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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 32, No. 3, March 1965

THE DETERMINATION OF TRACE AMOUNTS OF ZIRCONIUM, HAFNIUM, THORIUM AND CERIUM IN SILICATE ROCKS

A method is described for the determination of traces of zirconium, hafnium, cerium and thorium in rocks. After the sample has been opened up, these elements are separated from the major component elements by extraction from 10 *N* nitric acid with a 40% solution of tri-*n*-butyl phosphate, cerium being oxidised with bromate. After back-extraction the elements are separated from each other and from other extracted elements by cation exchange. Zirconium is determined photometrically with quinalizarin sulphonic acid which gives about twice the sensitivity of alizarin red S. Thorium is determined photometrically with thorin, and cerium by utilizing its bleaching action on iron(II) phenanthroline. Hf is determined spectrographically.

F. Culkin and J. P. Riley,
Anal. Chim. Acta, 32 (1965) 197–210.

A PROCEDURE FOR SILICATE ROCK ANALYSIS BASED ON ION EXCHANGE AND COMPLEX-ION FORMATION

A procedure for the analysis of silicate rocks based on ion exchange and complex-ion formation is described. Moisture (H_2O^-), SiO_2, TiO_2, Al_2O_3, P_2O_5, total iron, MgO, MnO, and CaO are determined in a 1-g sample. Other oxides, such as FeO, Na_2O and K_2O, and H_2O^+ are determined in separate portions. The results for 6 silicates, including G-1 and W-1, compare favorably with those obtained by established procedures. Six complete analyses may be carried out in about 8 days.

A. D. Maynes,
Anal. Chim. Acta, 32 (1965) 211–220.

SPECTROPHOTOMETRIC DETERMINATION OF CALCIUM WITH 8-QUINOLINOL

The spectrophotometric determination of calcium with 8-quinolinol is described. Interference from all the commonly encountered metals and elements with the exception of magnesium and strontium can be eliminated by preliminary carbamate–chloroform and cupferron–chloroform solvent extractions. The proposed method is adapted to the determination of calcium in battery lead.

C. L. Luke,
Anal. Chim. Acta, 32 (1965) 221–226.

THE DETERMINATION OF GLYCEROL

PART II. ABSORPTIOMETRIC DETERMINATION AS THE COPPER COMPLEX

Spectrophotometric studies of the copper–glycerol complex are reported. A single 1:1 complex is formed under the experimental conditions employed. The interference of precipitated or colloidal copper(II) hydroxide can be overcome by filtration through glass-fibre discs or by application of a correction factor. Filtered solutions of the complex in 90% ethanol obey Beer's law over a wide range of concentration. The stability of the complex and the effects of variation in alcohol and alkali concentration have been studied.

An absorptiometric method for the determination of 0.5–40 mg of glycerol is proposed and the effect of possible interferences is considered.

(The late) J. T. McAloren and G. F. Reynolds,
Anal. Chim. Acta, 32 (1965) 227–234.

INVESTIGATION OF THE IRON(II) COMPLEX OF BIS-3,3′-(5,6-DIMETHYL-1,2,4-TRIAZINE)

The reagent, bis-3,3′-(5,6-dimethyl-1,2,4-triazine) (BDMT), forms intensely colored complexes with selected transiton metal ions. The reagent is water-soluble and easily prepared. An intense orange complex, $Fe(BDMT)_3^{2+}$, is formed on reaction of iron(II) with the reagent in aqueous solution at pH 4.0–7.0. Nuclear magnetic resonance data show that chelation occurs between the 2,2′-nitrogens of the reagent. The complex exhibits absorption maxima at 408 mμ and 493 mμ, with molar absorptivities of 12,200 and 15,000 respectively. The perchlorate salt of the complex is readily extracted into nitrobenzene. A proposed spectrophotometric method for the determination of iron is both accurate and precise.

R. E. Jensen and R. T. Pflaum,
Anal. Chim. Acta, 32 (1965) 235–244.

VAPOR PRESSURE–TEMPERATURE DATA FOR VARIOUS METAL β-DIKETONE CHELATES

Vapor pressure–temperature data, molar heats of sublimation, and sublimation temperatures are given for 29 metal β-diketone chelates. The chelates studied were those of Be(II), Al(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with acetylacetone, acetyltrifluoroacetone, benzoylacetone, benzoyltrifluoroacetone, 2-furoyltrifluoroacetone, and 2-thenoyltrifluoroacetone. The observed difference in volatilities of the various metal chelates of a given ligand is the basis for a suggestion that various mixtures of metal ions can be resolved by a fractional sublimation scheme.

E. W. Berg and J. T. Truemper,
Anal. Chim. Acta, 32 (1965) 245–252.

SOME CAUSES OF BENDING OF ANALYTICAL CURVES IN ATOMIC ABSORPTION SPECTROSCOPY

Some factors affecting the shape of analytical curves in atomic absorption spectroscopy are considered and the influence of the emission and absorption line profiles is discussed in detail. An empirical equation expressing the analytical curves for different ratios of emission line width to absorption line width is given. The possible influence of resonance line broadening and resonance line shift in atomic absorption flame photometry is also discussed.

I. Rubeška and V. Svoboda,
Anal. Chim. Acta, 32 (1965) 253–261.

THE NATURE OF LIGHT

PART I. A PHYSICAL MODEL OF THE PHOTON

The dualistic behavior of light has always presented a problem to scientists in general, and spectroscopists in particular.

A model of a photon has been proposed which has mass, and a matched positive and negative charge. The properties of the proposed particle would be expected to behave as a particle usually behaves, but under certain circumstances a group of such particles would exhibit wave-like properties. Several classical phenomena are examined and interpreted in terms of the proposed model.

J. W. Robinson,
Anal. Chim. Acta, 32 (1965) 262–268.

THE USE OF POORLY RESOLVED GAS CHROMATOGRAPHIC CURVES FOR THE ANALYSIS OF BINARY MIXTURES OF PETROLEUM FRACTIONS

Blends of petroleum products are usually made from fractions which contain preponderantly the same compounds. Only the relative abundances vary. A calculation of the contribution of each blended fraction is theoretically possible with the aid of the gas chromatographic elution curve even though resolution is uniformly poor in such complex systems. An elementary mathematical analysis is made to show what conditions must maintain. Experimental evidence is presented to indicate that the necessary conditions can be realized for petroleum blends. Binary mixtures of complex fractions may be analyzed with an accuracy of better than 10% and only normal attention to detail need be observed.

G. Perkins, Jr., R. E. Laramy and E. E. Smith,
Anal. Chim. Acta, 32 (1965) 269–277.

THE APPLICATION OF THIN-LAYER CHROMATOGRAPHY AND PHOSPHORIMETRY FOR THE RAPID DETERMINATION OF NICOTINE, NORNICOTINE AND ANABASINE IN TOBACCO

Tobacco is ground and extracted with chloroform, and thin-layer chromatography is used to separate the 3 major tobacco alkaloids — nicotine, nornicotine and anabasine. Each of the alkaloids is quantitatively removed by scraping the spot into a container and dissolving in ethanol–sulfuric acid. A small volume of the ethanol solution is then measured phosphorimetrically. Excellent recoveries of each of the tobacco alkaloids were obtained; the relative standard deviation of analysis was 6% or less for all analyses. The total time for analysis of the 3 alkaloids was less than 90 min. This method is considerably faster and more accurate than previous methods.

J. D. WINEFORDNER AND H. A. MOYE,
Anal. Chim. Acta, 32 (1965) 278–286.

A NEW NEOCUPROINE–CARBAMATE SPECTROPHOTOMETRIC DETERMINATION OF COPPER
(Short Communication)

C. L. LUKE,
Anal. Chim. Acta, 32 (1965) 286–287.

THE DETERMINATION OF TRACE AMOUNTS OF ZIRCONIUM, HAFNIUM, THORIUM AND CERIUM IN SILICATE ROCKS

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(Received June 25th, 1964)

Zirconium can frequently be detected by direct optical spectrographic methods in rocks since its average abundance in the lithosphere is approximately 5 times the minimum detectable concentration (*ca.* 30 p.p.m.). A simple fluorimetric method of greater sensitivity, using morin, has been described[1] for the determination of the element in silicate rocks, but it is lacking in precision. DEGENHARDT[2] has described a procedure for the determination of zirconium in silicates, in which the element is concentrated by co-precipitation with titanium hydroxide and determined photometrically with alizarin sulphonic acid.

Thorium, cerium and hafnium do not possess lines of sufficiently high sensitivity for their direct spectrographic determination at the concentrations at which they normally occur in rocks. Neutron activation procedures[3,4] have been used for the determination of thorium in rocks, but it is generally necessary to concentrate these elements before they can be determined by spectrographic or photometric methods. Solvent extraction processes using mesityl oxide[5] and *cyclo*-hexanone[6,7] have been used for the concentration of thorium from rocks and sediments prior to photometric determination. Thorium has also been concentrated by co-precipitation with calcium oxalate[8,9]. A cation-exchange method has been employed[10] for concentration of rare earth elements and cerium from rocks prior to their spectrographic determination.

This paper describes the development of a solvent exchange method for the concentration of traces of zirconium (+ hafnium), thorium and cerium from silicate rocks and recent marine sediments. These elements are then separated from one another by ion-exchange procedures and determined by spectrophotometric, or in the case of hafnium, spectrographic methods.

Solvent extraction of microgram amounts of zirconium, hafnium, thorium and cerium

Little work appears to have been carried out on the concentration of zirconium by extraction. Extractions with 2-thenoyltrifluoroacetone in benzene[11,12] or xylene[13] and with cupferron in chloroform[14] or in benzene–isoamyl alcohol mixture[15] have been used, but many other metals, particularly iron, are also extracted. Tri-*n*-butyl phosphate, usually diluted with an inert solvent has proved a satisfactory

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solvent for extracting zirconium from nitric or hydrochloric acid medium[16,17]. Partial separation of zirconium and hafnium can be achieved with this solvent using 4–5 M nitric acid as the aqueous phase.

