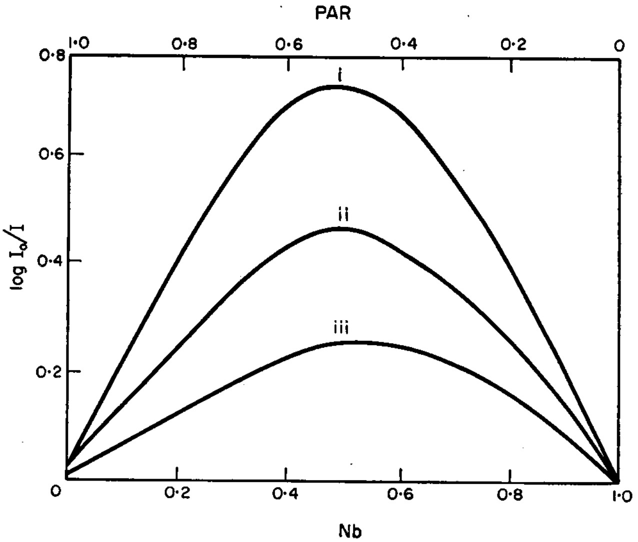


FIG. 4.—Harvey-Manning (*a*) and Yoe-Jones (*b*) Plots for niobium-PAR
(KCl medium; μ = 0·5/100 ml volume; 4-cm cuvettes; 550 mμ)
(*a*) Curve *i*; 10 ml of $10^{-3}M$ PAR solution + x ml of $10^{-4}M$ Nb^V solution.
Curve *ii*; 10 ml of $10^{-3}M$ Nb^V solution + x ml of $10^{-4}M$ PAR solution.
Both in presence of 10 ml of 0·02M EDTA + 5 ml of buffer.
(*b*) 5 ml of $10^{-4}M$ Nb^V solution + 10 ml of 0·02M EDTA + 5 ml of pH 5·8 buffer + x ml of $10^{-4}M$ PAR; measured against x ml of PAR in each instance.



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100 ml of solution containing 10 ml of 0·02M EDTA + 5 ml of pH 5·8 buffer:
(*i*) Total concentration of Nb + PAR solutions = 20 ml of $10^{-4}M/100$ ml.
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These curves are uncorrected for PAR absorption since this is very slight at 550 mμ.

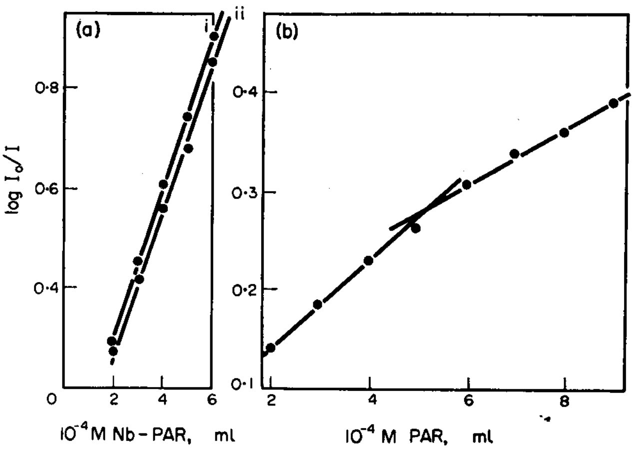

Fig. 4.—Harvey-Manning (*a*) and Yoe-Jones (*b*) Plots for niobium-PAR (KCl medium; μ = 0·5/100 ml volume; 4-cm cuvettes; 550 mμ)
(*a*) Curve *i*; 10 ml of $10^{-3}M$ PAR solution + x ml of $10^{-4}M$ Nb^V solution.
Curve *ii*; 10 ml of $10^{-3}M$ Nb^V solution + x ml of $10^{-4}M$ PAR solution.
Both in presence of 10 ml of 0·02M EDTA + 5 ml of buffer.
(*b*) 5 ml of $10^{-4}M$ Nb^V solution + 10 ml of 0·02M EDTA + 5 ml of pH 5·8 buffer + x ml of $10^{-4}M$ PAR; measured against x ml of PAR in each instance.

On the basis of the previous experiments if a mono-nuclear complex, MD, is assumed, it is possible to write the stability constant as K = [MD]/([M] [D]) and hence the conditional constant as K = $(1-\alpha)/\alpha C$ where C represents the concentration of the complex. Thus the conditional constant, *cf.* Table I, is readily evaluated. (*Av. value* K = 8·36 × 10^4).

The continuous variations curve may be used similarly to obtain a measure of the conditional stability constant. This was done from curves I and II of Fig. 3. Using the same symbols for K as above, it may be said that at some point, x, on the curve, corresponding to a certain concentration of the complex, $K = x/[(M - x)(D - x)]$, where M and D would represent the total concentrations of M (niobium) and D (PAR) if no reaction had taken place between them. If we chose another point, x', on the opposite side of the maximum or, as was done here, on a curve of different concentration such that the optical densities are the same, then

TABLE I

Volume of $10^{-4}M$ Nb^{V}, *ml*	Optical density stoichiometric amount of PAR, ϵ_s	Optical density 20 ml of $10^{-3}M$ PAR, ϵ_m	Degree of dissociation	Conditional constant, *K*
4	0·135	0·65	0·792	8.3 × 10^4
5	0·205	0·84	0·756	8·5 × 10^4
6	0·260	1·00	0·740	8·3 × 10^4

$$\mathrm{K} = \frac{x}{(\mathrm{M} - x)(\mathrm{D} - x)} = \frac{x'}{(\mathrm{M}' - x')(\mathrm{D}' - x')}$$

and of course $x = x'$,

whence
$$x = \frac{\mathrm{MD} - \mathrm{M'D'}}{[\mathrm{M} + \mathrm{D}] - [\mathrm{M}' + \mathrm{D}']}$$

Substitution of x in the expression for K, the conditional stability constant, then provides the numerical values shown in Table II. Two values of K were calculated, one for each curve, *i.e.*, x and x'. The average value for K in this instance is 2.67 × 10^4.

The nature of the complex was not investigated further, though some preliminary experiments with solvent extraction revealed that only the excess of PAR would be extracted by non-miscible solvents such as benzene, carbon tetrachloride, chloroform, methylisobutylketone, *etc.* This indicates that the complex is either quite heavily

TABLE II. VALUES OF CONDITIONAL CONSTANT FROM CONTINUOUS VARIATIONS CURVE

Optical density $\times 10^{-1}$	M	D	M′	*D′*	K	
		(10^{-4}*M* solution, *ml*)			x	x'
1	19·25	0·75	14·175	0·825	3·3 × 10^4	2·52 × 10^4
2	1·8	18·2	2·4	12·6	3·25 × 10^4	2·8 × 10^4
1·5	1·3	18·7	1·725	13·275	4·07 × 10^4	3·3 × 10^4
2·5	2·3	17·7	3·0	12·0	1·34 × 10^4	1·2 × 10^4
1·25	1·1	18·9	1·35	13·65	3·3 × 10^4	2·8 × 10^4
1·75	1·6	18·4	2·1	12·9	3·6 × 10^4	3·0 × 10^4
2·25	2·1	17·9	2·7	12·3	1·5 × 10^4	1·4 × 10^4

solvated by water molecules or is probably co-ordinated extensively by the acetate or tartrate ions of the reaction medium. It is possible to extract the reagent and the complex quantitatively by certain amine-containing organic solvents; further work is proceeding on this aspect. A few electrophoresis experiments on both PAR and its niobium complex were carried out in tartrate buffer (pH 5·8), acetate buffer (pH 4), and borate buffer (pH 10). In all cases, the complex began to move towards the anode, but decomposed too rapidly thereafter to permit further useful results to be obtained. The spot caused by PAR diffused and decomposed without migrating. The extractive and electrophoretic evidence both indicate the anionic nature of the complex, thus suggesting the presence of tartrate or acetate in the complex. It is conceivable, though improbable, that the niobium could react with *both* phenolic groups in the molecule, for resorcinol itself has been used as a means of detecting niobium.[4] Evidence of this might be obtained from a pH titration curve, but the situation is complicated by the presence of large amounts of tartrate, and therefore this aspect was not pursued in this instance. It is almost certain, however, that the azo nitrogen group participates in the co-ordination. The reagent PAN [4-(2-pyridylazo)-naphthol] also forms an orange-coloured complex with niobium, but the compound formed in this instance is a precipitate rather than a soluble colour-body. On these grounds it is open to question whether the hydroxyl group remote from the azo bond in PAR contributes to the complex formation. Its function may therefore be mainly to maintain the complex in solution by ionisation, with perhaps some auxochromic contribution to the colour system.

Effect of foreign ions on the colour system

The effects of thirty-four cations and of eight anions on the niobium determination were examined. In the cation experiments the amount of niobium used was *ca.* 45 μg and in each instance 1 mg of the foreign ion was added and its effect was noted. The amount of EDTA present in each experiment was 10 ml of 0·02M disodium salt; the amount of pH 5·8 sodium acetate buffer was 5 ml. In the few instances where EDTA does not form a stable complex, *e.g.*, Ag, or where the EDTA complex is coloured, *e.g.*, Cu^{II} and Co^{II}, 5 ml of 1 % potassium cyanide were added in addition to the EDTA. With Ce^{IV}, 5 ml of 0·5 % aqueous ascorbic acid were added to prevent oxidation of the PAR. The ions examined were Pb, Cu^{II}, Bi, Cd, Hg^{II}, Fe^{II}, Fe^{III}, Al, Cr^{III}, Ag, Zn, Mn, Co, Ni, Ca, Sr, Ba, Mg, Be, Sn^{II}, Sn^{IV}, NH_4, As^{III}, Zr, Th, V^V, Ta, Ti, U^{VI}, La, Ce^{IV}, Mo^{VI}, W^{VI}. Of these ions, only U^{VI}, V^V and Ta were found to interfere and give high results. The interference of V^V was readily overcome by addition of zinc ions as suggested by Cheng and Goydish[5] and U^{VI} was masked by ammonium oxalate. A final concentration of $10^{-2}M$ oxalate reduces the molecular extinction coefficient from 35,600 only to 35,000 in the presence of the same amount of EDTA. The interference of tantalum was prevented by adding a higher concentration of tartrate to the solution. Fig. 5 shows calibration curves for the niobium in the absence (*i*) and presence (*ii*) of EDTA and in the presence of both EDTA and 5 g of tartaric acid (*iii*). No interference was found from 1,000 μg of Ta under these conditions. When dealing with ions which hydrolyse readily, *e.g.*, Bi^{III}, Ti^{IV}, Zr^{IV}, *etc.*, it was found that the order of addition of reagents was important. Thus, results low by *ca.* 20 % were found with 1 mg of Zr unless the buffer was added last. The best order of addition of reagents is (1) EDTA, (2) PAR, (3) buffer. When buffer was added first, low recoveries were generally obtained because of coprecipitation of the niobium with the hydrous oxides of these metals.

The anions examined included cyanide, thiocyanate, fluoride, oxalate, citrate, sulphite, sulphide and phosphate. Sulphide produced a turbidity, and both sulphite and phosphate produced serious interference. No interference was observed from cyanide or thiocyanate and the effect of fluoride, oxalate and citrate was a very slight reduction in sensitivity. The slight effect of fluoride was readily overcome by addition of excess of borate. Because both sulphide and sulphite would not survive the normal fusion procedure by which niobium is brought into solution, it may be said that the only serious anionic interference is that from phosphate.

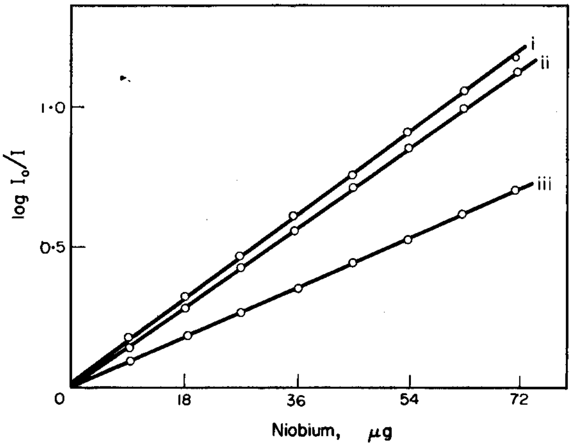

FIG. 5.—Comparison of calibration curves:
(*i*) 4-cm cuvettes; 550 mμ; 10 ml of $10^{-3}M$ PAR; 5 ml of pH 5·8 buffer + x ml of $10^{-4}M$ Nb^V solution/100 ml; 1 hr development time.
(*ii*) As (*i*) but plus 10 ml of 0·02*M* EDTA.
(*iii*) As (*ii*) but plus 5 g of tartaric acid.

DISCUSSION

From the foregoing experiments it will be seen that the reagent 4-(2-pyridylazo)-resorcinol provides a valuable means of determining niobium^V by spectrophotometry. Table III utilises data provided by Sandell[6] and Charlot[7] for the sensitivity of various niobium reagents and supplies comparable values for the PAR reagent and two recently described reagents, Xylenol Orange[5] and tribromopyrogallol.[8]

From this Table it will be seen that the PAR method is, according to reported values, as sensitive as, or slightly more sensitive than the thiocyanate based procedures. We have, however, checked the data reported for the (ether extraction) thiocyanate procedure, and find it to be somewhat more sensitive, with $\epsilon_{385} = 41,000$ and a sensitivity index of 0·0022 μg. In terms of sensitivity, therefore, there is little to choose between the PAR method proposed here and that based on thiocyanate, which has hitherto been the most sensitive method available. In the presence of EDTA plus a large amount of tartrate the sensitivity of the PAR method is reduced by *ca.* 30%, but it is still more sensitive than the oxine and peroxide procedures by a very considerable margin. The addition of a large amount of tartrate is necessary only when tantalum is present. The proposed PAR method is easier to operate than the thiocyanate method in that the time schedule is not critical, and the interferences are considerably less. The freedom from cationic interference in the method recommended here results entirely from the presence of EDTA and, in some cases, cyanide. EDTA would have little masking action in conjunction with the thiocyanate procedure because of the acidity of the medium. In the oxine extraction method, however, we have established that EDTA eliminates nearly all interferences except those of iron^{III} and aluminium. Nevertheless the PAR procedure does not require an extraction and therefore is quicker and easier to apply, as well as being several times more sensitive.

TABLE III. SENSITIVITY OF NIOBIUM REAGENTS

Reagent	Molecular extinction coefficient	Sensitivity index for Log $I_0/I = 0{\cdot}001$, *μg. cm*$^{-2}$
Thiocyanate (acetone addition)	$\epsilon_{383m\mu} = 35{,}000$(b)	0·0024(a)
Thiocyanate (ether extraction)	$\epsilon_{385m\mu} = 32{,}400$	0·0029(a)
8-Hydroxyquinoline	$\epsilon_{345m\mu} = 10{,}000$(b)	0·009(a)
Hydrogen peroxide	$\epsilon_{340m\mu} = 892$(b)	0·110(a)
PAR	$\epsilon_{550m\mu} = 38{,}700$(c)	0·0024(c)
PAR-EDTA ($2 \times 10^{-3}M$)	$\epsilon_{550m\mu} = 35{,}600$(c)	0·0026(c)
PAR-EDTA ($2 \times 10^{-3}M$)-tartrate (5%)	$\epsilon_{550m\mu} = 23{,}500$(c)	0·0039(c)
Xylenol Orange[5]	$\epsilon_{535m\mu} = 16{,}000$	0·0058
Tribromopyrogallol[8]	$\epsilon_{410m\mu} = 6{,}170$	—

(*a*) Sandell's values; (*b*) Charlot's values; (*c*) Our values.

While this manuscript was being prepared for publication, Cheng and Goydish[5] reported on the use of Xylenol Orange for the spectrophotometric determination of Nb^{V}, and independently suggested that PAN and PAR might be applied as reagents. They comment that the colour reaction must be carried out at pH 2.5–3·0 and necessitates heating. However, as demonstrated above, and as already detailed in our previous communication,[1] at pH 5·8–6·4 the PAR colour reaction proceeds normally at room temperature. The Xylenol Orange method appears to necessitate a carefully timed heating procedure; the stability of the colour system is unknown. The complex appears to be weaker than the PAR complex, since EDTA cannot be used as masking agent, though zinc-EDTA may be used successfully; and in addition fluoride and oxalate interfere seriously. The sensitivity ($\epsilon_{535m\mu} = 16{,}000$) is less than that of the PAR method.

In the same issue of the journal in which the Xylenol Orange method is proposed, Ackermann and Koch[8] describe tribromopyrogallol as a reagent for niobium. The latter is considerably less sensitive ($\epsilon_{410m\mu} = 6{,}170$) than the methods described above, but is an interesting addition to the series of reagents based on molecules containing vicinal phenolic groups. In this area we ourselves have also examined reagents containing this grouping, but in addition containing auxochromic groups to aid the colour development and have made a preliminary report on one of these, *viz*, Bromopyrogallol Red.[9] This reagent is less selective than PAR, but, with a molecular extinction coefficient of 60,000 it is the most sensitive (visible-region) reagent for niobium known to us.

Lastly, as noted in our previous communication, PAR may be used in the presence of EDTA as a highly sensitive and selective spot-test for niobium in the presence of over 30 different cations. The concentration of EDTA used in the experiments described in this paper was sufficient to cater for the amount of foreign ions used in the interference studies, but we have confirmed that much higher concentrations of EDTA, *e.g.*, 10 ml of 0·1*M* EDTA/100 ml, may safely be used to mask larger amounts of interfering ions. This results in a slightly lower over-all sensitivity, but the effect is not very pronounced and, provided a similar amount is used in drawing up the calibration curve, it does not cause any difficulty. Care must be exercised to allow for the buffering effects of high concentrations of EDTA or potassium cyanide when used in appreciably larger amounts.

EXPERIMENTAL

Reagents

Niobium solution, $10^{-4}M$: Fuse 0·266 g of Nb_2O_5 (B.D.H.) with 7·5 g of $KHSO_4$. Extract the melt into boiling tartaric acid solution (20 g). Cool and dilute with water to 1 litre. Standardise the solution gravimetrically with *N*-benzoylphenylhydroxylamine. From this stock solution, transfer 50 ml to a beaker, add about 20 g of tartaric acid, and neutralise the solution with sodium hydroxide to pH 5·8–6·4 (using pH paper). Allow the solution to cool, transfer to a l-litre flask, and dilute with water to the mark.

PAR *solution,* $10^{-3}M$; Dissolve 0·2951 g of PAR disodium salt (B.D.H.) in 1 litre of water.

Buffer solution, pH 5·8 (*cf.* Note 1): Dissolve 80 g of ammonium acetate (AnalaR) in water, add 6·5 ml of glacial acetic acid, and dilute to 1 litre.

EDTA *solution,* 0·02*M*: Dissolve 7·445 g of EDTA disodium salt in 1 litre of water.

Apparatus

Unicam SP 600 *spectrophotometer:* Operated from stabilised 12–V transformer.

Cuvettes: 4-cm.

Determination of niobium

Calibration curve: Transfer 1–8 ml of $10^{-4}M$ niobium solution, adjusted to *ca.* pH 5·8, to 100-ml standard flasks, add 10 ml of 0·02*M* EDTA, 10 ml of $10^{-3}M$ PAR, and 5 ml of buffer (Note 2). Allow to stand for about 1 hr, dilute to the mark with water, and measure the optical density, in 4-cm cuvettes at 550 mμ, against a blank containing all the reagents except the niobium solution. The plot of optical density against niobium concentration (9–70 μg of Nb) is a straight line, and passes slightly above the origin.

When tartrate or oxalate is used to mask tantalum or uranium, respectively, a similar amount of the masking agent should be incorporated in the calibration solutions because of the slight effect on the sensitivity of the colour reaction.

Procedure: Determine niobium by the method described for the preparation of the calibration curve. In the presence of tantalum add 5 g of tartaric acid, dissolved in water and nearly neutralised with NaOH, before the addition of PAR, and then proceed as described above. In the presence of vanadium the addition of 1 ml of 0·01*M* $ZnSO_4$ before addition of the EDTA and other reagents is sufficient to mask at least 1 mg of VO_3^-. To mask a similar amount of uranium^{VI} add 10 ml of 0·1*M* ammonium oxalate.

$$1 \text{ ml of } 10^{-4}M \text{ Nb}^{V} \equiv 9{\cdot}29\ \mu g \text{ of Nb.}$$

Note 1: An ammonium acetate buffer is recommended for the analytical procedure rather than the sodium acetate used in exploratory experiments because of its higher buffer index, *ca.* pH 6.

