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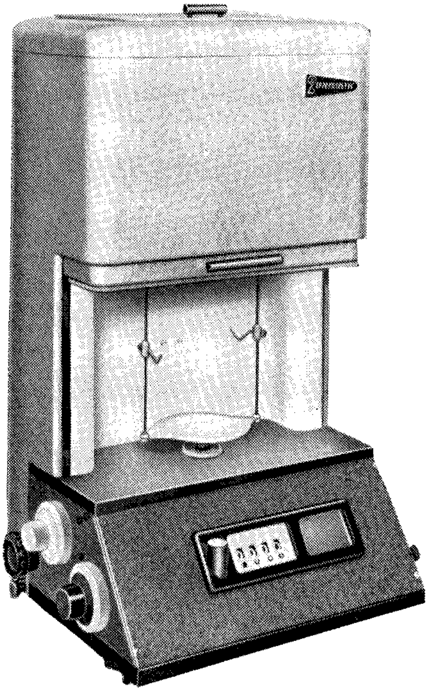

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Analytical applications of second order electrodes: JOHN O. FROHLIGER and RONALD T. PFLAUM *Talanta*, 1962, **9**, 755.

Summary—Second order electrodes of silver-silver bromide, silver-silver iodide, silver thiocyanate, silver-silver chromate and silver-silver tetraphenylboron have been investigated. Suitable electrodes for the last two systems could not be prepared. The indicator electrodes were coupled with a saturated calomel reference electrode and the potentials of various solutions measured. The response of the electrodes to anion activities was determined and compared with calculated potentials. The effects of ionic strength and diverse ions on the observed potentials were determined. Results on selected samples indicate that direct potentiometric measurements can be used for the determination of bromide, iodide and thiocyanate ions in aqueous solution. In the concentration range of $1 \times 10^{-1} - 1 \times 10^{-4}M$, measurements can be made with an accuracy comparable to that obtained in usual potentiometric work.

Spectrophotometric determination of palladium and platinum; J. T. PYLE and W. D. JACOBS, *Talanta*, 1962, **9**, 761.

Summary—Palladium^{II} and platinum^{II} form water-insoluble coloured complexes with dibenzyldithio-oxamide which are extractable into chloroform. Factors affecting the analytical use of this reagent have been investigated. The yellow palladium complex and the rose-coloured platinum complex show absorption maxima at 450 and 520 mμ, respectively. Beer's law is obeyed over the range investigated, and a close control of conditions of colour development is not necessary. The tolerance to a number of diverse ions has been established with favourable results. A procedure for the simultaneous determination of palladium and platinum has been developed.

Complexometric determination of copper in the presence of other ions: O. B. BUDEVSKY and L. SIMOVA, *Talanta*, 1962, **9**, 769.

Summary—Copper^{II} ions form stable complexes with EDTA, whereas copper^{I} ions do not. Thus, if the copper^{II} in a copper^{II}-EDTA complex is reduced to copper^{I}, an equivalent quantity of EDTA is liberated. To a solution containing copper^{II} and other ions an excess of EDTA is added, the solution is brought to pH 5·5–6·0 and titrated with lead nitrate solution in the presence of Xylenol Orange as indicator. At this pH all ions forming stable complexes, including copper^{II}, are firmly associated. Thiourea is then used for the reduction of copper^{II} to copper^{I}, in a strongly acidic media where the copper^{II}-EDTA complex is dissociated. The solution is re-adjusted to pH 5·5–6·0 and the liberated EDTA titrated with lead nitrate solution. Most common ions (Ag^{I}, Pb^{II}, Zn^{II}, Ni^{II}, Bi^{III}, Sb^{III}, As^{III}, Fe^{III}, Al^{III}, Sn^{IV}, *etc.*) do not interfere with the determination. The present method has been used successfully for the determination of copper in copper alloys, concentrates and minerals.

Separation of certain cations from mixtures of various cations on ion-exchange papers—I: JOSEPH SHERMA, *Talanta*, 1962, **9**, 775.

Summary—Development with solutions providing selective complexation and pH control permits the complete separation of silver or thallium ions from multicomponent mixtures of various ions on ion-exchange papers. Complete recovery as well as separation is demonstrated for silver on columns of ion-exchange resin.

Determination of major and minor alkalies in silicates by differential flame spectrophotometry: C. O. INGAMELLS, *Talanta*, 1962, **9**, 781.

Summary—By attaching an external galvanometer circuit to a Beckman DU spectrophotometer and making use of an improved and highly stable air-natural gas flame, it is possible to apply the principle of differential measurement to the flame spectrophotometric determination of the major and minor alkalies and alkaline earths. Although it is doubtful that any reasonably rapid, purely flame photometric, method can ever equal the best flame-supported gravimetric techniques in determinations of major alkali constituents, procedures have been worked out whereby rubidium and caesium can be determined with improved precision, and the accuracy of sodium and potassium determinations is significantly increased.

Submicro determination of Iron in Organic Materials: T. R. F. W. FENNELL and J. R. WEBB, *Talanta*, 1962, **9**, 795.

Summary—A method for the determination of iron in solid organic compounds, such as ferrocene and its derivatives, has been developed. Sample weights between 25 and 400 μg were used, the optimum sample size being such as to contain between 10 and 20 μg of iron. All results obtained from the analysis of standard compounds were within $\pm 0{\cdot}5\%$ absolute. An indication is given of the utility of working on the small scale in detecting inhomogeneity of materials.

New colour reactions of elemental sulphur and carbon disulphide: T. URBAŃSKI, *Talanta*, 1962, **9**, 799.

Summary—Simple colour reactions are described for the detection of elementary sulphur and carbon disulphide

The determination of gallium: G. R. E. C. GREGORY and P. G. JEFFERY, *Talanta*, 1962, **9**, 800.

Summary—An improved separation of gallium from other elements, using an ion-exchange column, and subsequent determination of the element by titration with EDTA, using morin as indicator, are described. The method has been applied to determination of gallium in the presence of a large excess of aluminium.

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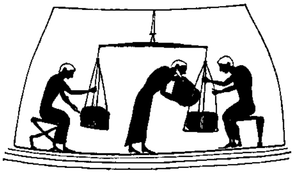

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.

[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.

[4] W. Jones, *Brit. Pat.* 654321, 1959.

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TALANTA

1962 VOLUME 9 SEPTEMBER

CONTENTS

Talanta, 1962, Vol. 9, pp. 755 to 760. Pergamon Press Ltd. Printed in Northern Ireland

ANALYTICAL APPLICATIONS OF SECOND ORDER ELECTRODES

JOHN O. FROHLIGER* and RONALD T. PFLAUM
Department of Chemistry, State University of Iowa, Iowa City, Iowa, U.S.A.

(*Received* 5 *February* 1962. *Accepted* 20 *April* 1962)

Summary—Second order electrodes of silver-silver bromide, silver-silver iodide, silver thiocyanate, silver-silver chromate and silver-silver tetraphenylboron have been investigated. Suitable electrodes for the last two systems could not be prepared. The indicator electrodes were coupled with a saturated calomel reference electrode and the potentials of various solutions measured. The response of the electrodes to anion activities was determined and compared with calculated potentials. The effects of ionic strength and diverse ions on the observed potentials were determined. Results on selected samples indicate that direct potentiometric measurements can be used for the determination of bromide, iodide and thiocyanate ions in aqueous solution. In the concentration range of $1 \times 10^{-1} - 1 \times 10^{-4}M$, measurements can be made with an accuracy comparable to that obtained in usual potentiometric work.

INTRODUCTION

A NON-DESTRUCTIVE method of analysis which has found little analytical application is the method of direct potentiometry using second order indicator electrodes. Development of the method has been hindered by the lack of suitable indicator electrodes and insufficient data on the activity coefficients of many ions. However, Chanin[1] recently was successful in determining chloride ion in biological fluids with a silver, silver chloride-mercury^{I}, mercury^{I} sulphate electrode system. He reported that the indicator electrode was useful over the concentration range of 0·1–1·0 mequiv/l. of chloride ion, but that the potential of the cell was unstable. Helmkamp and coworkers[2] analysed chlorinated insecticide residues with a silver-silver chloride indicator electrode and a saturated calomel reference electrode at 40°. In 1958, Stern and coworkers[3] used a silver-silver chloride inidcator electrode and a saturated calomel reference electrode with a Beckman Model G pH meter. The system was used for the determination of chloride ion in samples of sweat, urine and cerebrospinal fluid. In this work, the authors related the activity of chloride ion to the observed cell potential and developed the concept of pCl analogous to pH. Work similar to that of Stern and coworkers on the chloride system has been carried out on the bromide system.[4] The authors investigated the response of a silver-silver bromide indicator electrode and a saturated calomel reference electrode to bromide ion and developed a method for the direct potentiometric determination of bromide ion in aqueous solutions.

In this paper, electrode systems that respond to bromide, iodide and thiocyanate ions are described. Electrode systems that would respond to chromate and tetraphenylborate ions were investigated. Data are presented for the performance of the bromide, iodide and thiocyanate electrodes under varying conditions of ionic strength

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and diverse ion concentrations. The analytical possibilities of these direct potentiometric measurements are discussed.

EXPERIMENTAL

Apparatus

All potential measurements were made with a Beckman Model G pH meter equipped with the appropriate second order indicator electrode and a Beckman No. 1170 asbestos fibre calomel reference electrode at 25°. A Beckman No. 1281 platinum electrode with a shielded lead or a platinum bead sealed in a soft-glass envelope equipped with a shielded lead (leads from discarded glass electrodes are convenient for this purpose) forms the base of the indicator electrode.

Reagents

Analytical grade potassium bromide, potassium iodide, and potassium thiocyanate were obtained from the Mallinckrodt Chemical Works and were used as received. Potassium argentocyanide was prepared according to recommended procedures.[5,6] All other chemicals used were of reagent grade quality.

Preparation of the indicator electrodes

The platinum bead electrodes were silver plated in an electrolysis cell containing a 10% solution of cyanide-free potassium argentocyanide.[6] The resulting silver electrode was washed first with $6M$ ammonia solution, then with distilled water to remove decomposition products from the electroplating process. Second order electrodes for the bromide, iodide and thiocyanate systems were prepared by anodising the silvered beads for 15 sec in acidic solutions of the potassium salt of the respective anion. The anion concentrations were approximately $1M$. The resulting electrodes were thoroughly washed with distilled water. The electrodes were stored in $1M$ solutions of the respective anions when not in use.

Potential measurements with second order electrodes

A 300-ml tall-form beaker fitted with a rubber stopper to hold the electrodes was used as the cell vessel. A magnetic stirrer was used to stir the solutions. The electrodes were rinsed twice with portions of the test solution prior to measurement. Separate aliquots of the solution were used for measurement. Potential readings were taken at 1-min intervals on quiescent solutions until reproducible readings were obtained.

RESULTS AND DISCUSSION

Physical characteristics of the indicator electrode

The platinum beads, which form the base of the indicator electrodes, had an exposed surface area of about 3 mm^2. The silver deposit adhered firmly to the platinum beads and had a smooth dull grey appearance. The anodised electrodes varied in appearance with the silver salt deposited. The anodised layers adhered firmly to the silver deposit, but could be removed by direct contact with cleansing tissue. For this reason, the electrode surfaces were not wiped dry between measurements.

Because of the small surface area of the electrodes, they can easily be polarised by the passage of a very small current. Since a potentiometer passes sufficient current at all times except at the balance point to polarise the electrodes, this instrument was impractical as a measuring device. The current drawn by a vacuum tube voltmeter causes negligible polarisation of the small electrodes. For this reason, a pH meter was used for all potential measurements. The use of this instrument necessitated the use of shielded electrode leads in order to observe stable readings.

The silver-silver bromide electrodes functioned with no change in potential for a period of 6 months. There is apparently no effect of sunlight, artificial light, or ageing with these electrodes. The silver-silver iodide electrodes, which were originally yellow in colour, darkened to blue after about 6 weeks and required replating. The silver-silver thiocyanate electrodes functioned for about 1 month, then portions of the silver-silver thiocyanate deposit loosened and fell off the electrode.

Response of the indicator electrodes

The electrical characteristics of the indicator electrodes were determined from the cell

$$\mathrm{Ag, Ag\,X} \mid \mathrm{X^-}\ (\mathrm{x}M) \parallel \mathrm{KCl(sat)} \mid \mathrm{Hg_2Cl_2, Hg}.$$

The potential of the cell at 25° is expressed as

$$\mathrm{E\ cell} = \mathrm{E^\circ(Ag^+, Ag)} + 0{\cdot}05916 \log \mathrm{K_{AgX}} - 0{\cdot}05916 \log \mathrm{a_{(x-)}} + \mathrm{Ej} - \mathrm{E_{SCE}}.$$

In this work, E° was taken to be 0·7995 V and E_{SCE} as 0·245 V. Values of $6{\cdot}0 \times 10^{-13}$, $9{\cdot}5 \times 10^{-17}$ and $1{\cdot}2 \times 10^{-12}$ were used for the ion products of silver bromide, iodide, and thiocyanate, respectively. These are averages of the values tabulated by Schwarzenbach.[7] Activity coefficients used in the log $a_{(x^-)}$ values were obtained from Latimer's tables.[8] Cell potentials were calculated neglecting the contribution of the liquid junction potential.

TABLE I.—POTENTIAL VALUES FOR POTASSIUM BROMIDE SOLUTIONS AT 25°

Concn. KBr, *M*	$-\log \alpha_{(Br^-)}$	E.m.f. (calc.), *mV*	E.m.f. (obs.), *mV*	Δ e.m.f. *mV*
$1{\cdot}95 \times 10^{-1}$	0·846	−118	−116	−2
$8{\cdot}46 \times 10^{-2}$	1·178	−98	−99	+1
$4{\cdot}72 \times 10^{-2}$	1·412	−85	−84	−1
$1{\cdot}89 \times 10^{-2}$	1·782	−63	−64	+1
$7{\cdot}56 \times 10^{-3}$	2·159	−41	−39	−2
$3{\cdot}78 \times 10^{-3}$	2·452	−24	−25	+1

Comparisons were made between the calculated potentials and the measured potentials of solutions of known anion concentration. The data for the bromide and iodide systems are presented in Tables I and II. The observed potential values presented here and in the following tables represent the averages of replicate readings on at least two identical aliquots of the test solution. A deviation of 2 mV obtained between the observed and calculated potentials is the limit of sensitivity of the meter. The potentials listed in the tables show that the electrodes respond to the activity of the anion and that the liquid junction potential is less than the meter error and can be neglected. Although activity coefficients are not available for the thiocyanate system, the thiocyanate electrode did respond to changes in the thiocyanate concentration in the manner predicted by the Nernst equation.

TABLE II.—POTENTIAL VALUES FOR POTASSIUM IODIDE SOLUTIONS AT 25°

Concn. KI, *M*	$-\log \alpha_{(I^-)}$	E.m.f. (calc.), *mV*	E.m.f. (obs.), *mV*	Δ e.m.f., *mV*
$1{\cdot}05 \times 10^{-1}$	1·076	−329	−330	+1
$5{\cdot}25 \times 10^{-2}$	1·326	−314	−314	0
$2{\cdot}10 \times 10^{-2}$	1·733	−290	−292	+2
$1{\cdot}05 \times 10^{-2}$	2·022	−273	−274	+1
$5{\cdot}25 \times 10^{-3}$	2·282	−257	−255	−2
$2{\cdot}10 \times 10^{-3}$	2·699	−233	−232	−1
$1{\cdot}05 \times 10^{-3}$	2·996	−215	−215	0

Effect of ionic strength

In order to utilise second order electrodes in an analytical application, the measured potential should be related to concentration rather than to activity. For any system, there is a limited region of ionic strength in which the activity coefficient of a particular anion will be invariant. In this concentration range, usually achieved by the addition of a high concentration of an inert electrolyte, a direct relationship between potential and concentration is permissible. Table III shows the effect of varying concentrations of potassium nitrate on the potentials of bromide, iodide and thiocyanate solutions. At concentrations of potassium nitrate of 1·0–1·4*M*, the activity coefficient of the measured anion is essentially constant since constant potential values were obtained. These potentials can then be expressed as

TABLE III.—EFFECT OF IONIC STRENGTH ON THE RESPONSE OF SECOND ORDER INDICATOR ELECTRODES

Anion concn., *M*	Cell potentials, *mV*					
	Concn. KNO_3, *M*					
	0	0·2	0·6	1·0	1·4	1·8
$9{\cdot}45 \times 10^{-3}$ KBr	−56	−46	−40	−36	−36	−34
$1{\cdot}05 \times 10^{-2}$ KI	−276	−268	−264	−262	−262	−261
$7{\cdot}68 \times 10^{-3}$ KSCN	−39	−31	−27	−25	−24	−23

$$\text{E cell} = \text{E}' - 0{\cdot}0591 \log [\text{X}^-]$$

where E′ is the summation of all constant terms in the Nernst equation.

Effect of diverse ions

It was found that the bromide, iodide and thiocyanate electrodes responded equally well in both acidic and basic solutions. No effect of hydrogen ion was noted over a pH range of 1 to 11. Naturally, bromide ion interferes in the thiocyanate system, iodide in the bromide and thiocyanate systems, and thiocyanate in bromide solutions. Oxidising agents, such as dichromate and permanganate ions, act as interferences in all three systems. Cyanide and thiosulphate ions form soluble silver complexes and interfere in the measurements. Other common anions have no effect in concentrations of 2000 ppm.

The three systems studied are relatively free of cationic interferences. The presence of metallic ions which form complexes or insoluble salts with the anion being measured leads to errors. Thus, iron^{III} ion is undesirable in a thiocyanate solution and copper^{II} ion in an iodide system.

Analytical applications of the indicator electrodes

The determination of bromide ion, iodide ion and thiocyanate ion can be carried out using a silver-silver bromide, silver-silver iodide and a silver-silver thiocyanate indicator electrode, respectively.

Weighed samples of the anion are dissolved in distilled water and potassium nitrate added so that the final concentration of potassium ion in the solution is 1*M*. The solution is brought to constant temperature at 25°. The pH of the final solution should be between 1 and 11. The potential of the solution is then measured as previously described. The concentration of the anion is determined from a calibration curve constructed from potential measurements on solutions of known concentration.

The results of measurements on a series of synthetic samples of bromide, iodide and thiocyanate ions are shown in Table IV. The potential of the solutions can be measured with an accuracy of 2 mV. A 1-mV deviation in the potential measurement will cause a deviation of 3 to 5% in the determination of the concentration of the solution. Best results are obtained in the concentration range of 1×10^{-1} to 1×10^{-4}M.

Determination of pSCN

The use of the pH scale of the pH meter has been recommended for the potentiometric measurements of solutions of chloride[3] and bromide[4] ions. The use of the pH scale of the meter increases the sensitivity of the instrument by a factor of 100 to 59. The zero adjust control compensates for slight variation in the individual indicator electrodes. The potentials of iodide ion solutions are too large to be measured on the pH scale of the meter. However, the potentials of solutions of thiocyanate ion can be measured. The value of 11 on the pH scale was chosen as a convenient value for a 1*M* solution of thiocyanate ion concentration or zero pSCN. In order to use the pH scale, the meter must be standardised. A solution of known thiocyanate ion concentration is used to standardise the meter. For example, a 0·1*M* solution of thiocyanate ion concentration would have a pSCN of 1 and the meter would then be standardised at 10 on the pH scale; for a 0·01*M* solution, the meter would read 9.