The complexes which thorium forms with a number of organic reagents, such as acetylacetone[18], 2-thenoyltrifluoroacetone[19–21], cupferron[22,23], 8-hydroxyquinoline[23], mesityl oxide[24,25], 1-nitroso-2-naphthol[26] and 2-nitroso-1-naphthol[26] can be extracted with various solvents. These reagents are unspecific and many of the commoner elements such as iron and titanium are also extracted. Thorium can be extracted from nitric acid solutions, in the presence of high concentrations of nitrate ion, by a number of oxygen-containing organic solvents, such as ketones and organic phosphates. HESFORD *et al.*[27] have employed extraction with tri-*n*-butyl phosphate for the separation of thorium from the rare earth elements. The same reagent has been used[28] as a 10% solution in methyl isobutyl ketone for the determination of thorium in ores. Thorium can also be extracted from hydrochloric acid solution, by means of tri-*n*-butyl phosphate, and this effects a separation from scandium and zirconium, which are not extracted[29].

Cerium(III) and the rare earths are not extracted appreciably from nitrate solution. If cerium is oxidised to the cerium(IV), it can be extracted from nitric acid solution with solvents such as diethyl ether[30–32], methyl isobutyl ketone[33,34], hexyl alcohol and tri-*n*-butyl phosphate[35,36].

The above review of the literature suggested that the choice of solvents for the simultaneous extraction of thorium, cerium, zirconium and hafnium was limited, particularly if the other major components of rocks, such as iron and titanium, were not to be simultaneously extracted. Tri-*n*-butyl phosphate appeared to be a suitable solvent for the separation. The optimum nitric acid concentrations for the extraction by this solvent of decimilligram amounts of these 4 tetravalent elements were investigated, since most of the data in the literature apply to the extraction of deci- or centigram amounts of these elements.

Extraction of zirconium, hafnium, thorium and cerium with tri-n-butyl phosphate

A series of extractions was carried out, in which 20-ml aliquots of various strengths of nitric acid, containing 100 μg of zirconium and 0.5 g of sodium bromate, were shaken with 20 ml of a 40% (v/v) solution of tri-*n*-butyl phosphate in isooctane, which had been equilibrated with the same strength of nitric acid. After shaking for 10 min, the nitric acid phase was run off, and the organic phase was washed twice with 2-ml portions of the same strength of nitric acid. Zirconium was back-extracted by shaking the organic phase with two 25-ml aliquots of 0.1 M oxalic acid. The combined back-extracts were allowed to stand overnight with 0.5 g of sodium bromate in order to oxidise oxalic acid. Excess of bromate, and bromine which was formed during the oxidation, were reduced by adding 1 ml of 20% (w/v) hydroxyammonium chloride solution. The solution was passed through a column of Zeo-Karb 225, which was then washed with 100 ml of 1.5 N nitric acid to remove phosphate and bromide. After the resin had been washed with water until free from acid, zirconium was eluted with 30 ml of 0.025 M oxalic acid. The eluate was evaporated to fuming with 1 ml of 60% perchloric acid and zirconium was determined as described on p. 201. A similar series of extractions of hafnium was also carried out.

Extraction of 100 μg of thorium, back-extraction and adsorption were carried out as described for zirconium; elution was performed with 150 ml of 0.5 *M* oxalic acid. After destruction of oxalic acid with hydrogen peroxide and perchloric acid, thorium was determined photometrically with thorin. For comparison, a similar series of extractions was made using a 20% (v/v) solution of tri-*n*-butyl phosphate in isooctane.

An investigation of the extraction of 50 μg of cerium with both 20% and 40% (v/v) tri-*n*-butyl phosphate was performed as described for thorium, with the exception that cerium was eluted from the ion-exchange column with 75 ml of 5% citric acid of pH 5.0. After destruction of the citrate, cerium was determined spectrophotometrically with iron(II) phenanthroline.

The results of the extraction experiments are summarised in Table I. They show that a 20% solution of tributyl phosphate in isooctane was not a satisfactory solvent for the quantitative extraction of thorium and zirconium. With a 40% solution of tri-*n*-butyl phosphate, all 4 elements were extracted with an efficiency of 94%, or better, from a 10 *N* nitric acid solution. A double extraction under these conditions was therefore employed to separate zirconium, hafnium, thorium and cerium from the major components of rocks and minerals.

TABLE I

EXTRACTION OF Zr, Hf, Th AND Ce WITH TRIBUTYL PHOSPHATE IN ISOOCTANE

	N HNO_3	*Percentage extraction*			
	(aq. phase)	*Zr*	*Hf*	*Th*	*Ce*
20% T.B.P.	1	2		37.6	6.0
	2	4		48.2	9.5
	4	18		64.4	28.0
	6	48		67.1	75.0
	8	70		63.9	94.0
	9	76		63.0	99.0
	10	79		62.1	97.6
	12				80.5
40% T.B.P.	1			55.3	4.5
	2			71.6	11.0
	4	45.5	9.0	86.4	33.8
	6	79.3	28.0	90.2	88.5
	8	96.0	74.0	91.4	100.0
	10	99.3	96.5	94.0	100.0

Oxalic acid (0.1 *M*) was found to be a satisfactory reagent for the back-extraction of these elements from the organic phase. Since ion-exchange procedures are used for the separation of the elements present in the back-extract, its acidity is of importance. The acidity of the two combined 25-ml back-extracts of 2 × 25 ml of 40% tri-*n*-butyl phosphate, which had been previously equilibrated with 10 *N* nitric acid, was 1.46 *N* with respect to nitric acid. This acidity did not interfere with the adsorption of zirconium, thorium or cerium by the resin.

The tributyl phosphate used for the extraction is saturated with nitric acid, and this inevitably produces some hydrolysis of the ester. The presence of large amounts of phosphate in the back-extract is undesirable because of the danger of the precipitation of zirconium phosphate, and because of the possibility of its interference in the adsorption of the cations by the ion-exchange resin. The total phosphorus content of the combined back-extracts was determined and found to be 2.8 mg of phosphorus (as phosphate). No precipitation of zirconium from the back-extracts (after destruction of oxalic acid) was noted, even when 2 mg of zirconium was present, which suggested that most of the phosphorus was present as organic phosphate.

Investigation of extraction of other elements from 10 N nitric acid

Since iron, titanium, manganese and chromium interfere in the photometric determination of zirconium, thorium and cerium, their extraction with 40%tributyl phosphate from 10 *N* nitric acid containing sodium bromate was studied as described above, using two extractions with 25 ml of the extractant.

When 5 mg of manganese was present, the combined oxalic acid back-extracts contained 6 μg of manganese corresponding to *ca.* 0.1% of the manganese initially present. Filtration of the back-extract removed all traces of manganese, which suggested that it was present as manganese dioxide; this compound was formed rapidly in the nitric acid phase during the extraction. Treatment of the back-extract with 1 ml of water saturated with sulphur dioxide dissolved the manganese dioxide without interfering with the ion-exchange behaviour of the other elements.

Extraction of titanium (50 mg) showed that the element is partly extracted from 10 *N* nitric acid. The first and second 25-ml oxalic acid back-extracts contained 3.73 and 0.05 mg of titanium respectively, corresponding to 7.5% extraction.

Investigation of the extraction of iron (5 mg), showed that 50 μg of the element was present in the combined oxalic acid back-extracts, corresponding to 1.0% extraction of the element. Chromium (50 mg) was not detectably extracted from 10 *N* nitric acid.

Destruction of oxalic acid in the back-extracts

Oxalic acid (0.1 *M*) was a satisfactory reagent for the back-extraction of zirconium, thorium and cerium from the tri-butyl phosphate phase, but it had to be destroyed before the back-extract could be applied to a cation-exchange column, since it inhibited their uptake by the exchanger. It was found that a 100% excess of sodium bromate added to the combined back-extracts (which is *ca.* 1.5 *N* in nitric acid extracted from the organic phase) destroyed all the oxalic acid within 16 h at room temperature. Bromine and any remaining bromate could then be reduced by means of hydroxyammonium chloride.

Ion-exchange separation of zirconium, thorium and cerium

Ion-exchange methods seemed to offer the best prospects of separating zirconium (+ hafnium), thorium and cerium from one another and from other elements such as iron, thorium and manganese which will also be found in small amounts in the oxalic acid back-extracts. With Zeo-Karb 225 columns (see p. 198), it was found that zirconium, thorium and cerium (100 μg each) were quantitatively adsorbed from their solution in 60 ml of 1.5 *M* nitric acid even in the presence of 3.5 mg of phosphate-P. Complete adsorption also occurred if the back-extracts from tri-butyl phosphate extractions, after destruction of oxalic acid, were passed through the columns. However, if manganese (1 mg), iron (50 mg), or titanium (50 mg) were applied to the column in 50 ml of nitric acid, they were only slightly adsorbed and could be completely removed without loss of zirconium, thorium or cerium, by washing the column with 100 ml of 1.5 *M* nitric acid. Zirconium and hafnium could be completely eluted from the column with *ca.* 25 ml of 0.025 *M* oxalic acid, without removal of thorium or cerium.

The elution of thorium was complete if 150 ml of 0.5 *M* oxalic acid was passed through the column, and this treatment did not remove cerium from the resin. If the combined back-extract from the tri-butyl phosphate extraction of thorium (after destruction of oxalic acid) was put through the ion-exchange process and thorium was eluted with 0.5 *M* oxalic acid, it was found that the overall recovery of the element was only 92 ± 1%. The recovery of thorium was complete, however, if a solution of thorium in 1.5 *N* nitric acid was examined by the ion-exchange process. This suggested that partial hydrolysis products of tri-butyl phosphate prevented adsorption of thorium by the exchanger by forming strongly bound complexes with it. Since the recovery of thorium from the whole process was reproducible, the final results could be corrected for the 8 ± 1% loss of the element.

Hydrochloric acid (6 *N*) was effective for the removal of cerium from the resin, but its repeated use led to decomposition of the latter and its use was therefore abandoned. It is probable, however, that *ca.* 500 ml of 3–4 *N* hydrochloric acid would prove satisfactory for the elution of cerium. It was found that 75 ml of 5% citric acid brought to a pH of 4–5 with ammonia quantitatively removed cerium from the resin, and this eluting agent was therefore used in subsequent work. Destruction of the eluting agent before photometric analysis was accomplished by evaporation and digestion with nitric and perchloric acids.