Note 2: The optimum pH range is 5·8–6·4, and care must be taken not to let the pH fall below 5·8 if reproducible results are to be obtained. In most respects it is preferable to work at pH 6·0, where the colour system is less likely to be affected by small fluctuations of pH. The buffer solution may be suitably modified by the addition of slightly less acetic acid.

Acknowledgement—We wish to thank W. T. Elwell and J. M. Sturton of I.M.I. (Kynoch) Ltd., Witton, Birmingham, for checking and verifying the experimental procedure independently in their own laboratory. We are also grateful for their comments on the procedure.

Zusammenfassung—4-(2-Pyridylazo-) resorcin bildet mit Nb^V einen purpurfarbigen 1:1-Komplex mit $\lambda_{max} = 550$ m in acetat- und tartrathaltiger Lösung, der sich für die spektralphotometrische Bestimmung von Nb bis 0,1 ppm eignet. Die Färbung tritt innerhalb 45 Minuten auf und bleibt mehrere Tage lang bestehen; der molare Extinktionskoeffizient bei 550 mμ beträgt 38 700, ist also so groß wie der für das bekannte Rhodanidverfahren, und die Stabilität ist viel besser. Der Einfluß von über 40 Ionen in Mengen von 1000 μg wurde in Gegenwart von Cyanid und ÄDTE untersucht; nur U^{VI}, V^V und Phosphat stören. V kann mit Zn^{II} und U mit Ammonoxalat maskiert werden. 1000 μg Tantal geben eine schwache Färbung mit dem Reagens, aber diese kann durch größeren Tartratzusatz beseitigt werden, wobei die Empfindlichkeit für Nb nur wenig leidet. Die neue Methode verlangt keine Extraktion und ist leichter durchzuführen als die Standardverfahren.

Résumé—L'(azo-2-pyridyl)-4 résorcinol forme un complexe 1/1 coloré en pourpre (λ max. 550 mμ), avec le niobium^V en milieu acétate/tartrate à pH 5,8. Ce complexe convient aux déterminations spectrophotométriques du niobium en quantité inférieure à 0,1 p.p.m. Le colorant se forme en 45 mns et reste stable même après plusieurs jours. Le coefficient d'extinction moléculaire à 550 mμ est de 38.700, soit aussi élevé que celui obtenu par la méthode classique au thiocyanate; de plus la stabilité de de complexe est très supérieur. Les interférences ont été étudiées sur plus de quarante ions dans des teneurs de 1000 μg et en présence d'un excès de cyanure et d'EDTA; seuls l'uranium (VI), le vanadium (V) et les phosphates sont gênants. Le vanadium peut être masqué par les ions zinc et l'uranium au moyen d'oxalate d'ammonium. 1.000 μg de tantale provoquent la formation d'une faible coloration avec le réactif, mais celle-çi peut être façilement éliminée par addition de fortes quantités de tartrate qui ne provoque qu'une faible diminution de la sensibilité de la réaction du niobium. Cette méthode nouvelle ne nécessite pas une extraction et présente une plus grande facilité d'emploi que les procédés standard.

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

SIMULTANEOUS POTENTIOMETRIC DETERMINATION OF VANADIUM^{V} AND URANIUM^{VI} (OR MOLYBDENUM^{VI}) IN MIXTURES

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Summary—The formal redox potential of the V^{V}/V^{IV} couple has been determined in a medium of varying phosphoric acid concentration. Potentiometric procedures have been developed for the simultaneous titrimetric determination of vanadium^{V} and uranium^{VI} (or molybdenum^{VI}) in mixtures, using iron^{II} as a reductimetric reagent in $12M$ phosphoric acid. Two breaks in potential are obtained, the first corresponding to the complete reduction of vanadium^{V} to vanadium^{IV} and the second to the simultaneous reduction of vanadium^{IV} to vanadium^{III} and uranium^{VI} to uranium^{IV} (or molybdenum^{VI} to molybdenum^{V}). Manganese^{II} and tungsten^{VI} do not interfere. These procedures have definite advantages over those involving titanium^{III}, tin^{II} and chromium^{II}.

In previous parts of this series Gopala Rao and Sagi[1,2] reported on the use of iron^{II} in a strong phosphoric acid medium as a new reductimetric reagent for the direct titration of uranium^{VI} and molybdenum^{VI}. Subsequently, Gopala Rao and Dikshitulu[3] used this reagent for the potentiometric titration of vanadium^{V} and observed two distinct breaks in potential in $12M$ phosphoric acid, the first corresponding to the reduction of vanadium^{V} to vanadium^{IV} and the second to the further reduction of vanadium^{IV} to vanadium^{III}.

The formal redox potentials of the U^{VI}/U^{IV}, Mo^{VI}/Mo^{V} and V^{IV}/V^{III} couples[1,2,3] have nearly the same value in $12M$ phosphoric acid medium, but they are lower than the formal redox potential of the V^{V}/V^{IV} couple which is reported in this publication. It is obvious, therefore, that when a mixture of vanadium^{V} and uranium^{VI} (or molybdenum^{VI}) is titrated with iron^{II} in a $12M$ phosphoric acid medium, two breaks in potential may be expected, the first corresponding to the reduction of vanadium^{V} to vanadium^{IV} and the second to the simultaneous reduction of vanadium^{IV} to vanadium^{III} and uranium^{VI} to uranium^{IV} (or molybdenum^{VI} to molybdenum^{V}). In view of the fact that these elements often occur together, the potentiometric titration of vanadium^{V} in mixture with uranium^{VI} (or molybdenum^{VI}) is now attempted.

DETERMINATION OF FORMAL REDOX POTENTIAL OF V^{V}/V^{IV} COUPLE IN MEDIA OF VARYING PHOSPHORIC ACID CONCENTRATION

Apparatus and reagents

The apparatus employed, the preparation of exactly $0.05N$ solutions of vanadium^{V} and vanadium^{IV} and the source of the syrupy phosphoric acid and its standardisation are as described previously.[3]

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* Part III: see reference 3.

Procedure

Take 5.0 ml each of the exactly 0.05*N* solutions of vanadium^{V} and vanadium^{IV} in a 50-ml calibrated flask and enough phosphoric acid is added to give the desired strength when made up to 50 ml. The mixture is then diluted to about 48 ml and allowed to cool to room temperature. After the mixture attains the room temperature, the volume is finally made up to 50 ml. The mixture is then carefully transferred to a 150-ml Pyrex beaker which is kept in a thermostat maintained at 28°. A bright platinum rod is used as the indicator electrode. The potential of the mixture is read against a saturated calomel electrode. Steady potentials are obtained immediately and there is no drift in potential with time. The mixture is not kept under inert atmosphere because such a precaution was found unnecessary. The platinum electrode is kept in concentrated hydrochloric acid when not in use and the electrode is heated to redness with a spirit lamp before each potential determination. It is obvious from the procedure described above that the mixed solution in all determinations contains 0.025*M* sulphuric acid (from the vanadium^{IV} solution) in addition to the phosphoric acid. The potentials obtained in a medium of varying phosphoric acid concentration are given in Table I. They are not corrected for the liquid junction potential.

TABLE I—FORMAL REDOX POTENTIALS OF V^{V}/V^{IV} COUPLE IN A MEDIUM OF VARYING PHOSPHORIC ACID CONCENTRATION
(Total vanadium concentration = 0.01*M*; temperature: 28°)

Concentration of phosphoric acid, *M*	Formal redox potential (N.H.E.), *V*
0.25	0.890
0.50	0.920
1.00	0.956
1.25	0 960
2.50	1.007
3.75	1.042
5.00	1.075
7.50	1.134
10.00	1.186
12.00	1.210

The data presented in Table I are shown graphically in Fig. 1.

POTENTIOMETRIC TITRATION OF A MIXTURE OF VANADIUM^{V} AND URANIUM^{VI}

A perusal of the literature shows that the reductimetric methods currently available for the determination of both uranium^{VI} and vanadium^{V} in a mixture are very few. Thus, Khopin and Kaufmann[4] determined vanadium^{V}, iron^{III} and uranium^{VI} in a mixture using titanium^{III} as reductant. The vanadium^{V} was titrated with a 0.05–0.1*N* titanium^{III} solution using a mixed solution of potassium hexacyanoferrate$^{(III)}$ and iron^{III} as indicator. Iron^{III} was titrated with titanium^{III} in another aliquot of the solution by the method of Knecht and Hibbert,[5] potassium thiocyanate being used as indicator, while uranium^{VI} was determined in a third aliquot of the solution by titration with titanium^{III} using Neublau G(c) as indicator.

Evidently this method is tedious because it requires three separate titrations. Nikolaeva[6] stated that the potentiometric titration of a mixture of vanadium^{V} and uranium^{VI} with chromium^{II} (in solutions which are 4*N* in hydrochloric or sulphuric acid) in a carbon dioxide atmosphere, gives two potential breaks; the first break corresponds to the reduction of vanadium^{V} to vanadium^{IV} and the second to the simultaneous reduction of uranium^{VI} to uranium^{IV} and vanadium^{IV} to vanadium^{III}.

The above methods suffer from the disadvantage that the reductants used, namely, titanium^{III} and chromium^{II}, need special storage conditions and an elaborate apparatus. Furthermore, titrations with these reductants must be made in an inert atmosphere. Because the new reagent, iron^{II} in a strong phosphoric acid medium, is free from these defects, the potentiometric titration of a mixture of vanadium^{V} and uranium^{VI} using this reagent should be advantageous.

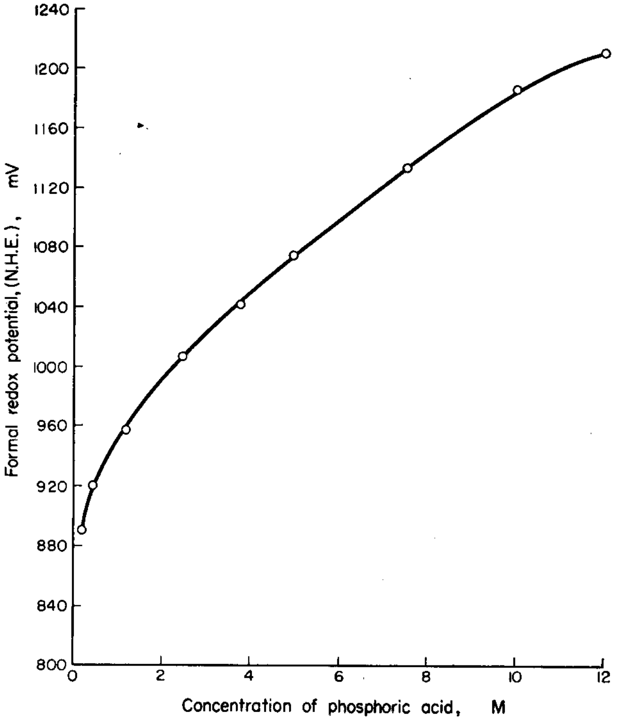

FIG. 1—Formal redox potential of V^{V}/V^{IV} couple in a medium of varying phosphoric acid concentration.

Reagents

The preparation and standardisation of a $0.1N$ solution of uranium^{VI} in $1N$ sulphuric acid[1] and of $0.1N$ solutions of vanadium^{V} and iron^{II}[8] are as described previously.

Syrupy phosphoric acid: B.P. grade acid (Albright and Wilson Limited, Birmingham, England) has been employed in this investigation.

Procedure

Take 0.5–3.0 ml of vanadium^{V} solution and 0.5–3.0 ml of uranium^{VI} solution in a beaker and mix with 45–50 ml of syrupy phosphoric acid. The mixture is then titrated with standard $0.1N$ iron^{II} solution using the potentiometric assembly described previously.[8] The first break in potential has been found to correspond to the reduction of vanadium^{V} to vanadium^{IV} and the second to the simultaneous reduction of uranium^{VI} to uranium^{IV} and vanadium^{IV} to vanadium^{III}. Satisfactory results are obtained even when the ratio of vanadium^{V} to uranium^{VI} is varied within wide limits; but, if the concentration of phosphoric acid is less than $12M$, a satisfactorily break in potential is not obtained at the second end-point. A typical titration curve is shown in Fig. 2. During the titration, the potential is established immediately after each addition of iron^{II} solution until the first break in potential is obtained; the potential at the first break shows considerable drift and becomes reasonably stable only after 7–8 min. The potential jump is about 150 mV/0.04 ml of $0.1N$ iron^{II} solution. After the first break, the potentials attain reasonably steady values only after waiting for 3 min after each addition of iron^{II} solution. The break in potential at the second end-point is about 80 mV/0.04 ml of

0.1*N* iron^{II} solution. Typical results presented in Table II show that in a simultaneous determination of vanadium and uranium, the error for vanadium varies from 0.4 to 0.6% and that for uranium varies from 0.5 to 1.0%.

TABLE II

Amount of vanadium^V, *mmoles*		Amount of uranium^{VI}, *mmoles*	
Taken	Found	Taken	Found
0.0560	0.0558	0.1015	0.1010
0.0834	0.0829	0.1573	0.1562
0.1098	0.1093	0.0995	0.1005
0.2186	0.2198	0.0503	0.0498
0.2357	0.2345	0.0353	0.0350
0.2747	0.2735	0.1244	0.1253

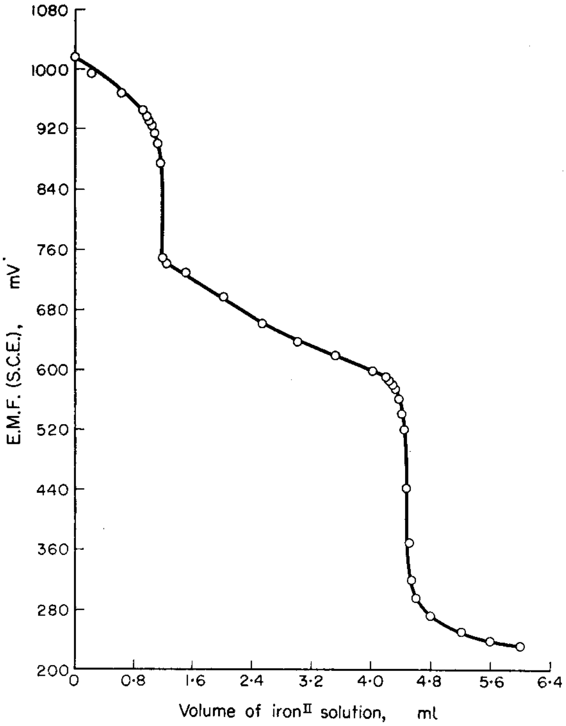

FIG. 2.—Potentiometric titration of a mixture of 0.1098 mmole of vanadium^V and 0.0995 mmole of uranium^{VI} with iron^{II} in a strong phosphoric acid medium.

Interferences

Manganese^{II} does not interfere. Tungsten^{VI} gives a white precipitate but it does not interfere in the titration.

The method now developed is likely to be of considerable use in the analysis of uranium minerals like carnotite and uranite.

POTENTIOMETRIC TITRATION OF A MIXTURE OF VANADIUM^{V} AND MOLYBDENUM^{VI}

Trzebiatowski[7] carried out the simultaneous determination of vanadium^{V} and molybdenum^{VI} by potentiometric titration at 30–40° (in a medium containing 30–40% sulphuric acid by volume), using tin^{II} chloride as the reductimetric reagent. After the first break in potential corresponding to the reduction of vanadium^{V} to vanadium^{IV} was obtained, enough sulphuric acid was added to the reaction mixture so that it still contained 35–40% of acid by volume at the second break in potential. The mixture was then heated to 90–100° and the titration with tin^{II} chloride continued; the second potential break corresponded to the simultaneous reduction of vanadium^{IV}

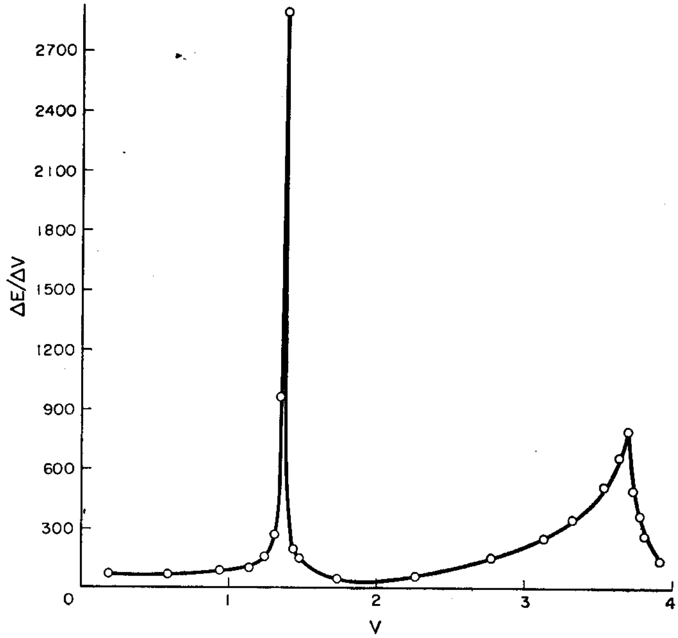

FIG. 3.—Potentiometric titration of a mixture of 0.2746 mmole of vanadium^{V} and 0.1766 *mmole* of molybdenum^{VI} with iron^{II} in a strong phosphoric acid medium.

TABLE III

Amount of vanadium^{V}, *mmole*		Amount of molybdenum^{VI}, *mmole*	
Taken	Found	Taken	Found
0.1170	0.1181	0.4396	0.4370
0.1538	0.1549	0.3873	0.3900
0.1593	0.1604	0.4134	0.4176
0.2900	0.2884	0.3721	0.3749
0.2955	0.2939	0.3473	0.3459
0.3692	0.3681	0.1544	0.1544

to vanadium^{III} and molybdenum^{VI} to molybdenum^{V}. Flatt and Sommer[8] titrated vanadium^{V} and molybdenum^{VI} potentiometrically in a 15% sulphuric acid medium at 90° using chromium^{II} sulphate as the reductant. The first potential break corresponded to the reduction of vanadium^{V} to vanadium^{IV} and the second to the simultaneous reduction of vanadium^{IV} to vanadium^{III} and molybdenum^{VI} to molybdenum^{V}. These methods using tin^{II} and chromium^{II} are inconvenient, firstly because the titrants require special storage conditions and secondly because the titrations have to be carried out at 90° in an inert atmosphere. In view of these inconveniences, the potentiometric titration of a mixture of vanadium^{V} and molybdenum^{VI} in a strong phosphoric acid medium with iron^{II} should be a distinct improvement.

Reagents

The preparation and standardisation of a 0.1*N* molybdenum^{VI} solution[2] and of a 0.1*N* vanadium^{V} solution and a 0.2*N* iron^{II} solution[3] are as described previously.

Procedure

Take 0.5–4.0 ml of vanadium^{V} solution and 0.5–4.0 ml of molybdenum^{VI} solution in a beaker and mix with 40–50 ml of syrupy phosphoric acid. The mixture is then titrated with standard 0.2*N* iron^{II} solution using the potentiometric assembly described previously.[3] During the titration it has been observed that the first break in potential corresponds to the reduction of vanadium^{V} to vanadium^{IV}; the second break in potential corresponds to the simultaneous reduction of vanadium^{IV} to vanadium^{III} and molybdenum^{VI} to molybdenum^{V}. Satisfactory results are obtained even when the ratio of vanadium^{V} to molybdenum^{VI} is varied within wide limits. The concentration of phosphoric acid should be 12*M* at the second end-point, otherwise the break in potential is too small to be located precisely. A typical titration curve is given in Fig. 3. The break in potential at the first end-point is about 150 mV/0.04 ml of 0.2*N* iron^{II} solution. At the second end-point, the break in potential will be of the order of only 30 mV/0.04 ml of 0.2*N* iron^{II} solution; hence, it is advisable to plot $\Delta E/\Delta V$ *vs.* V to locate the end-points. Some typical results are presented in Table III.