TABLE IV.—RESULTS ON SELECTED SAMPLES IN 1*M* POTASSIUM NITRATE AT 25°

Sample	E.m.f. (obs.), *mV*	Concn. X⁻ present, *M*	Concn. X⁻ found, *M*
KBr	−92	$8{\cdot}17 \times 10^{-2}$	$8{\cdot}20 \times 10^{-2}$
KBr	−75	$4{\cdot}72 \times 10^{-2}$	$4{\cdot}70 \times 10^{-2}$
KBr, NaCl	−51	$1{\cdot}89 \times 10^{-2}$	$1{\cdot}85 \times 10^{-2}$
KBr, NaF	−4	$2{\cdot}83 \times 10^{-3}$	$2{\cdot}90 \times 10^{-3}$
KBr, K_2SO_4	+20	$9{\cdot}45 \times 10^{-4}$	$1{\cdot}05 \times 10^{-3}$
KI	−304	$5{\cdot}25 \times 10^{-2}$	$5{\cdot}40 \times 10^{-2}$
KI	−283	$2{\cdot}45 \times 10^{-2}$	$2{\cdot}55 \times 10^{-2}$
KI, NaCl	−236	$4{\cdot}20 \times 10^{-2}$	$4{\cdot}21 \times 10^{-2}$
KI, KF	−218	$2{\cdot}10 \times 10^{-3}$	$2{\cdot}00 \times 10^{-3}$
KI	−199	$1{\cdot}05 \times 10^{-3}$	$9{\cdot}50 \times 10^{-4}$
KSCN	−67	$3{\cdot}84 \times 10^{-2}$	$4{\cdot}00 \times 10^{-2}$
KSCN	−35	$1{\cdot}15 \times 10^{-2}$	$1{\cdot}15 \times 10^{-2}$
KSCN, NaCl	−25	$7{\cdot}68 \times 10^{-3}$	$7{\cdot}60 \times 10^{-3}$
KSCN, K_2SO_4	−1	$3{\cdot}00 \times 10^{-3}$	$3{\cdot}07 \times 10^{-3}$
KSCN	+17	$1{\cdot}54 \times 10^{-3}$	$1{\cdot}50 \times 10^{-3}$

TABLE V.—pSCN VALUES FOR THIOCYANATE SOLUTIONS

Concn. SCN⁻, *M*	Meter reading	pSCN (calc.)	pSCN (obs.)
$3{\cdot}84 \times 10^{-2}$	9·60	1·42	1·40
$1{\cdot}54 \times 10^{-2}$	9·14	1·81	1·86
$7{\cdot}68 \times 10^{-3}$	8·89	2·11	2·11
$3{\cdot}84 \times 10^{-3}$	8·60	2·42	2·40
$1{\cdot}54 \times 10^{-3}$	8·08	2·81	2·92
$7{\cdot}68 \times 10^{-4}$	7·72	3·11	3·28

In general, pSCN is equal to 11-scale reading. The results in Table V show the determination of thiocyanate ion solutions using the pH scale of the meter. The accuracy obtained in these measurements is comparable to that obtained in pH measurements.

Zusammenfassung—Elektroden zweiter Ordnung wie Ag-AgBr, Ag-AgJ, AgCSN, Ag-Ag_2CrO_4 und Ag-AgTetraphenylborat wurden hergestellt. Die Indicatorelektroden wurden gegen eine ges. Calomelelektrode geschaltet und die Potentiale verschiedener Lösungen gemessen. Das Ansprechen der Elektroden auf Anionenaktivitäten wurde ermittelt und mit berechneten Potentialen verglichen. Der Einfluss der Ionenstärke und verschiedener Ionen wurde studiert. Ergebnisse mit ausgewählten Systemen zeigen, dass direkte potentiometrische Messungen zur Bestimmung von Bromiden, Jodiden und Rhodaniden in wässriger Lösung angewendet werden können. Im Konzentrationsbereich 10^{-1}—10^{-4} sind die Messungen etwa von gleicher Genauigkeit wie in üblicher potentiometrischer Arbeitsweise.

Résumé—Les auteurs ont préparé des électrodes du deuxième genre: argent-bromure d'argent, argent-iodure d'argent, thiocyanate d'argent, argent-chromate d'argent et argent-tétraphénylborate d'argent. Les électrodes indicatrices sont couplées avec une électrode de référence au calomel saturée et les potentiels de diverses solutions sont mesurés. La réponse des électrodes aux activités de l'anion est déterminée et comparée aux potentiels calculés. Les effets de la force ionique et des différents ions sur les potentiels observés sont déterminés. Les résultats, pour des échantillons sélectionnés, indiquent que l'on peut utiliser des mesures potentiométriques directes pour le dosage des ions bromure, iodure et thiocyanate en solution aqueuse. Dans le domaine de concentration 10^{-1} à 10^{-4} M, des mesures peuvent être faites avec une précision comparable à celle obtenue dans une étude potentiométrique usuelle.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM AND PLATINUM WITH DIBENZYLDITHIO-OXAMIDE*

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(*Received* 1 *March* 1962. *Accepted* 10 *April* 1962)

Summary—Palladium^{II} and platinum^{II} form water-insoluble coloured complexes with dibenzyldithio-oxamide which are extractable into chloroform. Factors affecting the analytical use of this reagent have been investigated. The yellow palladium complex and the rose-coloured platinum complex show absorption maxima at 450 and 520 mμ, respectively. Beer's law is obeyed over the range investigated, and a close control of conditions of colour development is not necessary. The tolerance to a number of diverse ions has been established with favourable results. A procedure for the simultaneous determination of palladium and platinum has been developed.

INTRODUCTION

IN a recent study of a series of substituted dithio-oxamides,[1] it was found that the dibenzyl derivative showed promise of being a good reagent for the spectrophotometric determination of palladium and platinum. This derivative was selected for further investigation because of favourable absorbance curves for the palladium and platinum complexes and the sensitivities of the colour reactions. Xavier and Rây[2] have investigated dibenzyldithio-oxamide as a colorimetric reagent for certain elements of the transitional series, but these workers presented no quantitative data concerning palladium and platinum. Examination of the literature will reveal that there are many reagents proposed for the spectrophotometric determination of palladium and/or platinum. However, many of these require a close control over conditions of colour development, many are time consuming, and many require the complexation of diverse ions with agents such as EDTA if interference is to be minimised. Because of freedom from the control of variables and the simplicity of the colour reaction, dibenzyldithio-oxamide is proposed as a reagent which could find application in rapid, routine analyses for palladium and platinum.

EXPERIMENTAL

Apparatus

Spectrophotometer: All absorbance measurements were made with a Beckman Model DU spectrophotometer using matched silica cells of 1-cm light path.

Separatory funnels: Globe Separatory funnels of 125-ml volume, and stems shortened to approximately 1 cm were used for all extractions.

Reagents

Standard palladium solution: Prepared by dissolving about 1 g of palladium^{II} chloride in 500 ml of distilled water containing sufficient hydrochloric acid to give a final concentration 1*M* in the acid.

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* Paper presented at combined Southeastern–Southwestern Regional Meeting of the American Chemical Society, New Orleans, La., 7–9 December, 1961.

The palladium content was determined to be 1·15 mg/ml by the dimethylglyoxime gravimetric method.

Standard platinum solution: Prepared by dissolving about 7 g of chloroplatinic acid hexahydrate in 1 litre of distilled water with sufficient hydrochloric acid to give a final concentration 1*M* in the acid. The platinum content was determined gravimetrically by reducing the platinum to the metal with formic acid. The standard solution contained 2·83 mg of platinum per ml.

Reagent solution: Prepared by dissolving 1·00 g of dibenzyldithio-oxamide in 100 ml of acetone. The reagent, obtained from the Aldrich Chemical Company, Incorporated, Milwaukee, Wisconsin, was used without further purification. The solution was found to be stable for at least 3 weeks. Longer periods of time were not investigated.

Solutions of diverse ions: Stock solutions containing 1 mg/ml of the ion were prepared from nitrates or chlorides of the metal, except osmium, which was prepared from potassium osmate.

All other reagents were analytical grade, used without further purification.

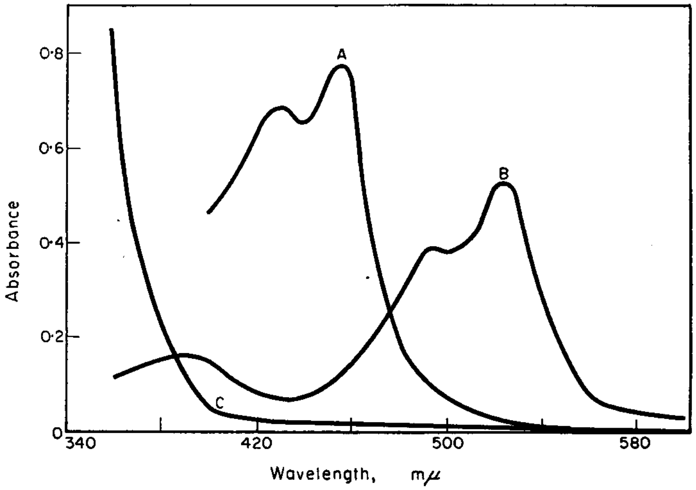

FIG. 1.—Absorbance curves for the palladium complex, platinum complex, and reagent:
(A) 4·2 ppm of palladium,
(B) 3·4 ppm of platinum,
(C) reagent, 6·6 × $10^{-3}M$.

Complex formation

Quadrivalent platinum reacts very slowly with the reagent in strong hydrochloric acid solution. However, when platinum^{IV} is reduced to platinum^{II}, the reaction proceeds fairly rapidly at room temperature, maximum colour intensity being attained in about 30 min. With palladium, the reaction is apparently instantaneous. One ml of 2*M* sodium sulphite solution, followed by hydrochloric acid, effects the reduction of platinum^{IV}. This treatment has no influence on the palladium complex formation.

Absorbance curves

The water-insoluble complexes of palladium and platinum are readily extractable into chloroform. In Fig. 1 are shown the absorbance curves for the chloroform solutions of the yellow palladium complex (4·2 ppm), the rose-coloured platinum complex (3·4 ppm), and the reagent (6·6 × $10^{-3}M$). In the case of both palladium and platinum, the colour was allowed to develop for 0·5 hr in approximately 9*M* hydrochloric acid before extraction. The maxima for palladium and platinum are 450 and 520 mμ, respectively. The reagent shows negligible absorbance above 425 mμ. The absorbances of the palladium and platinum complexes were measured against a reagent blank; the absorbance of the reagent was measured against chloroform.

Hydrochloric acid concentration

Fig. 2 shows that colour development is optimum in solutions which have an acid molarity greater than about 8. These results were obtained by varying the acid molarity of the aqueous solutions in which colour developments occurred from 0·77 to 10·0*M*, in the case of palladium, and from 2·5 to 10·6*M*, in the case of platinum. Each palladium sample contained 105·4 μg of palladium, sufficient concentrated hydrochloric acid to furnish predetermined increasing acid molarities, and 5 ml of the 10 mg/ml reagent solution. The samples were extracted with two 5-ml portions of chloroform, and diluted to 25 ml with chloroform. Each platinum sample contained 85·0 μg of platinum, 1 ml of 2*M* sodium sulphite solution, sufficient concentrated hydrochloric acid to furnish predetermined increasing acid molarities, and 5 ml of the 10 mg/ml reagent solution. The samples were extracted and diluted in the same manner as the palladium samples. The gain in sensitivity realised by increasing the acid molarity in the aqueous phase above 8*M* is so slight that reproducible results are obtained without rigorous control of the acid concentration. In practice, 25–30 ml of concentrated hydrochloric acid are used in a volume of 35–40 ml of solution before extraction.

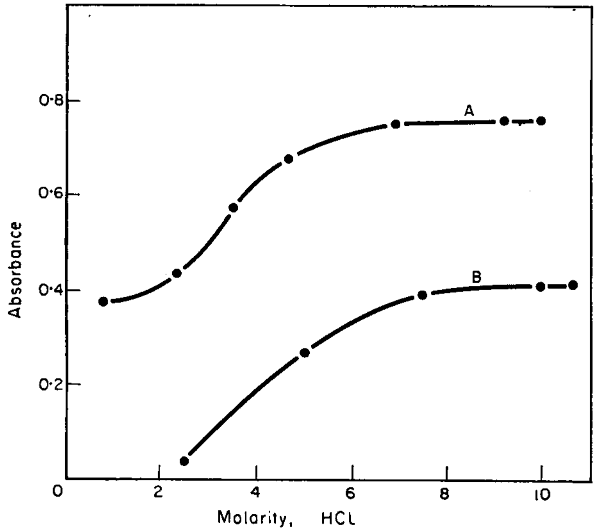

FIG. 2.—Effect of the molarity of hydrochloric acid on the palladium and platinum complexes:
(A) 4·2 ppm of palladium,
(B) 3·4 ppm of platinum.

Rate of colour formation

Studies reveal that the yellow palladium complex forms immediately, while the rose-coloured platinum complex forms more slowly. About 30 min are required for the platinum complex to develop maximum intensity. To determine the optimum time for colour development, samples of palladium and platinum were prepared containing 115·4 μg and 85·0 μg, respectively. The samples were allowed to develop colour for varying lengths of time, after which they were extracted and diluted to 25 ml with chloroform. The absorbances of the palladium and platinum complexes were measured at 450 and 520 mμ, respectively. Table I shows the findings of this experiment.

TABLE I—Rate of colour formation

	Absorbance	
Time, *min*	Pd (450 mμ)	Pt (520 mμ)
Immediately	0·812	0·290
15	0·815	0·405
30	0·815	0·445
45	0·812	0·443
60	0·815	0·446

Stability of colour

In order to investigate the stability of the extracted complexes on standing, the absorbances of a palladium sample and a platinum sample were measured at intervals of 10 min, 45 min, 3 hr, 24 hr and 48 hr. There was no change in absorbances observed over this period of time. Longer periods were not investigated.

Extraction of the complex

Extraction of prepared palladium and platinum complexes with one, two, three, and four 5-ml portions of chloroform, and subsequent determination of absorbances, indicate that the complexes are completely extracted by the use of two 5-ml portions of chlofororm.

Reagent concentration

It is desirable to use a large excess of reagent when determining palladium and/or platinum in the presence of other metals, because certain of these diverse ions appear to consume some of the reagent, even though interferences are not proportionately severe. In practice, 5 ml of the 10 mg/ml reagent solution are used. For samples containing 115·4 μg of palladium or 85·0 μg of platinum, this concentration of reagent furnishes a molar ratio of reagent to palladium and platinum of about 31:1 and 76:1 respectively.

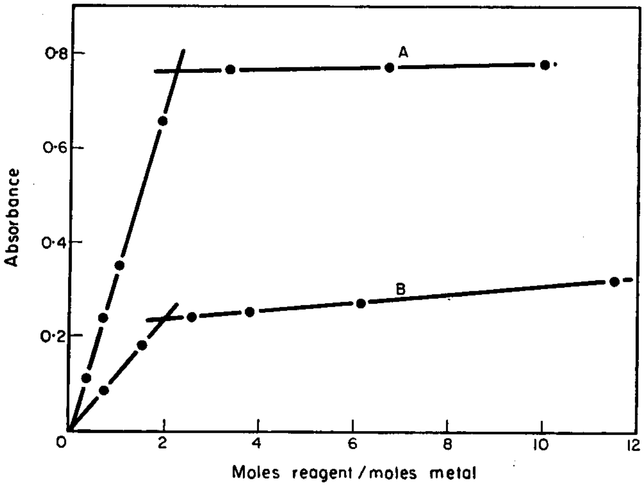

FIG. 3.—Mole ratio method applied to palladium and platinum complexes at 450 and 520 mμ, respectively:
(A) palladium, 3·96 × $10^{-5}M$,
(B) platinum, 1·74 × $10^{-5}M$.

Conformity to Beer's law

Beer's law is obeyed over the range investigated; 0·92 to 6·93 ppm in the case of palladium, and 0·68 to 5·10 ppm in the case of palladium.

Sensitivity

According to the Sandell notation,[3] the sensitivity of the reaction for palladium is 0·0055 μg per cm^2, and for platinum is 0·0075 μg per cm^2.

Nature of complex in solution

The empirical formulae for the complexes of palladium^{II} and platinum^{II} in solution were established by two independent methods, the mole-ratio method of Yoe and Jones,[4] and the slope-ratio method of Harvey and Manning.[5] The results of these experiments show that 2 moles of the reagent react with 1 mole of the bivalent metal ion. Fig. 3 shows the results of applying the mole-ratio method to the complexes of palladium and platinum at the respective wavelengths of maximum absorbance. The concentration of palladium was held constant at 3·96 × $10^{-5}M$ and that of platinum at 1·74 × $10^{-5}M$. These findings are in accord with earlier investigations of other derivatives of dithio-oxamide.[6,7,8]

Effect of diverse ions

Solutions containing 1 mg of the foreign ion per ml were prepared to determine the effect of selected ions on the colour reaction. These ions were added individually to solutions containing

TABLE II.—Effect of diverse ions on palladium complex*

Ion added	Quantity added, *mg*	Palladium found, *μg*	Error, %
Fe^{III}	5·7	77	−78·0
Fe^{III}†	5·7	110	+4·8
Co^{II}	5·0	106	+0·9
Ni^{II}	5·0	105	0·0
Ru^{III}	4·9	105	0·0
Rh^{III}	3·6	105	0·0
Os^{VI}	1·1	104	−0·9
Ir^{IV}	5·8	114	+8·5
Pt^{IV}	7·5	107	+1·9
Pt^{IV}	0·02	108	+2·9
Cu^{II}	5·0	106	+0·9
Au^{III}	2·5	141	+25·0
Au^{III}†	6·2	107	+1·9
Cr^{III}	5·0	105	0·0

* 105 μg of palladium present.

† These samples contained approximately 1 ml of 1*M* sodium sulphite.

TABLE III.—Effect of diverse ions on platinum complex*

Ion added	Quantity added, *mg*	Platinum found, *μg*	Error, %
Fe^{III}	1·0	79	−7·1
Co^{II}	0·5	80	−6·3
Ni^{II}	0·2	82	−3·5
Ru^{III}	1·0	90	+5·9
Rh^{III}	1·9	82	−3·5
Pd^{II}	0·06	88	+3·5
Os^{VI}	0·05	81	−4·6
Ir^{IV}	1·8	89	+4·7
Cu^{II}	0·2	81	−4·6
Au^{III}	2·2	79	−7·0
Cr^{III}	0·2	79	−7·0

* 85 μg of platinum present.

105·4 μg of palladium, and to solutions containing 85·0 μg of platinum. The palladium samples were extracted immediately while the platinum samples were allowed to develop colour for 30 min. An interference is arbitrarily chosen as that concentration which would give an error of greater than 3% in the amount of palladium or platinum found after extraction and dilution. The results of these findings are shown in Tables II and III.

Determination of palladium

Because the colour reaction with palladium is apparently instantaneous, the complex formed can be extracted immediately into chloroform. This technique obviates diverse ion interference markedly, because most of these ions do not form complexes immediately. A recommended procedure is as follows:

Introduce an aliquot of the sample (not over 5 ml), containing between 25 and 100 μg of palladium and no foreign ions in excess of those which would give a 3% error (see Table II), into a 125-ml separatory funnel. Add 25–30 ml of concentrated hydrochloric acid and 5 ml of the 10 mg/ml reagent solution. Swirl the funnel for a few sec, introduce about 5 ml of chloroform, stopper, and shake vigorously for about 10 sec. Let the layers separate, and draw the organic phase into a 25-ml volumetric flask. Repeat the extraction procedure, and bring the flask up to volume with chloroform. Measure the absorbance at 450 mμ against a reagent blank and determine the palladium content from a calibration curve.

Determination of platinum

Introduce an aliquot of the sample (not over 5 ml), containing between 35 and 135 μg of platinum and no foreign ions in excess of those which would give a 3% error (see Table III), into a 125-ml separatory funnel. Add 1 ml of 2*M* sodium sulphite solution, swirl, then add about 25–30 ml of concentrated hydrochloric acid. The order of this addition must not be reversed. Swirl the funnel again for a few sec and add 5 ml of the 10 mg/ml reagent solution. Allow 30 min for colour development with periodic swirling. Introduce about 5 ml of chloroform, stopper, and shake vigorously for about 10 sec. Let the layers separate and draw the organic phase into a 25-ml volumetric flask. Ignore the sulphite precipitate which may form, but remains in the aqueous phase. Repeat the extraction procedure and bring the flask up to volume with chloroform. Measure the absorbance of the sample at 520 mμ against a reagent blank and determine the platinum content from a calibration curve.

Simultaneous determination of palladium and platinum

The absorbance curves for the complexes of palladium and platinum, shown in Fig. 1, represent an almost ideal situation for the simultaneous determination of the two metals. At the wavelength of maximum absorbance shown by palladium, there is little absorbance from the platinum complex, and *vice versa.* Spectrophotometric equations may be derived from known values of the molar absorptivities of the palladium and platinum complexes, enabling one to calculate the concentrations of palladium and platinum from absorbance measurements made at 450 and 520 mμ.[9] For the equations to be valid, the absorbances of the complexes of palladium and platinum must be additive at the two wavelengths of consideration. In addition, Beer's law must be obeyed by the two complexes at both wavelengths. Both of these conditions have been verified experimentally. Molar absorptivities of the palladium and platinum complexes used for calculation of the spectrophotometric equations, and the equations derived from these values are given in Table IV. A recommended procedure for the simultaneous determination of palladium and platinum is identical to the determination of platinum alone, except that measurements are made at both 450 and 520 mμ. The molar concentrations of palladium and platinum may then be calculated with the aid of equations given in Table IV.

TABLE IV—Molar absorptivities of platinum and palladium complexes

	450 Mμ	520 Mμ
ϵ Pd	19,000	737
ϵ Pt	4,900	25,500

Equations derived from above values:

$$(\mathrm{Pd}) \times 10^5 = 5{\cdot}32\ A_{450} - 1{\cdot}02\ A_{520},$$

$$(\mathrm{Pt}) \times 10^5 = 3{\cdot}96\ A_{520} - 0{\cdot}154\ A_{450}.$$

The results of the analysis of a series of synthetic samples by this procedure are shown in Tables V and VI.