Photometric determination of the eluted elements

Photometric methods were selected for the determination of most of the elements eluted from the ion-exchange columns, on account of their sensitivity and simplicity. A spectrographic method was used for the estimation of hafnium, which is contained in the zirconium fraction.

Determination of zirconium. Although zirconium forms coloured complexes with many organic reagents in practically no case is the reaction specific. Methods based on the use of oxalohydroxamic acid[37], fast grey R.A.[38], haematoxylin[39], quercetin[40], morin[41–43], catechol violet[44,45], phenylfluorone[46] and solochrome violet R[47] have been recommended for the photometric or fluorimetric determination of the element but all suffer on this account. Arsonic acid derivatives of azo compounds, such as arsenazo, arsenazo III[48], thorin[49] and SPADNS[50] are sensitive and can be made more selective in their action, but nevertheless are subject to many interferences. The strongly coloured lakes which zirconium forms with several hydroxyanthraquinones, notably alizarin and its sulphonic acid, are stable in hydrochloric acid solution, in contrast to those of most other elements, and have formed the basis of a number of photometric procedures[1]. Alizarin blue S, a pyridine derivative of alizarin, has been recommended[51] as a more satisfactory reagent than alizarin. The greater sensitivity of quinalizarin compared with alizarin has been utilized[52] in a method in which interfering elements are masked with EDTA at pH 5.0. The low solubilities of quinalizarin and of its zirconium lake create difficulties in obtaining stable colours with this reagent. In order to overcome these difficulties quinalizarin sulphonic acid (probably 1,2,5,8-tetrahydroxanthraquinone-3-sulphonic acid)[53] was prepared by sulphonation of quinalizarin and its use for the determination of microgram amounts of zirconium was investigated. It was found that it gave intense red colours with zirconium in acid solution, but that the zirconium lake precipitated after a short time. The presence of 20% of acetone, by volume, in the final solution stabilized the colour for several hours and enhanced its intensity. The absorption maximum of the zirconium lake in acetone medium was at 565 mμ and the colour attained its maximum intensity after 3 h.

The effect of perchloric acid on the colour formed with zirconium under these conditions was investigated. It was found that perchloric acid up to a final concentration of *ca.* 0.5 *M* could be present without decreasing the intensity of the colour of the zirconium lake; above this concentration, the intensity of the colour was progressively decreased. In all subsequent work 1 ml of 60% (w/w) perchloric acid was added to each determination carried out in a 25-ml graduated flask. A concentration of 400 μg of quinalizarin sulphonic acid per 25 ml was sufficient for the determination of 50 μg of zirconium.

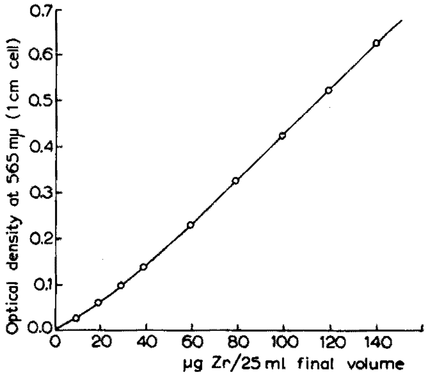

Fig. 1.

Under the above conditions, a calibration curve (Fig. 1) was prepared using 0–140 μg of zirconium (25 ml). It will be seen that there is a linear relationship between optical density and zirconium concentration in the range from 40–140 μg of zirconium. Below 40 μg there was a reproducible, but non-linear relationship, similar to that found for zirconium lakes by other workers[1]. The slope of the linear region of the calibration curve gave a value of 10,000 for the molar extinction coefficient of the zirconium complex* as compared with 5,000 for the zirconium–alizarin S lake. Replicate determinations carried out using 50 μg of zirconium showed that the method gave a coefficient of variation of 0.7%.

Alizarin and alizarin red S form slightly soluble lakes with a number of

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* Application of the method of continuous variations showed that the complex contains 1 atom zirconium per molecule of quinalizarin sulphonic acid.

elements, but most of these are decomposed in acid solutions. In view of this fact, the possible interference of a number of elements in the determination of zirconium with quinalizarin sulphonic acid was investigated. Each element was converted to its perchlorate and was placed in a 25-ml graduated flask together with 1 ml of 60% perchloric acid, 5 ml of 0.02% quinalizarin sulphonic acid and 5 ml of acetone. The solutions were diluted to volume, well mixed and their optical densities were measured at 565 mμ in 1-cm cells after 3 h. The following ions were found to produce no interference: Pb^{2+} (20 mg); Al^{3+} (10 mg); Cu^{2+}, Ag^{+}, Be^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} (1 mg of each); Ga^{3+} (200 μg); Sc^{3+}, Gd^{3+}, In^{3+}, Th^{4+}, Ge^{4+}, As^{5+}, Sb^{5+}, UO_2^{2+} (100 μg of each). Elements showing interference are given in Table II. Of these, only iron and titanium are present in silicate rocks in sufficient amounts to cause interference. However, these elements and all the other interfering elements are removed by the use of the combined solvent extraction–ion exchange procedure.

TABLE II

EFFECT OF INTERFERING IONS ON DETERMINATION OF ZIRCONIUM WITH QUINALIZARIN SULPHONIC ACID

Ion	*Amount of element (mg/25 ml)*	*Optical density produced*[a]	*Equivalent to μg of Zr*
Fe^{3+}	1	0.129	29.6
Fe^{3+}	10	0.617	141.0
Fe^{3+}[b]	10	0.000	0
Cr^{3+}	1	0.380	87.0
Ti^{4+}	10	0.056	12.8
Bi^{3+}	1	0.184	42.0
Au^{3+}	1	Precipitate	—
Tl^{+}	0.1	0.072	16.5
Sn^{2+}	1	0.098	22.4
Nb^{5+}	0.1	0.053	12.1
VO_3^{-}	1	0.235	53.7
MoO_4^{2-}	1	0.143	32.8

[a] Less reagent blank.
[b] Reduced with hydroxyammonium chloride before colour development.

Photometric determination of thorium. Thorin (1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid) was selected for the photometric determination of thorium concentration by the proposed separation scheme. This reagent forms a red complex with thorium in hydrochloric acid solution[54] and has been used in numerous spectrophotometric methods for thorium in materials as diverse as silicate rocks[55], monazite[56,57], and natural waters[58-60]. The optimum conditions for the formation of the complex have been investigated by several workers. THOMASON *et al.*[60] found that the optical density of a solution of the complex is fairly constant in the pH range 0.2–1.0, and CLINCH[57] recommends 0.5–1.5. MAYER AND BRADSHAW[61] found that these ranges were too wide and suggested that the solution should be 0.3–0.4 *N* with respect to hydrochloric acid. Since thorium recovered from the ion-exchange process is in perchloric acid solution it was decided to investigate the use of thorin in a perchloric acid medium. Thorium perchlorate (50 μg Th), 2 ml of an 0.1% (w/v) aqueous solution of thorin and various amounts of 60% (w/w) perchloric acid were mixed and diluted to 10 ml. A similar series of blank solutions containing no thorium was also made up. The optical densities of the solutions containing thorium were measured against a compensator cell containing the corresponding blank solution at 547 mμ (the wavelength of maximum absorption of the thorium complex). It was found that up to 3 ml of perchloric acid had no effect on the optical density. With 4–6 ml of perchloric acid a similar optical density was found, but after 1 h the colour faded rapidly. The stability of the complex in perchloric acid medium is presumably caused by the low complexing power of the perchlorate ion for thorium. Choride ion, however, has a quite strong complexing action and a close control of the acidity is necessary in methods employing a hydrochloric acid medium if erratic results are to be avoided. In all subsequent work thorium determinations were carried out in a medium containing 20% by volume of 60% perchloric acid.

The thorium–thorin complex was found to obey Beer's law up to at least 100 μg Th/10 ml. The molecular extinction coefficient of the complex was 16,000. The coefficient of variation of the method was *ca.* 0.5% with 60 μg of thorium.

For completeness, the interference of a number of elements in the determination of thorium with thorin in perchloric acid medium was investigated. The following ions were found to produce no interference: Pb^{2+} (20 mg); Al^{3+} (10 mg); Cu^{2+}, Ag^{+}, Be^{2+}, Zn^{2+}, Cd^{2+}, Ti^{4+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} (1 mg of each); Ga^{3+}, Sc^{3+}, Gd^{3+}, In^{3+}, Tl^{+}, Ge^{4+}, As^{5+}, Sb^{5+} and UO_2^{2+} (100 μg of each). Interfering cations are shown in Table III. Separation from all of these elements is achieved in the proposed solvent extraction–ion exchange scheme. It is important to note that sulphate, fluoride and oxalate interfere strongly in this method as in all other photometric methods for thorium.

TABLE III

INTERFERING CATIONS IN THE DETERMINATION OF THORIUM WITH THORIN IN PERCHLORIC ACID MEDIUM

Ion	*Amount of element (mg/10 ml)*	*Optical density produced*[a]	*Equivalent to μg Th*
Fe^{3+}	10	0.171	25
Fe^{3+}[b]	10	0.001	0
Ti^{4+}	10	0.217	31
Zr^{4+}	0.1	0.195	28
Sn^{2+}	1	0.149	22
Bi^{3+}	1	0.162	24
Cr^{3+}	1	−0.162	−24

[a] Measured against reagent blank.
[b] Reduced with hydroxyammonium chloride before colour development.

Determination of cerium. Cerium separated by the combined solvent extraction–ion exchange method was determined by the bleaching effect of the cerium(IV) on the red iron(II)-phenanthroline complex, as already described[62].

Determination of hafnium

Hafnium follows zirconium through the whole separation process and was determined spectrographically in the zirconium concentrate. The concentrate was treated with quinalizarin sulphonic acid solution and the zirconium complex (bearing the hafnium) was recovered by filtration in the presence of alumina (to act as a carrier) and ignited to oxide. The mixed oxides were thoroughly mixed with an equal weight of pure carbon and analysed spectrographically for hafnium using zirconium as an internal standard. The spectrographic conditions used were based on those described by WARING AND WORTHING[63] and are given in Table IV.