Interferences

Manganese^{II} does not interfere. Tungsten^{VI} gives a white precipitate during the course of the titration but it does not interfere.

Zusammenfassung—Das formale Redoxpotential des Systems V^{V}/V^{IV} wurde in einer Lösung variabler Phosphorsäurekonzentration bestimmt. Titrimetrische Verfahren für die gleichzeitige Bestimmung von V^{V} und U^{VI} oder Mo^{VI} mit Fe^{II} als Reagens in 12m Phosphorsäure wurden entwickelt. Es treten zwei Potentialsprünge auf, der erste für die vollständige Reduktion von V^{V} zu V^{IV}, der zweite für die gleichzeitige Reduktion von V^{IV} zu V^{III} und U^{VI} zu U^{IV} oder Mo^{VI} zu Mo^{V}. Mn^{II} und W^{VI} stören nicht. Diese Methode hat Vorteile gegenüber denen mit Ti^{III}, Sn^{II} und Cr^{II}.

Résumé—Le potentiel redox défini du couple V^{V}/V^{IV} a été déterminé en milieu avide phosphorique à des concentrations variées. Développement de certains procédés de titrage pour la détermination simultanée du vanadium^{V} et de l'uranium^{VI} (ou du molybdène^{VI}) en mélange, utilisant le fer^{II} comme agent réducteur en solution phosphorique à 12 M. On obtient deux cassures dans la courbe de potentiel, la première correspondant à la réduction complète du vanadium^{V} en vanadium^{IV}, et la seconde à la réduction simultanée du vanadium^{IV} en vanadium^{III} et de l'uranium^{VI} en uranium^{IV} (ou du molybdène^{VI} en molybdène^{V}). Le manganèse^{II} et le tungstène^{VI} ne sont pas gênants. Cette méthode présente des avantages marqués sur celles faisant intervenir le titane^{III}, l'étain^{II} et le chrome^{II}.

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SEMI-AUTOMATIC DETERMINATION OF CALCIUM AND MAGNESIUM HARDNESS IN WATER

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Summary—A photometric method is described for the determination in a single titration of both calcium and magnesium hardness in waters using only one indicator. The method involves the addition of Eriochrome Black T to the solution containing calcium and magnesium buffered to pH 10, followed by titration with EDTA. The course of the titration is followed on a simple semi-automatic apparatus which is described. The complete titration curve obtained from a potentiometric recorder shows two distinct end-points; this permits the determination of both calcium and magnesium from a single titration.

INTRODUCTION

THE use of photometric titrations[1–5] has increased considerably over the last few years and already there are quite a number of commercial instruments[6–7] available both for laboratory and plant use. One of the main applications of such instruments, however, has been in the determination of water hardness by the well known complexometric titration procedure using Eriochrome Black T as indicator.[8]

A simple instrumental method for the determination of hardness in softened waters was required to replace the present EDTA/Erio T visual titration procedure and to eliminate the human element in detection of the end-point. The method needed to be only semi-automatic, because automatic sampling and addition of reagents was not required. Also, because the method was intended for plant use it had to be simple to operate and to require a minimum of attention.

Because the commercial instruments available did not entirely meet the requirements of the plant, *e.g.*, they were either too costly or too insensitive, *etc.*, it was considered worthwhile to look into the possibility of developing a relatively simple semi-automatic instrument in our own laboratories, which could be used for the determination of hardness over the range 0·2–3 ppm.

The majority of the photometric titrators described in the literature have been modifications of commercial spectrophotometers. Such alterations, however, limit the usefulness of an otherwise general laboratory instrument.

Agazzi and Bond[9] have described a simple apparatus for photometric titrations consisting of a photo-tube and light source enclosed in separate glass tubes which can be immersed in the solution to be titrated. It was considered that with a number of modifications, this design, used in conjunction with a titrant delivery system and a recorder,[10] could be adapted for the determination of hardness in water. Such an arrangement would enable the complete titration curve to be recorded and would

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allow the operator to determine the hardness value merely by measuring a distance on the chart.

In addition to the determination of total hardness, the possibility of determining calcium also from the same titration was considered. Such a method would have a useful application in the analysis of raw waters when it is often necessary to determine both calcium and magnesium hardness.

During preliminary tests it was found that when a solution containing calcium and magnesium, buffered to pH 10, was titrated photometrically with EDTA using Erio T as indicator, a curve with two end-points was obtained. It was only after the work described in this paper had been completed that a paper by Flaschka and Sawyer[11] appeared in which a similar titration was reported but with the use of a different indicator. These authors describe a submicro method for the determination of both calcium and magnesium by photometric titration with EDTA using Calmagite as indicator. They also carried out a number of tests using Erio T but the results obtained were not very satisfactory and they abandoned the use of this indicator in favour of the more stable dye Calmagite.

As far as the author is aware, therefore, a satisfactory method for the determination of both calcium and magnesium in the same solution using the indicator Erio T has never been reported in the literature.

This paper describes the use of a simple semi-automatic apparatus for carrying out photometric titrations and its application to the determination of both calcium and magnesium hardness by evaluation of a single titration curve.

The apparatus, as it stands, is not intended as a plant instrument. It is considered, however, that it would be a relatively easy matter to design an instrument suitable for plant operation using as a basis the apparatus described here.

EXPERIMENTAL

Apparatus

The apparatus used consists of four essential parts—(1) an injection delivery system for delivering titrant at a definite rate, (2) a phototube and light source assembly, (3) a measuring circuit for measuring the potential of the phototube output, and (4) a recorder.

The phototube, light source and measuring circuit were constructed as a laboratory prototype from readily available materials but these could be varied without loss of accuracy.

1. *Injection delivery system.* This consists of a hypodermic syringe, usually 10 ml, the plunger of which is driven at a constant rate by means of a slow injection apparatus with a plunger drive speed of 1 inch in 10 min.

The injection apparatus, Model F 130, is manufactured by C. F. Palmer Ltd., London, England. The outlet of the syringe is joined, via a three-way tap, to a short length of narrow-bore polythene tubing, the end of which is attached to a capillary jet for insertion in the solution to be titrated. The other limb of the three-way tap is joined via polythene tubing, to a reservoir containing EDTA solution. This arrangement facilitates easy filling of the syringe. Using a 10-ml syringe the delivery rate of EDTA solution is approximately 0·6 ml/min.

2. *Phototube and light source assembly.* The unit shown schematically in Fig. 1 consists of two glass tubes, one housing the phototube and the other the light source. The glass tubes are inserted through holes in a Tufnol plate and held in place by two rubber rings and a glass spacer fused to both tubes as shown in Fig. 1.

The light source is a small 12-V, 2·2-W bulb screwed into a socket which is attached to a Paxolin tube (or similar material). A short brass tube with a small hole in it and closed at one end, is placed over the bulb and positioned so as to direct the light on the phototube. The whole assembly is inserted into a glass tube closed at one end and fitted with a B.19 glass joint at the other.

The phototube unit consists of a Mullard cadmium sulphide cell (Type ORP.61) placed inside a length of 18/8/Ti alloy steel tubing and fixed in position with Faraday's wax so as to protrude from the lower end. A short length of aluminium tubing with a small hole near the closed end is placed over the phototube and metal tubing and positioned so that the hole is directly opposite the sensitive part of the cell.

In order to provide light of the required wavelength, a small red filter (Kodak 608) approximately 1 cm^2, is positioned over the hole in the aluminium tube and held in place with a suitable cement. The whole unit is then inserted into a glass tube as shown in Fig. 1.

3. *Measuring circuit.* A circuit diagram for the photometric apparatus is shown in Fig. 2. Power for the lamp is obtained from the 12-V secondary of the constant voltage transformer via a variable resistor A which enables the light intensity to be adjusted. Two separate d.c. supplies of approximately 230 V are provided from the stabilised 12-V a.c. by two identical circuits consisting of a transformer, rectifier and an 8-microfarad reservoir condenser. The first supplies current to the ORP 61, the output meter and the 200-Ω resistor which are in series. Opposing this is the current supplied from the second circuit via a 1-MΩ potential divider and a 100,000-Ω series resistor. The standing current in the photocell can be backed off by adjustment of the 1-MΩ resistor so that the meter shows maximum deflection during the titration. When the indicator colour changes at the end-point from red to blue, the red filter prevents light passing and the meter deflection drops to zero.

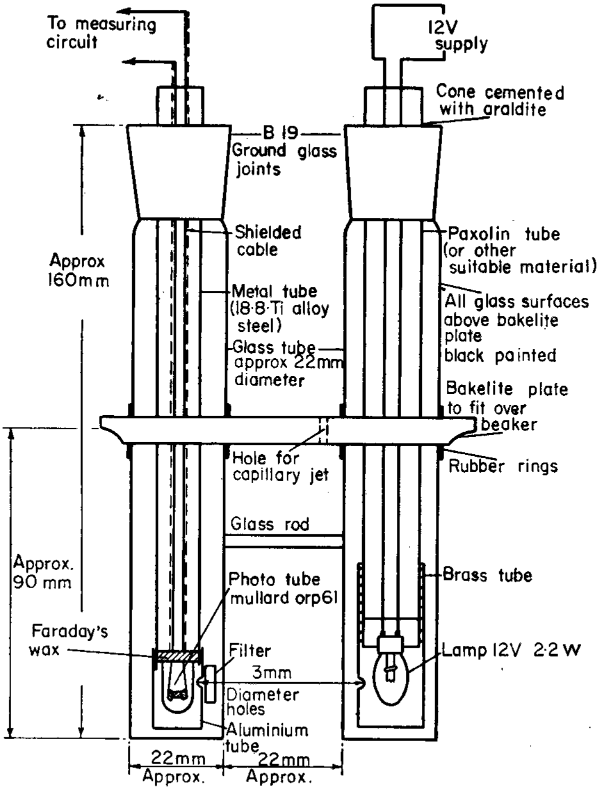

FIG. 1.—Light source and phototube assembly.

Provision is made for a recorder output by placing a 200-Ω resistance in series with the meter. The potential difference developed across this resistance is fed to the recorder terminals via a filter circuit for reducing the a.c. ripple and consisting of a 200-Ω resistor and 500-microfarad condenser. The two diodes in the circuit are to prevent damage to the movement of the meter by excessive current.

There is, of course, nothing unusual about the measuring circuit given here and any other high impedance measuring device would also suffice.

4. *Recorder.* A Honeywell Brown strip chart recorder modified to give 0-20 mV full-scale deflection was used. The chart speed on the recorder was 30 inch/hr.

Reagents

Buffer solution (pH 10): Dissolve 67·5 g of ammonium chloride in water, add 570 ml of aqueous ammonia (sp. gr. 0·88) and dilute to 1 litre with water.

Indicator solutions: Dissolve 0·5 g of Eriochrome Black T and 0·4 g of hydroxylamine hydrochloride in 100 ml of methanol.

0·002M EDTA solution: Dissolve 0·7440 g of the di-sodium salt of ethylenediaminetetra-acetic acid (previously dried at 80° for 1 hr) in water and dilute to 1 litre with water.

Standard calcium carbonate solution: 1 ml $\equiv$ 0·1 mg of $CaCO_3$.

Procedure

Transfer a volume of sample, containing not more than about 1·5 mg of hardness (as $CaCO_3$) to a 500-ml beaker (painted black). For hardness values ranging from 0-6 ppm, 250 ml of sample is a suitable amount. Dilute, if necessary, to 250 ml with distilled water and add 2·0 ml of buffer solution and 1·0 ml of indicator solution. Place the beaker on a magnetic stirrer and adjust the speed of stirring so that the turbulence cone does not obstruct the light path. Immerse the phototube and light source assembly, together with the delivery jet from the hypodermic syringe in the solution. Switch on the apparatus and recorder and turn the zero adjustment until the pen of the recorder is at a suitable position on the chart. When the pen is passing a convenient zero line, switch on the slow injection motor driving the plunger of the syringe containing EDTA and mark the position on the chart. Allow the titration to proceed until it is evident fron the recorder trace that both end-points have been passed. Carry out a blank determination using distilled water in place of the sample.

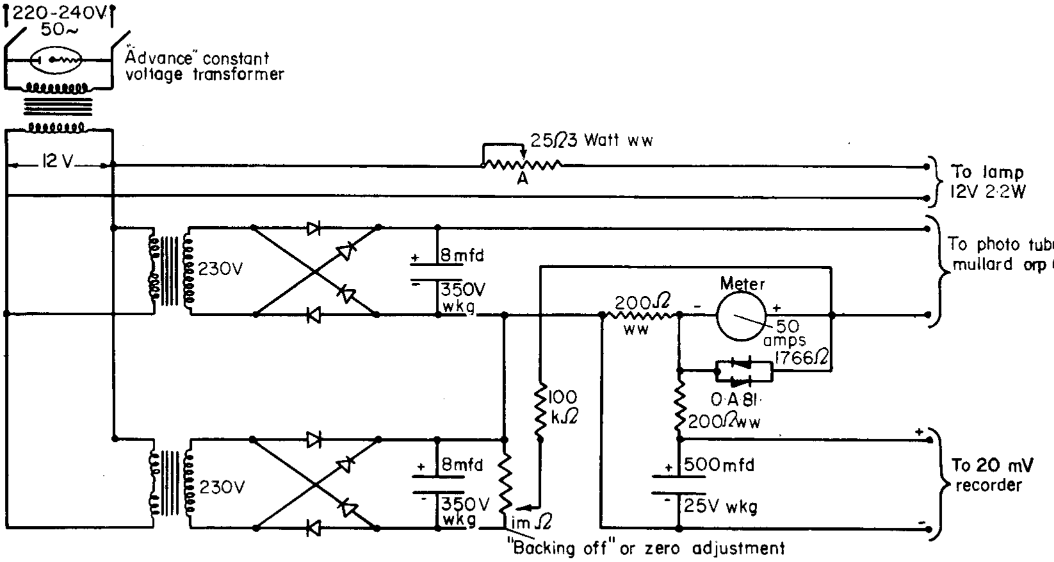

FIG. 2.—Circuit diagram for photometric titration apparatus.

Standardisation

Standardise the apparatus by measuring into separate 500-ml black-painted beakers containing 250 ml of distilled water, 2·5, 7·5 and 12·5 ml of standard calcium solution, then proceeding as described previously. Calculate the mean factor, *i.e.*, mg of hardness (as $CaCO_3$)/mm = F, Hence:

$$\text{Calcium hardness in sample (as } CaCO_3) = \frac{1000 \times B \times F}{V} \text{ ppm}$$

and

$$\text{Total (calcium plus magnesium) hardness in sample (as } CaCO_3) = \frac{1000 \times A \times F}{V} \text{ ppm}$$

where A = distance (mm) to the total end-point,

B = distance (mm) to the calcium end-point,

and V = volume of sample (ml).

RESULTS

Determination of calcium and magnesium in waters of low hardness content

The apparatus was first calibrated with water solutions to which known amounts of calcium and magnesium, or calcium alone, had been added. The range tested covered 0–5 ppm. of total hardness (calculated as $CaCO_3$) and the results obtained are shown in Table I. These results clearly show that, over the range considered, there is a linear relationship between ppm of hardness and distance on the chart.

TABLE I.—CALIBRATION DATA FOR TOTAL HARDNESS

0–5 p.p.m.[a]			0–1 p.p.m.[b]		
Total hardness (as $CaCO_3$) added, *ppm*	Distance on chart (less blank), *mm*	Factor *ppm/mm*	Total hardness (as $CaCO_3$) added, *ppm*	Distance on chart (less blank), *mm*	Factor, *ppm/mm*
0·1	3·0	0·033	0·1	5·0	0·020
0·2	6·0	0·033	0·2	10·0	0·020
0·5	13·0	0·038	0·3	16·0	0·019
1·0	28·5	0·035	0·4	20·0	0·020
1·0 {0·5 ppm Ca (as $CaCO_3$) + 0·5 ppm Mg (as $CaCO_3$)}	29·5 28·0	0·034 0·036	0·5	26·5	0·019
			0·6	31·0	0·019
			0·7	38·0	0·018
			0·8	40·5	0·020
			0·9	47·0	0·019
			1·0	51·5	0·019
1·0 {0·2 ppm Ca (as $CaCO_3$) + 0·8 ppm Mg (as $CaCO_3$)}	27·0	0·037			
1·0 {0·8 ppm Ca (as $CaCO_3$) + 0·2 ppm Mg (as $CaCO_3$)}	27·0	0·037			
1·5	41·0	0·037			
2·0	56·0	0·036			
2·5	68·0	0·037			
3·0	81·0	0·037			
3·0 {1·5 ppm Ca (as $CaCO_3$) + 1·5 ppm Mg (as $CaCO_3$)}	83·5 83·5	0·036 0·036			
3·5	95·5	0·037			
4·0	109·0	0·037			
4·5	123·0	0·037			
5·0	138·0	0·036			

[a] Using 0·002*M* EDTA

[b] Using 0·001*M* EDTA.

Typical recorder traces are shown in Figs. 3 and 4. It can be seen from Fig. 4 that for solutions containing both calcium and magnesium the shape of the recorder trace is different from that obtained when only calcium is present. The titration curve shows two end-points, the first one being due to calcium and the second due to the total of calcium and magnesium. Although the calcium end-point is not as sharp as the total end-point, nevertheless reasonably precise results can be obtained by measuring the distance from the start of the titration to the point of intersection of the lines DE and FG at X (Fig. 4).

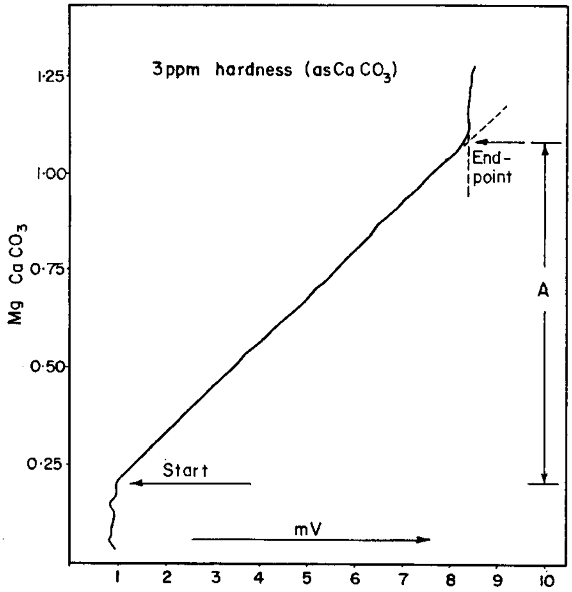

FIG. 3.—Typical recorder trace with only calcium present.

In order to assess the method, therefore, and determine its accuracy and precision, tests were carried out on water solutions to which had been added known amounts of calcium and magnesium. Determinations were also carried out on actual boiler water samples which had been previously analysed by the usual complexometric procedure.[12] The results obtained are shown in Tables II and III.

These results clearly show, therefore, that the determination of both calcium and magnesium from a single titration is satisfactory and gives good accuracy and precision.

Determination of calcium and magnesium hardness in raw waters

Although at times it is necessary to determine both calcium and magnesium hardness, as distinct from total hardness, in softened waters, it is not a frequent request in most laboratories. It was considered, therefore, that the photometric method for the determination of both calcium and magnesium on the same sample of water would have a wider application in the examination of industrial raw or process waters, in which it is often necessary to determine both elements.