TABLE V—Simultaneous analysis of synthetic samples

Pd, μg		Pt, μg	
Added	Found	Added	Found
23·1	22·9	85·0	85·0
57·8	59·2	85·0	85·0
115	117	85·0	83·0
115	115	17·0	15·5
115	115	42·5	39·5
11·5	11·5	34·0	34·5
46·2	47·8	128	129
23·1	23·7	128	127
11·5	11·6	68·0	67·0
59·8	58·3	8·5	7·8
11·5	11·0	8·5	7·7
11·5	10·3	85·0	84·8

CONCLUSIONS

Dibenzyldithio-oxamide has been shown to react with palladium and platinum in strong hydrochloric acid solutions to form water-insoluble complexes which may be

TABLE VI—Simultaneous analysis of synthetic samples

Sample no.	Pd, μg		Pt, μg		Diverse ions, *mg*
	Added	Found	Added	Found	
1	115	117	25·5	15·4	Ir, 0·45 Ru, 0·49 Rh, 0·52
2	23·1	24·9	128	129	Same as sample 1
3	23·1	25·8	25·5	13·0	Fe, 0·50 Co, 0·50 Ni, 0·50 Cu, 0·50
4	115	117	128	119	Same as sample 3

extracted with chloroform. Conditions for the development of colour do not have to be rigorously controlled. The reagent has a sensitivity for palladium and platinum which compares favourably with other reagents for these metals. The simplicity of the analytical procedure, and the favourable tolerance for other platinum metals and certain base metals are advantages to be considered in employing this reagent for palladium and platinum.

Acknowledgement—This investigation was supported by a research grant from the National Science Foundation.

Zusammenfassung—Palladium(II) und Platin(II) bilden wasserunlösliche, gefärbte Komplexe mit Dibenzyldithio-oxamid, Die Komplexe können mit Chloroform extrahiert werden. Faktoren, die die analytische Anwendung des Reagenses beinflussen, werden untersucht. Der gelbe Palladiumkomplex hat ein absorptionsmaximum bei 450 mμ, der rosa Platinkomplex bei 520 mμ. Beer's Gesetz wird über einen weiten Konzentrationsbereich befolgt; strenges Einhalten der Bedingungen ist nicht nötig. Eine Anzahl verschiedener Ionen übt keine Störung aus. Eine Methode zur gleichzeitigen Bestimmng von Palladium und Platin wurde ausgearbeitet.

Résumé—Le palladium(II) et le platine(II) forment des complexes colorés, insolubles dans l'eau, avec le dibenzyldithio-oxamide; des complexes peuvent être extraits par le chloroforme. Les auteurs ont étudié les facteurs influant sur l'utilisation analytique de ce réactif. Le complexe du palladium jaune et celui du platine rose montrent des maxima d'absorption respectivement à 450 et 520 mμ. La loi de Beer est suivie dans le domaine étudié, et un contrôle approfondi des conditions de développement de la couleur n'est pas nécessaire. La tolérance à un certain nombre d'ions variés a été établie avec des résultats favorables. Une méthode de dosage simultané du palladium et du platine a été mise au point.

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Talanta, 1962, Vol. 9, pp. 769 to 774. Pergamon Press Ltd. Printed in Northern Ireland

COMPLEXOMETRIC DETERMINATION OF COPPER IN THE PRESENCE OF OTHER IONS

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(*Received* 20 *March* 1962. *Accepted* 20 *April* 1962)

Summary—Copper^{II} ions form stable complexes with EDTA, whereas copper^{I} ions do not. Thus, if the copper^{II} in a copper^{II}-EDTA complex is reduced to copper^{I}, an equivalent quantity of EDTA is liberated. To a solution containing copper^{II} and other ions an excess of EDTA is added, the solution is brought to pH 5·5–6·0 and titrated with lead nitrate solution in the presence of Xylenol Orange as indicator. At this pH all ions forming stable complexes, including copper^{II}, are firmly associated. Thiourea is then used for the reduction of copper^{II} to copper^{I} in a strongly acidic media where the copper^{II}-EDTA complex is dissociated. The solution is re-adjusted to pH 5·5–6·0 and the liberated EDTA titrated with lead nitrate solution. Most common ions (Ag^{I}, Pb^{II}, Zn^{II}, Ni^{II}, Bi^{III}, Sb^{III}, As^{III}, Fe^{III}, Al^{III}, Sn^{IV}, *etc.*) do not interfere with the determination. The present method has been used successfully for the determination of copper in copper alloys, concentrates and minerals.

THE fact that copper^{II} forms stable complexes with EDTA[1] has been used for its easy and precise determination by complexometric titration. Because the reaction of EDTA with copper^{II} is not selective, most of the proposed complexometric methods necessitate the preliminary separation of copper^{II} from all other ions.[2,3] A few methods are available by which the determination of copper is possible in the presence of only one or two other ions, the interference of the latter being eliminated by a suitable masking agent.[4,5,6,7,8]

Many univalent ions do not form stable EDTA-complexes, so that their presence does not interfere with the complexometric determination of bi- and tervalent ions. The stability constant of the copper^{I}–EDTA complex is not known, but its value is small. This permits the determination of many bivalent ions in the presence of copper^{I}. Thus a method for the determination of zinc in brass has been devised, using thiosulphate as a reducing and masking agent for copper^{II}.[4]

The different behaviour of copper^{II} and copper^{I} in respect to EDTA is used in the present paper to develop a complexometric method for the determination of copper^{II} in the presence of other ions, based on reduction of the copper^{II} in a copper^{II}-EDTA complex to copper^{I} and titration of the liberated EDTA.

EXPERIMENTAL

Reagents

0·05*M EDTA solution:* Prepared by dissolving 37·22 g of Chelaton 3 (Chemapol, Prague) in 2 litres of distilled water. The solution was standardised against copper (E. Merck AG) in dilute ammonia solution (pH 7·5–8·0) using murexide as indicator.

0·05*M Copper*^{II} *nitrate solution:* Prepared by dissolving 24·16 g of $Cu(NO_3)_2.3H_2O$ (analytical grade) in 2 litres of distilled water. The solution was standardised against 0·05 *M*EDTA solution in a slightly alkaline medium, as described above.

0·025M Lead nitrate solution: Prepared by dissolving 16·52 g of $Pb(NO_3)_2$ (analytical grade) in 2 litres of distilled water and standardised against 0·05*M* EDTA solution at pH 5·5–6·0 using Xylenol Orange as indicator.[9]

10% Thiourea solution: Prepared by dissolving 100 g of thiourea (analytical grade) in 1 litre of cold distilled water and then filtered.

Acetate buffer solution (pH 5·5–6·0): Dilute 95 ml of glacial acetic acid (analytical grade) with 500 ml of distilled water, then add 135 ml of ammonia solution (analytical grade, sp. gr. 0·91) and make the solution up to 1 litre with distilled water. When the buffer is diluted ten times the pH of the buffer solution should have a value of 5·5–6·0 (measured with a pH-meter). If necessary it must be corrected.

Xylenol Orange indicator:[9] 0·1 g of Xylenol Orange (Chemapol, Prague) ground with 10 g of potassium nitrate in a porcelain mortar.

Solutions of various ions having a concentration of 10 mg/ml were prepared from salts (analytical grade reagents) of Ag^{I}, Hg^{I}, Hg^{II}, Zn^{II}, Ni^{II}, Cd^{II}, Co^{II}, Mn^{II}, Fe^{II}, Fe^{III}, Sb^{III}, Bi^{III}, As^{III}, Al^{III}, Cr^{III}, Sn^{IV}, Se^{IV}, Te^{IV}, V^{V}, Mo^{VI}, chloride and sulphate. All other reagents were analytical grade.

Apparatus

An officially verified 25-ml burette with 0·05-ml divisions and a sharpened tip covered with solid paraffin was used, thus permiting titration with 0·01-ml drops. The titrated solution was agitated with a magnetic stirrer. All of the volumetric flasks and pipettes were officially verified.

RESULTS

Investigation of the copper^{II}-EDTA reduction

Preliminary experiments indicated that in the presence of EDTA and at pH 5·5–6·0 reduction of the copper^{II}-EDTA complex is incomplete. The following reducing agents were used: thiosulphate, thiourea, thioglycollate, ascorbic acid and sulphite. The incomplete reduction is probably caused by the presence of EDTA which, by associating with copper^{II} in a complex, lowers the redox potential of the copper^{II}/copper^{I} system. The EDTA complexes of bivalent metals are stable in alkaline, neutral or weakly acid media, but not in strongly acidic media. In acidic solutions (pH 0–1) the bivalent ion complexes are dissociated. It is, therefore, to be expected that an increase of hydrogen ion concentration and hence of copper^{II} concentration should result in an improvement of the reduction conditions. Experiments showed that in strongly acidic solution copper^{II} ions are reduced quantitatively to copper^{I} by thiourea in the presence of EDTA and a colourless complex of copper^{I} is formed. Detailed investigations were performed to establish the optimum reduction time, the most suitable thiourea concentration, *etc.*, so that the best conditions for the quantitative determination of copper were found. Based on these experiments the following procedure for the determination of copper is proposed:

To a neutral solution containing 5–50 mg of copper^{II}, add an excess of 0·05*M* EDTA solution, 2 ml of buffer solution (pH 5·5–6·0) and Xylenol Orange indicator*. Titrate with 0·025*M* lead nitrate solution until the colour of the titrated solution just becomes permanently blue. Add 25 ml of 10% thiourea solution, followed by nitric acid (1:1) dropwise until the colour of the solution changes to yellow†. Stir for 10 min, then neutralise with ammonia solution (1:1) until a violet colour appears. Add 5 ml of buffer solution (pH 5·5–6·0). The precipitate of elemental sulphur which is formed is no obstacle to the further analysis. Titrate the liberated EDTA with 0·025*M* lead nitrate solution in the presence of the Xylenol Orange indicator until a colour change from yellow to violet takes place. The volume of 0·025*M* lead nitrate solution used for the second titration is equivalent to the copper^{II} content of the solution.

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* The colour of the solution should be green (a mixed colour from the blue of the copper^{II}-EDTA complex and the yellow of the Xylenol Orange). If the solution is blue, it is an indication that the volume of 0·05*M* EDTA solution is insufficient or that the pH is above 6·0.

† The copper^{II}-EDTA complex is dissociated and the blue component disappears.

Interferences

Standardised solutions of different amounts of foreign ions and equivalent amounts of EDTA were added to a solution containing 15·90 mg of copper^{II}. The pH of the solution was adjusted to 5·5–6·0, excess EDTA titrated with 0·025*M* lead nitrate solution and the determination completed as described above.

The results of these investigations are shown in Table I. They indicate that the ions most commonly encountered (Ag^{I}, Zn^{II}, Ni^{II}, Bi^{III}, Sb^{III}, As^{III}, Fe^{III}, Al^{III}, Cr^{III}, Sn^{IV}, *etc.*) over a wide range of concentrations, do not interfere with the determination of copper^{II}. The presence of the lead^{II} used as titrant has no effect on the determination. The influence of magnesium^{II}, calcium^{II} and barium^{II} was not studied, because no interference is to be expected from them. A certain amount of interference was encountered at very high concentrations of foreign ions. This is probably caused by the adverse effect of the large quantities of EDTA (added to complex foreign ions) on the reduction of the copper^{II} ion and also by the increase of the ionic strength of the solution. Aluminium^{III} and tin^{IV} are easily masked as fluoride complexes.

Iron^{II} and cobalt^{II} interfere with the determination and their contents must not exceed 5–10 mg. Cobalt^{II} ions have a negative effect and those of iron^{II} a positive one. The effect of the latter can be diminished by preliminary oxidation of the solution.

Cadmium^{II}, manganese^{II}, mercury^{I} mercury^{II}, vanadium^{V} and molybdenum^{VI} should be absent. Even small quantities of these ions have an unfavourable effect on the results. Manganese^{II} is easily removed as $MnO_2.xH_2O$ by oxidation with persulphate in a nitric acid medium. The effect of mercury^{I} ions could probably be eliminated if they were oxidised to mercury^{II}, then the latter masked with potassium iodide. In the presence of molybdates, the titration could be carried out with a zinc salt instead of lead nitrate solution.

Regarding anions, it was found that chloride and sulphate have no effect, whereas selenium and tellurium are precipitated in the elemental form and make observation of the colour changes in the vicinity of the equivalent point difficult.

Determination of copper in copper alloys, concentrates and minerals

From the results obtained with pure solutions it seemed that the method might be very convenient for the determination of copper in materials rich in copper (above 10%). A number of analyses of copper alloys, a concentrate and a mineral (bornite) were performed. The results are to be seen in Table II. They indicate good reproducibility and agreement with the results obtained by electroanalytical determination.

Procedure for copper alloys: Dissolve 0·1 g of sample in a 100-ml volumetric flask with 5-ml of nitric acid (1:1) (in the presence of tin boil the solution for 5 min). Cool the solution, then dilute to the mark with distilled water. Transfer a 25-ml aliquot to a 150-ml beaker and add 15 ml of 0·05*M* EDTA solution and Xylenol Orange indicator. Add ammonia solution dropwise until the green colour of the solution receives a blue tint, then add 2 ml of buffer solution (pH 5·5–6·0) and complete the analysis as described previously.

Procedure for copper concentrates and minerals: Dissolve 0·3–0·5 g of sample in 10 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid, then evaporate the resulting solution to a dry residue. Add a further 2–3 ml of nitric acid and repeat the evaporation. Pour over the residue 50 ml of 1% nitric acid solution and boil for 1 min, then filter into a 100-ml volumetric flask. Wash the filter with warm 0·1% nitric acid solution. Cool and made up the solution to the mark with distilled water. Depending on the quantity of copper, transfer an aliquot of 10–20 ml to a beaker, add 0·5 g of ammonium fluoride (to complex aluminium^{III}), then 10–20 ml of 0·05*M* EDTA solution. Boil for 2–3 min and cool. Add Xylenol Orange indicator and neutralise the solution with ammonia solution (1:1) until a blue tint appears. Add 2 ml of buffer solution (pH 5·5–6·0) and complete the analysis as described previously.

TABLE I.—RESULTS FOR THE DETERMINATION OF 15·90 MG OF COPPER IN THE PRESENCE OF FOREIGN IONS.

Foreign ion taken, *mg*		Weight ratio of Cu: foreign ion	Cu found, *mg*	Deviation	
				mg	%
Ag^{I}	100	1 :6·3	15·76	−0·14	−0·6
Zn^{II}	25	1 :1·5	15·95	0·05	0·3
	50	1 :3·1	15·91	0·01	0·06
	100	1 :6·3	15·93	0·03	0·2
Ni^{II}	10	1 :0·6	15·86	−0·04	−0·2
	25	1 :1·5	15·76	−0·14	−0·9
	50	1 :3·1	15·73	−0·17	−1·1
Bi^{III}	5	1 :0·3	15·90	0·00	0·0
	50	1 :3·1	15·93	0·03	0·2
	100	1 :6·3	15·71	−0·19	−1·2
Sb^{III}	50	1 :3·1	15·96	0·06	0·4
	100	1 :6·3	15·91	0·01	0·06
As^{III}	100	1 :6·3	15·87[a]	−0·03	−0·2
Fe^{III}	10	1 :0·6	15·90	0·00	0·0
	20	1 :1·2	15·91	0·01	0·06
	30	1 :1·9	15·78	−0·12	−0·8
	40	1 :2·5	15·74	−0·16	−1·0
Al^{III}	5	1 :0·3	15·94[b]	0·04	0·2
	10	1 :0·6	15·85[b]	−0·05	−0·3
Cr^{III}	5	1 :0·3	15·78	−0·12	−0·7
Sn^{IV}	50	1 :3·1	15·79[c]	−0·11	−0·7
	100	1 :6·3	15·96[c]	0·06	0·4
Fe^{II}	5	1 :0·3	15·91	0·01	0·06
	25	1 :1·5	16·10	0·20	1·3
Co^{II}	2	1 :0·1	15·92	0·02	0·1
	5	1 :0·3	15·74	−0·16	−1·0
	10	1 :0·6	15·72	−0·18	−1·1
Cd^{II}	2	1 :0·1	16·19	0·29	1·8
	5	1 :0·3	16·20	0·30	1·9
	10	1 :0·6	16·18	0·28	1·8
	50	1 :3·1	76·30	0·40	2·5
Mn^{II}	2	1 :0·1	16·22	0·32	2·0
	5	1 :0·3	16·34	0·44	2·8
Hg^{II}	10	1 :0·6	18·27	2·37	14·9
Hg^{I}	5	1 :0·3	—[d]	—	—
Cl^{-}	200	1 :12·6	15·91	0·01	0·06
SO_4^{2-}	200	1 :12·6	15·95	0·05	0·3
SeO_3^{2-}	1	1 :0·06	15·93	0·03	0·2
	5	1 :0·3	—[e]	—	—
TeO_3^{2-}	5	1 :0·3	—[e]	—	—
VO_3^{-}	5	1 :0·3	—[f]	—	—
MoO_4^{2-}	20	1 :1·2	—[g]	—	—

[a] A precipitate forms, which disappears during titration.
[b] Preliminary boiling of the solution with ammonium fluoride.
[c] Preliminary boiling of the solution with sodium fluoride.
[d] A black precipitate of elemental mercury appears.
[e] A red precipitate of elemental selenium and tellurium appears.
[f] The solution cannot be titrated because the indicator is blocked.
[g] A precipitate of lead molybdate appears when the solution is titrated.

TABLE II.—RESULTS FOR THE DETERMINATION OF COPPER IN ALLOYS, ETC.

Sample	Copper found by electroanalysis, %	Copper found by the present method, %	Number of analyses	Standard deviation relative, %
Brass[a]	60·40	60·51	17	0·34
Copper alloy[b]	78·39	78·52	6	0·22
Copper concentrate	11·96	12·17	9	0·73
Bornite	44·70	44·50	4	0·94

[a] The alloy contains also 38·65% of zinc and 0·92% of lead.
[b] The alloy contains also 3·80% of tin, 4·65% of lead and 6·57% of zinc.

DISCUSSION

Existing complexometric methods have not solved the problem of determining copper^{II} in the presence of more than one or two foreign ions. The present method achieves this by making use of a selective reduction of copper^{II} in the copper^{II}-EDTA complex to copper^{I}, whereupon an equivalent quantity of EDTA is liberated. The ions most commonly encountered, over a wide range of concentrations, do not interfere with the determination. Interfering ions (*i.e.* cadmium^{II}, mercury^{I}, mercury^{II}, *etc.*) are not usually met in copper alloys and concentrates. The method is rapid and especially convenient for the determination of copper in materials rich in copper.

Zusammenfassung—Die Methode beruht auf die Tatsache, daß Cu(II) stabile Komplexe mit ÄDTE bildet, wobei Cu(I) von der ÄDTE nicht gebunden wird. Bei einer Reduktion von komplexgebundenem Cu(II) zu Cu(I) wird aus diesem Grunde eine äquivalente Menge ÄDTE freigesetzt. Die Versuchslösung wird mit einem Überschuß von Na_2ÄDTE versetzt, auf pH 5,5–6 korrigiert und mit $Pb(NO_3)_2$-Lösung in Gegenwart von Xylenolorange zurücktitriert. Alle Ionen (einschließlich Cu(II)), die stabile Komplexe mit ÄDTE bilden, werden auf diese Weise Komplex gebunden. Jetzt wird die Lösung angesäuert, das frei gewordene Cu(II) mit Thiokarbamid zu Cu(I) reduziert, wieder auf pH 5,5–6 neutralisiert und die freigesetzte ÄDTE mit 0,025 m $Pb(NO_3)_2$ weitertitriert. Die Ionen, die sehr oft das Kupfer begleiten (Ag(I), Pb(II), Zn(II), Ni(II), Bi(III), Sb(III), As(III), Fe(III), Al(III), Sn(IV) u.a.) stören bei der Bestimmung des Kupfers nach dieser Methode nicht. Der Einfluß anderer Ionen wurde auch untersucht. Die Methode wurde bei der Bestimmung des Kupfers in Kupferlegierungen, Kupferkonzentraten und Kupfermineralien mit Erfolg angewendet.

Résumé—La méthode est basée sur le fait que Cu^{II} donne de complexes stables avec l'EDTA, par contre de Cu^{I} qui ne forme pas de complexes de la sorte. On réduit le Cu^{II} à Cu^{I} de manière qu'on délibère une quantité équivalente d'EDTA. A la solution qui contient Cu^{II} et d'autres ions, on ajoute un excès de Na_2EDTA, après quoi on ajuste le pH à 5,5–6 et on titre avec une solution de $Pb(NO_3)_2$ en présence de xylenol orange. De cette façon, tous les ions formant chez ce pH des complexes stables avec EDTA sont liés. On accomplit la reduction de Cu^{II} à Cu^{I} à l'aide de thiourea dans un milieu fort acide, où les complexes de Cu^{II} avec EDTA sont dissociés. On amène le pH de la solution à 5,5–6 et on titre avec 0,025 m $Pb(NO_3)_2$ la quantité libérée d'EDTA. La détermination peut être accomplie en présence des ions qui d'habitude accompagnent le cuivre. L'influence des autres ions a aussi été étudiée. En appliquant cette méthode, nous avons fait des dosages de cuivre dans les alliages de cuivre, les concentrates et différents minéraux.