TABLE IV

SPECTROGRAPHIC CONDITIONS USED IN THE DETERMINATION OF HAFNIUM

Spectrograph	Hilger Littrow with quartz optics
Condensing system	Mirror–lens system as used for Cathode Layer method
Step sector	6-step sector rotating at 1500 rev./min
Slit	25 μ
Lower electrode (anode)	Carbon (Ship Brand 0.63 cm diameter). Crater 0.5 cm deep, internal diameter 0.25 cm
Upper electrode (cathode)	Carbon (Ship Brand 0.63 cm diameter). Pointed
Arcing current	7 A
Arcing time	3 min
Arc gap	4 mm
Photographic emulsion	Ilford Chromatic
Development	ID2, 3 min at 20° with constant agitation
Densitometer	Hilger non-recording microdensitometer
Spectrographic lines	2461 Å Hf, 2583 Å Zr

The method gave a linear response between log % Hf and log I_{Hf2461}/I_{Zr2583} for hafnium concentrations between 0.6 and 30% in the mixed oxides. The sensitivity of the method for hafnium is therefore *ca.* 0.5 p.p.m. if a 2-g sample of rock is analysed. Replicate determinations (6) carried out on a synthetic mixture of hafnium and zirconium oxides containing 2.0% ZrO_2 gave an average result of 1.94% and a coefficient of variation of 5.7%.

EXPERIMENTAL

Reagents

Extracting agent. Dilute 400 ml of redistilled tri-*n*-butyl phosphate to 1 l with 2,2,4-trimethyl-pentane.

Ion-exchange columns. Zeo-Karb 225 resin (8% crosslinked, 40–80 mesh) was heated on a water bath for 2 h with 3 *N* hydrochloric acid; the acid was then decanted and the digestion was repeated. The acid-washed resin was washed with a rapid current of water to remove "fines" and then packed into 0.8 cm diameter glass columns to give a packed length of 16.5 cm. Before use the columns were washed with 100 ml of 0.5 *N* nitric acid.

Quinalizarin sulphonic acid solution. Prepare quinalizarin sulphonic acid (1,2,5,8-tetrahydroxyanthraquinone-3-sulphonic acid)[53] by heating quinalizarin with fuming sulphuric acid (60% (w/v) SO_3) at 130° for 6 h. Pour the reaction mixture on to ice, filter the solution and partially neutralize the filtrate with sodium bicarbonate. Filter off the sodium salt of the sulphonic acid which precipitates, wash it with ice-cold water and dry at 110°. The yield is *ca.* 63%. The reagent for the photometric determination of zirconium is a 0.02% (w/v) solution of the sodium salt in water; a 0.5% solution is used for precipitating zirconium + hafnium before spectrographic determination of the latter.

Standard zirconium solution. Prepare a solution of zirconium containing 500 µg Zr/ml by dissolving the appropriate weight of spectrographic grade zirconium nitrate (analysed by ignition to oxide) in 100 ml of 1 *N* nitric acid. Prepare from it, as required, a working solution containing 10 µg Zr/ml in 0.5 *N* perchloric acid.

Standard thorium solution. Prepare a solution containing 500 µg Th/ml by dissolving the appropriate weight of thorium nitrate A.R. (analysed by ignition to oxide) in 100 ml of 0.5 *N* nitric acid. Prepare from it a working solution containing 10 µg Th/ml in 0.1 *N* nitric acid.

Standard cerium solution. Digest 0.1228 g of spectroscopically pure cerium dioxide with 10 ml of concentrated sulphuric acid at 250° for 8 h. After cooling, dilute with 50 ml of water, boil gently until all the cerium(IV) sulphate has been dissolved and dilute to 250 ml. Prepare a working standard solution containing 10 µg Ce/ml from this stock solution (which contains 400 µg Ce/ml).

Procedures

Weigh accurately 2–3 g of the finely ground sample (to pass 100 mesh) in a 40-ml platinum crucible, and add 6 ml of 60% (w/v) perchloric acid and *ca.* 30 ml of 40% (w/v) hydrofluoric acid. Cover the crucible and heat it on a water bath overnight. Then remove the crucible lid and again heat on the water bath. When all fumes of hydrofluoric acid have disappeared, heat the crucible under an infrared heater until most of the perchloric acid has been removed. Cool the crucible and add 5 ml of 60% (w/v) perchloric acid while stirring with a platinum rod. Replace the crucible under the infrared heater and again fume down to remove most of the perchloric acid. Repeat the evaporation using a further 5 ml of perchloric acid to ensure removal of all fluoride. Dissolve the contents of the crucible by warming with *ca.* 45 ml of 10 *N* nitric acid. Remove any insoluble matter by centrifuging and after washing it with *ca.* 5 ml of 10 *N* nitric acid return it to the crucible. Retain the combined nitric acid solution and washings.

Dry the insoluble residue, add *ca.* 0.5 g of sodium carbonate and fuse at red heat for 30 min. After cooling, dissolve the cake in water and acidify by the gradual addition of 8 ml of 5 *N* sulphuric acid, followed by 2 ml of hydrofluoric acid. Evaporate to dryness on the water bath, gently heat the covered crucible over a low gas flame to expel all the water and then raise to very dull redness for 10 min. After cooling, add 3 ml of 10 *N* nitric acid and warm until the cake has dissolved. Combine this solution with the main nitric acid solution.

Add 0.25 g of sodium bromate to the combined solution and extract twice with 25 ml of 40% (v/v) tri-*n*-butyl phosphate in isooctane, shaking for 10 min in each case. Wash the extracts twice with 2-ml portions of 10 *N* nitric acid. Back-extract the trace elements by shaking twice with 25-ml aliquots of 0.1 *N* oxalic acid. Add 0.5 g of sodium bromate to the combined back-extracts; after *ca.* 16 h the destruction of oxalic acid will be complete. Remove excess of the bromate and any free bromine by addition of 2 ml of 20% (w/v) hydroxyammonium chloride and dissolve any traces of manganese dioxide by adding 1 ml of water saturated with sulphur dioxide and warming to 60–70°.

Pass the solution through a column of Zeo-Karb 225 in its hydrogen form, and elute any traces of manganese, titanium, or other common elements with 100 ml of 1.5 *M* nitric acid. Wash the resin free of acid with distilled water and then elute zirconium and hafnium with 30 ml of 0.025 *M* oxalic acid; collect the eluate in a 50-ml conical flask. Add 1 ml of 60% (w/w) perchloric acid to the eluate and heat on a hot plate until dense white fumes are evolved. Cover the flask with a bulb stopper and maintain at fuming temperature for 2 h to destroy oxalic acid. Dilute to 25 ml after adding 1 ml of 60% (w/v) perchloric acid. Use this solution (Solution A) for the determination of zirconium and hafnium (see below).

Elute thorium from the column with 150 ml of 0.5 *M* oxalic acid and collect the eluate in a 200-ml conical flask. Add 10 ml of hydrogen peroxide (100 volume) and 2 ml of 60% (w/w) perchloric acid to the eluate and heat it on the water bath for 30 min. Evaporate on the hot plate until dense white fumes are evolved, loosely stopper the flask and maintain the solution in the fuming conditions for 2 h. Wash the liquid into a 25-ml conical flask and evaporate to dryness. Add 2 ml of 60% (w/w) perchloric acid and 2 ml of water to the residue and heat until the latter has dissolved. Determine thorium in the solution (Solution B) as described below.

Elute cerium from the column with 75 ml of 5% citric acid which has been adjusted to pH 4.5 by cautious addition of ammonia. Evaporate the eluate to a small volume on the water bath, and add 25 ml of concentrated nitric acid. Heat the loosely stoppered flask on the hot plate overnight and then gently evaporate the acid. Repeat the evaporation with nitric acid until most of the organic matter has been removed. Transfer the residue to a 25-ml conical flask using water. Complete the destruction of organic matter by fuming to dryness with 2 ml of 60% (w/w) perchloric acid. Dissolve the residue in 0.13 ml of concentrated sulphuric acid and add 5 ml of water. Determine cerium in this solution (Solution C) as described below.

It is not normally necessary to carry a blank through the whole process, since with each set of determinations the level of contamination of the reagents with the elements being determined has not been found to be significant. Blank determinations should be carried out with fresh batches of reagents.

Determination of zirconium + hafnium. Pipet a suitable aliquot of Solution A (< 150 μg Zr) into a 25-ml graduated flask, add 1 ml of 60% (w/w) perchloric acid, 5 ml of 0.02% quinalizarin sulphonic acid reagent and 5 ml of acetone. Dilute to volume with distilled water. After 3 h measure the optical density at 565 mμ in a 1-cm cell against a compensator cell containing distilled water. Determine the reagent blank in the same manner but omitting the sample. Calibrate the method using 10, 25, 50, 75, 100, 150 μg of zirconium.

Determination of hafnium. Treat the remainder of Solution A with an excess of 0.5% quinalizarin sulphonic acid solution and 5 ml of acetone. Precipitate the zirconium (+ hafnium) complex by boiling the solution gently for 15 min. Filter the solution through a 7-cm Whatman No. 42 paper covered with 2.0 mg of pure aluminium oxide. Wash the filter with a few ml of water and ignite it in a platinum crucible. Determine hafnium spectrographically using zirconium as internal standard using the conditions shown in Table IV.

Determination of thorium. Quantitatively transfer solution B (0–80 μg Th) to a 10-ml graduated flask, add 2 ml of 0.1% thorin solution and dilute to volume with water. After 15 min measure the optical density of the solution at 547 mμ in a

1-cm cell against a similar compensator cell containing the reagent blank. Prepare the reagent blank solution by diluting a mixture of 2 ml of 60% perchloric acid and 2 ml of aqueous 0.1% thorin solution (filtered if necessary) to 10 ml. Calibrate the method by passing aliquots of standard thorium solution containing 40 and 80 μg of thorium through the ion-exchange column, eluting thorium with 0.5 *M* oxalic acid, destroying oxalic acid, and determining thorium as described above. Measure the optical densities of these solutions against the reagent blank at 547 mμ. Multiply the optical densities by 1.08 to correct for the fact that the recovery of thorium is 92%.