This being the case, it was decided to test the photometric titration method on a number of raw waters which had been obtained from different localities. These samples were also analysed for calcium and magnesium hardness by the usual chemical

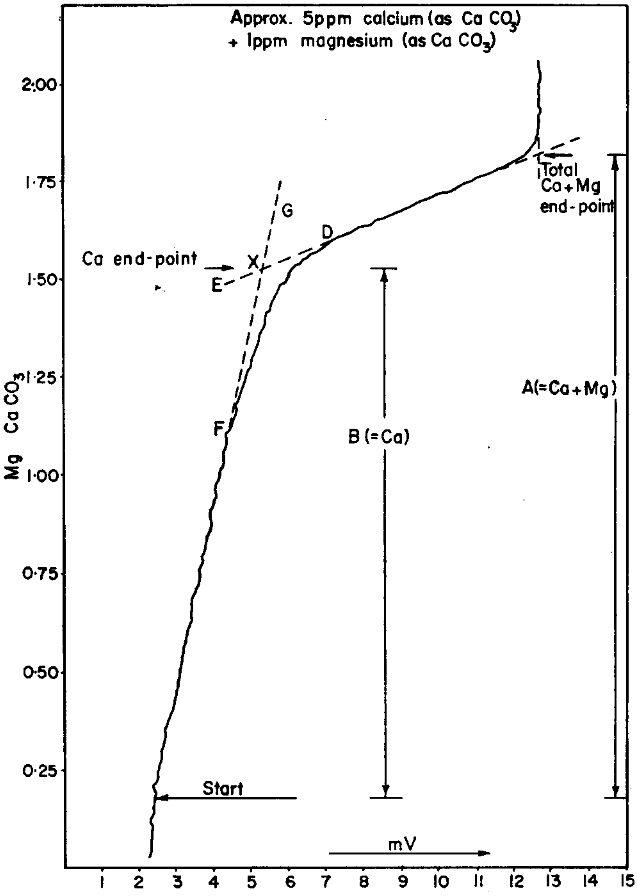

FIG. 4.—Typical recorder trace with both calcium and magnesium present.

TABLE II.—ACCURACY AND PRECISION OF PHOTOMETRIC TITRATION METHOD FOR DETERMINATION OF LOW HARDNESS CONTENTS

[p.p.m. w/v hardness (as $CaCO_3$)]

Total hardness				Calcium hardness		Magnesium hardness	
Added	Found	No. of detns.	Std. devn.	Added	Found	Added	Found
0·40	0·40	10	0·026	—	—	—	—
3·00	2·98	10	0·075	—	—	—	—
2·5	2·5	1	—	1·3	1·3	1·2	1·2
2·7	2·6	1	—	1·9	1·8	0·8	0·8
2·9	2·8	1	—	2·5	2·4	0·4	0·4
7·9	8·3	1	—	6·3	6·8	1·6	1·5

methods, *i.e.*, Murexide was used for the calcium titration and Erio T for the total calcium and magnesium titration. All determinations were made in random order over a period of about 3 weeks. Frequent checks were also carried out on the calibration and it was found to remain almost unchanged throughout the tests. The results obtained are shown in Table IV.

TABLE III.—DETERMINATION OF TOTAL HARDNESS IN BOILER WATER SAMPLES
[ppm hardness w/v (as $CaCO_3$)]

Sample No.	Total hardness found by usual chemical method	Total hardness found by photometric titration method
1	0·2	0·14
2	0·2	0·23
3	0·5	0·47
4	0·6	0·54
5	0·8	0·83
6	2·6	2·50

TABLE IV.—DETERMINATION OF CALCIUM AND MAGNESIUM HARDNESS IN RAW WATERS[a]
[ppm w/v hardness (as $CaCO_3$)]

	Total hardness			Calcium hardness			Magnesium hardness		
Sample No.	Chemical method	Photometric method Mean[b]	Standard deviation of mean	Chemical method	Photometric method Mean[b]	Standard deviation of mean	Chemical method	Photometric method Mean[b]	Standard deviation of mean
1	36·0	35·7	0·2	21·4	21·2	0·5	14·6	14·5	0·4
2	36·7	36·0	0·4	20·5	19·9	0·2	16·2	16·1	0·3
3	42·4	41·8	0·1	26·3	25·6	0·2	16·1	16·2	0·2
4	42·8	42·3	0·3	26·1	25·4	0·4	16·7	16·9	0·5
5	48·2	47·9	0·3	28·0	27·8	0·6	20·2	20·1	0·5
6	60·1	59·1	0·3	34·3	33·6	0·5	25·8	25·5	0·4
7	61·2	62·7	1·8	50·0	50·7	1·5	11·2	12·0	0·4

[a] All samples were diluted ten times before analysis, the final volume in all cases being 250 ml.

[b] Mean of 6 determinations for samples Nos. 1, 2, 3, 4, 5 and 7; mean of 5 determinations for sample No. 6.

It is evident from Table IV that the results obtained by the photometric titration method compare very favourably with those obtained by the conventional procedure. The slight negative bias in the instrumental results could be caused by a very small error in the calibration, but there are insufficient results to be conclusive on this point. No direct comparison between the precision of the two methods can be made from the results in Table IV, but experience suggests that the precision of the photometric method is at least as good as that of the conventional procedure.

Effect of possible interferences

Because the method might be used in practice for the determination of calcium and magnesium hardness in waters containing small amounts of other metals, the effect of copper, zinc, nickel, *etc.*, on the photometric titration procedure was investigated.

To two solutions containing known amounts of both calcium and magnesium 10 ppm of a number of metals were added separately and the titration carried out in the normal way. The results obtained are shown in Table V.

With iron, nickel, aluminum and copper there appears to be only a negligible interference, if any, at both calcium and total end-points. Zinc is titrated at the total end-point but exhibits only slight interference with the calcium determination, whereas with manganese both end-points are affected.

TABLE V.—EFFECT OF POSSIBLE INTERFERENCES ON THE DETERMINATION OF CALCIUM AND MAGNESIUM BY PHOTOMETRIC TITRATION
[ppm w/v hardness (as $CaCO_3$)]

Metal added (10 ppm)	Metal added calculated as $CaCO_3$	Calcium found		Total found	
		Sample No. 1	Sample No. 2	Sample No. 1	Sample No. 2
Fe^{II}	17·9	53,54	216,208	66,66	379,379
Zn^{II}	15·3	60,59	214,214	81,81	396,399
Ni^{II}	17·0	55,56	216,214	66,66	381,383
Mn^{II}	18·2	77,77	189,189	91,90	388,388
Al^{III}	37·1	55,56	203,205	68,68	379,378
Cu^{II}	15·7	56,55	202,207	67,68	383,378

Sample No. 1: total 66 ppm Ca 55 ppm.
Sample No. 2: total 379 ppm Ca 205 ppm.

With the exception of iron, all of the other metals examined altered the shape of the titration curve, the sensitivity being reduced in the case of nickel, aluminium and copper.

On the other hand, when zinc and manganese were present the sensitivity was increased. The amounts of foreign metals added are, however, vastly in excess of those found in raw waters, which seldom contain as much as 1 ppm of these metals. In the exceptional case, the reagent could be modified to mask the interferences.

Conclusions

It has been shown that both calcium and magnesium hardness can be determined by means of a single titration with EDTA solution using Eriochrome Black T as indicator. The method is free from operator errors because the end-point is detected photometrically and gives results which compare very favourably with those obtained by the more usual methods.

Although the photometric titration apparatus described in this paper proved to be very reliable and completely trouble-free during the 3 or 4 month period in which it was used, it is obviously not suitable in its present form for operation on a plant. It is considered, however, that it could be used as a basis for the development of a simple, compact and inexpensive plant instrument suitable for semi-automatic operation by plant operators.

Acknowledgements—The author is indebted to Mr. S. C. Smith and Mr. C. Crowther of the Research Services Department under whose direction the apparatus was made, and to Mr. M. J. Wicks for helpful discussion and for carrying out most of the experimental work.

Zusammenfassung—Eine photometrische Methode für die Bestimmung von Calcium- und Magnesiumhärte in Wässern mit einer Tritation und nur einem Indikator wird beschrieben. Der auf p_H 10 gepufferten Lösung, die Ca und Mg enthält, wird Eriochromschwarz T zugesetzt, dann wird mit Äthylendiamintetraessigsäure (EDTA) titriert. Ein einfaches halbautomatisches Gerät zur Verfolgung des Titrationsverlaufes wird beschrieben. Die auf einem Potentiometerschreiber aufgezeichnete Titrationskurve zeigt zwei scharfe Endpunkte; aus diesen können Ca und Mg nach nur einer Titration bestimmt werden.

Résumé—Une méthode de dosage photométrique est utilisée au cours d'un dosage unique d'un mélange de calcium et de magnésium en solution aqueuse et par l'emploi d'un seul indicateur. Cette méthode consiste à ajouter de l'Eriochrome noir T à la solution tamponnée à pH 10 et contenant le calcium et le magnésium; on titre ensuite par l'acide éthylène-diamine tétracétique. Le dosage est repesé dans un appareil semi-automatique dont la description est donnée. La courbe complète de dosage obtenue à partir d'un enregistreur potentiométrique montre deux produits équivalents distincts; ceci permet de déterminer le calcium et le magnésium au cours d'un seul dosage.

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SHORT COMMUNICATION

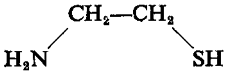
Use of masking agents in chelatometric titrations—II *: β-Aminoethylmercaptan†

(*Received* 24 *December* 1962. *Accepted* 2 *March* 1963)

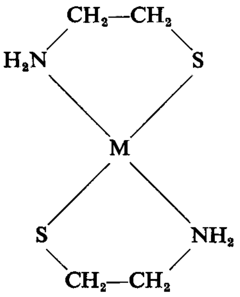
THE proper use of masking agents plays an important role in the practical application of chelatometric titrations, and many selective masking agents have been reported in the literature. Heavy metals are most effectively masked with potassium cyanide, in alkaline media, but this reagent is not widely accepted in routine work because of its extreme toxicity. Therefore, many other masking agents have been proposed to replace potassium cyanide and to attain a different spectrum of selectivity in chelatometric titrations in alkaline media. Among these, reagents such as 1,2-dimercaptopropanol (BAL),[1] 1,2-dimercaptopropanesulphonic acid (Unithiol),[2] thioglycolic acid (TGA)[3] and triethanolamine (TEA),[4] are being successfully used in practical applications.

During the course of our synthesis of new chelating agents, an intermediate product, β-aminoethylmercaptan (AEM), has been isolated. This interesting building block of chelating agents, having amino and mercapto groups as co-ordinating sites, drew our attention to its possible application as a masking agent in chelatometric titrations.

The free base of AEM is a white crystalline solid which is rather unstable and easily oxidised in the air. Its aqueous or alcoholic solution is also not very stable. However, its hydrochloride aqueous solution can be stored for 1 month. Furthermore, the hydrochloride has no objectionable odour of mercaptan and this reagent is not toxic.



(I)



(II)

AEM (I) forms water-soluble chelates with many multivalent metal ions (II) and most of them are sufficiently stable that the metal ions can be masked by AEM against titration with EDTA or with 1,2-diaminocyclohexane-*N,N,N′,N′*-tetra-acetic acid (CDTA).

Because AEM behaves as a bidentate ligand with sulphur and nitrogen as donor atoms, its selectivity is more or less similar to that of BAL, Unithiol and TGA. However, the selectivity of masking with AEM is so different in minor points from the above mentioned masking agents that the use of AEM makes it possible to carry out new selective titrations.

For example, with AEM the titration of alkaline earth metals is possible in the presence of bivalent heavy metals except lead and manganese^{II}. Titration of manganese^{II} is also possible while other heavy metals are masked by AEM.

EXPERIMENTAL

Reagents

β-Aminoethylmercaptan: Free base was prepared by the reaction of ethylene-imine and hydrogen sulphide according to a published procedure[5] with a slight modification.[6] The crude product was

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* Part I: *Japan Analyst*, 1963, **12,** 55.

† Contribution No. 38 from Department of Organic Synthesis, Kyushu University, Japan.

purified by vacuum sublimation, and the purified material stored in an atmosphere of nitrogen. The pure sample is white and melts at 98–99°, but is easily oxidised in the air. The hydrochloride is more stable both in the solid state and in solution. In this investigation a 4% methanol solution of the hydrochloride was used. AEM hydrochloride is now commercially available from Evans Chemetics Inc., New York, U.S.A., and in the later part of our investigation, a sample kindly donated by this company was used without further purification. The purity of the reagent ranged from 97 to 99%.

Buffer solution: A standard composition of aqueous ammonia and ammonium chloride (pH 10).

Erio T indicator solution: Used as a 1% solution in a 3:1 mixture of triethanolamine and methanol.

Solutions of the various cations and of EDTA and CDTA were prepared in 0·01*M* concentrations from reagent-grade chemicals. The strengths of the solutions were determined against primary standard metallic zinc.

TABLE I.—SCREENING TESTS FOR β-AMINOETHYLMERCAPTAN (AEM)

Metal ion	Colour reaction (1)	(2)	(3)	Masking against Erio T
Mg	colourless	red	red	no
Ca	colourless	violet	violet	no
Mn^{II}	colourless	red-violet	red-violet	no
Co	yellow-brown	blue-green	red-violet	yes
Ni	pale orange-brown	blue-green	red-violet	yes
Cu	pale yellow	blue-green	red-violet	yes
Zn	colourless	blue	red	yes
Cd	colourless	blue	red-violet	yes
Hg^{II}	colourless	blue	red	yes
Pb	colourless	blue	violet	yes(not quantitative)
Al	colourless	violet	violet	indicator is blocked
Fe^{III}	pale-brown	red	red	indicator is blocked

(1) Colour reaction observed after adding buffer solution (pH 10) and AEM to the metal ion solution.

(2) Colour reaction observed after adding Erio T indicator to the above solution.

(3) Colour reaction observed after adding buffer solution (pH 10) and Erio T indicator to the metal ion solution.

Preliminary investigation

In order to get a brief estimation of the selectivity of masking by AEM, the following experiments were carried out:

A few drops of a 0·01*M* solution of cation were diluted to about 5 ml. To this 0·5 ml of buffer solution and a few drops of AEM solution were added. A similiar test was carried out in the presence of Erio T indicator with or without adding AEM. The resulting colours of the solutions were compared.

Although this does not always suggest the possibility of masking in the EDTA or CDTA titration of a certain metal, it can be a useful guide in the screening test of masking agents.

The results are shown in Table I, and it was found that cations, except the alkaline earth metals and manganese^{II}, could be masked by AEM. A similiar test was carried out at pH 5 using Xylenol Orange as indicator. However, the stabilities of AEM complexes were found to be insufficient for it to be used as a masking agent under these conditions.

Titration of calcium, magnesium or a mixture of both in the presence of heavy metal ions

To a mixture of 10 ml of a 0·01*M* solution of calcium and/or magnesium and 1–10 ml of 0·01*M* solution of another multivalent metal ion, the appropriate amount of AEM, 3 ml of buffer solution and a few drops of Erio T indicator solution were added. After diluting to 100 ml, the solution was titrated with 0·01*M* EDTA solution.

In the titration of calcium, 0·1 ml of 0·1*M* magnesium-EDTA solution was added along with Erio T indicator solution in order to sharpen the magnesium end-point colour change.

Titration of manganese^{II} in the presence of heavy metal ions

A similar procedure was followed to that for the calcium and magnesium titrations, but about 50 mg of ascorbic acid were added to the sample solution to maintain the manganese in the bivalent state.

RESULTS AND DISCUSSION

Zinc, cadmium and mercury can be masked effectively in the titration of calcium. The end-point colour changes for nickel, copper and cobalt were from red to grey, from red to green and from red to yellow-green, respectively, because these metals form coloured complexes with AEM. However, the end-point could be detected clearly if the concentration in the final solution did not exceed $10^{-3}M$ for nickel and copper and $10^{-4}M$ for cobalt. In the case of lead the masking was not quantitative, even when a large excess of AEM was used.

Masking agent	Alkaline earths	Zn	Cd	Mn^{II}	Cu	Ni	Co	Pb	Hg	Fe^{III}	Al
Aminoethyl-mercaptan		▨	▨		▨	▨	▨	△	▨		
Thioglycolic acid		▨	▨		▨			▨	▨	×	
Potassium cyanide		▨	▨	▨	▨	▨	▨		▨		
Unithiol		▨	▨	▨	×	▨	×	▨	▨	×	
Dimercapto-propanol		▨	▨	×	×	×	×	▨	▨	×	
Triethanol-amine				▨ ^{III}						▨	▨

FIG. 1.—Masking properties of various masking agents in the EDTA titration at pH 10 with Erio T indicator:

//// Metal ions which can be masked,

× Metal ions which form intensely coloured complexes and interfere in the indicator end-point detection,

△ Metal ions which are not quantitatively masked.

The results for magnesium titrations were almost the same as in the case of calcium titrations. However, it was found that zinc and cadmium could only be masked at the $10^{-4}M$ level by AEM (a large excess necessary) in the presence of small amounts of magnesium, although they could be masked successfully when CDTA was employed as a titrant instead of EDTA. These findings are hard to understand from a general knowledge of the stability constants of the complexes involved in the titration solution. A full explanation may be expected after the stability measurements of AEM-metal chelates, now under way, are finished. The end-point was indistinct at the $10^{-3}M$ level of cobalt.

When mixtures of calcium and magnesium were titrated, similar results were obtained to the case of titrating calcium or magnesium alone. However, when the amount of magnesium increased far beyond that of calcium, the masking of zinc or cadmium again became incomplete.

Titrations of manganese were conducted in the presence of ascorbic acid at pH 10 with Erio T as an indicator. Under these conditions zinc and cadmium could be masked if their concentrations were kept at the $10^{-4}M$ level, although the masking became incomplete at the $10^{-3}M$ level. The maximum allowable concentrations for copper, nickel and cobalt, which form coloured complexes, were also found to be the $10^{-4}M$ level in the final solution. Mercury^{II} was reduced to the metallic state by ascorbic acid. Masking of lead was found to be incomplete.

Similar experiments were carried out using CDTA instead of EDTA titrant with a hope of finding any difference in the spectrum of metals being masked. However, almost the same results were obtained for all titrations, with the one exception which has already been pointed out in the titration of magnesium.

The amount of AEM which is necessary to mask a given cation depends not only on the metals to be masked but also on the metal to be titrated. In general, more masking agent was needed in the titration of manganese^{II} than in the titration of calcium or magnesium.

In order to compare the masking ability of AEM with other masking agents which can be used at pH 10, their spectra of metals which can be masked are represented in Fig. 1. As shown in the figure, most of the interfering metals except lead and manganese can be masked by AEM against the EDTA or CDTA titration of the alkaline earth metals. The difference of masking ability between AEM and TGA lies in that nickel and cobalt cannot be masked by TGA. In this point, AEM is a more selective masking agent in the titration of manganese in the presence of other heavy metals. This is also true for other masking agents such as Unithiol and BAL. They are less selective and sometimes form intensely coloured complexes or precipitates. It may not be fair to compare the masking property of AEM with TEA because the latter reagent has been most exclusively used in the masking of manganese^{II}, iron^{III} and aluminium, and has been being employed in combination with other masking agents listed above.

Upon considering the properties of AEM, one may conclude that it is a useful masking agent in the EDTA titration of the alkaline earth metals with Erio T as indicator at pH 10, where moderate amounts of interfering cations can be masked by AEM plus TEA. It is also a useful masking agent in the titration of manganese with Erio T indicator at pH 10 in the presence of other heavy metals. Moreover, AEM is not toxic and its hydrochloride can be stored for many months.

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Summary—The masking properties of β-aminoethylmercaptan (AEM) and its possible use in chelatometric titrations have been studied. AEM has been found to mask selectively at pH 10, many bivalent metals, such as cobalt, nickel, copper, zinc, cadmium and mercury, resulting in the formation of colourless or slightly coloured soluble complexes. Thus it is possible to titrate the alkaline earth metals at pH 10 with Erio T indicator, where moderate amounts of interfering cations are masked by AEM plus triethanolamine. It is also possible to titrate manganese^{II} in the presence of other heavy metals.

Zusammenfassung: Maskierungseigenschaften von β-aminoäthylmercaptan (AEM) und seine Verwendbarkeit bei der chelatometrischen Titration wurden untersucht. AEM tarnt bei pH 10 viele zweiwertige Metalle wie Co, Ni, Cu, Cd, Zn und Hg selektiv unter Bildung farbloser oder schwachfarbiger löslicher Komplexe. So kann man Erdalkalien bei pH 10 mit Erio T als Indikator titrieren, wobei mäßige Mengen störender Kationen mit AEM und Triäthanolamin maskiert werden. Man kann auch Mn (II) in Gegenwart anderer Schwer metalle titrieren.