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Talanta, 1962, Vol. 9, pp. 775 to 780. Pergamon Press Ltd. Printed in Northern Ireland

SEPARATION OF CERTAIN CATIONS FROM MIXTURES OF VARIOUS CATIONS ON ION-EXCHANGE PAPERS—I

SILVER AND THALLIUM

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(*Received* 30 *January* 1962. *Accepted* 19 *March* 1962)

Summary—Development with solutions providing selective complexation and pH control permits the complete separation of silver or thallium ions from multicomponent mixtures of various ions on ion-exchange papers. Complete recovery as well as separation is demonstrated for silver on columns of ion-exchange resin.

ONE of the important uses of ion exchange is for the separation of cations from anions.[1] In this report, solvents which selectively cause one cation to remain positively charged while all other cations are anionically complexed are used in conjunction with filter paper impregnated with anion-exchange resins to provide a complete separation of that one cation from a complex mixture. As the solvent flows, the cation migrates rapidly while the anions undergo ion exchange and migrate slowly or not at all.

Differential migration in an ammonical solution of oxalate plus cyanide permits the separation of thallium^{I} ions from univalent silver and mercury ions and from various multivalent cations. Differential migration in an ammoniacal solution of ammonia-triacetic acid (nitrilotriacetic acid) permits the separation of silver from univalent thallium and mercury ions and from various multivalent cations.

Separate studies with silver ions show that the qualitative separation procedures developed on ion-exchange papers can be rendered accurately quantitative by use of columns of ion-exchange resin. As has been reported for other ion-exchange procedures,[2] the results of ion exchange on papers and in columns of the same resin are entirely analogous.

EXPERIMENTAL

Studies on ion-exchange papers

Migration apparatus. Paper chromatograms were developed by the downward flow of solvent in a bench-top Chromatocab (Research Specialties Co., Model C-350). Amberlite SB-2 ion-exchange papers (batch No. 7804) were used in sheets 18 in. long (except in one experiment) by up to 10 in. wide, exactly as supplied (Rohm and Haas Co.). This paper contains about 45% by weight of Amberlite IRA-400 strong-base anion-exchange resin in the chloride form. Migrations were performed perpendicular to the machine direction of the paper.

Samples were applied to the dry paper at marked locations by means of a micropipette. The origin was close to the developer and always the same distance from the surface of the developer. A migration distance of about 40 cm was available between the origin and the bottom of the sheet. The spots were dried for 15 min after application by hanging the paper in a hood and using a hair dryer. The paper was placed in the chamber, with the end closest to the origin line in a solvent trough, and allowed to equilibrate for 45 min in the presence of a container of developer. The developer was then introduced into the trough through a hole in the top of the cabinet, and development was allowed to proceed until the solvent front was close to the bottom of the paper; this required about 3 hr with the solutions used. The paper was then removed from the chamber, and the solvent front was marked; the paper was dried for 30 min and sprayed with the proper reagents to make the zones of the substances visible.

Developing solvents. Three solvents were used to develop the chromatograms in this work. To separate silver, 0·0125M ammonia-triacetic acid in 3·0M ammonia, pH 11·0, was used. For studies involving thallium (1) 0·05M potassium cyanide and 0·05M ammonium oxalate in 0·185M ammonia, pH 9·5, and (2) 0·05M potassium cyanide and 0·075M ammonium oxalate in 0·20M ammonia were employed. These solvents were chosen because electrochromatographic studies[3] had indicated that they would give the desired separations and would not interfere with detection tests.

Initial zones. To compare the migrations of various cations (listed below) in the systems chosen, single spots [10 μl for all ions except Ni (20 μl), and Al, Sb, and Sn^{IV} (25 μl)] were developed at a concentration of 0·05M. The amount of sample was chosen so that the zone could be detected after migration and concomitant dilution.

Sample solutions were prepared by dissolving the proper amount of reagent-grade nitrate, chloride, or acetate. Antimony and arsenic chloride, mercurous nitrate, and cerium ammonium sulphate solutions were stabilised with acid.

Synthetic mixtures of ions were tested to ascertain whether there was any variance in behaviour from the single cation solutions to the mixture. A mixture of all cations studied could not be used because of the incompatibility of some of the ions. A representative compatible mixture contained Ag, Cd, Co, Cu, Fe, Pb, Ni, Tl, Al, Ce, Mg, Zn, Cr, Mn, and Ba. The concentration of each ion was 0·05M except that nickel was 0·10M and aluminium was 0·15M.

Detection of zones. Four spray reagents were sufficient to detect all ions studied. All the ions which reacted with a given reagent were run on one piece of paper, which was then treated with this reagent. Likewise, when a synthetic mixture was separated, four spots of mixture were run under identical conditions on four separate pieces of paper, which were sprayed with the four reagents so as to account for every ion.

Many ions were converted to coloured sulphides by spraying the paper with a 2% solution of yellow ammonium sulphide. These included Ag, Tl, Pb, Cu, Cd, Fe^{III}, Co, Ni, Sb, Hg^{I}, Hg^{II}, As, and Sn^{IV}. Some of these ions formed coloured zones when spotted on the dry ion-exchange paper and required no spray for detection. For nickel with the ammonia-triacetic acid solvent and copper with the oxalate solvents, no sulphides formed upon spraying with the reagent. For these cases, it was necessary to spray the paper with 3·0M hydrochloric acid and allow it to stand several hr before spraying with sulphide.

Al, Ce^{IV}, Mg, and Zn were detected by spraying with 8-quinolinol (0·5 g in 60 ml of absolute ethanol, diluted to 100 ml with water), and viewing the resultant fluorescent spots in a darkened room under ultraviolet light.

Mn^{II} and Cr^{III} were located with alkaline ammoniacal silver nitrate (0·1M silver nitrate in 2M ammonia, mixed with an equal volume of 6M sodium hydroxide).

Barium ions were located by spraying with 3M acetic acid followed by a freshly prepared 0·1% solution of potassium rhodizonate.

Studies on columns of ion-exchange resin

Ion-exchange resin. Amberlite CG-400 (lot No. SW-3203), strong-base anion-exchange resin, 200-400 mesh, in the chloride form, was used (Rohm and Haas Co.). The resin was treated before use by the recommended procedure.[1]

Ion-exchange column. In all experiments, columns of resin 10 cm high were used. They were prepared by pouring a slurry of resin and eluent into columns, 15 cm × 3·90 cm^2 (Ace Glass Co., drawing T-3422). A glass-paper disc was placed on top of the bed of resin to prevent its disturbance as solutions were added.

Exploratory studies. The separation of silver was studied on ion-exchange columns in order to compare the results with those obtained on ion-exchange papers, and to indicate the quantitative usefulness of the systems studied. The only eluent employed was the ammoniacal ammonia-triacetic acid solvent described above.

A series of solutions, each 0·1M in silver and 0·1M in one of the ions listed in the mixture above, was eluted in turn through a column of resin. Five ml of solution were mixed with eluent, loaded on to the column with a pipette, and washed into the bed with several portions of eluent. A separatory funnel containing a supply of eluent was attached to the column with a rubber stopper. The flow rate of eluent was regulated at 1–2 ml per min. Effluent was automatically collected from the point of sample addition in constant fractions of about 5·0 ml.[4] Each fraction were tested qualitatively for silver and the other metal ion in the pair. The elution was stopped when all the silver had been eluted from the column.

To test qualitatively for the presence of each metal, common spot tests were used, such as hydrochloric acid (after neutralisation with HNO_3) for Ag; sulphide for Cd, Co, Cu, Fe, Pb, and Tl; Eriochrome Black T (purple colour) for Al, Mg, Mn; potassium rhodizonate (brown precipitate) for Ba; dithizone in CCl_4 for Ni and Zn; and Xylenol Orange (pH 4·5-red) for Cr.

Later, a series of elutions of the fifteen-component mixture above was run. The solution used was a standard solution of 0·09943*M* silver nitrate which was also 0·025*M* in each other ion. Exactly 5 ml of this mixture, mixed with eluent, were added to the column and all the silver was collected in a single effluent fraction. To check the recovery of the silver, it was determined gravimetrically by neutralising the ammonia with about 40 ml of 0·15*M* nitric acid, precipitating silver chloride with a carefully controlled excess of 0·12*M* hydrochloric acid, and continuing as usual.[5] The ammonia-triacetic acid in the eluent did not at all interfere with this determination.

RESULTS

Separation of silver ions from thallium and multivalent cations in ammoniacal ammonia-triacetic acid on ion-exchange papers

In the interpretation of results, use is made of the familiar equation

$$R_F = \frac{\text{distance travelled by leading edge of solute zone}}{\text{distance travelled by solvent front}} \quad . \qquad (1)$$

Ammonia-triacetic acid forms anionic chelate complexes with multivalent cations and silver and thallium^I ions. In strongly ammoniacal ammonia-triacetic acid, however, the silver becomes cationic, forming $Ag(NH_3)_2{}^+$, while thallium^I and multivalent ions remain anionic. This has been proven by electrochromatographic studies, by noting the direction of migration of various ions in background solutions of this nature.[3]

Development with this solvent on anion-exchange paper causes silver to move with a mean R_F value of 0·77. Of all other ions tested, only thallium shows appreciable movement (R_F = 0·21); copper has R_F = 0·092 and cadmium has R_F = 0·070. No other ion leaves the origin. The significant movement of thallium indicates that ammonia-triacetic acid complexes multivalent ions much more strongly than it does univalent thallium. Univalent mercury is unstable in ammoniacal solutions, decomposing to mercury and mercury^{II} ions, neither of which leaves the origin.

When developed over the full 40 cm of paper afforded in the present apparatus, the rear of the silver zone is separated from the front of the thallium zone by 17·5 cm. The silver zone has an average length of 2·7 cm and an average width of 1·0 cm after development.

In the course of this study, 12 migrations of silver, both from single spots and from mixtures, were performed. The standard deviation of the resultant R_F values was ±0·03 R_F unit.

Because thallium is the only other ion with significant movement in the system used, studies to determine how quickly silver could be separated from the other ions were made using only thallium and silver ions. The separation was considered complete when the rear of the silver zone was separated from the front of the thallium zone by one cm. It was found that on a sheet of paper 14 in. long and 6 in. wide, this requirement was met in 15 min. During this short period of time the solvent front moved about 4·5 cm past the origin, which was more than expected from the results of the usual 3-hr migrations. This indicates that the rate of downward flow of solvent substantially decreases with time, an effect noted in other studies.[6] As was expected, the silver zone measured only 1·2 cm after this short period of migration, compared with the greater tailing (above) during the usual 3-hr migrations.

These results indicate that by development for only 15 min in the system described silver can be completely separated from all ions studied. The procedure can be further shortened by omitting the pre-equilibration of the paper (which is often omitted when one-phase solvents are employed) and omitting the drying of the paper before spraying with the developing reagents.

Separation of thallium ions from silver and multivalent cations in ammoniacal oxalate plus cyanide on ion-exchange papers

Electrochromatography[3] has proved that all multivalent cations and silver ions are converted into complexes in the presence of oxalate and cyanide ions, while thallium ions remain as cations. These are separable by ion exchange. Univalent mercury again is unstable in the presence of ammoniacal cyanide, forming mercury and mercury^{II} ions.

Of the two ammoniacal oxalate-cyanide developing solvents which were studied in the attempt to find a solution which would facilitate the separation of thallium from the other ions, solvent (2) (above) proved the more successful. In it, thallium migrated with an $R_F = 0{\cdot}30 \pm 0{\cdot}02$ (standard deviation, 7 trials), while no other cation, except magnesium, showed movement from the origin. The thallium zone had an average length of 5·3 cm after the usual 3-hr development period, which means that the rear of the zone was 7·3 cm from the origin.

With solvent (2), the magnesium zone moves with an average value of $R_F = 0{\cdot}20$ having a zone length of 3–4 cm after a 3-hr development period. Results of several trials indicate that under the conditions used, an average thallium zone would separate completely from an average magnesium zone by about 0·75 cm, but that the separation was not complete every time. The separation of thallium from all other ions tested ($R_F = 0$) is easily accomplished.

Solvent (1) contained a lower concentration of oxalate ions and ammonia than solvent (2). When solvent (1) was used as the developing solvent, thallium moved more slowly with less tailing [$R_F = 0{\cdot}30 \pm 0{\cdot}01$ (standard deviation, 6 trials); average length = 5·3 cm; rear of zone moved 5·1 cm from the origin] than in solvent (2). Magnesium also moved more slowly, the rear of its zone barely leaving the origin. With solvent (1) however, the ions studied, when applied to the paper separately, did not behave in the same way as they did when applied as part of the mixture. Some of the ions showed movement from the initial zone of mixture, but not when present as a single component. This indicated that there was too low a concentration of complexing agent in solvent (1); results for a given ion with solvent (2) were the same whether that ion was alone or part of a mixture.

The significant movement of the magnesium zone in the two solvents which were used indicates that the magnesium ions are either in the form of weak anionic oxalate complexes, or un-ionised covalent oxalate complexes[7] (or both), and therefore do not undergo ion-exchange reactions with the resin in the paper to the same extent as do the other multivalent ions.

These studies show that thallium can be completely separated from all ions studied, except perhaps magnesium ions, by development as directed above.

Separation and analysis of silver ions in ammoniacal ammonia-triacetic acid on columns of ion-exchange resin

As well as being used to separate silver or thallium, the techniques described above can be used to determine these ions quantitatively by resorting to the usual methods for determining the amount of material in a spot of a developed paper chromatogram. These methods include cutting-out the spot followed by elution of the material and analysis, or relating the area of the spot to the amount of material present. The most accurate method of making these separation techniques quantitative, at least for macro amounts of silver and thallium, was to perform the separations in the same way, but on columns of that ion-exchange resin which was contained in the papers. Results for the two systems were found to be entirely analogous.

Elutions of samples containing silver and each metal of the mixture in turn proved that no metal appeared in the effluent before all the silver had emerged. In many cases the metals formed a coloured band when sorbed on top of the bed; this was found not to move significantly on elution with the ammoniacal ammonia-triacetic acid eluent. In all cases, qualitative analysis of the effluent proved the absence of any ion except silver. The break-through volume for silver was 25 ml, and the elution was complete by the time 45 ml of effluent had been collected. The break-through volume for thallium, the only other ion to show movement on the ion-exchange papers, was found to be greater than 200 ml.

Elutions of the standard solution of silver in admixture with the other ions proved that the silver was eluted between the same volumes of effluent as above. Gravimetric analysis of the effluent for silver ion showed an average recovery (6 trials; standard deviation = 0·40%) of 71·1 mg of silver chloride compared to a theoretical value of 71·2 mg for a mean error of −0·1 mg and a relative mean error of −0·14%.

These results prove that silver can be completely separated and recovered from mixtures containing any or all of the ions studied. Because analogous results were obtained with silver on columns and on paper containing the same ion-exchange resin, the thallium separations can undoubtedly be made quantitative on columns of chloride-form anion-exchange resin.

DISCUSSION

This paper is the first in a series in which certain ions are separated by ion exchange from multicomponent mixtures of various ions because of the selective complexing of the developing solvent. Within Strain's definition,[8] the separations are chromatographic in nature, because they are based upon selective differential migration of the ionic complexes formed.

The experiments were performed with cations representative of many elements of the Periodic Table. Therefore, it should be possible to separate silver or thallium from almost all cations except those of the alkali metals, which are not anionacally complexed by any known reagent.

Zusammenfassung—Entwicklung mit Lösungen, die selektive Komplexformer enthalten, sowie pH-Kontrolle gestatten die vollständige Trennung von Silber oder Thallium von Mehrkomponentensystemen mittels Ionenaustauscherpapieren.

Vollständige Trennung und Wiedergewinnung von Silber mittels Ionenaustauschersäulen wird demonstriert.

Résumé—Sur papier échangeur d'ions, le développement par des solutions qui conduisent à une formation sélective de complexes et à un contrôle du pH permet la séparation complète des ions argent ou thallium de mélanges de différents ions. La récupération complète, ainsi que la séparation, sont montrées, dans le cas de l'argent, sur des colonnes de résine échangeur d'ions.

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Talanta, 1962, Vol. 9, pp. 781 to 793. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF MAJOR AND MINOR ALKALIES IN SILICATES BY DIFFERENTIAL FLAME SPECTROPHOTOMETRY*

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(*Received* 5 *February* 1962. *Accepted* 4 *April* 1962

Summary—By attaching an external galvanometer circuit to a Beckman DU spectrophotometer and making use of an improved and highly stable air-natural gas flame, it is possible to apply the principle of differential measurement to the flame spectrophotometric determination of the major and minor alkalies and alkaline earths. Although it is doubtful that any reasonably rapid, purely flame photometric, method can ever equal the best flame-supported gravimetric techniques in determinations of major alkali constituents, procedures have been worked out whereby rubidium and caesium can be determined with improved precision, and the accuracy of sodium and potassium determinations is significantly increased.

INTRODUCTION

In 1955, Ellestad and Horstman[3] described an air-natural gas flame attachment for use with a spectrophotometer in the determination of lithium. In 1956, Horstman[6] used the same apparatus for rubidium and caesium as well as for lithium, and a later paper[7] reported a large number of determinations of these elements in igneous and sedimentary rocks.

Horstman estimates an accuracy of 5 ppm of caesium and 10 ppm of rubidium for his determinations in the range 10–200 ppm, and 5–10% of the amount present with larger amounts.

By modifying the apparatus and the chemical techniques, the limit of detection for rubidium and caesium has been extended to about 2 ppm of Rb_2O and 1 ppm of Cs_2O in the sample, and by differential measurement, precision in the determination of both the major and the minor alkalies has been considerably improved.

Separate samples are required for sodium and potassium, for rubidium and caesium, and for lithium. In the preparation of sample solutions, a variation of the method of Abbey and Maxwell[1] is used in preference to the longer procedure of Horstman; however, lithium is not completely recovered in this procedure, and for its accurate determination the method of Ellestad and Horstman[3] is recommended, with some slight refinements. The Ellestad-Horstman procedure for lithium cannot be used for the other alkalies.

Rubidium and caesium emission in the flame is greatly enhanced by potassium, and if this enhancement is to be used to advantage, the potassium content of the sample solutions must be controlled. Perhaps the simplest way to do this is to add potassium to the sample up to a standard concentration, and this expedient is here

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adopted. Because the potassium content of the sample must be accurately known, the determination of this element must be made a part of any flame photometric method for the determination of rubidium and caesium.

Horstman preferred to make standard solutions to correspond to each unknown. This requires, in effect, a recalibration for each sample, but nevertheless may be an advantageous procedure, especially for samples of widely varying potassium content.

It is difficult to obtain potassium salts completely free from rubidium, so that the rubidium content of the potassium salt used as an additive and as a standard must be determined, and suitable corrections made.

The sensitive rubidium lines available for flame photometry are those of wavelength 780·02 $m\mu$ and 794·76 $m\mu$. These are unfortunately so close to the potassium lines 766·49 and 769·90 $m\mu$ that the Beckman DU monochromator resolves the two elements only imperfectly. Despite the proximity of Rb 780 to K 770, this line was chosen after many experiments in preference to the Rb 795 used by Horstman, largely because reproducibility is slightly better at this wavelength. Actually, there is little to choose between the two; the greater potassium interference at Rb 780 is compensated for by the lower sensitivity at Rb 795.

The 852·11 line is used for the measurement of caesium. Although there is no direct potassium interference at this wavelength, the flame background is relatively high, and thus an absolutely steady and reproducible flame is as necessary with caesium as with rubidium.

The determination of sodium and potassium is only slightly affected by the small amounts of lithium, rubidium and caesium normally found in silicates. Provision is made in the procedure to correct for the inter-effects of potassium and rubidium.

While lithium is best determined on a separate sample, an approximate preliminary figure may be obtained on the solutions used for the other alkalies.

EXPERIMENTAL

Apparatus

Changes in the original design of the flame attachment described by Ellestad and Horstman[8] improve stability, and make practicable the use of a more sensitive indicating ammeter than that provided in the Beckman DU spectrophotometer; an external galvanometer circuit, specifically that of a Coleman Universal spectrophotometer, is used. Presumably, a 'Galv-o-meter' or similar instrument—or a recording device—would serve as well.

Sensitivity is increased by the use of an additional 1·5-V dry battery in the Coleman instrument, increasing available voltage to 3·0. The phototube is the red-sensitive caesium oxide tube normally used for flame photometry with the Beckman DU spectrophotometer.