Determination of cerium. Add 0.5 ml of silver sulphate solution (100 μg Ag/ml; 0.145 g dissolved in 1 l of water) and 1 ml of freshly prepared 0.2% ammonium persulphate solution to Solution C. Heat the mixture in a boiling water bath for 10 min in order to oxidise cerium to cerium(IV) and to decompose excess of persulphate. After cooling, transfer the solution to a 10-ml graduated flask and add 1 ml of iron(II)–phenanthroline solution (1 g of 1,10-phenanthroline and 0.0635 g of iron(II) ammonium sulphate in 250 ml of 0.1 *N* sulphuric acid) followed by 1 ml of 4.5 *M* sodium acetate solution. Dilute to volume and mix thoroughly. Measure the optical density of the solution at 510 mμ in a 1-cm cell against distilled water. Prepare a reagent blank in the same manner using 5 ml of water containing 0.13 ml of concentrated sulphuric acid. Calibrate the method using 50 μg of cerium dissolved in 5 ml of water containing 0.13 ml of concentrated sulphuric acid.

TABLE V

RECOVERIES FROM SYNTHETIC MIXTURES

	Taken							*Recovered (%)*			
	Zr(μg)	*Hf(μg)*	*Th(μg)*	*Ce(μg)*	*Fe(mg)*	*Ti(mg)*	*Mn(mg)*	*Zr*	*Hf*	*Th*[a]	*Ce*
1	—	—	—	—	300	30	30	—	—	—	—
2	500	5.0	10	—	—	—	—	97.8	108	99.9	—
3	250	—	25	—	—	—	—	95.8	—	99.6	—
4	100	—	50	—	—	—	—	96.8	—	99.8	—
5	500	5.0	100	—	300	30	30	97.0	112	100.0	—
6	250	—	50	—	300	30	30	97.0	—	100.4	—
7	100	—	25	—	300	30	30	97.7	—	102.0	—
8	50	—	10	—	300	30	30	96.0	—	99.2	—
9	—	—	—	50	—	—	—	—	—	—	100.5
10	—	—	—	20	—	—	—	—	—	—	100.0
11	—	—	—	100	—	—	30	—	—	—	100.8
12	—	—	—	50	—	—	30	—	—	—	99.0
13	—	—	—	10	—	—	30	—	—	—	97.0
14	250	2.5	10	100	—	—	—	95.9	116	100.1	97.4
15	500	5.0	25	50	—	—	—	98.0	102	101.0	102.0
16	750	7.5	50	40	—	—	—	97.2	98	99.7	97.5
17	500	5.0	100	20	300	30	30	99.0	92	98.6	100.0
18	750	7.5	50	40	300	30	30	98.9	98	100.5	98.0
19	1000	10.0	25	20	300	30	30	96.9	101	99.6	93.0
							Mean	97.2	103	100.1	98.7

[a] Corrected for 92% yield.

Results

Since rocks containing accurately known concentrations of zirconium, hafnium, cerium and thorium were not available, synthetic mixtures containing known amounts of these elements together with iron, titanium and manganese were prepared and analysed by the above method. The results, which are given in Table V, show that satisfactory recoveries were obtained in all cases.

SUMMARY

A method is described for the determination of traces of zirconium, hafnium, cerium and thorium in rocks. After the sample has been opened up, these elements are separated from the major component elements by extraction from 10 *N* nitric acid with a 40% solution of tri-*n*-butyl phosphate, cerium being oxidised with bromate. After back-extraction the elements are separated from each other and from other extracted elements by cation exchange. Zirconium is determined photometrically with quinalizarin sulphonic acid which gives about twice the sensitivity of alizarin red S. Thorium is determined photometrically with thorin, and cerium by utilizing its bleaching action on iron(II) phenanthroline. Hf is determined spectrographically.

RÉSUMÉ

Les auteurs décrivent une méthode pour le dosage de traces de zirconium, hafnium, cérium et thorium dans les roches. Ces éléments sont séparés en solution nitrique, par extraction au moyen de tri-*n*-butylphosphate, après oxydation du cérium par le bromate. Finalement, le zirconium est dosé photométriquement au moyen de l'acide quinalizarinesulfonique; le thorium est dosé photométriquement à l'aide de thorin et le cérium en utilisant sa réaction de décoloration du complexe fer(II)–phénanthroline. Hf est dosé par spectrographie.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Spuren Zirkonium, Hafnium, Cer und Thorium in Gesteinen beschrieben. Nach dem Aufschluss der Probe werden diese Elementen von den Hauptbestandteilen durch Extraktion aus 10 *N* Salpetersäure mit einer 40%igen Lösung von Tri-*n*-butylphosphat abgetrennt; Cer wird mit Bromat oxydiert. Nach der Rückextraktion werden die Elemente mit einem Kationenaustauscher voneinander und von anderen extrahierten Elementen getrennt. Zirkonium wird photometrisch mit Chinalizarinsulfonsäure bestimmt, die etwa die doppelte Empfindlichkeit wie Alizarinrot S besitzt. Thorium wird photometrisch mit Thorin bestimmt und Cer durch die Anwendung seiner Bleichwirkung auf Eisen(II)–phenanthrolin.

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A PROCEDURE FOR SILICATE ROCK ANALYSIS BASED ON ION EXCHANGE AND COMPLEX-ION FORMATION

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Many procedures of wet-chemical rock analysis are based on the classical methods, which have been summarized by several authors[1-3]. The difficulty in applying these procedures has been well documented by LARSEN[4] and in papers summarizing the analyses of two rocks, G-1 and W-1[5-7]. Although classical procedures can yield reliable results, they are inherently long and complicated, and therefore subject to accidental error. The procedure reported in this paper has been developed to replace the difficult and tedious separations of the classical methods with ion-exchange separations.

The first successful alternative to the classical methods was reported by SHAPIRO AND BRANNOCK[8]. By the use of relatively specific colorimetric and titrimetric procedures, a rapid, simple and direct scheme of analysis was developed. The accuracy of the results was limited by the use of colorimetric procedures for the determination of some major components. RILEY[9] modified this procedure to increase accuracy without loss of speed. He reported that 6 or 7 samples could be analyzed in 5.5 days.

OKI *et al.*[10] developed a procedure based on ion-exchange separation. An analysis could be completed in 3 days with an accuracy reported to be comparable to the classical procedure. AHRENS *et al.*[11] have reported the work which has been done towards the development of a scheme for the analysis of common silicates and meteorites based on spectrochemical methods, ion exchange and solvent extraction.

In the procedure outlined in this paper, moisture (H_2O^-), SiO_2, TiO_2, Al_2O_3, P_2O_5, total iron, CaO, MgO and MnO were determined in one portion of the rock. Separate portions were used to determine Na_2O and K_2O, iron(II), and total water. To complete 6 analyses by the recommended procedure required about 8 days.

EXPERIMENTAL

Solutions and chemicals

Solutions of silicon (0.495 mg of SiO_2/ml), iron (10.00 mg of Fe_2O_3/ml), titanium (1.06 mg of TiO_2/ml), aluminum (15.04 mg of Al_2O_3/ml), calcium (10.12 mg of CaO/ml), magnesium (9.94 mg of MgO/ml), manganese (0.299 mg of MnO/ml), and phosphorus (0.474 mg of P_2O_5/ml) were prepared from reagent-grade chemicals and standardized by conventional procedures. Aliquots of these solutions were used in the development of the ion-exchange procedure and to establish the standard curves for the colorimetric procedures.

Reagent-grade chemicals were used. Concentrated ammonia solution (s. g. 0.90) was prepared by dissolving gaseous ammonia in chilled, distilled water and stored in a polyethylene bottle. Special reagents required for the column separations included 5-sulfosalicylic acid and 8-hydroxyquinoline-5-sulfonic acid. The concentration of solutions prepared from solid reagents are weight/volume percentages.

Apparatus

Colorimetric determinations were made in 1-cm cells with a Beckman Model B spectrophotometer. pH values were measured with a Beckman pH meter, Model G.

Ion-exchange columns

Anion-exchange column. Dowex 1-X8, 50–100 mesh, was leached with concentrated hydrochloric acid for 1 day or more to dissolve most of the soluble organic matter, washed with water to remove the acid, and treated with ammonia solution to a pH of 7.3 ±0.2. A 50-cm bed of resin was prepared in a glass tube 4 feet long, 1.7 cm O.D., fitted with a delivery tube extending above the top of the resin bed. The resin was discarded after each analysis.

Cation-exchange column. Amberlite I.R.C.-50, 16–50 mesh, was converted to the ammonium form with excess ammonia solution, and washed with water to remove most of the excess ammonia. A 30-cm bed of resin was prepared in a glass column 2 feet long, 1.5 cm O.D., fitted with a delivery tube extending above the top of the resin bed. No evidence of the need to replace the resin was observed.

Preliminary work

Preliminary experiments were carried out to establish procedures for the ion-exchange separation of iron, titanium, aluminum, calcium, magnesium and manganese into groups which could be readily analyzed by the classical gravimetric and volumetric procedures. It was considered essential that no element be divided between two groups.

It was shown that in the presence of sulfosalicylic acid at pH 7.3, iron, titanium and aluminum were quantitatively adsorbed on an anion-exchange resin; calcium, magnesium and manganese were not adsorbed. Further separations of iron, titanium and aluminum from each other by washing the anion-exchange resin with weakly acidic solutions were not possible. OLIVER AND FRITZ[12] have reported the use of sulfosalicylic acid in the anion-exchange separation of a number of binary mixtures of cations. The essential separation in this group, namely aluminum from iron with titanium accompanying either component, was accomplished by a procedure based on the results reported by KRAUS AND NELSON[13]. Iron was adsorbed on an anion-exchange resin as the complex chloride and thus separated from aluminum and titanium. It was subsequently shown that phosphate accompanies titanium and aluminum.

The separation of calcium from magnesium and manganese was accomplished with 8-hydroxyquinoline-5-sulfonic acid. These components were first adsorbed on a carboxylic acid cation-exchange resin directly from the effluent of the anion-exchange resin. Then magnesium and manganese were eluted with a solution of 8-hydroxyquinoline-5-sulfonic acid at pH 10.0.