Résumé—On a fait une étude des propriétés masquantes de l'amino-ethylmercaptan (AEM), et des possibilités de son emploi dans les dosages par chélatométrie. A pH 10 l'AEM masque sélectivement des métaux divalents tels le Co, Ni, Cu, Zn, Cd, et Hg. Il en résulte des complexes solubles incolores ou légèrement colorés. Ainsi il est possible de doser des métaux alcalino-terreux à pH 10 au moyen de l'ériochrome T, en présence de cations gênants qui se trouvent masqués par l'AEM et l'éthanolamine. On peut également doser le Mn (II) en présence d'autres métaux lourds.

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LETTER TO THE EDITOR

Potassium dichromate in strong phosphoric acid medium as a new oxidimetric reagent

SIR,

Gopala Rao and Sagi[1,2] have recently reported that iron^{II} sulphate serves as a powerful reductimetric reagent for the titrimetric determination of uranium^{VI} and molybdenum^{VI} in a strong phosphoric acid medium (11·6*M* to 13·1*M*) with a potentiometric end-point or a visual end-point using methylene blue or thionine as redox indicators. Iron^{II} reduces uranium^{VI} to uranium^{IV} and molybdenum^{VI} to molybdenum^{V} stoichiometrically in these titrations. Gopala Rao and Dikshitulu[3] have observed that iron^{II} reduces vanadium^{IV} to vanadium^{III} and that the reaction can be used as a basis for the potentiometric titration of vanadium^{IV} in a strong phosphoric acid medium. These titrations in strong phosphoric acid medium involve reversal of the normal redox reactions, for it is well known that in dilute aqueous sulphuric or hydrochloric acid media uranium^{IV}, molybdenum^{V} or vanadium^{III} reduces iron^{III}. Gopala Rao and collaborators have shown that this new reductimetric reagent has several advantages over chromium^{II} or titanium^{III}. During these investigations, it has been accidentally observed that the phosphoric acid obtained from one manufacturer gave a pink colour when used as a medium in the titrimetric determination of chromium^{VI} with iron^{II} sulphate. Detailed experiments have now shown that the pink colour is caused by manganese^{III} formed by the reaction of chromium^{VI} with the manganese^{II} present as an impurity in the phosphoric acid. A search of the literature at this stage has revealed that Ingamells[4] has made a somewhat similar observation that manganese^{II} gives manganese^{III} when treated with excess of chromic acid in phosphoric acid medium. We have now been able to establish conditions under which manganese^{II} can be directly titrated with a standard solution of potassium dichromate, with either a potentiometric end-point or a photometric end-point, at room temperature. Cobalt^{II}, nickel^{II}, chromium^{III}, tungsten^{VI}, uranium^{VI}, molybdenum^{VI} and iron^{III} do not interfere in either method of titration. Chloride ion does not interfere in the photometric titration but interferes in the potentiometric titration by preventing the attainment of steady potentials; sulphate ion does not interfere with either method of titration. Perchlorate ion above 1·0*M* concentration interferes with the photometric titration, forming a precipitate with the potassium ions from the potassium dichromate. From the results in Table I, it will be noted that the error of determination is ±0·4% in the potentiometric method for a manganese content of 20–150 mg

TABLE I.—DETERMINATION OF Mn^{II} WITH Cr^{VI} IN STRONG PHOSPHORIC ACID MEDIUM

Potentiometric indication of end-point		Photometric indication of end-point	
Manganese^{II}, *mg*		Manganese^{II}, *mg*	
Taken	Found	Taken	Found
28·42	28·45	4·998	5·054
31·62	31·52	6·735	6·782
40·31	40·31	7·650	7·643
48·28	48·07	8·678	8·624
55·34	55·34	8·802	8·843
62·53	62·75	9·716	9·730
70·65	70·53	10·09	10·15
72·38	72·30	13·31	13·34
108·1	108·3	17·14	17·12
116·3	116·5		
131·7	131·6		
145·1	144·7		

per 50 ml; and ±1·0% in the photometric titration for a manganese content of 5–18 mg per 40 ml.

It will be observed that the method now developed for the determination of manganese^{II} is much more convenient and rapid than the numerous methods proposed from time to time during the last century. Potassium dichromate is a primary reagent of high purity, giving very stable solutions in water. The titration of manganese^{II} in phosphoric acid medium can be carried out at room temperature without the need for any inert atmosphere. Guaranteed Reagent phosphoric acid of E. Merck or AnalaR grade of B.D.H. have been found very satisfactory as titration media, although they may contain traces of hypophosphorous acid or phosphorous acid. It is expected that the method now proposed will be of great use in routine analysis of alloy steels or minerals, because of its speed and convenience. Iron^{II}, uranium^{IV}, vanadium^{IV}, cerium^{III}, molybdenum^{V} and several other reducing agents are also oxidised by this new, powerful oxidising agent. Further work is in progress and detailed results will be published as available.

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16 *April* 1963

REFERENCES

[1] G. Gopala Rao and Seetarama Raju Sagi, *Talanta*, 1962 **9**, 715.
[2] *Idem, ibid.*, 1963, **10**, 169.
[3] G. Gopala Rao and L. S. A. Dikshitulu, *ibid.*, 1963 **10**, 295.
[4] C. O. Ingamells, *ibid.*, 1959, **2**, 171.

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NOTICES SECTION

UNITED KINGDOM

Wednesday 18 *September* 1963: **Contributions to Analytical Chemistry by Younger Members of the Profession:** *Society for Analytical Chemistry, Midlands Section:* Chemistry Department, University, Edgbaston, Birmingham 15: 3.30 p.m.

The following papers will be presented:

Afternoon	
Developments in the Periodate Oxidation of Organic Compounds.	G. Dryhurst
Some Aspects of Cathode Ray Polarography.	M. L. Richardson
Gas Chromatographic Determination of Impurities in Dicloran.	J. R. Ellis
Stereoisomerism of α-Dioximes.	S. Thompson
Evening	
Friedal-Crafts Acylation of Cycloalkenes.	E. J. Rudd
Reduction Methods for Determination of Trace Quantities of Sulphate.	D. B. Adams
Proposals for Modifications to the British Standard dealing with Analysis of Raw Copper.	K. H. Denmead

Tuesday 15 *October* 1963: **Sugars in Foodstuffs—Some Newer Methods:** J. L. Buchan: *Society for Analytical Chemistry, Midlands Section:* Nottingham and District Technical College, Burton Street, Nottingham: 7.00 p.m.

Monday–Thursday 6–9 *January* 1964: 1964 **Exhibition of Scientific Instruments and Apparatus:** *Institute of Physics and Physical Society:* Halls of Royal Horticultural Society, Vincent Square, London S.W.1.

British Standards Institution has announced the following *New British Standard:*

B.S. 3406: *Methods for the determination of particle size of powders: Part* 3: 1963: *Air elutriation methods.* This describes methods of determination of the size distribution of particles in those fractions of powders which pass through a 75-micron B.S. test sieve, using the principle of gaseous elutriation. Air is the most usual elutriating medium, but the methods are equally applicable to other gases. Three methods are described, *viz.* The Gonnell, the Roller (modified ASTM) and the miniature elutriator. The basic principle (Stokes's Law) is described in the foreward. The appendices describe methods of evaluating a size analysis instrument and the correlation of results from different methods of size determination. (*Price* 7s. 6d.)

The following *Revised British Standards* have also been announced:

B.S. 809: 1963: *Methods for sampling milk and milk products.* This provides guidance for the sampling of dairy products for both chemical and bacteriological examination and covers the following—milk, skimmed milk, whey, unsweetened condensed milk (evaporated milk), sweetened condensed milk, butter, cheese, dried milk, dried buttermilk, dried whey, dried malted milk, dried milk sugar, rennet casein, acid casein, ice-cream, water ices and similar frozen confections. Details of suitable containers and sampling tools are provided. (*Price* 6s).

B.S. 1417: 1963: *Methods for the sampling and analysis of acid casein.* This describes methods for the sampling and analysis of acid casein and provides for the preparation of the sample for tests, determinations of coarse particles of foreign matter, range of particle sizes, moisture, total ash, residue on ignition at 850°, fat, pH, total acidity, free acidity, iron and solubility index. Colour standards (see B.S. 1417C are also specified. (*Price* 5s.)

The following *Amendment Slip* has been announced:

B.S. 1428: *Part F*1: 1957: *Filtration apparatus for microchemical purposes. Amendment No.* 1, *PD* 4913.

UNITED STATES OF AMERICA

Monday–Thursday 9–12 *September* 1963: **Eighteenth Annual Instrument-Automation Conference and Exhibit:** *Instrument Society of America:* McCormick Place, Chicago, Ill.

The conference programme is as follows:

Monday—Thursday 9-12 *September* 1963: *18th Annual ISA Instrument-Automation Conference and Exhibit:* **Frontiers in Instrumentation:** McCormick Place, Chicago.

The following parts of the programme may be of interest to analytical chemists:

Monday, 9 September, Afternoon: Spectrophotometric Instruments for Atmospheric Measurements

A Balloon-Borne Photometer for Measuring Atmospheric Attenuation.	Paul M. Furukawa and I. H. Blifford, Jr.
An Ozone Spectrophotometer with High Resolution and Spectral Purity.	W. T. Welford and I. H. Blifford, Jr.
Photoelectric Skylight and Polarimeter.	Z. Sekera and C. R. Magaraja Rao
A Balloon-Borne Infrared Spectrometer for Water Vapour Measurements.	Walter J. Harrop and David M. Gates

Monday, 9 September, Afternoon: Electrical Measurement Standards

Comparison Calibration of Inductive Voltage Dividers.	Raymond V. Lisle and Thomas L. Zapf
High Voltage Measurements.	Winston W. Scott, Jr.
Measurement of Very High Resistances.	John Parnell
A New Average-To-DC Transfer Standard and AC Monitor.	Peter Richman

Monday, 9 September, Afternoon: Problems of Heat-Flux Measurement

Applications and Advancements in the Field of Direct Heat Transfer Measurements.	Fred C. Stempel
A Method for the Determination of Local Transient Heat Flux in Uncooled Rocket Motors.	Walter B. Powell
Thermal Perturbations Caused by Heat-Flux Transducers and Their Effect on Accuracy of Heating-Rate Measurements.	David R. Hornbaker and Dieter L. Rall
Measurement of Heat Flux in Solid Propellant Rocketry.	Charles E. Brookley
Design and Application of a Steady-State Heat Flux Sensor for Hypersonic Wind Tunnel Aerodynamic Heat Transfer Measurements.	David J. Johnson

Monday, 9 September, Afternoon: Strain Gauges applied to Control Systems and Semi-Conductor Strain Gauges

Semi-Conductor Strain Gauge in Bio-instrumentation.	Roger B. Grau

The Strain Gauge, Key Element in a Force Control System.	Louis R. Islander
Design of a Semiconductor Load Cell.	Charles F. Sikorra
Strain Indicator for Semi-Conductor Strain Gauges.	Charles Dean Bradley
Skew Epitaxial Strain Bridge Sensor.	Arthur R. Zias

Monday, 9 *September, Afternoon: Process Control in the Metals Industry*

Optimising Control of Slab Re-Heating Furnace.	Yasuo Nozaka, Susumu Hagiwara, Akito Yoshida and Toshiya Morisuye
Control of Batch-Type Annealing Furnaces by Optimum Heat Head Computer.	J. L. Garrison and W. R. Haden, Jr.
Development of an Optimum Heating Policy for a Batch-Type Heating Furnace.	Julius L. Marcus

Monday, 9 *September, Afternoon: New Techniques in Process Instrumentation*

A Continuous Vacuum Distillation Analyser for Process Control.	Robert D. Clark
On-Line Application of X-Ray Emission Analysers to Rock Product, Mining and Related Industries.	A. D. Furbee and F. Bernstein
A New, High-Speed Process Gas Chromatograph.	Eugene L. Szonntagh
Continuous Process Analysis by Magnetic Resonance.	Forrest A. Nelson
Performance and Applications of the Automatic Gas Chromatography Distillation Analyser.	Helmut J. Maier, C. J. Bossart and H. Heller

Tuesday, 10 *September, Morning: Electronic Power Instrumentation with Special Emphasis on Power Reactors*

Controls and Instrumentation at Pathfinder Atomic Power Plant.	D. H. Leppke and L. C. La Tourette
Features of AC Servomechanism Control Systems.	Charles H. Smoot

Tuesday, 10 *September, Morning: Temperature Measurement in the Cryogenic to 1500°C Region*

Practical Aspects of Temperature Measurements in the Cryogenic Range.	Joseph D. Evans
Semiconductor Cryogenic Temperature Measuring Device.	Daniel S. Schwartz and Conrad C. Schilling

Platinum Resistance and Conductance Thermometry Down to 4°K.	Richard D. Royle, Howard T. Mooers and Frank D. Werner
Airborne Temperature Measurements.	Howard W. Clark

Tuesday, 10 *September, Morning: Metals Instrumentation*

A Non-Contacting Hardness Gauge for the Continuous Annealing Line.	Walter A. Wilson
Continuous Temperature Measurement of Molten Metals.	J. Ward Percy
Disposable-Type Immersion Thermocouples for Use at Elevated Temperatures and in Vacuum Systems.	S. Ramachandran and T. R. Acre

Tuesday, 10 *September, Morning: Computer Control and Systems Engineering*

A Batch Reactor Control Study.	Marvin D. Weiss and L. A. Schafer
Advanced Instrumentation and the Control Computer.	H. H. Flum
Instrumentation Systems and Instrument Development for Paper Industry Process Control.	Charles W. Carroll
Application of a Digital Computer in a Cement Plant.	D. D. Bedworth and J. R. Faillace

Tuesday, 10, *September, Nuclear Instrumentation*

High Energy Particles.	A. V. Crew
Use of Isotopes in Industry.	Stanley Bristol and Leonard Reiffel
Transfer Function of a Linearised Multi-Region Reactor.	Thomas J. Higgins

Tuesday, 10 *September, Afternoon: Reference Voltage Devices and Techniques*

Operating Characteristics of Zener Reference Diodes and Their Measurement.	Woodward G. Eicke Jr.
Establishment and Maintenance of the Unit of Voltage at the NBS Boulder Laboratories.	Barbara A. Wickoff
Zener Diode Power Supply as a Fundamental Reference.	John Nagy, Jr.
Maintenance of an Industrial Reference Standard of Voltage	George D. Vincent

Tuesday, 10 *September, Afternoon: Temperature Measurement above 1500°C*

A Thermocouple for Measuring Temperatures in the 3000°C Region in Oxidising Atmospheres.	C. Howard Mellor
Requirements for a Direct-Reading 5000°F Thermocouple	Earl W. Hicks, Jr.

Temperature Measurements and Heat Transfer Calculations in Rocket Nozzle Throats and Exit Cones.	Jacob Nanigian

Tuesday, 10 *September, Afternoon: Automatic Control Systems*

Matrix Valve: A Programmable Fluid Power Control Valve.	Russel W. Henke
A New Approach to Control System Communications.	J. K. Loeser and J. J. Sadauskas
Investigation of a Self-Adaptive Three-Mode Controller.	David W. Pessen
Sampled-Data Representative System: An Effective Concept for Use in Analysis and Synthesis of Distributed-Parameter Systems.	Thomas J. Higgins and Donald Pierre

Tuesday, 10 *September, Afternoon: New Techniques in Process Instrumentation*

ASTM and TBP Distillations by Chromatography.	Robert L. Sinek and Roger Serne
Potentials of Laser-Excited Emission Spectroscopy for On-Stream Analysis.	Frederick Brech
Use of Radioisotopes in On-Stream Analysis.	James W. Haffner
Controlling a High Viscosity Process with an On-Stream Torsional Viscometer.	Richard W. Scott

Wednesday, 11 *September, Morning: Developments in Solid State Controls*

High Accuracy Electromagnetic Flowmeter Integration.	Roy F. Schmoock
A New Controller for Central Station Use.	Donald R. Hyer
Ignition Energy of Hazardous Atmospheres.	Alfred H. McKinney and Bradford S. Brown
Silicon-Controlled Rectifier Power Systems.	Harry B. Cordes and Donald D. Perry

Wednesday, 11 *September, Morning; Digits at Work*

Supervisory Control of an Operational Pipeline with Computer Assistance.	Alvin C. Winter
Multi-Element Liquid Blending of Digital Techniques.	Fred Jenny
Digital Sub-System Control of Steel Mill Processes.	Kenneth W. Clarke

Wednesday, 11 *September, Morning: Food Industry Instrumentation*

New Developments in Food Processing Automation.	Joseph A. Perry, Jr.
Automatic Control of Dissolved Solids.	G. E. Stackhouse
Automation of a Sugar Pan.	Norman Rosenberg

Wednesday, 11 *September, Morning: High Frequency Standards*

Precision Detector for Complex Insertion Ratio Measuring Systems.	Robert A. Lawton and C. McKay Allred
High Frequency Microvolt Measurements.	Francis X. Ries and Gregorio Rebuldela
A Photometric Bolometer for High Frequency Voltage and Power Measurements.	Kingsley H. Klarer
An Unmodulated Twin-Channel Microwave Attenuation Measurement System.	David H. Russell

Wednesday, 11 *September, Morning: Pipe Line Systems*

A Multi-Station Remote Control and Data Handling System with Flexibility.	Donald E. Stark and Robert A. Sylvester
Rapid Solution of Gas Pipe Line Flow Problems.	M. A. Pai and R. A. Mugele
Must Pipe Line Compressor Stations be Manned for Safe and Reliable Operations.	Robert W. Smith, Jr.

Wednesday, 11 *September, Morning: Analogue Computation and Process Control*

Future Development in Chemical and Petroleum Process Control.	Peter N Nikiforuk
Use of an Analogue Computer to Simulate Process Control Elements.	C. Roy Horney
On-Line Data Reduction Using an Analogue Computer.	Robert M. Howe
Computer Control in Refining and Petrochemicals.	Gerald L. Farrar
Application of Statistical Methods in Evaluating Accuracy of Analogue Instruments and Systems.	Clinton S. Zalkind

Wednesday, 11 *September, Afternoon: Advanced Electronic Transmitters and Transducers*

A Solid-State Tunnel Diode Strain Gauge.	Terrence R. Kiggins and Arthur G. Milnes
Solid-State Current Transmitter for Magnetic Flowmeter Primary.	Roy F. Schmoock
Developmental Studies on Nuclear Digital Transducers.	James L. Hyde
Piezo-Junction Strain Transducers.	R. Rindner, R. Nelson and A. P. Schmid
Use of Hall Effect in New Solid State Instrumentation.	A. L. Aden and N. G. Sakiotis

Wednesday, 11 *September, Afternoon: Digits at Work*

Collection, Analysis and Display of Meteorological Data by Digital Techniques.	W. E. Eggert
Computer Positioning, Analysis and Adaptive Control of an X-Ray Diffraction Mechanism.	Frank W. Chambers
Collection and Computer Analysis of Gas Chromatographic Data by Digital Techniques.	H. W. Johnson, Jr.