To attach the external galvanometer, a telephone plug is mounted in the base of the DU spectrophotometer and wired across the indicating ammeter. A lead from this plug through a 100,000-Ω variable resistance carries a controlled portion of the current from the DU spectrophotometer to the galvanometer plug of the Coleman instrument. The resistance box also contains a reversing switch and an additional series-connected 100,000-Ω resistor which may be switched in and out of the circuit at will.

As in the original apparatus, the burner is mounted in a cylindrical mirror of polished aluminium sheet. The mirror is enclosed in a brass tube, from which a light-pipe of polished aluminum projects to within about 2 cm of the entrance tunnel of the DU spectrophotometer. This device increases the radiation striking the instrument mirror by about 20%. The burner and chimney are mounted on movable supports so that the optimum portion of the flame may be sampled. It would seem advantageous to mount the spectrophotometer in such a way that the slit is horizontal instead of vertical, but this has not yet been investigated.

Natural gas is supplied to the spray chamber itself, rather than to a mixer in the spray tube leading from it, and enters through an inverted funnel, which increases turbulence and protects the water seal at the bottom of the chamber. The spray tube is extended into the chamber to increase mixing efficiency. A second trap at the bottom of the burner compartment requires a small addition of water from time to time.

The aspirator itself is identical to that used by Ellestad and Horstman.[3] Air pressure at the atomiser is about 70 cm of mercury, and gas flow is roughly adjusted to the maximum at which no peaking of the flame occurs. A final adjustment of gas flow should be made to give maximum instrument response for each element at the time of measurement. Undoubtedly air pressure will have to be changed to suit gas composition. Air pressure and gas flow must be held constant within very close limits; this is easily done by placing two or more pressure and flow regulators in series on the air and gas lines. The flame attachment is illustrated in Fig. 1.

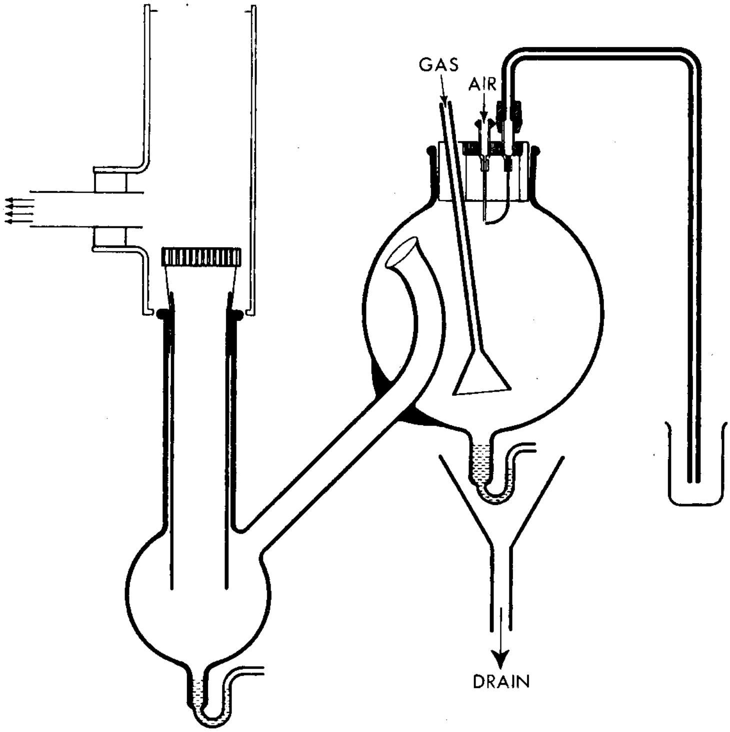

FIG. 1—Flame Attachment. The atomiser consists of two hypodermic needles mounted in a brass plug in the rubber stopper closing the spray chamber. Air enters through a No. 15 needle, and the test solution through a No. 21 needle. The arrangement is similar to that suggested by Barnes *et al.*[2] The spray chamber is made from a 2-litre round flask, and the burner chamber from a 250-ml flask with a special neck to accept the Meker burner cap. The burner tube is installed by grinding off the flange which holds the burner grid and removing the latter. Best results are obtained if the grid is returned to the burner cap without reflanging. The capillary through which solution is drawn into the spray chamber should be selected to give a flow rate of about 2–3 ml per min. A capillary bore of 0·5 to 0·6 mm is satisfactory.

Features which are of particular importance in the determination of trace alkalies are the almost perfect stability and reproducibility of the flame, and the minimum of maintenance required. As long as solutions are free from foreign solids, the burner and atomiser will operate for weeks without need for cleaning or attention of any kind, even when solutions containing several g/litre of salts are routinely passed through it. The memory of the flame is surprisingly short; distilled water will completely remove all traces of a sodium flame in about 30 sec after aspirating a solution containing 10,000 ppm of Na_2O. If salts become deposited on the burner grid, they may be removed simply with a jet of water, without dismantling the apparatus.

It is possible that even greater sensitivity might be attained with a red-sensitive photomultiplier tube instead of the arrangement described; however, the controlling factor is the steadiness and reproducibility of the flame background, rather than the sensitivity of the detector. This is particularly true in the case of rubidium, for this element nearly always is associated with much larger amounts of potassium, so that in practice it must always be measured over a large potassium background. Even if a monochromator which completely resolves the two elements is available, the enhancement effect must still be quantitatively dealt with, and control of this effect likewise requires a completely steady flame.

Attempts to use the Beckman flame attachment with oxygen and acetylene in a similar procedure to that described were not successful.

Reagents

Standard alkali solutions: Neutral alkali sulphate solutions to be used as standards should be prepared from the purest salts available.

Mix the salt thoroughly, and weigh 0·1 to 0·2 g into a weighed 55-ml flat-bottom platinum dish. Add a little water and about 1 ml of 1:1 sulphuric acid, and evaporate to dryness. Increase the temperature until excess acid is removed, and hold the dish and contents at the highest plate temperature for some time to remove bisulphate. Heat cautiously with a small flame, then at the full heat of a good Meker burner for 1 min. Weigh, and repeat the ignition to constant weight.

On the basis of the assay, weigh enough of the salt to give a solution of the desired concentration, dissolve in somewhat less than the required volume of water, and heat the solution to 95–100° for a few hr to destroy organisms which otherwise precipitate after standing. Dilute to volume with boiled water, and filter into Pyrex bottles which have been thoroughly cleaned and dried.

Solutions containing 10,000 or 20,000 ppm of Na_2O and K_2O, and 1000 ppm of the other alkalies are convenient, and may be diluted as needed.

All solutions should be examined for foreign alkalies and alkaline earths on the flame photometer. Determination of rubidium in the standard potassium solution is a matter of some difficulty, because of interference and enhancement effects. A satisfactory procedure is as follows:

By dilution of stock solutions, prepare a series of solutions with 1000 ppm of K_2O, 1000 ppm of MgO, and increasing amounts of Rb_2O in increments of 0·2 or 0·5 ppm, up to 2·0 ppm. At the rubidium wavelength setting near 780 mμ (established as accurately as possible with a pure rubidium solution, not a potassium-rubidium solution) and a slit of 0·14 mm, set the Beckman and Coleman controls so that the galvanometer index on the latter instrument reads at one end of the scale with 2·0 ppm of Rb_2O, and at the other end with no rubidium added. Read each of the intermediate solutions directly from the galvanometer scale, adjusting the dark current to zero between readings. Plot galvanometer readings against ppm of Rb_2O. Extrapolate the straight portion of the curve (or rather, draw a straight line asymptotic to it) to meet the ordinate at a point representing a negative Rb_2O content (Fig. 2). This gives a preliminary estimate of the rubidium content of the potassium solution. Repeat the procedure, adjusting the instrument settings so as to take the estimated rubidium impurity into account, and again plot the results, Repeat, changing settings as necessary, until a straight line between 0 and 100 on the galvanometer scale is obtained. Once the T scale reading on the DU spectrophotometer has been established for zero Rb_2O, there is no further difficulty in determining the absolute rubidium content of any solution containing 1000 ppm of K_2O and 1000 ppm of MgO.

Because of uncertainties in this procedure (for instance, it is assumed that a straight line relationship exists down to the limit of detection), it seemed desirable to check results by independent methods, *viz.*, emission spectrography and also isotope-dilution mass spectrometry. Fair agreement between methods was obtained with samples of potassium salts (both 'Spec-pure') containing 20 and 40 ppm of rubidium.

Preparation of sample solutions

Weigh 0·5000 g (for rubidium and caesium) and 0·0500 g (for sodium and potassium) of the suitably prepared sample into 55-ml platinum dishes. Other sample weights may, of course, be used. Add a little water and 1 ml of 1:1 nitric acid, and warm gently to remove carbonate, keeping the dish covered. Wash down and add 1 ml of 1:1 sulphuric acid and 5–15 ml of hydrofluoric acid, then evaporate slowly, increasing the plate temperature gradually until fumes of sulphuric acid appear. Cool, dilute with water, and warm gently until soluble salts are in solution. If sample attack is incomplete, repeat the hydrofluoric acid treatment and again evaporate to fumes and dilute. Repeat until a clear solution is obtained. Two or three evaporations without hydrofluoric acid addition may be required to remove fluoride.

Add 2 ml of a magnesium sulphate solution containing 25 mg of MgO per ml, or, if the magnesium content of the sample is known, add just enough to make a total of 50 mg of magnesium oxide. Evaporate to fumes, and gradually increase the plate temperature until excess acid has been removed. Continue heating at the maximum plate temperature for 2–4 hr to decompose bisulphate. Transfer the dish to a platinum triangle, and heat first with a small flame, then finally for 1 min at the full heat of a good Meker burner.

Cool the residue, add 15–25 ml of water, and digest on the steam bath for 30 min or more. Up to this point the 50-and 500-mg samples are treated similarly.

Evaporate the suspension of the 50-mg sample to about 5 ml, and filter into a 50-ml volumetric flask through a 5·5-cm Whatman No. 44 paper. Wash thoroughly with hot water.

Filter the suspension of the 500-mg sample into a 150-ml beaker, breaking up the flakes of oxide with a rubber-tipped rod. Wash very thoroughly with hot water to a volume of 100 ml or more. Add about 50 mg of pure calcium carbonate to the filtrate, and evaporate to small volume on the steam bath. In this process, any traces of free acid remaining after the ignition are neutralised, and the final solution should have a pH close to 6. The precipitate of hydrous oxides formed as a result of the neutralisation should be small. If a large precipitate forms, heating over the Meker burner was inadequate. With the 50-mg sample, there should be no difficulty in obtaining a neutral solution without the additional step.

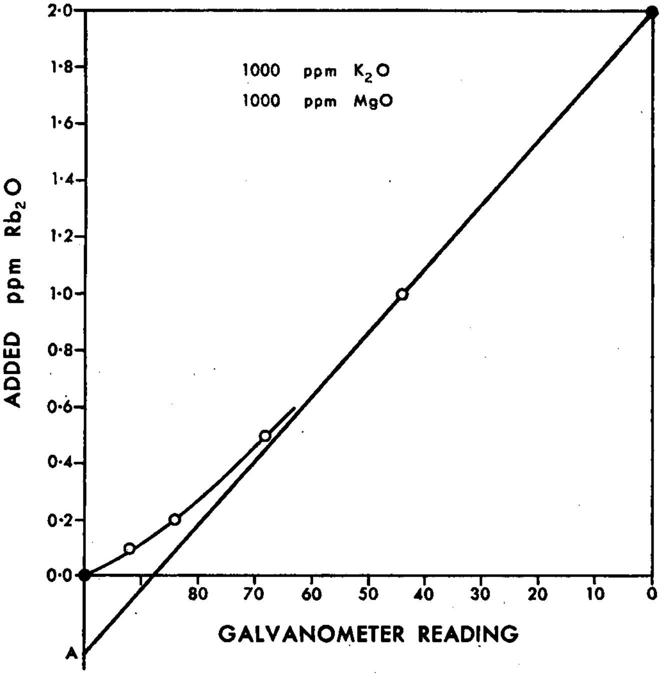

FIG. 2.—Extrapolation method of determining contamination of the standard potassium solution. A similar procedure may be followed for any alkali or alkaline earth trace constituent in strong stock solutions. The distance OA gives a first approximation to the concentration of the contaminant.

When the volume of the solution has been reduced to about 10 ml, filter through a small Whatman No. 44 paper into a 50-ml volumetric flask, and wash thoroughly with hot water, leaving enough room in the flask for later addition of standard alkali solutions. In some cases, where very little rubidium or caesium is expected, it is advantageous to use a 25 ml flask. The magnesium addition earlier in the procedure should then be halved.

The pH of all final solutions should be very close to 6·0, and it is most advisable to check this. Unless sodium is to be determined, the check is easily made by dropping a small piece of nitrazine paper into the solution just before filtration, and observing the colour it assumes. Nitrazine is an ideal indicator for the purpose.

For the determination of lithium, weigh 0·1 to 0·5 g of the sample into a platinum dish, and treat exactly as above, up to the point where heating has been continued for 2–4 hr to remove bisulphate. Wash the residue into a 150-ml beaker, dilute to about 100 ml, heat to boiling, and add to the boiling solution small portions of basic lead carbonate until it is no longer acid to methyl red. Filter at once into another beaker, and wash thoroughly with hot water. Add about 50 mg of basic lead carbonate to the filtrate, and evaporate to 10–15 ml on the steam bath. *Do not evaporate to dryness.* Filter while still hot into a 50-ml volumetric flask and wash the residue thoroughly with hot water, leaving room in the flask to accept later addition of standard sodium solution.

Flame photometric procedure

Determination of sodium and potassium: Dilute the solution of the 50-mg sample to 50 ml and mix. For potassium, adjust the wavelength setting to give maximum response at about 766 mμ, and the sensitivity control to give 100 × ·1 T reading with a neutral sulphate solution containing 100 ppm of K_2O and 1000 ppm of MgO, using a 0·05-mm slit. Obtain a preliminary value for the unknown from a calibration curve prepared from standards with 100, 92, 84, *etc.*, ppm of K_2O. Magnesium has a depressing effect on the potassium emission, so it is important that all readings be made with very nearly the same concentration of magnesium ion in solution (Fig. 3). To help control the effect of rubidium in the unknown, all readings must be made at the same slit setting.

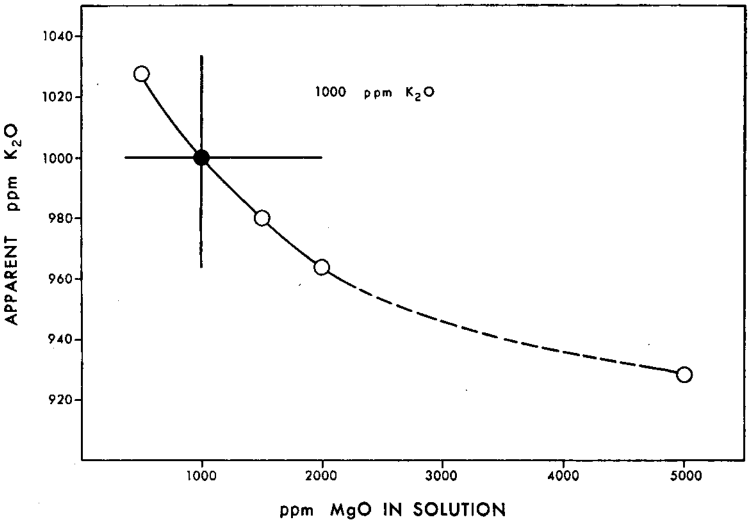

FIG. 3—Effect of magnesium on potassium emission. Instrument settings are made so that a solution with 1000 ppm of K_2O and 1000 ppm of MgO gives a reading of 100 × ·1 on the Beckman T scale. The graph shows the variation in apparent potassium content with change in the concentration of magnesium.

Make a preliminary sodium reading in the same way, using a wavelength near 589 mμ. Use of the external galvanometer is not necessary for these preliminary readings.

Obtain accurate values by setting the instrument controls using solutions with slightly less or slightly more Na_2O and K_2O than the unknown, and measuring the difference with the external galvanometer. Standards containing both sodium and potassium in appropriate concentration, as well as magnesium, should be prepared for each sample. Galvanometer sensitivity is conveniently adjusted so that the full scale represents 20 ppm of Na_2O or K_2O in solution. A separate calibration curve should be prepared for each 20-ppm range, because the relation between galvanometer reading and alkali content is not exactly linear.

Preliminary readings on the 50-mg sample may be made for lithium, rubidium and caesium, but there is seldom sufficient of these elements to make it worthwhile. Lithium values thus obtained are very approximate.

Reserve the solution for a final potassium reading to be made after the rubidium and caesium determinations are completed.

On the basis of the potassium determination, add to the solution of the 500-mg sample enough standard potassium sulphate solution to bring its concentration up to 1000 ppm of K_2O after dilution. Dilute to 50 ml and mix. Other standard potassium concentrations may be used; however, below about 500 ppm the K_2O concentration becomes increasingly critical, and above 2000 ppm flame stability is adversely affected.

Determination of rubidium: Using a pure rubidium sulphate solution (containing no potassium), adjust the wavelength setting near 780 mμ to give a maximum response, using a 0·14-mm slit. The external galvanometer should be used in making this setting as precisely as possible, and it should be checked at intervals because temperature changes cause a slight drift. Slit and wavelength settings must be identical for all readings.

Make a preliminary reading of the rubidium content of the sample solution, using a calibration curve prepared from standards all of which contain 1000 ppm of K_2O and 1000 ppm of MgO. Establish the rubidium concentration to the nearest ppm.

Using a standard solution with slightly less rubidium than the unknown, set the variable resistor, the galvanometer controls, and the T knob and dark current control on the DU spectrophotometer so that the galvanometer and the Beckman indicating ammeter read full scale and zero, respectively, both with the shutter open and with it closed. Adjust the sensitivity of the galvanometer circuit so that the index moves full scale with a known increase in the rubidium content of the solution (conveniently 2 or 10 ppm of Rb_2O). The excess Rb_2O in the unknown over that in the standard may then be obtained from the galvanometer scale reading. For small amounts of rubidium (<2 ppm), the relation between galvanometer reading and ppm of Rb_2O is almost linear (Fig. 4); with larger amounts, a calibration curve should be prepared for each 2-ppm range.

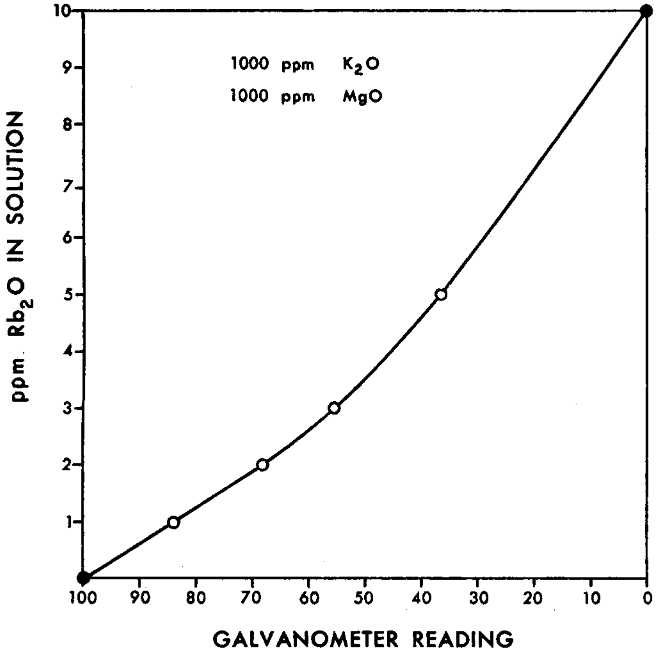

FIG. 4—Working curve for rubidium, 0–10 ppm. The relation between Rb_2O concentration and galvanometer reading is nearly linear up to 2 ppm of Rb_2O. Similar curves may be prepared for Cs_2O and Li_2O. Instrument settings may be adjusted so that the full scale galvanometer reading represents any desired range of the element being determined.

During these measurements, it is best to leave out of consideration the rubidium content of the standard potassium solution, correcting for it later.

Readings made in this way are reproducible, when all adjustments are properly made, to 1 division on the galvanometer scale, corresponding to 0·02 ppm of Rb_2O in solution or 2 ppm in a 0·5-g sample diluted to 50 ml; however, there are six readings or settings involved in a differential determination; two each in establishing (a) the rubidium content of the standard potassium solution, (b) the sensitivity setting against the standard rubidium solution, and (c) the excess rubidium in the unknown over the standard. The actual probable reading error in a differential rubidium determination is therefore close to the equivalent of ±3 divisions, or ±0·06 ppm of Rb_2O in solution. Near the limit of detection, this is reduced to about ±0·04 ppm, because only four readings are involved. This corresponds to ±2 ppm of Rb_2O in a 0·5-g sample diluted to 25 ml.