In applying these ion-exchange separations to silicate rocks, a three-column procedure was initially used. Silica was determined in a separate portion of the rock essentially as recommended by JEFFREY AND WILSON[14]. Silica remaining in solution after a single dehydration was determined colorimetrically with a 1-ml aliquot of the filtrate and diluted to a final volume of 25 ml, instead of with a 5-ml aliquot diluted to 100 ml. The principal advantage in the use of the smaller aliquot was that soluble silica could be determined without significant error due to the presence of iron(III) oxide equivalent to over 40% of the rock sample, and of phosphorus pentoxide and titanium oxide equivalent to over 20%. Hence only rarely would it be necessary to separate the silica from these potentially interfering elements before its determination.

The portion of the rock used for the column separations was dissolved in hydrofluoric and sulfuric acids, heated to expel fluoride ion, and taken up in 2:1 hydrochloric acid. Iron was adsorbed on a Dowex-1 column as the complex chloride. After evaporation of the effluent to remove hydrochloric acid, titanium and aluminum were adsorbed on a second Dowex-1 column with the aid of sulfosalicylic acid at pH 7.3 and subsequently recovered with 480 ml of 1:9 hydrochloric acid. Aluminum and titanium were determined in aliquots of the solution. Calcium, magnesium, and manganese were separated with an Amberlite I.R.C.-50 column as outlined in the recommended procedure.

Results obtained with this procedure on synthetic samples were satisfactory. Continued tests with rock samples gave low and erratic values for Al_2O_3, although the values obtained for the other oxides were in good agreement with the values obtained by the classical procedure. The difficulty was traced to the incomplete removal of sulfosalicylate from the Dowex-1 resin when aluminum and titanium were removed. With continued use, some of the aluminum passed through the column as the sulfosalicylate complex.

Concurrent with the explanation of the difficulty with aluminum, the feasibility of the one-step, two-column separation outlined in the recommended procedure was demonstrated. As a precaution, fresh resin was used in the Dowex-1 column for each analysis.

Problems with the silica determination were not immediately apparent. Initial determinations (Tables I and II) agreed reasonably well with the values obtained by the conventional procedure. Subsequent determinations tended to be low. Tests with reagent-grade silica suggested the problem was due to failure to dehydrate the silica effectively before the recovery and gravimetric determination of the main portion. The results reported in Table III were obtained with samples in which the evaporation on the steam bath was continued until the odor of hydrochloric acid was absent, or only very faint.

Recommended procedure

Flow rates through the columns should not exceed 3 ml per min.

Determination of H_2O^-. Weigh accurately 1 g of the powdered rock sample and transfer to a tared platinum crucible. Heat the sample at 105° for 1 h and determine moisture (H_2O^-) from the loss in weight.

Determination of SiO_2. Fuse the sample with 3.7 g of sodium carbonate, transfer the cake to a platinum dish, and leach with water containing a few ml of ethanol. Acidify with hydrochloric acid and evaporate the solution on a steam bath until the odor of hydrochloric acid is not detected. Add 50 ml of 1:4 hydrochloric acid and warm to dissolve the soluble salts. Collect the dehydrated silica on a 9-cm retentive filter paper and wash 20 times with water. Collect the filtrate and washes in a 200-ml volumetric flask and dilute to volume with water. Reserve the solution for the colorimetric determination of soluble silica and other determinations.

Transfer the paper with silica to the fusion crucible and burn the paper in a muffle furnace. Heat the sample at 1200° for 1 h, cool, and weigh. Volatilize the silica with hydrofluoric acid containing a few drops of 1:1 sulfuric acid, heat to dryness, and ignite for 10 to 15 min over a Meker burner. Cool, weigh, and subtract the weight from the initial weight to obtain the amount of silica recovered. Fuse the residue in the crucible with 0.3 g of sodium carbonate, cool, and dissolve with 10 ml of 1:9 hydrochloric acid. Reserve the solution.

Transfer a 1-ml aliquot of the solution in the 200-ml volumetric flask to a 25-ml volumetric flask. Reserve all portions of the solution used to pre-rinse the pipet in a 250-ml beaker. Add 4 ml of 1:19 hydrochloric acid to the 25-ml flask and determine soluble silica colorimetrically[14]. The amount is added to that recovered by dehydration to calculate the concentration of silica.

Separation of iron, titanium, aluminum, and phosphorus from calcium, magnesium and manganese. Rinse the 1-ml pipet, used to remove the aliquot for the determination of soluble silica, into the 250-ml beaker containing the pre-rinses, and quantitatively transfer the solution remaining in the 200-ml volumetric flask to the beaker as the solution is evaporated. Continue the evaporation to a small volume (say 5 ml). If the solution is evaporated to dryness, add 1:1 hydrochloric acid, digest to redissolve titania and evaporate to a small volume. Note that some of the silica that escaped dehydration (usually 6 mg or less) is often rendered insoluble during the evaporation and should not be confused with titania.

Combine the hydrochloric acid solution of the residue from the dehydrated silica with the evaporated filtrate in the 250-ml beaker. Add 3.5 g of sulfosalicylic acid and dilute the solution to approximately 100 ml with water. Add ammonia solution to a pH of 7.3 ± 0.2.

Arrange the ion-exchange columns so that the effluent from the Dowex-1 column flows into the Amberlite I.R.C.-50 column.

Pass the sulfosalicylate solution through the two columns. Iron, titanium, aluminum and phosphorus are adsorbed on the Dowex-1 resin; calcium, magnesium and manganese on the Amberlite resin. Rinse the sample beaker 3 times with dilute ammonium chloride solution at pH 7.3 and transfer to the column. Wash the columns with 300 ml of the same solution. The effluent from the Amberlite column is discarded. Treat the columns individually to effect further separations and recovery of the adsorbed ions.

Separation of aluminum, titanium and phosphorus from iron. Insert a glass wool plug at the top of the resin bed in the Dowex-1 column and backwash with concentrated hydrochloric acid until the color of the iron–sulfosalicylate complex is not apparent. Close the outlet tube and fill the column with portions of concentrated hydrochloric acid used to rinse the 250-ml beaker which contained the sulfosalicylate solution. Open the outlet tube and drain the solution in the column into a 500-ml volumetric flask until the level is slightly above the resin bed. Wash the column with 1:1 hydrochloric acid until the volumetric flask is almost filled. Approximately 350 ml are required. Fill the flask to volume with water and reserve for the determination of titanium, aluminum and phosphorus. Most of the sulfosalicylic acid is in this solution.

Wash the column with 300 ml of 1:19 sulfuric acid to recover the iron.

Separation of magnesium and manganese from calcium. Wash the Amberlite I.R.C.-50 column with 550 ml of a 1% solution of 8-hydroxyquinoline-5-sulfonic acid at pH 10.0 with ammonia to remove magnesium and manganese. Wash the column with 400 ml of 1:9 hydrochloric acid to remove calcium.

Determinations

The procedures used to determine the various oxides are essentially those of the classical scheme. Details will be found in many reference texts. Note that the values obtained must be multiplied by 200/199 to correct for the 1-ml aliquot used to determine soluble silica.

TiO_2. Titanium may be directly determined in the hydrochloric acid effluent from the Dowex-1 column with hydrogen peroxide provided that a portion of the solution is used as a blank to compensate for the yellow color due to organic material leached from the resin. Sulfosalicylic acid does not interfere.

Al_2O_3. Add 4 ml of 1:1 sulfuric acid to a 100-ml aliquot of the hydrochloric acid effluent from the Dowex-1 column and evaporate to a small volume. Add nitric acid and heat to destroy the sulfosalicylic acid. Evaporate the solution to dense fumes of sulfuric acid. Add 1:19 hydrochloric acid, digest and filter the solution. Determine alumina with 8-hydroxyquinoline. In the analyses reported in Tables I and II, peroxide was not added to the solution and the weight of the oxinate was corrected for the titanium oxinate present.

P_2O_5. Direct colorimetric determination of phosphorus in the hydrochloric acid effluent from the Dowex-1 column is not possible because of the yellow color sometimes imparted to the solution by organic material leached from the resin and the necessity of a reagent blank.

Evaporate a 100-ml aliquot of the effluent to dryness on a steam bath. Dissolve the sample, precipitate phosphorus with ammonium molybdate, filter and wash. Dissolve the precipitate with dilute ammonia and determine phosphorus colorimetrically as molybdivanadophosphoric acid.

Total iron. Evaporate the 1:19 sulfuric acid effluent from the Dowex-1 column to a small volume. Add nitric acid and heat to destroy sulfosalicylic acid, some of which is present in spite of the hydrochloric acid wash. Evaporate to fumes of sulfuric acid, cool, and dilute to about 80 ml with water. Add 4 g of ammonium chloride and digest if necessary to dissolve iron salts. Add 15 ml of concentrated ammonia solution, reduce iron with a silver reductor and titrate the solution with standard potassium dichromate solution.

MgO and MnO. Acidify the 8-hydroxyquinoline-5-sulfonic acid wash solution from the Amberlite I.R.C.-50 column with 25 ml of concentrated hydrochloric acid and 4 ml of 1:1 sulfuric acid. Evaporate, and destroy 8-hydroxyquinoline-5-sulfonic acid and ammonium chloride with nitric acid. Evaporate the excess nitric acid. Precipitate magnesium and manganese twice as the phosphate, and weigh as pyrophosphate.

TABLE I

ANALYSIS OF STANDARD ROCKS

	Rock G-1					*Rock W-1*				
	"Selected"	*Ion exchange*				*"Selected"*	*Ion exchange*			
	values	*I*[a]	*II*[a]	*III*[b]	*IV*[b]	*values*	*I*[a]	*II*[a]	*III*[b]	*IV*[b]
SiO_2	72.64	72.44	72.48	72.50	72.40	52.65	52.67	52.67	52.54	52.44
TiO_2	0.26	0.25	0.27	0.28	0.25	1.07	1.10	1.09	1.06	1.07
Al_2O_3	14.04			14.18	14.15	14.85			14.75	14.99
Fe_2O_3[c]	0.87	0.88	0.79	0.87	0.95	1.41	1.28	1.17	1.34	1.35
FeO	0.98				0.97	8.74				8.82
MnO	0.03	0.02	0.02	0.02	0.02	0.16	0.15	0.15	0.16	0.14
CaO	1.39	1.35	1.33	1.38	1.38	10.96	10.90	10.93	10.91	10.90
MgO	0.41	0.37	0.37	0.37	0.39	6.62	6.57	6.57	6.51	6.58
Na_2O	3.32				3.32	2.07				2.21
K_2O	5.45				5.36	0.64				0.65
H_2O^+	0.34				0.35	0.53				0.48
H_2O^-	0.06			0.02	0.03	0.16			0.13	0.14
P_2O_5	0.09				0.10	0.14				0.15
Total iron as Fe_2O_3	1.96	1.96	1.87	1.95	2.03	11.12	11.08	10.97	11.14	11.15
Total	99.88	99.61	99.56	99.72	99.67	100.00	99.99	99.90	99.71	99.92
Total with SiO_2 from Table III		99.73	99.64	99.78	99.83		100.02	99.93	99.87	100.18

[a] Three-column procedure.
[b] Recommended procedure.
[c] Fe_2O_3 obtained by subtracting the iron(III) oxide equivalent of FeO reported in analysis IV from Total iron.