Wednesday, 11 *September, Afternoon: Final Control Elements*

Valve Flow Characteristic.	Orval P. Lovett, Jr.
Development of a Universal Gas Sizing Equation for Control Valves.	James F. Buresh and Charles B. Schuder
Precise Mass Flow Measurement Using Inferential Methods.	Ralph Kuttner
Cv Determination at System Operating Conditions.	Sal F. Luna and Thomas J. Grogan

Wednesday, 11 *September, Afternoon: Food Industry Instrumentation*

Research in Food Instrumentation.	Gerald S. Birth
Automatic Package Weight Control on a Volumetric Filling Operation.	Thomas G. McBrady

Wednesday, 11 *September, Afternoon: Microwave Measurements and Microwave Standards*

A Survey of Microwave Power-Measurement Techniques Employed at NBS.	Glenn F. Engen
Application of NBS Standards and Commercially-Available Equipments to Measurement of RF and Microwave Power as an Industrial Primary Standards Laboratory.	James F. Warren and Merlin H. Wiese
Precise Impedance Measurements with Emphasis on Connector VSWR Measurements.	John Zorzy
A Survey of Techniques in Microwave Noise Measurements.	Tadao Mukaihata
A Survey of Precision Microwave Attenuation Measuring Techniques.	Karl Wolters, Gunther U. Corger and J. Ebert

Wednesday, 11 *September, Afternoon: High Temperature Strain Gauges and Temperature Measurements*

Calibration of Strain Gauges at High Temperature: Second Report.	William E. Bostwick and William L. Russell
High Temperature Strain Gauge Developments.	B. R. Anderson

Long Term Static High Temperature Strain Measurements on Power Plant Components.	Irwin Berman

Wednesday, 11 *September, Afternoon: Shock and Vibration Instrumentation*

Computation of Transfer Functions from Dynamic Response.	Arthur H. McMorris and W. Ray Busby
Development and Application of a Piezoresistive Strain Gauge Accelerometer.	Donald E. Lovelace
Calibration of Piezoelectric Accelerometer Using Hopkinson's Bar.	G. W. Brown
Conversion of Electromagnetic Energy into Shock Pulses.	Thomas F. Meagher

Wednesday, 11 *September, Afternoon: Special Instrument and Control Problems in the Pipe Line Industry*

Essential Liquid Pipe-Line Controller Characteristics.	Henry A. Brainerd
Overlooked Step in Pipe Line Automation.	Max M. Levy
Computers for Scheduling and Dispatching.	Harvey H. Ammerman

Wednesday, 11 *September, Afternoon: Sampling Systems for Analysis Instrumentation*

Basic Design Considerations for Analyser Sampling Systems.	Bruce A. Ritzenthaller
Gas Sampling: "The Neglected Science."	Lyle K. Barnes
Sample Conditioning for Process Analysers.	P. Taylor Bannerman
Progress in Standardising Process Analyser Sample Systems.	George N. Ehly
Sample Conditioning for Process Analysers.	Robert Duff Clark

Thursday, 12 *September, Morning: Compact and Integrated Circuits and Devices*

An Application of Integrated Thin-Film Electronics to Telemetry Systems.	Everett Eberhard and William C. Whitworth
An All-Solid-State Acceleration Switch.	A. E. Sobey, Jr. and Jack K. Gilbert
Solid State Instrumentation Techniques for Over-Temperature Protection.	Arthur L. Aden

Thursday, 12 *September, Morning: Computer Control Clinic*

The First Computer-Directed Food Plant.	Glenn A. Puncochar
Automation of a Steam Turbine Power Plant: The Final Step.	Hugh S. Drewry

Multiplexing Thermocouple Signals to a Computer-Controlled Data System.	Loren E. Sheldon
Control Systems.	M. L. Martin

Thursday, 12 *September, Morning: State of the Art of Measuring and Control Systems* (Panel)

Industrial Measurement and Control Systems.	E. J. Otis
Test Facilities Measurement and Control Systems.	Harry E. Burke, Jr.
Aerospace Measurement and Control Systems.	
Ground Support Measurement and Control Systems.	

Thursday, 12 *September, Morning: Temperature Measurement Standards*

Complete Immersion Testing of Liquid-in-Glass Thermometers.	Robert B. Foster, Jr.
Commercial Laboratory Temperature Calibrating Services with References Traceable to NBS.	A. M. Bonanno
Reference Tables for Tungsten vs. Rhenium and Platinum 6% *Rhodium vs. Platinum* 30% *Rhodium Thermocouples.*	Douglas B. Thomas and George W. Burns
A Freezing Apparatus for the Triple Point of Water Cell.	Claus O. Dengler

Thursday, 12 *September, Morning: Cement and Lime Instrumentation*

Closed Circuit Television: Its Advantages and Limitations in the Cement and Lime Industry.	Phillip L. Gantt
Nuclear Continuous Weighing Scale for Dry Solids on Conveyors.	Snowden Rowe
Modern Cement Plant Controls.	J. P. Puckett

Thursday, 12 *September, Morning: In-Transit Weighing*

Effect of Belt-Conveyor Parameters on Belt-Scale Accuracy	H. Colijn

Thursday, 12 *September, Morning: Radiation Methods of Analysis*

Applications of Nucleonic Gauges to Measure and Control Density, Percent Solids and Mass Flow of Chemicals and Plastic Processes.	H. T. Sessions
Performance Optimisation of Nuclear Density Gauges.	Sanford I. Shapiro and F. E. Sleeper
Calibration of Nuclear Radiation-Type Density Measuring Instruments.	Fred R. Gilmer and C. M. Drummond

Thursday, 12 *September*, *Morning: Instrumentation Techniques for Difficult Process Measuring and Control Applications*

Continuous Measurement of Trace Moisture Content in Liquid Hydrocarbons.	Chester N. White
Introduction to Relief Valve Applications: Sizing and Vent Header Design.	Joseph Conison
Industrial Measurement and Control of Slurries Using Radioisotope Gauges.	H. L. Cook, Jr.
Feed Forward Control Applied.	Francis G. Shinskey
A New Process Analyser for Hydrogen.	J. J. McKinley, Jr. and E. A. Hinkle
Operations and Applications of the Pneumatic Servo-Pump.	J. N. Swarr

Thursday, 12 *September*, *Afternoon: Computor Control Clinic*

Spacecraft Automatic Verification Equipment.	L. S. Klivans and A. D. Slor
Integrated Large-Scale Analogue-Digital Control Systems.	Richard K. Hovey
Automatic Reading and Interpolation of Strip Charts and Film Records.	Kenneth Larsen

Thursday, 12 *September*, *Afternoon: Oceanographic Instrumentation*

In Situ *Determination of Electrical Conductivity.*	Elmer A. Sperry, III
Solid State Digital Seawater Current Measuring System.	George Senseney

Thursday, 12 *September*, *Afternoon: Techniques for Control Loop Analysis*

Computer Techniques for Frequency Response Analysis.	G. N. Wolfgang, Leslie M. Zoss and C. A. Wagner
In-Plant Applications of Analogue Computers.	G. R. Marr, Jr. and E. E. L. Mitchell
Dynamic Analysis of Process Control System.	George L. Rock
Cascade and Model Control Methods for Superheater Temperature Control.	Tai-Seng Chen and John W. Schwartzenberg

Thursday, 12 *September*, *Afternoon: Dynamic Physical Measurement Standards*

Total Energy Balance Method of Precise Primary Measurements.	Eugene Norman
Production of Dynamic Pressure Environments.	Neal L. Vinson
An Accurate Timer for Positive Displacement Flow Meters.	Eshmal L. Porter

Thursday, 12 *September*, *Afternoon: Glass Instrumentation*

Automatic Control of Recuperative Glass Tank.	W. C. Trethewey
Unique Combustion Control of a Regenerative Furnace.	H. Bevins
Development of a Diameter Control System for the Tube Blowing Process.	R. Mouly

Thursday, 12 *September*, *Afternoon: In-Transit Weighing*

Pneumatic Gravimetric Feeder.	E. W. Wittke

Thursday, 12 *September*, *Afternoon: Standards as Applied to Automotive Instrumentation*

Typical Certification and Calibration Services Offered by an Independent Standards Laboratory.	J. D. Ghesquiere
Dynamic Pressure Transducer and Accelerometer Calibration.	Voigt R. Hodgson
Why Do Automotive Instrumentation Groups Need Standards?	Raymond A. Schnurr

Further information may be obtained from the Conference Programme Co-ordinator, Thomas A Abbot, American Oil Co.

Monday–Thursday 7–10 *October* 1963: **Thirteenth Annual Instrument Symposium and Research Equipment Exhibit:** National Institutes of Health, Bethesda, Maryland.

The symposium programme is as follows:

Monday Afternoon, October 7
Research Applications of Laser Beams

Clinical Applications of Lasers.	Milton M. Zaret
Use of the Laser in the Study of an in vivo Energy Transfer System.	R. A. Olson
Non-linear Optical Effects.	Norman Adams

Monday Evening, October 7
Atomic Absorption Spectroscopy

Progress in Atomic Absorption Spectrometric Determination of Previously "Unrealised" Elements.	Velmer A. Fassel, Richard N. Kniseley and Victor G. Mossotti
Recent Studies in Atomic Absorption Spectroscopy.	B. L. Vallee and K. Fuwa
Determination of Serum Calcium by Atomic Absorption Spectrophotometry.	Alfred Zettner and David Seligson
Preliminary Experience with Atomic Absorption Spectrophotometry with Respect to Body Composition and Growth.	Donald B. Cheek

Tuesday Morning, October 8
Automation in Biochemical Analyses

Application of Automatic Equipment in the Performance of Protein Bound Iodine Analyses.	Evelyn C. Wilson, Wesley J. Fletcher and Alan Keltz
Impact of Automation on a Large Clinical Chemical Laboratory	R. E. Sterling, A. A. Wilcox and H. A. Davis

Tuesday Afternoon, October 8
Determination of Macromolecular Structure

State of Aggregation of the Genetic Variants of Lactoglobulin.	SERGE N. TIMASHEFF
Ribonuclease-s in Solution and in the Solid State.	FREDERIC M. RICHARDS
Formation and Stabilisation of the Collagen Helix.	PETER H. VON HIPPEL

Tuesday Evening, October 8
New Methods in Immunology and Immunochemistry

Fluorescence Quenching of Purified Antibody.	J. R. LITTLE and H. N. EISEN
Autoradiography of Immunoelectrophoresis in the Study of ^{14}C-*-labelled Amino Acid Incorporation into Serum Proteins by Tissues in vitro and in vivo.*	G. J. THORBECKE
Study of the Kinetics of Antibody-hapten Reactions with the Temperature-jump Apparatus.	A. FROESE and A. H. SEHON
Quantitative Immunogenetic Studies Using Electronic Measurements of Hemagglutination.	MARY B. GIBBS

Wednesday Morning, October 9
High Resolution Microscopy

Modern Electron Microscopes.	W. C. BIGELOW
Electron Microscopy of Biological Molecules and Particles.	CECIL E. HALL
Tissue Preparation for Electron Microscopy.	DANIEL C. PEASE

Wednesday Afternoon, October 9
Radiation Biology

Radiation Biology Review.	CHARLES L. DUNHAM
Extracorporeal Irradiation of the Blood, Lymph Duct Cannulation and Isotopic Labelling in the Study of Lymphocyte Behaviour.	EUGENE P. CRONKITE
Biological Uses of Radiation Beams of Subcellular Dimensions.	RAYMOND E. ZIRKLE
Free Radical Concentration Measurements by Electron Spin Resonance	M. L. RANDOLPH

Wednesday Evening, October 9
Advanced X-ray and Electron Technique Spectroscopy

Low-energy Fluorescence and Photoauger Electron Analysis for Elementary Chemistry of 0.01 *to* 0.01-*mg Samples.*	BURTON L. HENKE
Study of Excited Molecules by Electron Velocity Analysis.	J. KARLE
Subcellular elemental Analysis of Tissues with the Electron Probe.	ROBERT C. MELLORS

Thursday Morning, October 10
Molecular Separation by Size and Charge

Sorting Rod-shaped Particles on Basis of Length by Agar gel Chromatography.	R. L. STEERE
Fractionation according to Charge and Size.	J. O. PORATH
Preparative Disc Electrophoresis	LEONARD ORNSTEIN
Complementary Interactions among Nucleic Acids: A Molecular Approach to the Study of Genes and their Products.	E. T. BOLTON

Thursday Afternoon, October 10

Physiological Monitoring

Biophysical Monitoring of Experimental Animals.	Harry A. Gorman
Bioinstrumentation for Space Flight.	S. P. Vinograd
An Instrumentation System for Cardiac Surgery.	Gerald S. Cohen and Andrew G. Morrow
An analysis of the need for, and a clinical trial of an intensive care monitor.	K. C. Rock and Jesse H. Meredith

Further information may be obtained from Dr. Fred Alt, National Institutes of Health, Bethesda 14, Md., U.S.A.

Tuesday–Thursday 8–10 *October* 1963: **Seventh Conference on Analytical Chemistry in Nuclear Technology:** Oak Ridge National Laboratory, Gatlinburg, Tennesse (see *Talanta*, 1963, **10**, June, v).

The programme is as follows:

Tuesday Morning, October 8

Instrumental Methods for Analysis of Molten Salt Systems

Electroanalytical Measurements in Molten Salts.	H. A. Laitinen
A Chronopotentiometric and Chemical Rate Study of the Third Order disproportionation of Eu(II), *Yb*(II) *and Sm*(II) *in molten KCl-LiCl Eutectic.*	L. C. Hall and G. M. Campbell
Electrochemical Studies in Molten Fluorides.	Gleb Mamantov
Electronic Absorption Spectroscopy of Molten Salt Solutions.	D. M. Gruen
Spectrophotometric Studies of Lanthanides and Actinides in Molten Salt Media.	W. T. Carnall
Analytical Aspects of Fused Salt Spectrophotometry—U(III) and U(IV) Species in Fused Chlorides.	J. R. Morrey
Spectrophotometric Studies of Molten Fluoride Salts.	J. P. Young

Instrumentation and Techniques for Nuclear Analysis

Radiation Detection, Analysis and Data Reduction at Phillips Petroleum Company, National Reactor Testing Station.	D. G. Olson
Instrumentation for Absolute Radioactivity Measurements.	P. Crowther and J. S. Eldridge
Analysis of Total Beryllium by Gamma Activation.	Harry L. Rook
Standardisation of Electron-capturing Nuclides.	S. B. Garfinkel
Routine Absolute Alpha and Beta Counting in a Four Pi Proportional Counter.	Mary Lou Curtis

Tuesday Afternoon, October 8

Instrumentation for Remotely Controlled Analysis of Radioactive Materials

Simple Method for Determination of Free Acid and Uranium in Uranium(VI) Solutions by Alkalimetry.	Kenji Motojima and Kimie Izawa
Automated Specific Gravity Apparatus for Highly Radioactive Samples.	F. W. Dykes
Automation of Wet Chemical Analyses.	J. C. Gillespie
Recent Developments in "In-line" Chemical Instrumentation at Windscale.	J. K. Foreman, C. R. McGowan and R. W. Dickinson
A Versatile, Low-cost, Remote Handling System for Chemical Analysis.	A. J. Howarth
Analytical Methods and Remote Handling Facilities for MSRE and TRU Programmes at ORNL.	L. T. Corbin

An Automatic, Electrically Controlled, Analytical Balance.	Lynne L. Merritt and Robert Ensman

Panel Discussion on Availability and Use of Radioactivity Standards

Wednesday Morning, October 9

Instrumentation and Techniques for Nuclear Analysis

Alpha Partical Spectroscopy: Instrumentation and Applications.	A. Chetham-Strode and J. R. Tarrant
Determination of Thorium-230 (*Io*) *in Thorium*-232 *Using a Solid State Detector.*	J. C. Nelson, Jr. and H. Bussell
Application of a Thermal Neutron Fission Counter to Nuclear and Radiochemical Problems.	R. F. Buchanan, James Gray, Jr. and French Hagemann
Rapid Determination of Yttrium in Aqueous Solutions Containing Dysprosium and in Ore Samples by Neutron Activation and γ-Ray Spectrometry.	Minoru Okada
Intermediate Level Gamma-ray Spectrometer for a High Radiation Level Experimental Laboratory.	V. A. McKay and G. W. Allin
A Portable Fluorescent X-Ray Instrument Utilising Radioactive Sources.	J. O. Karttunen, H. B. Evans, D. J. Henderson, R. L. Niemann and P. J. Markovich
Interlaboratory Quality Control of Iodine-131 *Surveillance Measurements in milk.*	Marvin Rosenstein and A. S. Goldin

Electroanalytical Instrumentation

Recent Developments in Hanging-Drop Voltammetry.	Irving Shain
Applications of Operational Amplifiers in Electroanalytical Chemistry at ORNL.	M. T. Kelley
A Versatile Automatic Electrometric Titrator.	Giulio Milazzo
High Precision (Comparative) Polarography.	H. I. Shalgosky
Differential Cathode-Ray Polarography.	H. M. Davis
An Automatic Method for Measuring the Slope of Kinetic Curves: Application to Quantitative Analyses.	Harry L. Pardue
Continuous Detection of Hexavalent Chromium for Control of a Darex Process.	T. M. Gayle and T. A. Gens

Wednesday Afternoon, October 9

A Round-Table Discussion of Recent Developments in Analytical Instrumentation

Thursday Morning, October 10

Analytical Spectroscopy

Practical Implications of Some Excitation Phenomena Occurring in Combustion Flames.	R. Mavrodineanu
Direct Reader for Flame Emission and Absorption Measurement.	R. C. Hughes, R. Mavrodineanu and T. R. Kohler
A Flameless Method for Producing Atomic Vapour for Atomic Absorption Spectrophotometry—I: Determination of Cadmium.	J. P. Mislan
Application of the Integration Method to Analytical Instrumentation.	Shigeki Hanamura
New Instrumentation for Emission Microspectroscopy.	R. S. Vogel
Spectrographic Determination of Beryllium in Oilfield Waters Using a Plasma Arc.	A. G. Collins and Cynthia A. Pearson

Direct-Reading Spectrometer for Determination of Beryllium in Paper Samples.	R. N. Whittem
Chemical Separation and Spectrographic Determination of Trace Amounts of Rare Earths in SAP Material.	Z. Hainski, E. Cerrai, G. Rossi and R. Trucco
X-Ray Fluorescence Spectrographic Determination of Zirconium and Molybdenum in Presence of Uranium.	E. A. Hakkila, R. G. Hurley and G. R. Waterbury

Thursday Afternoon, October 10

Analytical Spectroscopy and Gas Chromatography

Casting of Radioactive Samples into Plastic for X-Ray Fluorescence Analysis.	J. P. Hughes, F. J. Schmitz and Carol A. A. Bloomquist
Hypeac Interference Spectrometer and its Applications to Nuclear Technology.	David Bandel
Problems in Development of a Thermal Emission-type Mass Spectrometer for Use in Isotopic Analysis.	W. C. Taylor, Jr., W. J. Mordarski and R. H. Gale
Off-line Machine Reduction of Gas Chromatographic Data.	J. H. Karohl
Application of Gas Chromatography to Determination of Carbon in Sodium	H. L. Bradley and C. R. Moore
A Programmed Analyser with Direct Digital Readout for Measuring Dissolved Gases in Out-of-pile Corrosion Facilities.	M. Siegler and D. T. Snyder
Analysis of Uranium Carbide.	B. D. La Mont, J. D. Johnson and J. V. Derby
Analysis of V.P.M. Impurities in Helium by Gas Chromatography and Ionisation.	P. J. Bourke, R. W. Dawson and W. H. Denton

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Monday–Thursday 14–17 *October* 1963: **77th Annual Meeting:** *Association of Official Agricultural Chemists:* Shoreham Hotel, Washington D.C.

Enquiries should be addressed to Mr. Luther G. Ensminger, AOAC, Box 540 Benjamin Franklin Station, Washington 44, D.C.

Wednesday–Friday 16–18 *October* 1963: **Tenth National Symposium:** *American Vacuum Society:* Statler Hilton Hotel, Boston, Massachusetts.

Further information may be obtained from the Programme Chairman, G. H. Bancroft, 398 Kilbourn Road, Rochester 18, New York.

Monday–Friday 14–18 *October* 1963: **Second National Meeting:** *Society for Applied Spectroscopy:* El Cortez Hotel, San Diego, California.