It is very desirable to check the potassium content of the unknown solution in which rubidium and caesium are determined. This should of course be 1000 ppm. The check is best made by adjusting the DU spectrophotometer controls so that a solution with 1000 ppm of K_2O, 1000 ppm of MgO, and a rubidium content near that of the unknown reads 100 × ·1 on the T scale, and reading the unknown at that setting. The difference should be less than 1 × ·1 T, except with samples which contain much magnesium, which tend to give low readings. If the potassium content of the sample solution appears low, a correction should be made, based on a calibration curve (Fig. 5) giving the variation in apparent rubidium content with potassium content at the Rb_2O level of the unknown. Such a correction is seldom required if the potassium determination was carefully done, unless an unusually high Rb:K ratio exists in the sample, or much magnesium is present.

The correction for the rubidium content of the standard potassium solution will normally be positive, corresponding to the difference in Rb_2O content between the volume added to the unknown and that containing 50 mg of K_2O. Thus, if the standard potassium solution contains 10,000 ppm of K_2O, and x ml is added to the unknown, the correction is $+(5 - x)R$, where R is the Rb_2O content of the potassium solution. A method of determining this is given above.

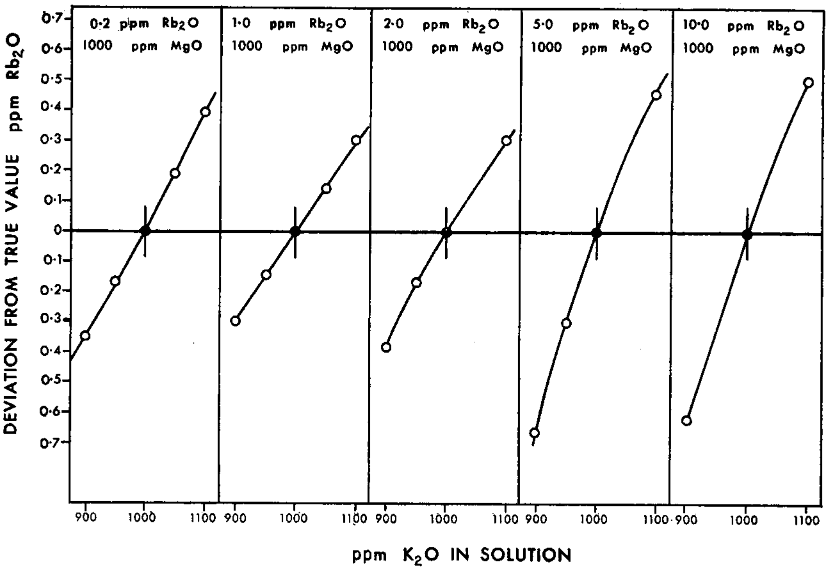

FIG. 5—Effect of potassium concentration on the determination of traces of rubidium. The variation of apparent Rb_2O content with potassium concentration results from a combination of interference and enhancement effects.

Determination of caesium: Caesium may be determined in the same way as rubidium, using a 0·4-mm slit and a wavelength setting near 852 mμ. Maximum sensitivity is about twice that for rubidium, and adjustments can conveniently be made so that a full scale galvanometer reading corresponds to 1·0 ppm of Cs_2O in solution, or 0·01% in the sample. Since in naturally occurring materials, the caesium content is frequently about one-tenth that of rubidium, some of the standard solutions used for the latter may to advantage have caesium added as well, in about a 1:10 ratio. The same set of standard solutions may then be used for both elements.

Little difficulty was experienced with caesium impurity in the potassium salts used, except when attempts were made to determine the element in samples containing 1 ppm or less. It is advisable to determine the caesium content of the standard potassium solution in a manner similar to that described for rubidium.

When the rubidium and caesium determinations are completed, a final reading for potassium should be made on the solution of the 50-mg sample, using standards containing the correct amounts of these elements as well as sodium and magnesium.

Determination of lithium: Add to the solution prepared for the lithium determination enough standard sodium solution to bring its concentration up to a standard value (conveniently 500 or 1000 ppm of Na_2O), and proceed as for rubidium or caesium, using a 0·4-mm slit and a wavelength setting near 671 mμ. If an indicator (methyl red) was added during the preparation of the solution, its sodium content should be taken into consideration; however, the effect of sodium on the lithium determination, while appreciable, does not require as accurate adjustment of the major alkali concentration as is necessary with rubidium and cesium.

RESULTS AND DISCUSSION

Some comparative results are given in Tables I, II and III. In the case of caesium, no comparable method was available, and the procedure was checked by carrying

TABLE I.—COMPARATIVE RESULTS FOR SODIUM AND POTASSIUM

Sample	Na_2O present[a]	Na_2O found	K_2O present[a]	K_2O found
Granitic rock	4·30	4·35	1·01	1·02
Granitic rock	4·69	4·70	1·31	1·32
Granitic rock	4·71	4·70	0·90	0·88
Lepidolite	0·30	0·32	9·88	9·90
Mica	—	—	9·32	9·40
Obsidian	4·28	4·25	4·60	4·60

[a] Separated by Lawrence Smith procedure: potassium weighed as chloroplatinate, sodium by difference from weight of chlorides. Corrections for the minor alkalies determined by flame photometry after conversion of chloroplatinates of potassium and of sodium to sulphates.

TABLE II.—DETERMINATION OF RUBIDIUM IN BIOTITE: COMPARISON OF RESULTS BY FLAME PHOTOMETRY AND BY MASS SPECTROMETRY

K_2O, %	Rb, *ppm*	
	Proposed method	Isotope dilution[a]
8·64	415	430
	406	
	415	
8·18	272	250
		253
8·68	572	549
7·78	694	677
8·96	540	538
	534	531
9·23	587	594
8·84	536	516
	520	
8·35	487	484
8·60	659	688
8·43	359	361
	359	356
		352
9·96	320	289
	319	
	293	

[a] Determined at U.S. Geological Survey laboratories, Washington, D.C., U.S.A.

known amounts of the element through the procedure, using a sample of mica which was salted with measured amounts of caesium sulphate. Rubidium was also added to these samples, and results are given in Table IV. Some results with reference samples are given in Table V.

The methods described have been applied to a variety of silicates and related

TABLE III.—DETERMINATION OF POTASSIUM IN BIOTITE

Sample	K_2O present[a]	K_2O found
KA 272 B	9·08	8·88
KA 76 B	7·02	6·98
KA 14 B	8·20	8·10
KA 48 B	3·50	3·46
KA 320 BM	8·72	8·84

[a] Values reported by Goldich and others.[4]

TABLE IV.—DETERMINATION OF RUBIDIUM AND CAESIUM ADDED TO A SAMPLE OF MICA

Sample	Rb_2O added, %	Rb_2O found, %	Cs_2O added, %	Cs_2O found, %
Mica	none	0·0305	none	0·0000
Mica + Rb, Cs	0·0200	0·0503	0·0040	0·0036
Mica + Rb, Cs	0·0400	0·0703	0·0100	0·0096
Mica + Rb, Cs	0·100	0·136	0·0200	0·0194
Mica + Cs	none	0·0307	0·0300	0·0308
Mica + Rb	0·100	0·132	none	0·0002

TABLE V.—POTASSIUM AND RUBIDIUM DETERMINATIONS IN REFERENCE SAMPLES

Sample	K_2O present, %	K_2O found, %	Rb present, *ppm*	Rb found, *ppm*
Granite G-1	5·52[a]	5·52	220[b]	216
Diabase W-1	0·62[a]	0·62	22[b]	20
Biotite B-3203	9·03[c]	9·00	466[d]	460

[a] Values reported by Goldich and Oslund.[5]

[b] Values recommended by Stevens *et al.*[9]

[c] Determined by Lawrence Smith procedure with flame corrections. A compilation of values obtained on this sample by different laboratories is given by Abbey and Maxwell.[1] The sample was prepared as a reference biotite[8] for laboratories engaged in K-Ar determination.

[d] Isotope dilution value, U.S. Geological Survey.

materials, including micas, feldspars, amphiboles, granites, basalts, shales, clays, frits and glasses. No serious difficulties were encountered with any of these materials. With sedimentary rocks, a preliminary ignition at low temperature to remove organic matter is advisable. Samples containing sulphides are best roasted before acid treatment. Some manganese minerals require the addition of hydrogen peroxide or sulphurous acid at intervals during the solution procedure.

The ignition of alkali sulphates must be carried out under oxidising conditions, or there is a possibility of reducing sulphate to sulphide, particularly if a large amount of material is present in the dish. This may lead to losses of potassium (and presumably of caesium and rubidium) by volatilisation; it also results in solutions of high pH. It is for this reason that the standard alkali salts are assayed as directed and weighed out on the basis of the assay, rather than after direct ignition.

A good test for an oxidising flame may be made by heating a nickel crucible at the correct position in the flame and observing its behaviour. The supply of air to the burner should be increased to the point where the bright metallic nickel surface becomes coated with oxide.

In preparing the sample solutions, it is quite necessary to use a flat-bottom platinum dish and a platinum triangle, particularly with 500-mg samples. If round dishes and silica triangles are used, it may prove difficult, if not impossible, to satisfactorily decompose the metallic sulphates. Re-evaporation of the residue with water, followed by re-ignition, as recommended by Abbey and Maxwell[1] may, however, overcome the difficulty.

It is most advisable to check the standard alkali solutions by pipetting 10 or 20 ml into a platinum dish, adding sulphuric acid, evaporating, igniting, and weighing. This will not only make certain of the alkali concentration, but will give a check on the ignition procedure; the rate of loss of the various alkalies under the actual conditions of heating may be followed, and if it is found to be serious, appropriate steps can be taken. The weighed residual salt should be dissolved in water, and a pH measurement made.

Procedures similar to those described can also be applied to solutions obtained by other chemical techniques, for example the Lawrence Smith method for the separation and collection of the alkali metals.[5] The differential measurement procedure can also be used for the alkaline earth elements, and this technique has been found most useful for the determination of strontium in the presence of large amounts of calcium. Nitrate solutions are used for the alkaline earth elements.

Lithium is not recovered completely by the sulphate ignition procedure described for the other alkalies, nor by the Lawrence Smith procedure, except in the case of certain samples containing no alumina. It is necessary to use a lead carbonate separation for this element, or to follow Horstman's procedure. The lead carbonate procedure is unsuitable for the other alkalies.

Galvanometer stability is improved by grounding the case of the DU spectrophotometer to a water pipe, but the Coleman instrument and its power supply should not be grounded. Instrument drift was found to be caused in part at least by temperature changes, and was largely eliminated by insulating the DU spectrophotometer from the hot flame chimney by means of sheet aluminium, and allowing a 2–3 hr warm-up period before making any settings. The wavelength setting for rubidium is particularly sensitive in this respect, and should be checked before all final readings.

During the differential measurements, and during the caesium determination in particular, the entrance end of the DU spectrophotometer should be shielded from even diffuse daylight, especially when clouds or moving vehicles cause fluctuations in room lighting.

The 1·5-V dry battery in the Coleman Universal spectrophotometer deteriorates rapidly at the sensitivity settings required. The 'Galv-o-meter', which is provided with a mercury battery, might be better in this respect, but the lower voltage will lead to lower sensitivity. The use of two 1·5-V dry batteries in series as recommended is satisfactory.

The differential method of measurement has not been used for rubidium in materials containing more than about 5000 ppm of Rb_2O. Above this amount, flame photometric readings are made by the technique of Horstman,[6] without the use of the galvanometer. With large amounts of rubidium, the preliminary potassium determination is affected to the extent that the 'salting up' to 1000 ppm of K_2O becomes progressively less accurate, to the point where it is difficult to take meaningful advantage of the increased precision of differential measurement.

With samples containing much manganese, appropriate additions of this element should be made to the final standards. The large magnesium addition which is always made during the solution procedure minimises the effect of small amounts of manganese and other foreign elements. Its depressing effect on both rubidium and potassium emission does not seriously affect sensitivity.

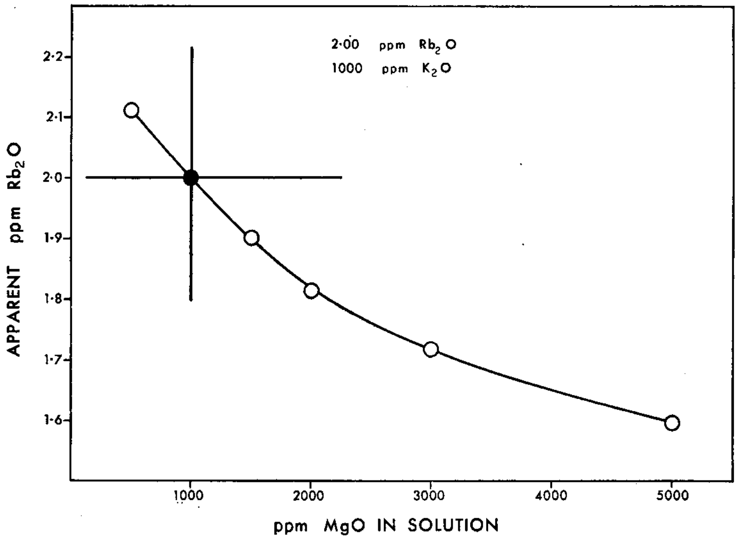

FIG. 6—Effect of magnesium on rubidium emission. Instrument settings are made so that the external galvanometer reads at mid-scale with solutions containing 1000 ppm of K_2O, 1000 ppm of MgO, and the indicated Rb_2O concentration. Variations in apparent Rb_2O content with changes in magnesium concentration are shown.

Large amounts of calcium interfere with the determination of lithium, and highly accurate lithium values can only be obtained if this is taken into account. The amount of calcium in the final solution for lithium determination is, of course, limited by the solubility of calcium in the lead carbonate-sulphate suspension.

The interference of magnesium cannot be entirely overcome unless the magnesium content of the sample is known. However, in most cases the error is small. The effect of magnesium originating in the sample is, of course, greater with the larger samples, and is revealed on checking the potassium content of the 500-mg sample used in the determination of rubidium and caesium. A discrepancy observed at this stage in the procedure may be treated as though it were caused by a deficiency of potassium, even though it is in fact a result of magnesium excess, with satisfactory results so far as the correcting of the rubidium value is concerned. The effect of magnesium on the rubidium emission is shown in Fig. 6.

While results by the techniques described in many cases approach in accuracy and precision those obtained by the most refined methods involving gravimetric determination of the major alkalies and flame photometric determination of the minors, it seems doubtful that any purely flame photometric method can compete with flame-supported gravimetric procedures in the determination of alkali contents in excess of about 5%, except in special cases. It should be noted, however, that procedures following acid attack of the sample have one major advantage over the Lawrence Smith method when applied to hydrous minerals such as biotites. The sample can be weighed in the unground condition, or after a minimum of grinding, whereas, with many such materials, fine grinding must precede weighing for the Lawrence Smith method. Problems of loss or gain of water and of oxidation of iron^{II} during sample preparation are thus avoided.

Acknowledgment—The author is indebted to S. S. Goldich, Chief, Isotope Geology Branch, U.S. Geological Survey, for invaluable assistance and advice, and for supplying analysed samples which are reported in Tables II and III. Full credit for the basic design of the flame attachment must be accorded R. B. Ellestad, P. T. Gilbert, E. L. Horstman, H. Baadsgaard and other workers in the Rock Analysis Laboratory of the University of Minnesota, where a similar apparatus was used and analytical methods for the alkali metals were developed over a period of many years.

Zusammenfassung—Wenn ein äusserer Gelvanometerstromkreis an ein Beckman DU-Spektrophotometer angeschlossen wird, ist es möglich differentielle Flammphotometrie der Alkalien und alkalischen Erden auszuführen. Eine verbesserte, hochstabile Luft- Naturgas-Flamme muss verwendet werden. Wenn es auch zweifelhaft ist, dass rein flammphotometrische Methoden jemals gravimetrische Genauigkeit erreichen kennen (für Alkalihauptbestandeteile) so wurde immerhin eine Methode ausgearbeitet, durch die Rubidium und Cäsium mit erhöhter Reproduzierbarkeit bestimmt wurden und die Genauigkeit der Natrium- und Kalium bestimmung beträchtlich erhöht wurde.

Résumé—En reliant un circuit galvanométrique externe à un spectrophotomètre Beckman DU et en utilisant une flamme air-gaz naturel très stable, il est possible d'appliquer le principe de la mesure differentielle au dosage par spectrophotométrie de flamme des alcalins et des alcalino-terreux importants et secondaires. Il est douteux que toute méthode par photométrie de flamme raisonnablement rapide puisse jamais égaler les meilleures techniques gravimétriques, dans les dosages des principaux constituants alcalins; cependant des méthodes permettant de doser le rubidium et le césium avec une précision améliorée ont été mises au point, ainsi que d'autres augmentant de façon significative la précision des dosages du sodium et du potassium.

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Talanta, 1962, Vol. 9, pp. 795 to 797. Pergamon Press Ltd. Printed in Northern Ireland

SUBMICRO DETERMINATION OF IRON IN ORGANIC MATERIALS

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(*Received* 27 *April* 1962. *Accepted* 33 *May* 1962

Summary—A method for the determination of iron in solid organic compounds, such as ferrocene and its derivatives, has been developed. Sample weights between 25 and 400 μg were used, the optimum sample size being such as to contain between 10 and 20 μg of iron. All results obtained from the analysis of standard compounds were within ±0·5% absolute. An indication is given of the utility of working on the small scale in detecting inhomogeneity of materials.

RECENT reviews of small-scale organic analysis have been given by Belcher,[1] using 30–50 μg samples, and by Kirsten[2] who used sample weights of about 500 μg. Several potential methods for the determination of iron in the range 10 to 100 μg existed. It appeared reasonable, therefore, to attempt the determination of iron in ferrocene derivatives, where iron contents between 5 and 30% were expected, using sample weights within the range covered by these two workers.

Titrimetric and colorimetric techniques only were considered for the determination of iron. Of the former, potentiometric titration with 0·01*N* mercury^{I} nitrate,[3] under a nitrogen atmosphere, showed promise (deviations on one day of ±0·2 μg of iron) but it was found that the titrant needed frequent restandardisation. Photometric titration with the apparatus available was not sufficiently sensitive although results to ±0·4 μg of iron were achieved by titration with 0·05*M* EDTA at pH 3·5 using potassium thiocyanate or sulphosalicylic acid as indicator.

Of the many colorimetric reagents available, previous experience indicated that 1:10-phenanthroline would be most likely to meet the requirements. Indeed, it was found, both during preparation of the calibration curve and also during checks using independently prepared standard iron solutions, that a precision of ±0·1 μg could be expected in the range 5 to 25 μg of iron using 4-cm fused silica absorption cells in a spectrophotometer.

EXPERIMENTAL

Procedure

Weigh by difference,[4] on the submicro balance[5] sufficient of the sample to give between 5 and 25 μg (optimum 10 to 20 μg) of iron and transfer from the platinum weighing boat into a hard glass digestion tube (9 mm internal diameter, 12.5 mm external diameter, 8 cm long). Add 0.1 ml of acid digestion mixture (95 ml of conc. nitric acid + 5 ml of conc. sulphuric acid) and seal off the tube with a blowpipe flame. Place the sealed tube vertically in a metal rack and transfer to an oven at 300 ± 20°. After 1 hr, remove the rack and allow to cool. Release pressure in the tube by heating the tip in a blowpipe flame. Place the digestion tube in a larger glass tube on a steam bath and apply suction (water pump) to remove volatile material. Remove the digestion tube, allow to cool and cut off the top in the usual way. Wash the contents of the tube and its top into a 25-ml volumetric flask (via a 25-ml beaker) with distilled water. Add 2 ml of hydroquinone (1% aq.), 2.5 ml of acetate buffer (225 ml of 2*N* acetic acid + 25 ml of 2*N* sodium acetate) and 2 ml of 1:10-phenantholine (0.25% aq.), swirling between additions. Make up to the mark with distilled water, mix and leave for 1 to 1.5 hr. Measure the optical density, at 509 mμ, in 4-cm cells* against a reagent blank. Compute the iron in the flask from a calibration curve prepared after similar development of standard iron solutions.

* When a sample is found to contain over 25 μg of iron the use of matched 2-cm or 1-cm cells is recommended.

RESULTS

Table I shows the results obtained after the analysis of four compounds using the procedure described and illustrates the range of weights that may be taken. A high proportion of the results lie within ±0·2% absolute and none are more than ±0·5% in error. It would appear that the dicarboxylic acid may not have been quite pure.

TABLE I—ANALYSIS OF COMPOUNDS

Compound	Range of sample wt., μg	Iron, %		No. of detns.	Standard deviation	Range of errors, %
		Calc.	Found (mean)			
Ferrocene	29·4–157·8	30·02	30·11	8	0·27	−0·34 to +0·43
1,1′-Dibenzoyl ferrocene	44·0–158·0	14·17	14·22	8	0·12	−0·15 to +0·23
Ferrocene 1,1′-dicarboxylic acid	63·4–99·3	20·38	20·13	8	0·14	−0·45 to −0·10
Ferrocene 1,1′-dicarboxyanilide	50·5–179·6	13·16	13·21	10	0·21	−0·30 to +0·40

Because of the volatility of ferrocene, which caused weighing difficulties with finely divided samples, the results quoted above were obtained from the analysis of material sublimed to give small but dense crystals. As a further precaution against loss, the crystals were dropped straight into digestion acid previously pipetted into the glass tubes.