TABLE II

COMPARISON OF THE CONVENTIONAL AND PROPOSED SCHEMES

	Rock A				*Rock B*				*Rock C*			*Rock D*			
	Conventional	*Ion exchange*			*Conventional*	*Ion exchange*			*Conventional*	*Ion exchange*		*Conventional*	*Ion exchange*		
		I[a]	*II*[b]	*III*[b]		*I*[a]	*II*[b]	*III*[b]		*I*[b]	*II*[b]		*I*[a]	*II*[b]	*III*[b]
SiO_2	60.43	60.35	60.32	60.30	53.64	53.65	53.55	53.47	66.70	66.01	66.20	62.05	62.04	62.07	62.04
TiO_2	0.99	1.01	0.99	0.99	1.05	0.94	0.97	1.08	0.86	0.80	0.85	0.69	0.64	0.68	0.70
Al_2O_3	15.07		15.26	15.24	15.06		15.06	14.97	12.98	13.04	12.97	16.43		16.43	16.40
Fe_2O_3[c]	3.08	3.19	3.06	3.22	7.71	7.96	7.86	7.97	4.96	5.35	5.40	0.99	0.83	0.76	0.86
FeO	4.57				3.72				2.03			5.59			
MnO	0.18	0.17	0.15	0.15	0.14	0.12	0.11	0.12	0.13	0.12	0.12	0.07	0.07	0.07	0.07
CaO	4.88	4.87	4.84	4.82	8.41	8.39	8.45	8.29	1.51	1.56	1.55	2.21	2.27	2.19	2.17
MgO	2.56	2.45	2.52	2.53	4.87	4.88	4.90	4.86	2.42	2.54	2.49	3.64	3.66	3.64	3.63
Na_2O	4.45				3.49				6.06			3.52			
K_2O	1.19				0.37				0.33			2.69			
H_2O^+	1.61				0.88				1.69			1.78			
H_2O^-	0.39	0.42	0.45	0.43	0.28	0.24	0.31	0.30	0.19	0.18	0.17	0.06	0.01	0.06	0.05
P_2O_5	0.19			0.23	0.10		0.11	0.11	0.16	0.17	0.17	0.18		0.19	0.19
Total iron as Fe_2O_3	8.16	8.27	8.14	8.30	11.84	12.09	11.99	12.10	7.21	7.61	7.66	7.20	7.04	6.97	7.07
												S 0.11			
												O for S−0.05			
Total	99.59	99.76	99.64	99.73	99.72	99.77	99.78	99.63	100.02	99.88	100.03	99.96	99.77	99.73	99.75
Total with SiO_2 from Table III		99.98	99.89	100.00		99.90	100.01	99.94		100.15	100.11		99.85	99.78	99.83

[a] Three-column procedure.

[b] Recommended procedure.

[c] Fe_2O_3 obtained by subtracting the iron(III) oxide equivalent of FeO reported in conventional analysis from Total iron.

Determine manganese in the pyrophosphate colorimetrically as permanganate.

Calculate magnesium after correcting the weight of the pyrophosphate for the manganese present.

CaO. Evaporate the calcium solution to a small volume to remove most of the hydrochloric acid. Dilute the solution with water, precipitate calcium once as the oxalate and weigh as calcium oxide.

Na_2O, K_2O, iron(II) and total water. These oxides must be determined in separate portions of rock sample by any suitable procedure. In the analyses reported below, Na_2O and K_2O were determined by flame photometry[15], iron(II) oxide by titration with a standard dichromate solution after dissolution of the sample with hydrofluoric and sulfuric acids, and total water by the PENFIELD method with lead oxide as a retainer. Time not required to process the portion used for the ion-exchange procedure should be used to complete these determinations.

RESULTS AND DISCUSSION

The analyses of G-1 and W-1 are recorded in Table I. Values for FeO, Na_2O, K_2O and H_2O^+ obtained in this laboratory are included for completeness and to obtain the summations. The "selected" values have been taken from FLEISCHER AND STEVENS[7].

In Table II, the analyses of 4 rocks obtained by the ion-exchange procedures are compared with the "conventional" analyses obtained with the procedure based on classical methods in use in this laboratory. Summations for the ion-exchange analyses were obtained with the values for FeO, Na_2O, K_2O and H_2O^+ reported in the "conventional" analysis. In the analyses lacking Al_2O_3 and P_2O_5, the values obtained in subsequent analyses of the rock with the ion-exchange procedure were used to obtain summations. The lack of a value for Al_2O_3 indicates analysis with the three-column procedure referred to above. Redeterminations of silica in all samples, with care to assure evaporation to dryness on the steam bath, are recorded in Table III. Summations obtained with these values are also recorded in Tables I and II.

The precision obtained with the ion-exchange procedures is generally good. The accuracy of the data is much more difficult, if not impossible, to appraise. The "conventional" values of rocks A to D are single analyses of samples selected primarily to provide a compositional range between G-1 and W-1, and are subject to the accidental error inherent in the classical methods. The "selected" values of G-1 and W-1 are arithmetic means of values obtained by a variety of procedures, and though less subject to accidental error, may yet be biased from the true value. In fact, there may not be a true value if errors due to inhomogeneity and sampling are measurable. Furthermore, the distribution of minor constituents, such as barium and strontium, will be a factor in a detailed comparison of the results.

With these limitations in mind, the agreement between the results obtained by the column procedures and the other values is very good. The differences in the total iron values are of random sign and, with the exception of rock C, not large. Silica values for G-1 and W-1 reported in Table III agree with the "selected" values reported in Table I. Silica values for rocks A, B, and D are somewhat higher than those obtained by the conventional procedures, which is consistent with the general conclusion that conventional procedures tend to give low results for silica. It is

TABLE III

REDETERMINATION OF SILICA, WITH CARE TO ASSURE EVAPORATION TO DRYNESS

	G-1	*W-1*	*Rock A*	*Rock B*	*Rock C*	*Rock D*
SiO_2	72.54	52.69	60.55	53.74	66.27	62.12
	72.58	52.71	60.58	53.82	66.29	
Average	72.56	52.70	60.57	53.78	66.28	62.12

apparent that there is an error in the values for total iron and silica reported in the conventional analysis of rock C.

Within the compositional range of the rocks tested, the precision and accuracy of the results obtained with the new procedure compare favorably with the results obtained by conventional procedures.

Samples of G-1 and W-1 were supplied by the United States Geological Survey, Washington 25, D.C. Rock samples A to D, and permission to report the conventional analyses were obtained from LEON T. SILVER and JAMES GRANT.

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SUMMARY

A procedure for the analysis of silicate rocks based on ion exchange and complex-ion formation is described. Moisture (H_2O^-), SiO_2, TiO_2, Al_2O_3, P_2O_5, total iron, MgO, MnO, and CaO are determined in a 1-g sample. Other oxides, such as FeO, Na_2O and K_2O, and H_2O^+ are determined in separate portions. The results for 6 silicates, including G-1 and W-1, compare favorably with those obtained by established procedures. Six complete analyses may be carried out in about 8 days.

RÉSUMÉ

L'auteur propose une méthode d'analyse de roches silicatées, basée sur échange d'ions et formation d'ions complexes. L'humidité, SiO_2, TiO_2, Al_2O_3, P_2O_5, fer total, MgO, MnO, et CaO sont dosés sur 1 g d'échantillon. D'autres oxydes (FeO, Na_2O et K_2O) sont dosés individuellement. Il est possible d'effectuer 6 analyses complètes en 8 jours environ.

ZUSAMMENFASSUNG

Es wird ein Verfahren für die Analyse von Silikatgesteinen beschrieben, das auf der Anwendung von Ionenaustauschern und der Bildung von Komplexionen beruht. In einer Probe von 1 g werden die Feuchtigkeit (H_2O^-), SiO_2, TiO_2, Al_2O_3, P_2O_5, Gesamteisen, MgO, MnO und CaO bestimmt. Andere Oxide wie FeO, Na_2O und K_2O und H_2O^+ werden in besonderen Proben bestimmt. Die Ergebnisse von 6 Silikaten einschliesslich der Standardproben G-1 und W-1 sind günstig, verglichen

mit denen, die mit bewährten Verfahren erhalten wurden. Sechs vollständige Analysen können in etwa 8 Tagen durchgeführt werden.

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SPECTROPHOTOMETRIC DETERMINATION OF CALCIUM WITH 8-QUINOLINOL

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Calcium can be extracted at high pH with 8-quinolinol–chloroform solution if 2-butoxyethanol is present[1,2]. It seemed therefore that, if potentially interfering metals were removed by preliminary solvent extractions with wide-spectrum organic reagents, it might be possible to develop a good spectrophotometric quinolinol method for the determination of calcium. Tests have shown that this is the case. By means of a carbamate–chloroform extraction followed by a cupferron–chloroform extraction, it is possible to eliminate interference of 100-μg amounts of all of the common metals and elements with the exception of magnesium and strontium. The new proposed method has been adapted to the determination of 0.02 to 0.1% of calcium in battery lead.

EXPERIMENTAL

Reagents

The organic reagents used must be of AR quality, otherwise the 8-quinolinol and cupferron–chloroform solutions may be straw-colored, the sodium carbamate may not dissolve completely in water and the 2-butoxyethanol may be immiscible in water. The reagents should be refrigerated if they are to be stored for any length of time. All basic reagent solutions used should be prepared in, stored in, and dispensed from polyethylene ware and the glass ware used should be of the acid resistant type such as Pyrex or Vycor.