The programme, subject to minor changes, is as follows:

Monday Morning, October 14

Gamma-Ray and Nuclear Particle Spectrometry

Semiconductors as Detectors of Charges Particles, X-rays and Gamma-rays.	C. Borkowski
Cerenkov Counter in Determination of Oxygen.	H. R. Lukens, Jr. and J. E. Lasch
Magnetic Charged Particle Analyser.	H. Bichsel
A Study of Flux Monitoring for Instrumental Neutron-Activation Analysis.	F. A. Iddings

Mass Spectrometry

Competitive Processes for Formation of Tryoplium Ion in Electron Impact Studies of Toluene.	J. G. Burr and R. A. Meyer
Accuracy in Spark Mass Spectrometry.	C. M. Judson and R. F. Howard
Electron Collisions with Atoms and Molecules.	W. Fite

Monday Afternoon, October 14

Gamma-ray and Nuclear Particle Spectrometry

Present State of Gamma-ray Scintillation Spectrometry.	R. Heath
Use of Gamma-ray Spectrometry in Study of Fission Product Release from Nuclear Fuels.	D. R. Lofing, E. E. Anderson and L. R. Zumwalt
Non-destructive Analysis Using a Research Reactor.	W. Meinke
Appropriate Roles of Small Accelerators and Nuclear Reactors and of Instrumental and Radiochemical Techniques in Neutron-activation Analysis.	V. P. Guinn

Mass Spectrometry—Collision Processes

Problems and Trends in Mass Spectrometric Study of Reactions between Gaseous Ions and Molecules.	D. Stevenson
Ion Cyclotron Resonance in Weakly Ionised Gases.	D. Malone
Aston Bands and Ion Collision Physics.	J. W. McGowan

Tuesday Morning, October 15

Mass Spectrometry—High Temperature Chemistry

Thermodynamics and Kinetics of Vaporisation Processes Studied by Mass Spectrometry.	W. A. Chupka and J. Berkowitz
Mass Spectrometric Study of Vaporisation of Mixed Oxides of Arsenic and Antimony.	J. H. Norman and H. G. Staley
Mass Spectrometric Study of the BeO–BeF_2 System.	J. Efimenko
Mass Spectrometric Study of Strontium Oxide Vaporisation.	H. G. Staley and J. H. Norman

Gamma-ray and Nuclear Particle Spectrometry

Use of Computers in Analysis of Gamma-ray Spectrum Data.	J. Trombka
Computer Analysis of Complex Gamma-ray Spectra.	A. K. Perkons, R. L. Hummel and R. E. Jervis
A Computer Programme for Rapid Optimisation of Experimental Conditions for Activation Analysis.	T. L. Isenhour and G. H. Morrison
Practical Computer Routines for Neutron-Activation Analysis.	D. E. Hull and J. T. Gilmore

Biochemistry and Molecular Biology

Theory of Fluorescence Polarisation and its Application to Biochemical Studies.	G. Weber
A Polarisation Fluorometer and its Use.	N. S. Bromberg, A. Pesce and N. O. Kaplan
Near Infrared Absorption Spectra of Native and Chemically Modified Wool and Related Structures.	G. F. Bailey
On the Ultraviolet Spectrophotometry for Measuring Proteins.	S. Gabay and D. E. Jordan

Geochemistry and Geophysics

Identification of Organised Elements in Meteorites.	B. Nagy
Application of a Nuclear Magnetic Resonance Spectrometer for Quantitative in-situ Measurements of Brine in Sea Ice.	C. Richardson
Abundances of Na, Sc, Mn, Cr, Fe and Co in Stony Meteorites via Instrumental Neutron-Activation Analysis.	R. A. Schmitt
Electron Microprobe Analysis of Some Minerals in Stony Meteorites.	K. Keil and K. Fredriksson

Tuesday Afternoon, October 15

Gamma-ray and Nuclear Particle Spectrometry

Computer Correction for Shifts in Gain and Baseline in Gamma Scintillation Pulse Height Spectra.	D. F. Covell
Application of a Rapid Print-out System for Analyser Dead-time Correction.	E. Steele, L. Fite, R. Wainerdi and W. Wilkins
Some New Techniques in Beta- and Gamma-ray Spectroscopy.	J. A. Eisele, J. F. McClary, E. R. Samecki and T. H. Adensam
Instrumental Activation Analysis for Identification of Forensic Specimens:	R. E. Jervis
New Applications of Neutron-activation analysis to Criminalistics.	R. R. Ruch, S. B. Madigan and V. P. Guinn

Tuesday Afternoon, October 15

Biochemistry and Molecular Biology—NMR and EPR Applications

Some Applications of Nuclear Magnetic Resonance Spectroscopy to Biochemical Problems.	M. Cohn
EPR Study of the Chlorpromazine Free Radical During Enzymic Oxidation.	L. H. Piette, I. Yamazski and G. Bulow
Application of EPR to Study of Some Transition-Metal Complexes in Biological Systems.	J. J. Windle
An NMR Study of Effect of Configuration on Proton Spin Coupling Constants in Some Five-membered Rings in Relation to Stereochemistry of Betamethyl-aspartase Reaction.	R. E. Lundin, H. J. Bright and I. L. Ingraham

Application of X-ray and Microprobe Analysis to Geochemistry and Geophysics

X-ray Fluorescence Analysis of Light Elements in Rocks and Minerals.	I. Adler, H. J. Rose, Jr. and F. J. Flanagan
Preparation of Silicate Rocks and Minerals for Light Element Analyses by X-ray Spectrography.	A. K. Baird and E. E. Welday
Use of a High-speed Computer in Light Element Analysis by X-ray Fluorescence.	D. B. McIntyre
Electron Microanalysis of Metallic Meteorites.	R. E. Ogilvie

Wednesday Morning, October 16

Gamma-Ray and Nuclear Particle Spectrometry

Applied Nuclear Geophysics.	R. L. Caldwell
Fast Neutron Techniques in Coal Analysis.	T. C. Martin, S. C. Mathur and J. T. Prud'homme
Photoactivation Analysis.	H. R. Lukens, Jr.

An Investigation into Utilisation of Metastable Isomers of Stable Isotopes in Activation Analysis.	H. H. Kramer and W. H. Wahl

Nuclear Magnetic Resonance and Electron Paramagnetic Resonance

*Some Recent Advances in Carbon-*13 *Magnetic Resonance.*	D. Grant
High Pressure EPR Spectroscopy: Emphasis—Paramagnetic Ions in Solids.	R. Sands

X-Ray

X-Ray Fluorescence Analysis for Light Elements Sodium Through Boron.	B. Henke
Experimental Determination of $M_{\text{II, III}}$ *Soft X-Ray Emission Spectra of Nickel, Copper and Zinc and their Alloys.*	B. J. Thompson
Determination of Microgram Quantities of Chloride in High-purity Titanium by X-Ray Spectrochemical Analysis.	J. S. Rudolph and R. J. Nadalin
Determination of Trace Elements in Solid Hydrocarbons and Related Materials by X-Ray Fluorescence Spectroscopy.	T. C. Yao and R. E. Harrison
An X-Ray Diffractometer for Diffractometry and or Spectroscopy.	W. Ashby, V. E. Buhrke and G. V. Patser

Wednesday Afternoon, October 16

Gamma-Ray and Nuclear Particle Spectrometry

Structural Chemical Applications of Neutron Diffraction.	J. Ibers
^{3}*He Activation Analysis: Oxygen, Carbon, Nitrogen and other Elements.*	S. S. Markowitz and J. D. Mahoney
Use of Radiochemistry and Mass Spectrometry for Fuel Depletion Studies.	J. E. Hudgens
Utilisation of Reactor Fast Neutrons for Activation Analysis.	H. P. Yule, H. R. Lukens, Jr. and V. P. Guinn

Nuclear Magnetic Resonance and Electron Paramagnetic Resonance

NMR Study of Keto-Enol Tautomerism in Beta-dicarbonyls.	M. T. Rogers and J. Burdett
An NMR Study of Competitive π *Bonding in* Ni^{II} *Chelates.*	D. R. Eaton and W. D. Phillips
Tautomerism—Exchange in B_3H_7:*N* Me_3 *and* B_3H_7:*THF.*	M. A. Ring, R. C. Greenough and E. F. Witucki

Electron Probe and Secondary Ion Emission Analysis

New Developments in Microanalysis.	R. Castaing and G. Slodzian
Electron Probe Analysis of Minerals.	I. Adler
New Techniques in Electron Probe Analysis.	D. Wittry
Quantitative Phase Determination in Polyphase Mixtures by X-Ray Diffraction.	G. O. Arrhenius, E. Bonatti and R. Fitzgerald
Interelement Effects in Analysis of Nickel-iron Thin Films.	J. C. Lloyd

Thursday Morning, October 17

Gamma-ray and Nuclear Particle Spectrometry

Applications of X-Ray, Gamma-ray and Nuclear Particle Spectroscopy to Lunar and Planetary Compositional Analysis.	A. Metzger
Some Applications of Thermal Neutron Capture Gamma-ray Analysis	R. C. Greenwood and J. H. Reed

Chemical Analysis Using Miniature Nuclear Accelerators and Inelastic Neutron Scattering Techniques.	J. A. WAGGONER, E. F. MARTIN and C. D. SCHRADER
Gamma-ray Spectrometry of Terrestrial Radioactivity.	B. ZEMEL

Electron Probe Analysis and X-Ray

Application of Kossel Technique to Metallurgical Problems.	R. E. OGILVIE
Fine Structure in Superconducting and Other Alloys, Studied by Electron Microprobe Analysis.	C. J. RAUB, C. A. ANDERSON, G. O. ARRHENIUS and B. T. MATTHIAS
Absorption and Fluorescent Effects in Inclined Targets in the Electron Microprobe.	V. G. MACRES and W. D. DONNELLY
X-Ray Diffraction and Microfluorescence Investigations of Hyaloclastic Aggregates.	G. O. ARRHENIUS, C. A. ANDERSON, E. BONATTI and N. KHARKAR
Design Considerations and Analytic Capabilities of an X-Ray Emission Spectrograph for Lunar Surface Analysis.	A. E. METZGER, R. A. SHIELDS and H. W. SCHNOPPER

Atomic Emission and Absorption

Recent Developments in Flame Atomic Absorption and Emission Spectroscopy.	V. FASSEL
An Arc Device for Spectral Excitation in Controlled Atmospheres.	B. F. SCRIBNER and M. MARGOSHES
Spectral Radiation Measurements of the Earth and Its Atmosphere from Onboard the X-15 Aircraft.	L. C. BLOCK, H. E. BAND and E. K. DANA
A Study of Spark Spectra of Selenium.	A. M. CROOKER and S. GEORGE

Thursday Afternoon, October 17

Gamma-ray and Nuclear Particle Spectrometry

Industrial Applications of Activation Analysis.	P. R. GRAY and L. M. CARTWRIGHT
Role of Instrumental Activation Analysis in a Diversified Chemical Research and Development Laboratory.	R. A. JOHNSON
Fast Neutron Activation vs. Vacuum Fusion Analysis for Oxygen in Metals.	F. BURNS
Silicon, Aluminum, and Silicon/Aluminum Analyses by Neutron Activation and Gamma-ray Spectrometry.	W. E. MOTT and D. F. RHODES
Reactor Pulsing in Activation Analysis.	H. R. LUKENS, JR., H. P. YULE and V. P. GUINN

Astrophysical

Spectroscopic Observations of Faint Galaxies and Stars.	J. OKE
Current Status of Far Ultraviolet Stellar and Nebular Spectroscopy.	J. KUPPERIAN
Space Instruments for Measurement of Ultraviolet Spectra of Planetary Atmospheres.	D. MARGETTS, E. F. MACKEY and C. A. BARTH

Infrared and Optical-molecular Structure

Vibrational Spectra of Excited Electronic States.	R. HEXTER
Spectrophotometric Studies of Molecules in their Triplet States.	M. W. WINDSOR and D. WEBER
Spectral Line Splitting in Europium Chelates.	M. L. BHAUMIK
Luminescence of Transition Metal Complexes.	L. S. FORSTER

Long-lived Luminescence from Organic Materials.	H. R. Lukens, Jr.
Optical Measurements of Radiation Damage Processes on a Fast Time Scale.	J. F. Bryant, D. M. J. Compton and J. Kirkbridge

Friday Morning, October 18

Atomic Emission and Absorption

A High Resolution Scanning System for Optical Study of Laser Crystals.	J. K. Powers and B. W. Harned
Instrumental Parameters in Atomic Absorption.	H. L. Kahn
Unsolved Problems in Spectrochemical Analysis.	R. Barras

Discussion Period—Unsolved Problems in Spectrochemical Analysis—ASTM Committee E-2

Infrared and Optical-structure

Evaluation of Transferable Force Constants.	J. Schachtschneider
Group Theoretical Vibrational Analysis of Impurities in Solids.	L. A. Veguille-Berdecia and G. C. Turrell
Optical Spectra and Energy Levels of Trivalent Thulium.	K. E. Lawson
Infrared Spectrum of B_2F_4.	J. N. Gayles and J. Self
Far Infrared Studies in Barbiturates.	W. F. Ulrich and J. E. Stewart

Friday Afternoon, October 18

Atomic Emission

Calculation and Measurement of Radial Distribution of Line Broadening in a Cesium Plasma.	D. L. Tipton and R. T. Schneider
Stabilised Plasma Jet for Spectroscopic Excitation.	M. Yamamoto
An Investigation into Analysis of Nitrogen for Hydrogen by Optical Spectroscopy.	G. W. Dickinson and G. V. Wheeler
Design Aspects of a New Compact Spectrographic Laboratory.	W. G. Shequen, H. Neuhaus, R. L. Gordon and A. J. Hartwick
Detection and Estimation of Some Trace Elements by D.C. Arc Excitation Using the Vacuum Cup Technique.	E. Bevege

Infrared-Solid State

Absolute Intensities of Infrared Absorption Bands in Molecular Crystals.	W. Person
Vibrational Spectrum of Single Crystals of Sodium Azide.	J. I. Bryant
Infrared Spectrum of Potassium Nitrate in Phases I, II, and III.	R. K. Khanna, J. Lingscheid and J. C. Decius
Infrared Micro Sampling Using Micro Specular Reflectance.	H. J. Sloane, T. Johns and W. F. Ulrich
Crystal Structure and Spectroscopic Study of the Potassium TCNQ Ion-radical Salt.	G. R. Anderson and C. J. Fritchie, jr.

Further information may be obtained from the Programme Chairman, Earl P. Wadsworth, Jr., Chemistry Department, San Diego State College, San Diego 15, California, U.S.A.

Monday–Wednesday 21–23 *October* 1963: **Eleventh Detroit Anachem Conference:** McGregor Memorial Conference Centre, Wayne State University.

The programme is as follows:

Monday Morning, October 21

Spectroscopic Sources

Vaporisation of Elements for Atomic Spectroscopy with Capacitor Discharge Lamps.	L. S. Nelson and N. A. Kuebler
Some Characteristics of Laser Excited Spectra.	E. F. Runge and F. R. Bryan

Symposium on Trace Analysis

An Optical Emission Spectrographic Method for the Analysis of Oxidation Products and Insoluble Phases of High Temperature Alloy Systems.	J. Cannon
Spectrographic Determination of Trace Impurities in High Purity Gold.	A. J. Lincoln and J. C. Kohler
Some Experiments on Trace Element Analysis by Vaporisation Concentration Methods.	Robert F. O'Connell
Application of a Direct-reading Spectrometer to Trace Element Determination in NaOH at the 0.1-*ppm Level.*	Stanley B. Smith, Jr.

Symposium on Activation Analysis in the Detroit Area

Principles of Activation Analysis.	W. W. Meinke
Experience with Neutron-activation Analysis at the Dow Chemical Company.	Oswald U. Anders
Activation Analysis in the Pharmaceutical Industry.	D. G. Kaiser
Fast Neutron-activation Analysis of Silicon IB Malleable Iron.	Robert J. Kinsey, Robert E. Kohn, Walter Kerwick and John P. Danforth
Activation Analysis with the Michigan Reactor: Application to Michigan Problems.	H. W. Nass
Panel: Use of Activation Analysis Services.	

Monday Afternoon, October 21

Analytical Spectroscopy

Some Physicochemical Aspects of Excitation in Graphite Electrodes.	C. L. Grant and W. M. Beasley
Analysis of Powder Samples with Spark Excitation.	D. C. Hargis and G. W. Smith

X-Ray Symposium

Electron Probe Microanalyser as a Metallurgical Tool.	Kurt F. J. Heinrich
An Investigation of Accuracy of Solution X-Ray Spectrometric Analysis: Copper-Base Alloys.	Robert Alvarez and Richard Flitsch
Determination of Nickel and Molybdenum in Cemented Titanium Carbides by X-Ray Spectrography.	J. C. Wagner and E. J. Violante
Rapid X-Ray Fluorescence Determination of Strontium in Samples of Biological and Geological Origin.	R. N. Wittem
Experience with an Inverted Co-ordinate Index for Searching X-Ray Powder Diffraction Data of Organic Compounds.	Harry A. Rose

Activation Analysis Symposium

Applications of Fast Neutron-Activation Analysis.	P. R. Gray and L. M. Cartwright

Neutron-Activation Analysis of Aluminium and Niobium in Ores Using Rapid Radiochemical Separation Procedures.	V. J. Molinski and Werner H. Wahl

Gas Chromatography

Assignment of cis-trans Configuration to Mono-olefin Pairs.	R. A. Hively
Backflush and Two-stage Operation of Capillary Columns in Gas Chromatography.	David J. McEwen
Applications of a New Pyrolysis Unit to the Analysis of Non-Volatile Materials by Gas Chromatography.	Ralph H. Waltz, John Wisniewski and Samuel Spencer

Tuesday Morning, October 22

Symposium on What Should Be Taught in Analytical Chemistry with Open Discussion

Status of and Trends in Analytical Chemistry.	I. M. Kolthoff
What Should Be Taught in Analytical Chemistry.	H. A. Liebhafsky and E. W. Balis
Comments from the Academic Viewpoint.	Louis Gordon

Symposium on Absorption Spectroscopy

Effect of High Pressures on Inorganic Crystalline Materials Using Optical and Spectroscopic Techniques.	Ellis R. Lippincott
Determination of Non-Ionic Ethylene Oxide Adduct in Commercial Products.	Khalid S. Bahjat, Elmer F. Degner and Joseph R. Weber
4,5-*Diamino*-6-*thiopyrimidine as a Reagent for Spectrophotometric Determination of Selenium.*	Frank L. Chan.
Differential Spectrophotometric Determination of Silicon in Boron Silicides.	Allan G. Boyes and Robert J. Hynek
Effect of Operating Conditions on Wavelength Calibration with the Holmium Filter.	J. M. Vandenbelt
Sensitive New Methods for Autocatalytic Spectrophotometric Determination of Nitrite through Free-radical Chromogens.	E. Sawicki, T. W. Stanley, J. Pfaff and H. Johnson
Determination of Trace Amounts of Titanium and Molybdenum in Tungsten.	K. F. Sugawara
Spectrophotometric Determination of Tungsten in Low Grade Ores.	R. H. Maurer and W. H. Price

Tuesday Afternoon, October 22

Anachem Award Symposium

Anachem Award Address: *Beginnings of Modern Microchemistry.*	A. A. Benedetti-Pichler
Simplicity and Effectiveness in Analysis.	Sidney Siggia
Morphological Analysis.	Walter C. McCrone
Applications of Ultramicrochemistry in the Clinical Laboratory.	James L. Whitehouse and Edwin M. Knights, Jr.