The results from analysis of research materials are given in Tables II and III.

TABLE II—ANALYSIS OF RESEARCH MATERIALS

Material	Range of sample wt., μg	Iron found (mean), %	No. of detns.	Deviations from mean, %
A	55·1–156·8	19·60	4	−0·18 to +0·17
B	38·0–299·3	13·63	8	−0·18 to +0·25
C	38·3–151·8	18·91	5	−0·18 to +0·28
D	162·7–220·6	6·60	3	−0·05 to +0·10

The results on materials A to D (Table II) were selected to illustrate the reproducibility attainable over a wide range of sample weights and on relatively high and low iron contents. It will be seen that all of the results lie within ±0·3% of the mean, even over the 40 to 300-μg sample range taken for compound B. This not only indicates the precision of the method, but also that the materials as submitted for analysis were homogeneous.

Considering now materials E to G (Table III), some erratic results are found. E was an unpurified sample of diacetyl ferrocene and it can be seen that four results are within ±0·3% of the theoretical (20·68% of iron). The other two are, however, over 1% high. F gave the even more striking result of 25·49% for one sample whereas the other five results lie within ±0·3% of the mean, 1·17%. Material G gave two results which are in reasonable agreement but the other two are more scattered than would be expected.

TABLE III—ANALYSIS OF OTHER RESEARCH MATERIALS

E	Wt. taken, μg	45·9	48·3	58·0	77·9	96·1	111·4
	Fe found, %	20·56	20·97	21·70	20·72	20·78	23·32
F	Wt. taken, μg	113·7	137·1	160·2	166·6	345·1	386·7
	Fe found, %	1·12	1·46	1·12	1·14	25·49	1·03
G	Wt. taken, μg	66·4	109·0	141·9	154·1		
	Fe found, %	23·87	23·66	21·95	26·19		

It is considered that these scattered results are not caused by any failure of the method but are rather an indication of inhomogeneity in the materials. An example was provided by the analysis of some commercially produced ferrocene where three crystals, varying in weight between 40 and 97 μg, gave iron contents of 29·6 ± 0·1% but a fourth, which was selected because of its slightly different colour and texture, gave 26·6% of iron.

Providing that sufficient precision is attainable on homogeneous samples, we suggest that the ability to work on the submicro scale has an added advantage in that the presence of impurities or mixtures may be detected by replicate analyses of the sample, or, more specifically, by analysis of suspect particles separated from the main bulk of the sample. This may be particularly useful in research on intractable polymeric materials.

Acknowledgements—We are indebted to Professor R. Belcher for an introduction to the techniques of submicro analysis and to Mr. E. J. P. Fear and Dr. W. A. Lee for the provision of samples.

Zusammenfassung—Eine Methode zur Bestimmung von Eisen in festen organischen Verbindungen, wie z.B. Ferrocen und seinen Derivaten wurde ausgearbeitet. Probenmengen von 25–400 μg wurden verwendet, wobei das Optimum bei einer Menge liegt, die etwa 10–20 μg Fe entspricht. Alle Ergebnisse mit Standardkomponenten waren inner halb einer Fehlergrenze von ±0·5% absolut. Es wird auf die Möglichkeit verwiesen unter Verwendung von so kleinen Probenmengen Inhomogenitäten in Präparaten nachzuweisen.

Résumé—Les auteurs décrivent une méthode de dosage du fer dans les composés organiques solides du type ferrocène et de ses dérivés. Des poids d'échantillon compris entre 25 et 400 μg ont été utilisés, le poids optimal de l'échantillon étant tel qu'il contienne de 10 à 20 μg de fer. La précision de la méthode est de l'ordre de ±0,5 pour 100. Le fait d'opérer sur des prises d'essai très petites permet de mettre en évidence l'hétérogénéité des produits utilisés.

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Talanta, 1962, Vol. 9, pp. 799 to 803. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

New colour reactions of elemental sulphur and carbon disulphide*

(*Received* 19 *December* 1960. *Accepted* 18 *February* 1961)

IT is often desirable to detect minute quantities of elementary sulphur in inorganic or organic raw materials, intermediates or finished products, and some attention has recently been devoted to this problem.[1,2] An excellent colorimetric determination has also been described.[3,4]

The present author has found that a solution of sulphur in acetone gives a transient green (at higher concentrations) or blue (at lower concentrations) colour when shaken with concentrated aqueous sodium or potassium hydroxide.

If the acetone is replaced by methyl ethyl ketone or methyl *n*-propyl ketone, a yellow colour develops on adding concentrated aqueous sodium or potassium hydroxide. The colour is stable and can serve for the colorimetric determination of sulphur, but the reaction is less sensitive than that with acetone.

When acetone and potassium hydroxide, but *not* sodium hydroxide, are used and the green or blue colour has disappeared, the addition of 1 drop of carbon disulphide produces a pink colour. This is more stable than the original green or blue and can be used to detect carbon disulphide.

Both reactions can be used to detect elementary sulphur in inorganic (*e.g.* gypsum) or organic (*e.g.* hydrocarbons) compounds.

Interferences

Sulphur-containing compounds, such as sodium sulphide, hydrogen sulphide, sodium hydrosulphide, sodium thiosulphate, thiophene, 2-aminothiazol, thiourea, do not give the green or blue colour. The presence of selenium does not interfere with the reaction. A large quantity of water in the acetone reduces the sensitivity of the test. No change of sensitivity was, however, observed when the content of water in acetone was below 10%. Therefore it is not necessary to use anhydrous acetone. A large quantity of ethyl alcohol (above 25%) also reduces the sensitivity of the test.

Neither water nor ethyl alcohol interferes with the pink colour developed on adding carbon disulphide. The presence of some organic compounds (*e.g.* thiourea) in the acetone solution interferes with the reaction. In such cases only a yellow colour appears.

EXPERIMENTAL

Reagents

0·01% *w/v Standard sulphur solutions:* Prepared by dissolving 20 mg of pure sulphur (pharmaceutical grade, recrystallised twice from carbon tetrachloride, m.p. 118°) in 200 ml of pure acetone, petroleum ether (boiling range: 75–110°; density: 0·73 at 25°), iso-octane, *n*-heptane and cyclohexane, respectively.

0·1% *Standard carbon disulphide solution:* Prepared by dissolving 1 g of pure carbon disulphide in 1 litre of pure acetone.

30% *Sodium and potassium hydroxide solutions:* Prepared by dissolving 300 g of sodium and potassium hydroxide, respectively, in distilled water followed by dilution to 1 litre.

Detection of sulphur in acetone solution

To a few ml of a solution of sulphur in acetone add a few ml of 30% aqueous potassium hydroxide and shake. When the concentration of sulphur in the solution is 0·01%, a dark grass-green colour develops in the acetone layer. A still higher concentration produces an olive-green colour. When the concentration is lower (0·001%), the colour is blue. The limit of sensitivity of the reaction is about 0·0002% of sulphur. No colour was observed when the concentration of sulphur was 0·0001%.

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* This work was completed in 1957, but for various reasons publication was delayed. In the meantime a similar test for the detection of elementary sulphur by means of acetone was described by G. Ingram and B. A. Toms, *Analyst*, 1960, **85**, 766.

After the green or blue colour fades, add 1 drop of carbon disulphide and shake. If the concentration of sulphur in acetone is relatively high (0·01 %), a strawberry colour appears. When the concentration is low (0·001 %), a light pink colour appears. At a higher concentration (0·05 %) an orange colour is formed. It is less characteristic than the colour developed at lower concentrations.

The colour appears within 0·5–2 min after adding the carbon disulphide and its intensity increases with time. The highest intensity is acquired after 3–5 min, and the colour fades within 20–30 min.

Detection of sulphur in hydrocarbons with acetone

Dilute 1 litre of the solution of sulphur in hydrocarbon (*e.g.* petroleum ether, iso-octane, *n*-heptane, cyclohexane) with pure acetone to 7–8 ml, then add 1–2 ml of 30% aqueous potassium hydroxide. A green (at higher concentrations of sulphur in the solution) or blue (at lower concentrations) colour develops. Sulphur in a concentration as low as 0·002% in the hydrocarbon can be detected.

After the colour fades, add 1 drop of carbon disulphide. A pink colour varying in intensity from light pink at lower concentrations to strawberry at higher concentrations (0·05% of sulphur in hydrocarbon) develops within a few min, reaching its maximum intensity after 3–5 min and lasting for about 30 min.

Detection of sulphur in hydrocarbons with methyl ethyl ketone or methyl n-propyl ketone

Dilute 1 ml of the solution of sulphur in hydrocarbon with 5 ml of methyl ethyl ketone or methyl *n*-propyl ketone and add 1–2 ml of 30% aqueous sodium or potassium hydroxide. A yellow colour develops in the ketone solution. The sensitivity limit is of the order of 0·05% of sulphur in hydrocarbon.

Detection of carbon disulphide

Add the solution of 0·01% of sulphur in acetone to the same volume of solution of carbon disulphide in acetone, then add 30% aqueous potassium hydroxide. A greenish-blue colour caused by the presence of sulphur in acetone develops and quickly disappears, then a strawberry or pink colour appears in the acetone layer within 5–10 min. This colour lasts for 20 min to 1 hr and finally changes to yellow. The sensitivity limit of the reaction is of the order of 0·01 % of carbon disulphide in acetone.

The potassium hydroxide layer is at the same time coloured yellow as a result of the formation of potassium trithiocarbonate.

The method can be applied to the detection of carbon disulphide in air. The air is drawn through a train of three or four tubes, containing a solution of 0·01% of sulphur in acetone cooled to 0–5°, at a rate of about 0·1 litre per min. The solution in the first two tubes is subsequently combined and tested with 30% aqueous potassium hydroxide as above.

T. URBAŃSKI

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Summary—Simple colour reactions are described for the detection of elementary sulphur and carbon disulphide.

Zusammenfassung—Einfache Farbreaktionen werden beschrieben, mittels derer elementarer Schwefel oder Schwefelkohlenstoff in azetonischer Lösung nachgewiesen werden können.

Résumé—L'auteur décrit des réactions colorées simples par lesquelles le soufre élémentarie ou le sulfure de carbone en solution dans l'acétone peut être decelé.

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The determination of gallium

(*Received* 29 *November* 1961. *Accepted* 12 *January* 1962)

DETERMINATION OF GALLIUM IN PURE SOLUTIONS

CLASSICAL methods for the determination of gallium were invariably completed by a gravimetric procedure involving precipitation of either hydroxide or cupferrate, followed by ignition to the oxide

Ga_2O_3.[1] Several titrimetric procedures using an excess of EDTA and a variety of titrants and indicators have been described[2] and direct titrations with EDTA have also been reported.[3-5]

When the direct determination of gallium using 0·01*M* EDTA was attempted, difficulty, in the form of delayed end-points, was experienced. This was particularly noted in cold solution. The replacement of EDTA by CyDTA gave no significant improvement.

Using morin as indicator, it was observed that an increase of fluorescence under ultraviolet light could be obtained by decreasing the pH of the solution from 4·0 to 1·7, for example by omitting the borax and sodium fluoride from the buffer solution described by Doležal *et al.*[4] A similar result was obtained by neutralizing the gallium solution to methyl red, and adding acetic acid to bring the solution to pH2. It was also noticed that the trace of red indicator colour effectively masked the slight residual fluorescence, and hence sharpened the end-point.

An increase in the fluorescence produced by gallium with morin was noted when certain water-miscible organic liquids were added to the solution. This is shown in Table 1. In all subsequent work equal volumes of methanol were added to the gallium solutions before titration.

Table I

Additive	Fluorescence	End-point	Gallium recovered,† *mg*
ethanol	good	delayed	6·99
iso-propanol	good	very poor	6·32
dioxan	good	slightly delayed	6·92
acetone	good	*normal	6·92, 6·92, 6·89
methanol	good	*normal	6·92, 6·92, 6·92 6·89, 6·96

* *i.e.* End-point in the absence of organic additive.

† Aliquots of a stock solution containing approximately 6·9 mg of Ga were used in each case.

A small amount of morin obtained in the early nineteen thirties was available for these determinations. This was a pale-buff powder giving a pale-yellow solution in methanol. More recent supplies of morin have been iridescent, black, crystalline materials giving brown solutions in methanol that do not fluoresce appreciably with gallium. Morin obtained from Dr. Theodor Schuchardt, G.m.b.H., Munich, however, compares very favourably with the pre-war material.

None of these improvements has significantly reduced the delay in reaching an end-point, although the increased fluorescence had made the end-point easier to detect. It is also possible to titrate in daylight, using only a small box to surround the vessel and ultraviolet lamp. On bright days it is possible to dispense with the lamp altogether. The quantitative recovery of gallium from a number of standard solutions by this procedure is shown in Table II.

Table II

Gallium taken, *mg*	Gallium recovered, *mg*
0·14	0·15*
0·35	0·38*
0·70	0·72,* 0·70,* 0·72
1·39	1·41,* 1·41
1·74	1·76
3·49	3·49
6·97	6·97, 6·96, 6·96
13·94	13·92, 13·81, 13·81
17·43	17·37

* By titration using 0·001*M* EDTA

SEPARATION FROM INTERFERING ELEMENTS

The presence of even a small amount of fluoride ion was found to quench the fluorescence at the pH2 used. Doležal *et al.* added sodium fluoride to remove the interference from aluminium, which also fluoresces with morin. This interference can, however, be eliminated by effecting a prior separation. A method for doing this had been described by Swift,[6] based upon repeated extraction of gallium from 6*M* hydrochloric acid with ether. An improved procedure for this extraction is described by Milner.[3]

An alternative although slightly longer procedure has now been devised following the work of Kraus *et al.*,[7] using strongly basic anion-exchange resins. These resins, used in the form of columns 1 cm in diameter and 4 cm in length, absorb gallium from 6*M* hydrochloric acid solution together with iron, zinc, cadmium, mercury, thallium, tin, antimony^{V} and bismuth. On washing the columns with 1*M* hydrochloric acid the gallium is removed, together with the iron^{III} and the antimony^{V}. It is therefore possible to separate gallium from all the other elements by this procedure, provided that iron and antimony are reduced to their lower valency states before passage through the ion-exchange column. For this purpose a silver reductor is employed.[1]

This method of separation has been used in the determination of the gallium content of Bayer liquor, containing approximately 40 g of aluminium per litre.

Procedure

Ten ml of the Bayer liquor were diluted to 20 ml with water and neutralized, and the acid strength was then increased to 6*M* with concentrated hydrochloric acid. This solution was passed through a silver reductor (6 cm in length, 1 cm in diameter), which was washed with 20 ml (about 3 column volumes) of 6*M* hydrochloric acid. The combined eluate and washings were immediately rinsed on to an anion-exchange column 4 cm in length (Dowex 1 × 4, 100–200 mesh) and the column was eluted with 60 ml (about 20 column volumes) of 6*M* acid. The gallium was eluted with 20 ml (about 6 column volumes) of 1*M* hydrochloric acid.

The eluate was carefully neutralised to methyl red with 10% aqueous sodium hydroxide, and 10 ml of glacial acetic acid were added. The volume was increased to 50 ml by dilution with water, and 50 ml of methanol were added. The solution was titrated with standard EDTA in ultraviolet light, using morin as indicator, until the vivid fluorescence was extinguished. Aliquots of the Bayer liquor to which additional gallium had been added were also analysed by this procedure. The results obtained are given in Table III.

Table III

Gallium added, *mg*	Gallium recovered, *mg*
nil	0·24,* 0·24*
	0·21,* 0·21*
6·92	7·11, 7·07
13·84	14·00, 14·00

* Titration with 0·001*M* EDTA

Acknowledgements—This note describes part of a research programme of Warren Spring Laboratory D.S.I.R. and is published by permission of the Director.

G. R. E. C. Gregory
P. G. Jeffery

Warren Spring Laboratory
Stevenage, Herts

Summary—An improved separation of gallium from other elements, using an ion-exchange column, and subsequent determination of the element by titration with EDTA, using morin as indicator, are described. The method has been applied to determination of gallium in the presence of a large excess of aluminium.

Zusammenfassung—Eine verbesserte Trennung fur Gallium vo anderen Elementen wird beschrieben. Ionenaustausch wird eingesetzt und Gallium wird mit ADTE titiert unter Verwendung von Morin al, Indicator. Die Methode wurde zu Bestimmung von Gallium in Gegenwart von grossen Mengen Aluminiums verwendet.

Résumé—Les auteurs décrivent une méthode de séparation du ga'lium d'autres éléments par échange d'ions, suivie d'un titrage par l'E.D.T.A avec le morin comme indicateur. La méthode a été appliquée au dosage du gallium en présence d'un grand exces d'aluminium.

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Talanta, 1962, Vol. 9, pp. 805 to 809. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

CZECHOSLOVAKIA

October 1962: **Seminary on Radiation Detectors:** *Association for Spectral Analysis.* Liblice.

POLAND

Saturday 20 *October* 1962: **Symposium on Chromatography in Analysis and Preparation of Alkaloids:** *Chromatographic Subcommittee of the Analytical Chemistry Commission, Polish Academy of Sciences.* Poznań (see *Talanta,* 1962, **9,** 627).

SWITZERLAND

Monday–Saturday 15–20 *October* 1962: **Second International Exhibition and Congress of Laboratory, Measurement and Automation Techniques in Chemistry.** Swiss Industries Fair, Basle (see *Talanta,* 1962, **9,** 627).

UNITED KINGDOM

Friday–Saturday 21–22 *September* 1962: **Joint Meeting** of *Society for Analytical Chemistry, Microchemistry Group* and *Royal Institute of Chemistry, Dublin and District Section.* Trinity Hall, Dartry Road, Dublin 6.

The following programme has been arranged:

Friday 21 *September*
3.00 p.m. Visit to the Distillery of John Jameson and Sons.
8.00 p.m. Meeting in Trinity Hall on *Modern Trends in Small-Scale Inorganic Analysis,* with the following speakers: Professor T. S. WHEELER, Mr. C. WHALLEY, Mr. R. C. CHIRNSIDE, Dr. R. A. CHALMERS and Dr. D. J. HINGERTY.

Saturday 22 *September*
9.30 p.m. All-day tour by courtesy of Bordna Mona (the Peat Board).
9.00 p.m. Discussion meeting in Trinity Hall on *Modern Trends in Analysis.*

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

B.S. 658: 1962: *Apparatus for the determination of distillation range (including flasks and receivers).* This specifies distillation flask (7 sizes), receiver (5 sizes), thermometer, draught screen (2 types), asbestos adaptor boards, wire gauze, heater (gas or electric), condenser (3 types), retort stand for a wide range of standard distillation tests. The section on flasks represents a revision of the former B.S. 571, and covers material, construction, dimensions and inscriptions. The dimensions ensure that the position of the side tube (and therefore of the thermometer), in relation to the top of the neck and the liquid surface when the flask is ready for use, is the same for all sizes of flask.

The section on receivers represents a revision of the former B.S. 605 and covers material, construction, tolerances, dimensions, graduation of scale and inscriptions, for both the cylindrical type and the Crow type with a conical lower portion. A standard method for determination of capacity is included as an appendix.

The correction of barometric readings to standard temperature and pressure is described in an appendix, which enables distillation temperatures to be corrected in accordance with the specification for the particular liquid concerned. (Price 8s. 6d.).

The following *Amendment Slip* is also announced:
B.S. 3406: *Methods for the determination of particle size of powders: Part* 1: 1961: *Sub-division of gross sample down to* 0.2 *ml. Amendment No.* 1: *PD* 4605.

UNITED STATES OF AMERICA

On 2 July, 1962, Dr. Nicholas Cheronis was fatally injured as a result of an automobile accident. Born in Sparta, Greece, Professor Cheronis arrived in the United States as a boy of fifteen to join his family which had already settled in Chicago. After earning his doctorate at the University of Chicago in 1929, he taught in the Chicago City College system until 1949. He joined the Brooklyn College Faculty the following year as Chairman of the Department of Chemistry.

He was the author of numerous articles and books in his field. Among his books are listed *Organic Chemistry*, *Semimicro and Macro Organic Chemistry*, and *Semimicro Experimental Organic Chemistry*. He was Chairman of the Editorial Board of *The Microchemical Journal*, which has its office at Brooklyn College. Professor Cheronis was a member of Sigma Xi, the American Chemical Society, the Illinois Academy of Science, the New York Academy of Sciences, the American Association for the Advancement of Science and the Metropolitan Microchemical Society.

He leaves his wife, Mrs. Nicholas Cheronis, and two children, both married, Dion, who lives in Chicago, and Mrs. Peter Selz, who resides in Manhattan.