Wednesday Morning, October 23

Clinical and Biochemistry Symposium

Chemistry of Gonadotropins of Pituitary and Placental Tissues.	Gregory S. Duboff
Serum Creatine-phosphokinase (CPK) Measurement for Diagnosis of Myocardial Infarction.	Roderick P. MacDonald and Joseph W. Hess
Electrophoresis and Immuno-electrophoresis in Urea Starch Gel.	M. D. Poulik

Testosterone Analysis by Glass Paper Chromatography.	E. Epstein and B. Zak

Fluorescence Analysis Symposium

Fluorescence of Purines and Pyrimidines.	Sidney Udenfriend
Thin Layer Chromatographic Separation and Fluorescence Analysis of Polynuclear Aza Hydrocarbons.	E. Sawicki, J. W. Stanley, W. C. Elbert and J. D. Pfaff
Semimicro X-Ray Fluorescence Analysis of Minerals, Rocks and Ores.	Harry J. Rose

Analytical Chemistry—General

Automation of Potentiometric Quantitative Analysis.	Albert F. Plant
Use of Phenylisothiocyanate for Determination of Tertiary Amines in Presence of Primary and Secondary Amines.	D. A. Keyworth and M. Miller
An Indirect Coulometric Titration of Trace Amounts of Organic Peroxides.	Stanley T. Hirozawa
Determination of Phosphorus in Aluminium-Silicon Alloys.	G. E. Fisher
Microchemical Analysis of Oil Additive Decomposition Films on Individual Bearing Balls.	Jack L. Johnson
Cycloidal Focusing Mass Spectrometer as a Structural Tool.	R. W. Geiger and G. W. Wilcox
Estimation of Formation Constants of Some Organo-silver Complexes Using Computer Methods.	David G. Bush, Albert D. Baitsholts and Edwin P. Przybylowicz

Wednesday Afternoon, October 23

Fluorescence Analysis Symposium

Fluorescence-Structure Relationships for Polynuclear Hydrocarbons by Automatic Triparametric Recording.	Myron M. Schachter and Edward O. Haenni
Several Applications for a New Spectral Fluorescence Attachment.	T. J. Porro, L. A. Hurlbut and H. T. Morse
Fluorescence Methods for Determination of Correction Factors for Excitation and Emission Spectra.	Robert Argauer and Charles E. White

Clinical and Biochemistry Symposium

Lead in Urine.	Vernon A. Nelson, R. A. Scheidt, Thomas Elmore and Diane Vogl
Factors Influencing Electrophroetic Migration of Lactic Dehydrogenase Isozymes.	N. Ressler, J. L. Schultz and R. R. Joseph
Identification of some Serum Proteins Responding to Injury in the Rat.	Otto W. Neuhaus
Constant Current Potentiometric Titration of Ascorbic Acid.	Calvin O. Huber and Heinz E. Staplefeldt

Analytical Chemistry—General

Comparative Studies on Critical Solution Temperatures of Aliphatic Compounds.	H. H. O. Schmid, H. K. Mangold and W. O. Lundberg
Gravimetric Determination of Rubidium and Cesium with N,N-Dimethylethanolammonium Orotate.	Nazhat Z. Babbie and W. Wagner
Analytical Studies of Cationic-sensitive Glass Electrodes.	Garry A. Rechnitz

Application of Stripping Analysis to Determination of Silver Using Graphite Electrodes.	S. P. Perone
Galvanic Monitoring of Nitrogen Dioxide and Nitric Oxide.	P. Hersch and R. Deuringer
Automated Dumas Instrumentation for Industrial Nitrogen and Protein Analysis.	Don Papievis and Lew Malter
A New Ultraviolet-visible Spectrophotometer Human Engineered for the Modern Laboratory.	Adrian Chisholm, J. J. J. Staunton and Lew Malter

Further information may be obtained from C. M. Gambrill, Ethyl Corporation, 1600 West 8 Mile Road, Detroit 20, Mich., U.S.A.

Monday–Friday 2–6 *March* 1964: **Fifteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy:** Penn-Sheraton Hotel, Pittsburgh, Pennsylvania.

Symposia on the following subjects are proposed for the conference:

1. *Coblentz Society Symposium.*
2. *Excitation Techniques.*
3. *Electron Probe.*
4. *Analysis of Polymers.*
5. *Analysis of Gases in Metals including Activation Methods.*
6. *Far Infrared.*
7. *Adsorb Molecules.*

Original papers on all aspects of analytical chemistry and spectroscopy are invited. Three copies of a brief abstract (150 words) of each paper, with a letter listing the names of the authors, the laboratory in which the work was done, and the current addresses of the authors, should be addressed, not later than 15 October 1963, to the Programme Chairman, Mr. Rudolf B. Fricioni, Allegheny Ludlum Steel Corporation, Corporate Quality Control Laboratory, Research Centre, Brackenridge, Pennsylvania, U.S.A.

The *Fifth Omnibus Conference on Experimental Aspects of NMR Spectroscopy* will be held the week preceding the Pittsburgh Conference, at Mellon Institute, Pittsburgh.

The **National Bureau of Standards** has recently issued four groups of metal standard samples. Included in the new standards are four high-temperature alloys and ten copper-base alloys for calibrating optical emission and X-ray spectrochemical procedures. Two new Zircaloy-2 standards primarily designed for optical emission spectrochemical analysis have been made available; in addition, a revised certificate of analysis has been issued for one Zircaloy-2 and two zirconium metal standards which were made available earlier. A leaded steel standard suitable for both optical emission and X-ray spectroscopic analysis has also been issued.

YUGOSLAVIA

Monday 30 *September–Friday* 4 *October* 1963: **XI Colloquium Spectroscopicum Internationale:** Beograd.

(*Material for this section should be sent directly to the Associate Editor*)

DEUTSCHE DEMOKRATISCHE REPUBLIK

24. und 25. *Oktober* 1963: Merseburger Hochschultagung über **Moderne Methoden der analytischen Chemie.** (Die Einzelheiten sind in *Talanta*, 1963, **10**, Juni, iii, zu finden.)

SWITZERLAND

17–22 *October* 1966: **Third International Exhibition and Congress of Laboratory, Measurement and Automation Techniques in Chemistry:** Basle.

The arrangements for this event, with the technical organisation of which the Swiss Industries Fair has again been entrusted, deliberately miss the year 1965 for reasons connected with the desire to avoid any clash with other events affecting industrial and trade fairs and exhibitions in that particular year. However, it is fully intended that, as a matter of principle, the three-yearly sequence will be a regular feature as already fixed, and that is why it has been decided to organise the Fourth ILMAC in October 1968 and the Fifth in October 1971.

ERRATUM

Volume 10, *page* 813, *fourth line of Zusammenfassung:* for 0,3 μg read 0,1 μg.

Talanta, 1963, Vol. 10, pp. xxv to xxvi. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Monographs on the Radiochemistry of Elements: The Sub-Committee on Radiochemistry, National Academy of Sciences. National Research Council, U.S.A.

THE most recent monographs in the series are listed below. Each monograph is written by an authority on the radiochemistry of the particular element, and an attempt has been made to produce a monograph which will be of the maximum value to the working scientist and which contains the latest available information on the subject. Each monograph has been written to a standard format, and the contents include general reviews of the inorganic, analytical and radiochemistry of the element, a table of its isotopes, a review of properties of particular interest to radiochemists, counting techniques pertinent to the element under consideration, and a collection of detailed radiochemical procedures.

The main part of the monograph is taken up by the last section, and a critical selection of known radiochemical techniques for each element has obviously been made.

(1) NAS-NS-3050	*The Radiochemistry of Uranium:* J. E. GRINDLER. March 1962, $3.50.
(2) NAS-NS-3051	*The Radiochemistry of Nickel:* L. J. KIRBY. November 1961, $0.50.
(3) NAS-NS-3053	*The Radiochemistry of Rubidium:* G. W. LEDDICOTTE. February, 1962, $0.50.
(4) NAS-NS-3055	*The Radiochemistry of Sodium:* W. T. MULLINS and G. W. LEDDICOTTE. March 1962, $0.50.
(5) NAS-NS-3056	*The Radiochemistry of Phosphorus:* W. T. MULLINS and G. W. LEDDICOTTE. March 1962, $0.50.

In the same series under a sub-title of *Radiochemical Techniques* the following publications are now available.

NAS-NS-3105	*Detection and Measurement of Nuclear Radiation:* G. D. O'KELLEY. April 1962, $1.50.
NAS-NS-3106	*Paper chromatographic and Electromigration Techniques in Radiochemistry:* R. A. BAILEY. June 1962, $0.50.

In the former publication an extensive survey of modern methods for the detection and measurement of nuclear radiation is given. This includes scintillation methods, ionisation chambers, semiconductor radiation detectors, gas multiplication counters, and auxiliary electronic instrumentation.

In the second publication the same general style as the monographs on the radiochemistry of the elements is used. This includes general reviews of the technique, discussion of the principles involved, a survey of applications to different systems, and a collection of selected procedures.

R. J. MAGEE

Comprehensive Analytical Chemistry. Volume 1C. Classical Analysis: Gravimetric and Titrimetric Determination of the Elements. Edited by CECIL L. WILSON and DAVID W. WILSON. Elsevier Publishing Company, Amsterdam, London, New York and Princeton. 1962. Pp. xxx + 728. 140s.

THIS volume completes the review of the classical methods of analysis of which the first eight chapters occupied the first two volumes. It is divided into two chapters discussing respectively the Main Group Elements and the Transition Group Elements of the Periodic Table.

It will be remembered that in reviewing the earlier volumes one tended to enquire into what might be expected of a compiler of such a work as this today, and one wondered whether the time had not come when it would prove impossible to compress all that was known and was of use into the compass of a single work. Certainly it is no longer possible for a single writer to do justice to the whole subject of analytical chemistry; and this point has been well taken by the editors, who have called in all—or so it seems—the experts on the determination of the various elements so that each can give his expert knowledge as a contribution to the whole. The danger that lay at the back of one's mind as the possible result of this approach was that each expert might be so immersed in his own branch of the subject that his section of the work might not integrate into the whole. It seems to me that this difficulty has been avoided to a very large extent in this volume. But, once again, one must realise that the editors are dealing here with the general means for the determination of the elements in relatively simple conditions where they are usually mixed with very few substances that might have interfering effects. The real test of skill, knowledge and information comes when the material to be determined is entangled with the kind of concomitants that appear with it in nature or in manufacturing conditions; and it may well be that we must still wait for the part of this work that deals with such situations before any final judgment of its real merits can be reached.

Nevertheless, this volume completes the description of the classical methods of analysis; that is those depending on the bench work of balance, filter and burette which for so long formed the basis of analytical chemistry. These methods are, of course, still practised on a very large scale, and probably form the bulk of the analytical operations undertaken by the analysts of the world. It is only right therefore that they should retain pride of place in a book on analytical chemistry, as they do here.

Let me say right out that the present volume goes a long way to establishing the eventual value of the whole work. It contains a very satisfactory account of almost all that one could want about classical analysis, and it follows naturally from the necessary preliminary study of the first two volumes. The impression formed on first dipping into it was extremely favourable, and this impression has been strengthened by more careful reading.

As has been said, the book is presented in two chapters. The sections of each chapter correspond to the Groups of the Periodic Table; each includes a treatment of the gravimetric and titrimetric methods available for the determination of the elements and a general discussion of their analytical chemistry. Each section is followed by a long list of references to original literature mostly ranging down to 1956 or 1957, but in some instances as up-to-date as 1961.

No doubt criticism could be levelled at a few items or at the omission of a few methods, but it seems churlish to draw attention to such small matters when there is so much that is extremely good. It must be remembered that even a volume of this size cannot cram into its pages—over 700 at rather under 2½d. per page—all that is known about the analytical chemistry of the elements. Selection is vital, and personal contact of the reviewer with most of the expert contributors to this volume leads him to say without hesitation that he trusts their judgment in the matter of selection of material for each part of the book fully and unquestioningly. If one may offer a regret, it is that a work of this size and calibre cannot possibly be produced quickly. Analytical chemistry is developing so quickly just now that the newer methods can never find their way into a text-book like this; but that is a general criticism and not one of this volume.

K. A. Williams

Talanta, 1963, Vol. 10, p. xxvii to xxviii. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Determination of uranium at microgram levels by derivative polarography: Clemens Auerbach and George Kissel. (19 *June* 1963).

Properties of bases in acetonitrile as solvent—III: Hydrogen bonding between protonated and free nitrogen bases: J. F. Coetzee, G. R. Padmanabhan and G. P. Cunningham. (19 *June* 1663).

A. C. polarographic studies on the influence of tensametric waves on reduction peaks of inorganic cations and vice-versa: S. L. Gupta and S. K. Sharma. (19 *June* 1963).

Some temperature effects in gas chromatography: W. E. Harris and H. W. Habgood. (19 *June* 1963).

Thermometric titrations in acetonitrile: Earl J. Foreman and David N. Hume. (19 *June* 1963).

Polarography of copper in diethylenetriaminepenta-acetic acid solutions: Einar Jacobsen and Gunnar Kalland. (19 *June* 1963).

Geometry-related errors in instrumental neutron-activation analysis: Raljh A. Johnson. (19 *June* 1963).

Bivalent thallium and the mechanism of the electrode reaction: $Tl^{+3} \overset{2e}{\rightleftharpoons} Tl^{+}$: H. A. Catherino and Joseph Jordan. (19 *June* 1963).

Polarographic determination of certain medicinal compounds containing dichloroacetamido groups: Clark A. Kelly. (19 *June* 1963).

Radiochemical determination of strontium-89 and -90 in uranium minerals and salts: P. K. Kuroda and Hirofumi Arino. (19 *June* 1963).

Schiff base complexes: A numerical study using a high-speed computer of the nickel^{II}-pyruvate-glycinate system: D. L. Leussing. (19 *June* 1963).

Potentiostatic determination of kinetic parameters of electrode reactions with generation of a reactant *in situ*: Y. Okinaka, S. Toshima and H. Okaniwa. (19 *June* 1963).

D_2O effect on $ZH^{\neq}$ and $ZS^{\neq}$ in the $Fe^{II} + Fe^{III}$ electron exchange reaction: Shouzow Fukushima and Warren L. Reynolds. (19 *June* 1963).

Analytical applications of radioactive vitamin B_{12}: Charles Rosenblum. (19 *June* 1963).

Lead-dithizone equilibria in water-carbon tetrachloride: Owen B. Mathre and E. B. Sandell. (19 *June* 1963).

The boron-carbon-hydrogen system: I. Shapiro. (19 *June* 1963).

Some physical properties of highly purified bromine: M. S. Chao and V. A. Stenger. (19 *June* 1963).

The anodic amperometric titration of low concentrations of nitrite with sulphamic acid or cerium^{IV} ion: John T. Stock and R. G. Bjork. (19 *June* 1963).

Polarographic reduction of manganese^{III} in alkaline tartrate solution: Nobuyuki Tanaka, Yasuko Kikuchi and Yuichi Sato. (19 *June* 1963).

A modification of the exponential exchange law in heterogeneous systems: B. van't Riet and L. J. Parcell. (19 *June* 1963).

Status of and trends in analytical chemistry: I. M. Kolthoff. (19 *June* 1963).

Izaac Maurits Kolthoff and the publications of Izaac Maurits Kolthoff: James J. Ligane. (19 *June* 1963).

Mutual radiation interference effects of the alkali elements and hydrogen upon the resonance line intensities of the alkali elements in flame spectrophotometry: E. L. Grove, C. W. Scott and Ferris Jones. (20 *June* 1963).

An investigation of 2-amino-4-chlorobenzenethiol hydrochloride as a spectrophotometric reagent for the determination of molybdenum: Gordon F. Kirkbright and John H. Yoe. (20 *June* 1963).

Precipitation from mixed solvents—V: Uranium 8-hydroxyquinolate: Lester C. Howick and Tony Rihs. (21 *June* 1963).

Precipitation from mixed solvents—VI: Nickel dimethylglyoximate: Lester C. Howick and Jerry L. Jones. (21 *June* 1963).

Determination of some metals and nitrogen-containing organic compounds on the ultramicro scale by turbidimetric titration: Einar Bladh. (28 *June* 1963).

Determinations of magnesium in biological samples by spectrophotometric measurement of the 8-quinolinolate extract: Taft Y. Toribara, Larysa Koval and Jorge F. P. Olive. (1 *July* 1963).

The development of the paper chromatographic method for orientative qualitative analysis: A. SCHNEER-ERDEY and T. TOTH. (8 *July* 1963).

The precipitation from homogeneous solution of palladium using indian-1:2-dioxime: L. S. BARK and D. BRANDON. (15 *July* 1963).

Photometric titrations—VII: The consecutive titration of cadmium and zinc: H. FLASCHKA and F. B. CARLEY. (16 *July* 1963).

Zur Entmischung der Lösungsmittel bei der chromatographischen Trennung—I: Selektive Sorption des Fliessmittels auf Cellulose und Entstehung der 2. Front in Der Papierchromatographie: JAN MICHAL und GERHARD ACKERMANN. (17 *July* 1963).

Zur Entmischung der Lösungmittel bei der chromatogaphischen Trennung—II: Selektive sorption der Mischungen Alkohol-Wasser und Alkohol-Wasser-Säure an der Cellulosesäule: JAN MICHAL und GERHARD ACKERMANN. (17 *July* 1963).

A source of error in the use of a cathode ray polarograph: J. M. BAKES, G. R. E. C. GREGORY and P. G. JEFFERY. (17 *July* 1963).

Cyanometric titrations in non-aqueous solutions: L. ERDEY, O. GIMESI and G. RÁDY. (17 *July* 1963)

Complexometric titration of yttrium and the lanthanons—I: A comparison of direct methods: S. J. LYLE and MD. M. RAHMAN. (19 *July* 1963).

Complexometric titration of yttrium and the lanthanons—II: Methods for the determination in oxalates: S. J. LYLE and MD. M. RAHMAN. (19 *July* 1963).

Colorimetric determination of vanadium with Xylenol Orange: OMORTAG BUDEWSKY and RUDOLF PŘIBIL. (24 *July* 1963).

Contribution to the basic problems of complexometry—XIII: Determination of aluminium and tervalent chromium in the presence of chromate: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (24 *July* 1963).

SOLUBILITIES OF INORGANIC AND ORGANIC COMPOUNDS

Volume I, Part I.

Edited by H. STEPHEN and T. STEPHEN

This work, in two volumes, is a compilation of published data on the solubility of elements, inorganic compounds, metallo-organic and organic compounds in binary, ternary and multicomponent systems. The extremely comprehensive material comprising the contents was obtained from a detailed survey of periodical literature, published in all languages and carried out by a panel of scientists specially appointed for the purpose by the Academy of Sciences of the U.S.S.R., Moscow.

In Volume 1, dealing with solubility in Water and Anhydrous Solvents, information is presented in the form of tables arranged systematically for easy reference. Table 1 lists the solubility of about 2,000 compounds in water; each subsequent table is devoted to the solubilities of a single compound, or a number of closely related compounds. There are in all 6,540 tables covering a vast number of compounds.

964 pages **£10 net**

THE APPLICATION OF MATHEMATICAL STATISTICS TO CHEMICAL ANALYSIS

V. V. NALIMOV

Translation Editor: M. WILLIAMS, *Birmingham College of Advanced Technology*

This translation of an important Russian book gives an up-to-date account of mathematical statistics as applied to problems connected with the chemical and physical methods of analysis, the emphasis being mainly on practice. The principal theorems of mathematical statistics are explained with examples taken from researches connected with the analysis of substances. Theoretical problems are considered only insofar as they are necessary for an understanding of the metrological aspect of the matter. A detailed account of contemporary literature in this field is included which demands from the reader only a knowledge of the mathematics normally included in the courses of technical colleges and an acquaintance with the principles of the theory of probability.

Invaluable as a handbook to engineers, physicists and chemists working in research laboratories, it will also act as a useful guide to further development in statistical methods of investigation.

Chapter headings include:

Problems of mathematical statistics; Classification of analytical errors; Chance variables and their characteristics; Normal distribution; Poisson's distribution and binomial distribution; Estimation of the results of analysis; Dispersional analysis; Statistics of linear connections; Some methods of work connected with the statistical planning of an experiment.

Distributed in the U.S.A. by Addison-Wesley Publishing Co. Inc. 304 pages **84s. net**

THE APPLICATION OF ORGANIC BASES IN ANALYTICAL CHEMISTRY

E. A. OSTROUMOV, *Academy of Sciences, Moscow*

The chemical analysis of naturally-occurring inorganic compounds—various rocks, ores and minerals—is often rendered difficult by the complex composition of the substance being analysed. The present work is a collection of systematic studies by the author, on the applications of a particular class of organic compounds—organic bases—in the analytical chemistry of inorganic substances. Accurate and rapid methods for the separation and determination of a number of elements have been developed, involving the use of the organic bases pyridine, α-picoline and hexamethylenetetramine. These methods have found extensive application in the analytical chemistry involved in geochemical studies. Since the Russians have a large background knowledge to call upon in the methods of analysis involving precipitation by pyridine, this book should prove of the utmost interest to all specialists in the field.

The book is divided into six parts: (1) The precipitation of metals using pyridine (2) The precipitation of metals by pyridine in the presence of its salts (3) The precipitation of metals with hydrogen sulphide in the presence of pyridine (4) The precipitation of metals using α-picoline (5) The precipitation of metals with hydrogen sulphide in the presence of hexamethylenetetramine (6) Methods for the separation of metals using pyridine α-picoline and hexamethylenetetramine; Conclusion; References.

180 pages **50s. net**

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VOLUME 10, NO. 9 SEPTEMBER 1963

CONTENTS

Short Communication

Letter to the Editor