Sunday 30 *September–Friday* 5 *October* 1962: **ASTM Fourth Pacific Area National Meeting:** *American Society for Testing and Materials.* Statler Hilton Hotel, Los Angeles, California.

The provisional technical programme contains the following items of interest to analytical chemists.:

Monday 1 *October*

9.00 a.m. *Symposium on Cleaning and Materials Processing for Electronics and Space Apparatus—Air Borne Contaminant Session*

A Review of the Gravity Settling Technique for Measuring Dust in Electron Device Processing Areas.	E. E. Selby
A Comparison of Dust Count Data Obtained from Different Measuring Methods.	R. C. Marsh
Enumeration of Air Borne Particulate Matter by the Scattered Light Technique.	J. F. Pudvin
Proposed Referee Method for Sizing and Counting of Air Borne Particulate Contamination in Clean Rooms and Other Dust Controlled Areas.	R. A. Cotton

2.00 p.m. Symposium continued—*Solvents and Processing Liquids Session*

Comparative Investigation of Methods of Producing Ultra-Pure Water.	V. C. Smith
The Silting Index—An Evaluation of Micron and Sub-Micron Contamination in Industrial Waters.	J. L. Dwyer
Resistance Measurements as a Means of Controlling the Quality of Ultra-Pure Organic Solvents.	S. Balsbaugh and V. C. Smith

Tuesday 2 *October*

9.00 a.m. Symposium continued—*Ultrasonic Analytical Techniques Session*

An Instrument for the Contactless Measurement of Minority-Carrier Lifetime.	C. G. Currin and F. A. Smith
Resistivity Measurements by Thermal Compression Bonding.	L. J. Droege
Theory and Performance of a Continuous Electrochemical Detector for Microgram Quantities of Atmospheric Cyanide.	C. O. Thomas
Measurement of Mass Using Quartz Crystal Resonators.	C. D. Stockbridge and A. W. Warner

Wednesday 3 *October*

9.00 a.m. *Symposium on Applied Statistics in Materials Testing*

Proposed Recommended Practice for Interlaboratory Study of a Test Method.	G. Wernimont and J. Mandel
Proposed Recommended Practice on Definitions of the Terms Precision and Accuracy as Applied to Measurement of a Property of a Material.	R. B. Murphy
Reliability Testing.	E. P. Coleman

Thursday 4 *October*

2.00 p.m. *Symposium on Industrial Water*

Methods of Determining Nitrates in Water.	E. Goldman
Application of the Technicon Auto Analyser to Steam Plant Boiler Silica Analysis.	R. C. Allen
Recent Advances in Automatic Colorimetric Analysis.	J. F. Baird
Water Analysis—As Interpreted by the Equipment Manufacturer.	W. C. Burns

Friday 5 *October*

9.00 a.m. *Symposium on Advancement in Methods of Air Pollution Measurement*

Particulate Air Contaminants from Combustion.	B. D. Tebbens
A Light Scattering Instrument for the Determination of Plume Opacity.	L. F. Dixon and H. H. Sonderling

2.00 p.m. Symposium continued

Methods for the Determination of the Size and Mass Distribution of Aerosols.	A. Goetz and T. Kallai
Quantitative Analysis by Gas Chromatography of NO and NO_2 at Low Concentrations in the Presence of Nitrogen.	W. H. Corcoran
Methods of Analysis, Available and Needed, for Evaluation of a Fluoride Pollution Problem.	R. H. Wade, H. M. Benedict and J. M. Ross

Further information may be obtained from ASTM, 1916 Race Street, Philadelphia 3, Pennsylvannia.

Monday–Friday 8–12 *October* 1962: **Twelfth Annual Instrument Symposium and Research Equipment Exhibit:** *National Institutes of Health.* Bethesda, Md.

During the scientific meeting, noted investigators will report on recent trends and developments in research methods and instrumentation. Symposium discussion topics will range from new ion-exchange techniques through nuclear magnetic resonance, optical masers, vacuum ultraviolet, X-ray microscopy, automation in chemical and biochemical research, physiological monitoring, and X-ray diffraction studies of proteins.

For additional information write to James B. Davis, National Institutes of Health, Public Health Service, Bethesda 14, Maryland.

Tuesday–Thursday 9–11 *October* 1962: **Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology** and **Third Conference on Nuclear Reactor Chemistry:** *Oak Ridge National Laboratory.* Gatlinburg, Tennessee (see *Talanta*, 1962, **9**, 471).

The preliminary programme for the **Conference on Analytical Chemistry** is as follows:

Tuesday 9 *October*

Morning—*Radiochemistry and Nucleonics Session*

Activation Analysis with a Research Reactor—New Developments.	V. P. Guinn
Identification and Comparison of Physical Evidence for Enforcement Purposes by Neutron Activation Analysis.	L. C. Bate, G. W. Leddicotte and M. J. Pro
The Texas A. and M. Mark I-Ia, Automatic Reactor and Computer-Coupled System for Activation Analysis.	L. E. Fite and R. E. Wainerdi
Determination of Germanium in Mineral Specimens by Neutron Activation Analysis.	M. A. Wahlgren and K. Orlandini
Precise Method for Determination of ^{235}U by Neutron Activation Analysis.	H. Bussell, C. L. Zyskowski and L. C. Nelson, Jr.
Analysis of Beryllium in Beryllium Metal by Activation Analysis.	F. W. Postma, Jr. and C. S. McMurray, Jr.
Radionuclides found at Equilibrium Conditions in Cooling Water of 5-Megawatt Pool-Type Research Reactor.	J. R. Pelrine

Afternoon—*Instrumentation Session*

Beta-Excited X-Rays in Analytical Chemistry.	R. H. Müller
Absorptiometry with Beta-Excited X-Rays.	D. C. Müller
Modified X-Ray Diffractometer for Medium-Level Radioactive Samples.	W. A. Ryder, G. V. Wheeler, H. H. Leigh and F. W. Schultz
Microscope for Ultrahigh Temperatures.	D. M. Olson

An In-Line Instrument for Automatic Determination of Gases in Simulated Boiling Water Reactor and Steam Loops.	M. Siegler and D. T. Snyder
Comparative Condensation-Pressure Analyser for Vapour Purity of Uranium Hexafluoride.	W. S. Pappas, S. A. MacIntyre and C. W. Weber
Determination of Hydrogen in Uranium, Utilising a Thermal Conductivity Detector.	D. E. Seizinger, L. A. Fergason and C. H. McBride

Spectrophotometry Session

Determination of Micro Quantities of Dibutylphosphate in Tributylphosphate-Kerosene.	M. A. Wade and S. S. Yamamura
Determination of Tungsten in Reactor Materials—Extraction and Spectrophotometric Determination with 8-*Quinolinol.*	A. R. Eberle
Spectrophotometric Determination of Technetium with 1,5-*Diphenylcarbohydrazide.*	F. J. Miller and H. E. Zittel
Separation and Spectrophotometric Determination of Technetium in "Fission".	R. J. Meyer, R. P. Larsen and R. D. Oldham

Wednesday 10 *October*

Morning—*Spectroscopy Session*

Advances in Atomic Emission Spectrochemistry.	P. T. Gilbert, Jr.
The Copper-Spark Method for Spectrographic Analysis—Twenty Years Experience.	J. Faris
Spectral Excitation of Solutions Using Stable Plasma Jets.	L. E. Owen
Collection and Flame Photometric Determination of Caesium.	C. Feldman and T. C. Rains

Afternoon—*Analytical Chemistry and the Actinides Session*

Plutonium Sulphate Tetrahydrate, A Primary Analytical Standard for Plutonium.	C. E. Pietri
Some Aspects of Measurement of Oxygen to Metal Ratio in Solid Solutions of Uranium and Plutonium Dioxides.	J. L. Drummond and V. M. Sinclair
Direct Volumetric Determination of Uranium or Plutonium in Nitric Acid Medium.	J. Corpel
Ion-Exchange Separation of Actinides with Nitric Acid-Methanol and with EGTA.	J. Hines, M. Wahlgren and F. Lawless
Ion-Exchange Purification of ^{147}*Pm and its Separation from* ^{241}*Am with Diethylenetriaminepentaacetic Acid as Eluant.*	P. B. Orr
Studies of Polymerisation of Quadrivalent Plutonium by Spectrophotometric Methods.	D. A. Costanzo and R. E. Biggers
Determination of ^{137}*Cs in Solutions of Irradiated* UO_2 *Fuel using Preformed Ammonium Molybdophosphate.*	G. M. Allison and R. A. Ferguson

Thursday 11 *October*

Morning—*Session on Use of Isotopes in Analytical Chemistry*

Radioactive Indicators in Analysis.	C. Rosenblum
Determination of Thorium and Alkaline-Earth Elements by Isotope Dilution.	S. A. Reynolds
Application of One-Step Radiometric Titration to Analysis of Aluminium Containing Silicates.	D. S. Berry and B. F. Scott
Determination of Phosphorus in Uranium by Isotope Dilution Analysis.	F. W. Lima and L. T. Atalla
Applications of Radioisotopes in Polarography.	W. B. Schaap and E. Wildman
Some Problems Involved in Utilising Radioisotopic Tracers.	G. Goldstein
Use of Radioisotopes in Determination of Distribution Coefficients of Alkali Metals in an Organic Phosphate-Aqueous System.	R. J. Klett and B. Wilkins, Jr.

Atomic Absorption and X-Ray Spectroscopy Session

Atomic Absorption Spectroscopy—A Review.	P. T. Gilbert, Jr.
An Atomic Absorption Tube for Use with an Atomiser-Burner: Application to Determination of Mercury.	C. Feldman and R. K. Dhumwad
Applications of Atomic Absorption Spectrophotometry to Isotope Analysis.	W. Slavin
A Grating Monochromator.	W. Kaye
An X-Ray Emission Method for Determining Uranium and Plutonium in Binary and Ternary Mixtures.	O. Menis, E. Halteman and E. E. Garcia

Analytical Techniques used in Evaluating High-Temperature Phase Equilibria· Application to the UO_2-ThO_2-O_2 System.	H. A. FRIEDMAN

Afternoon—*Mass Spectroscopy Session*

Utilisation of a Spark-Source Mass Spectrograph for Analysis of Reactor Materials.	W. J. SEWALK and H. D. COOK
Investigation of Burnup Determinations on Highly Irradiated Fuels by Mass Spectrometric Methods.	H. D. COOK, C. J. RETTGER and W. J. SEWALK
A Safe Semiautomatic Fluorination System for Preparation of UF_6 Mass Spectrometer Samples.	J. K. REUSCH and R. D. OHLINGER

General Session

Determination of Free Acid in an Organic Phase of Trilaurylamine.	A. CHESNE
Determination of Oxygen in Lithium.	R. J. JAWOROWSKI, J. R. POTTS and E. W. HOBART
Determination of Rubidium in Rubidium-Doped, Thalliated, Sodium Iodide Scintillation Crystal Using Sodium Tetraphenylboron.	K. J. JENSEN
Beryllium Determination as $Be_2P_2O_7$.	C. BAMBERGER and J. L. HUGUET
Dissolution of Irradiated, High-Fired, Refractory, Nuclear Materials.	H. KUBOTA and R. F. APPLE

Wednesday 31 *October–Saturday* 3 *November* 1962: **Ninth National Vacuum Symposium:** *American Vacuum Society.* Statler Hilton Hotel, Los Angeles, California (see *Talanta*, 1962, **9**, 406).

Monday–Thursday 20–30 *May* 1963: **International Symposium on Humidity and Moisture—Measurement and Control in Science and Industry:** *National Bureau of Standards, U.S. Weather Bureau, American Society of Heating, Refrigerating and Air Conditioning Engineers, Instrument Society of America* and *American Meteorological Society.* Washington D.C.

The symposium will review current progress and present the results of original research and development work on measurement and control of humidity and moisture in the physical, engineering, meteorological, agricultural and biological sciences.

Further details may be obtained from ARNOLD WEXLER, National Bureau of Standards, Washington 25, D.C.

Talanta, 1962, Vol. 9, p. 810. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Spectrophotometric study of *p*-nitrosodiphenylamine as a reagent for rhodium: JAMES R. STOKELY and WILLIAM D. JACOBS. (2 *July* 1962).

Triethylenetetraminehexa-acetic acid as a new volumetric reagent: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (2 *July* 1962).

Beobachtungen am Verbrennungsverlauf organischer Substanzen: E. PELL and H. MALISSA. (2 *July* 1962).

Precipitation of cadmium from homogeneous solution using 8-acetoxyquinoline: ROGER D. WHEALY and B. J. BLAND. (10 *July* 1962).

Differential coulometric analysis: A high precision technique and its application to the determination of dichromate by constant current generation of ferrous ion: R. G. MONK and G. C. GOODE. (13 *July* 1962).

Analytical applications of the flame emission spectra of lead and titanium: C. L. CHAKRABARTI, R. J. MAGEE and C. L. WILSON. (17 *July* 1962).

Spectrophotometric determination of the dissociation constant of the Woods reagent, 2-hydroxymethyl-6(2′-hydroxymethyl-5′-hydroxy-4′-pyrone-6′)pyranyl [3,2-B] pyran-4,8-dione: R. F. WILSON and G. W. LESTER. (17 *July* 1962).

4(2-Pyridylazo)resorcinol as a selective and sensitive spectrophotometric reagent for **niobium$^{(V)}$:** R. BELCHER, T. V. RAMAKRISHNA and T. S. WEST. (17 *July* 1962).

L'oxalate de *p*-dimethylaminoaniline dans la colorimétrie des aldehydes et des ceto-stéroides: MAURICE PESEZ et JAROSLAV BARTOS. (17 *July* 1962).

Some theoretical and practical problems in the use of organic reagents in chemical analysis—II: Effect of hydrogen bridge and donor π bond on the stability of transitional metal chelates of dioximes: K. BURGER and I. RUFF. (17 *July* 1962).

***p*-Thiocresol as a new reagent for technetium and rhenium:** M. AL-KAYSSI and R. J. MAGEE. (17 *July* 1962).

A study of the extraction and absorptiometric determination of titanium with 8-hydroxyquinoline: C. L. CHAKRABARTI, R. J. MAGEE and C. L. WILSON. (19 *July* 1962).

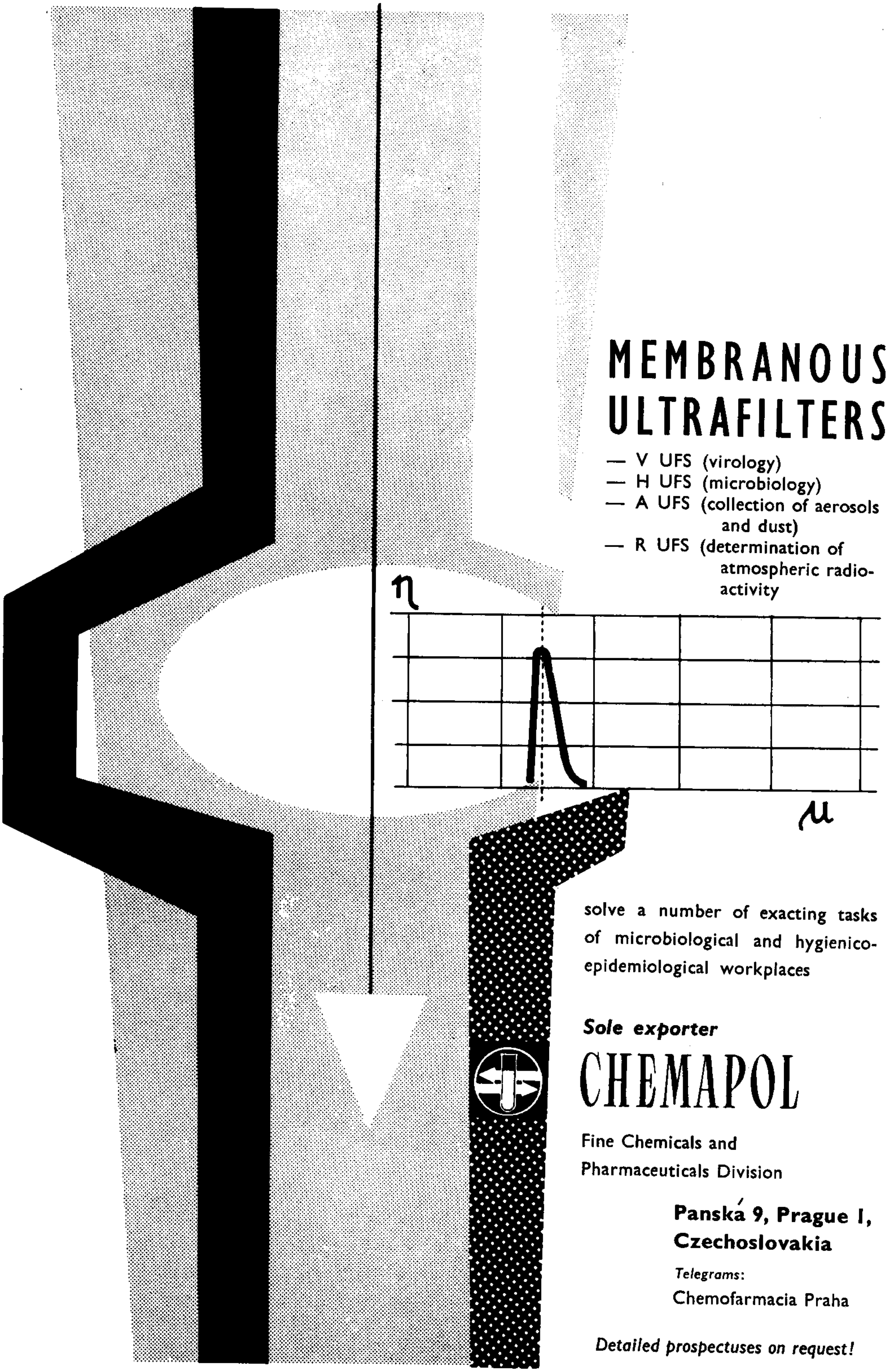
An investigation of the chelatometry of Cu$^{(II)}$ with ethylenediamine-N,N,N′,N′-tetra-*n*-propionic acid: I. P. SANDERSON and T. S. WEST. (19 *July* 1962).

Cation-exchange separation of scandium: HIROSHI HAMAGUCHI, ROKURO KURODA and KOREKAZU AOKI. (19 *July* 1962).

Voltammetry of silver in molten sodium nitrate–potassium nitrate: D. L. MANNING. (24 *July* 1962).

The chromatographic separation and determination of niobium, tantalum and titanium: I. MARTIN and R. J. MAGEE. (25 *July* 1962).

The iodometric estimation of tin: D. I. BOTHWELL and A. A. MOSS. (26 *July* 1962).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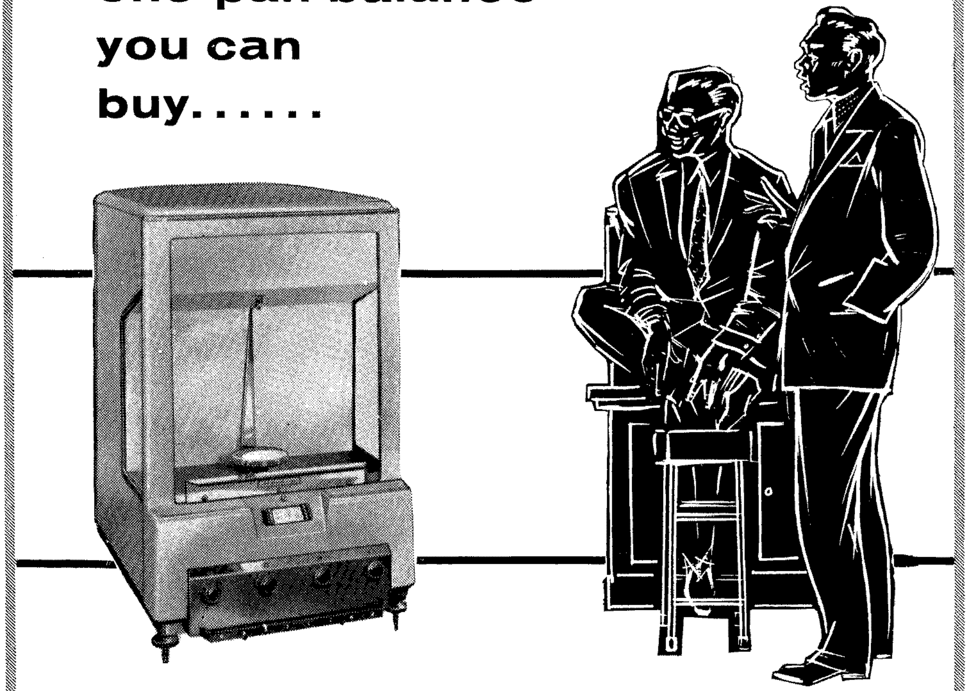

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