Procedure

Isolate the calcium from all but traces of other metals by conventional methods (*e.g.*, solvent extraction, mercury cathode separation, etc.). Obtain the calcium in 1 ml of 72% perchloric acid and dilute to 25 ml. Add 1 drop of an aqueous 0.1% (w/v) *m*-cresol purple indicator solution and neutralize just to the yellow color of the indicator with 20% (w/v) sodium hydroxide solution. Then add 1:1 perchloric acid dropwise until the orange or slight pink color of the indicator is obtained. Transfer the solution to a 125-ml separating funnel. Add 5 ml of freshly prepared aqueous 2% (w/v) sodium carbamate solution, add 25 ml of chloroform and shake for 30 sec. Allow the layers to separate and then drain off and discard the lower layer. If a small precipitate is seen to collect at the interface in the carbamate extraction, drain it completely through the stopcock each time it is observed in the carbamate and subsequent wash extractions. Make two consecutive 5-sec wash-extractions with 10-ml portions of chloroform.

If the amount of observed precipitate is appreciable, and especially if the sample is known to contain Al, Be or Sc, filter the solution and wash once, after removal of the 25 ml of chloroform and before the wash-extractions, through a 9-cm Whatman No. 40 filter paper to remove the precipitate. If Be or Al is known to be present, then add after the filtration 1 ml of a freshly prepared, aqueous 1% (w/v) cupferron solution followed by 1 drop of 20% sodium hydroxide solution. Add 1:1 perchloric acid dropwise until the solution just turns yellow. Allow to stand for 10 min. Extract with chloroform and wash-extract twice with chloroform. Discard the extracts.

Finally, add 10 ml of pH 12.6 buffer solution (10 g of sodium hydroxide plus 10 g of $Na_2B_4O_7$ dissolved in 1 l of water) plus 5 ml of 1:1 2-butoxyethanol solution plus 10.0 ml of a freshly prepared 3.0% 8-quinolinol solution in chloroform and shake for 30 sec. Drain most of the lower layer through a triply folded 9-cm Whatman No. 40 filter paper into a clean dry 50-ml conical flask. Immediately measure the solution spectro-photometrically in a 1-cm absorption cell at 400 mμ using pure chloroform as the reference liquid. Correct for a blank that has been carried through the entire procedure. Compare the transmittancies obtained with a calibration graph wherein known amounts of calcium (up to 150 μg) are carried through the appropriate procedure.

RESULTS AND DISCUSSION

Neither carbamate nor cupferron will precipitate magnesium or the alkaline earth metals. Of the two, carbamate is preferred for the removal of the bulk of the potentially interfering metals in the quinolinol method for calcium, since it does not introduce ammonium salts. Moreover, since the pH of the solution is raised as a result of extraction of the carbamate into the chloroform, many metals are precipitated as hydroxide and can be removed by passage through the stopcock of the separating funnel or by filtration.

In order to determine the efficiency of the carbamate extraction for removal of interference, the behavior of 56 of the common metals or elements[3] was tested individually. To do this, 0.1 mg of calcium plus 0.1 mg of each metal plus 2.5 ml of 1:1 perchloric acid were evaporated to 1 ml and the carbamate and 8-quinolinol extractions were made, draining any precipitate that collected at the interface through the stopcock. Of the 56 metals tested the following were seen to give precipitates on the addition of carbamate: Cu, Pb, Bi, Ga, Zn, Cd, In, Fe, Ni, Co, V, Mn, Cr, Mo, Ti, Se, Te, Pt, Pd, Ag, Sn and Hg.

Some of these metals gave only slight precipitates, indicating that only partial precipitation had occurred. Nevertheless, none appeared to be extracted subsequently with quinolinol at pH 12. The spectrophotometric data for calcium obtained showed that the only metals that interfered in the determination were Sc, Be, Al, Mn, Sr and Mg (Table I). Of course, it must be remembered that in all cases only 0.1 mg of metal or element was present and that the situation might be different if larger amounts were present.

Tests showed that when large amounts of phosphate or fluoride were present

TABLE I

INTERFERENCE OF VARIOUS METALS

Metal added (μg)	*Calcium found (μg)*	*Metal added (μg)*	*Calcium found (μg)*
None	100	100 Mn	125[a]
100 Sc	185[a]	100 Mn	160[a]
100 Sc	100[b]	100 Mn	101[d]
100 Be	190[a]	100 Mn	104[d]
100 Be	112[b]		
100 Be	105[c]	100 Sr	109
100 Al	250[a]	100 Mg	200
100 Al	160[b]	100 Mg	150[e]
100 Al	100[c]	100 Mg	91[f]

[a] Precipitate passed through stopcock; no cupferron extraction.
[b] Precipitate removed by filtration; no cupferron extraction.
[c] Precipitate removed by filtration; cupferron extraction made.
[d] Extra drop of indicator solution added.
[e] $Mg(OH)_2$ allowed to crystallize for 30 min.
[f] Crystallized $Mg(OH)_2$ removed by filtration.

the recoveries of calcium were low. However, it was established that the presence of as much as 10 mg of diammonium hydrogen phosphate or sodium fluoride and as much as 100 mg of oxalic acid caused no error in the determination of calcium.

Interferences

Scandium, aluminum and beryllium. The interference of scandium can be eliminated by filtration and that of aluminum or beryllium by cupferron extraction (Table I). Very little cupferron need be used since all of the metals that might be precipitated with cupferron at pH 3 to 4 are previously removed either by carbamate extraction or by precipitation as hydroxide.

Manganese. Some of the manganese appears to be oxidized by air during the neutralization before the carbamate extraction. The oxidized manganese tends to destroy the indicator, making the pH adjustment difficult to see. Moreover, some of the manganese precipitates and escapes removal in the carbamate extraction. Tests showed however, that these difficulties could be overcome if an extra drop of the indicator solution is added, just before the completion of the neutralization, to facilitate the pH adjustment and to reduce any oxidized manganese (Table I).

Magnesium and strontium. The interference of strontium is moderate. Magnesium, on the other hand, causes appreciable interference in spite of the fact that it is precipitated as hydroxide at pH 12. The latter interference can be reduced by allowing the $Mg(OH)_2$ to crystallize for 30 min after the addition of the pH 12.6 buffer and before the addition of 2-butoxyethanol. If the crystallized $Mg(OH)_2$ is removed by filtration low results for calcium are obtained, which suggests that coprecipitation of calcium occurs (Table I). It is therefore evident that, until such time as a better separation is found, the proposed method cannot be used when magnesium or more than traces of strontium are present.

Optimum pH of the aqueous solutions in the various solvent extractions

In order to assure removal of the maximum number of metals in the carbamate extraction, the acidity of the aqueous solution should not be lower than about pH 2 (*i.e.*, the orange or slight pink color of *m*-cresol purple). In fact, in the case of manganese, it is best to approach even closer to neutrality. In the presence of most metals the solutions can be adjusted to pH 3–4 before the carbamate extraction by neutralizing to the yellow color of *m*-cresol purple. However, in the presence of Al, Be and perhaps Sc, the chloroform layer may not separate well after the carbamate extraction if the neutralization is carried this far. Moreover, it has been noted that such metals as Pd, Pt, Ag, Sn and Hg do not precipitate as completely on adding carbamate to a solution that has been adjusted to pH 3–4 as they do when the neutralization is only taken to pH 2. Therefore, unless manganese is present, it is desirable to stop the neutralization at pH 2.

In preparing for the cupferron extraction it is necessary to neutralize to the purple color of the indicator and then just barely come back to the yellow with 1:1 perchloric acid in order to assure complete precipitation of aluminum and beryllium. The optimum pH for the quinolinol extraction of calcium is about 12. The aqueous solutions must contain appreciable amounts of salts in order to prevent emulsion formation in the extractions.

Blanks

In the proposed method the calibration blank usually gives a reading of about 80% transmittancy. Much lower transmittancies are obtained when quinolinol–chloroform solutions that have been allowed to stand for a day or two are used. This suggests that colored, chloroform-soluble degradation products are present or that such products induce extraction of other colored materials from the alkaline aqueous solution. Moreover, the transmittancies obtained are lower, the coarser the filter paper used to remove water droplets from the chloroform solution just before the spectrophotometric measurement. Filtration of alkaline solutions through filter paper usually causes higher blanks.

Determination of calcium in battery lead

The determination of 0.02–0.1% of calcium in battery lead is described below, as an example of the practical applicability of the proposed new method. In preliminary tests it was shown that such alloys could be analyzed by the quinolinol method after removal of most of the lead as sulfate. Subsequently, however, it was found that all of the lead could be removed by carbamate extraction. This is the method that is recommended, since it is simple and allows an analysis in less than 15 min.

In adapting the proposed method for calcium to the analysis of battery lead, no interference due to the 6 metals mentioned previously need be feared since they are not present in such alloys. Hence the filtration and cupferron extraction can be omitted.

Procedure

To analyze a lead–calcium alloy containing 0.02–0.1% of calcium, dissolve 0.1 g of the sample by warming with 1.5 ml of 5:1 perchloric acid–nitric acid. Take to fumes to expel nitric acid and all but 1 ml of the perchloric acid. Cool, add 25 ml of water, and then analyze by the proposed method but add 10 ml of 3% carbamate solution. Compare the transmittancies obtained with a calibration graph prepared with composite mixtures of known amounts of calcium plus an aliquot of lead perchlorate solution (0.1 g of Pb) plus 1 ml of perchloric acid.

In order to test this method, 4 samples of Bell System battery lead of varying calcium content were analyzed. The results obtained are shown in Table II. It is seen that the reproducibility obtained is reasonably good and that the results agree quite well with values obtained by T. Y. KOMENTANI using a direct atomic absorption method.

TABLE II

ANALYSIS OF LEAD–CALCIUM ALLOYS

Sample no.	*% Calcium found*	
	Proposed method	*Atomic absorption method*
1	0.023 0.022 0.024	0.024
2	0.087 0.085 0.086	0.087
3	0.086 0.086	0.088
4	0.101 0.100 0.097	0.100

SUMMARY

The spectrophotometric determination of calcium with 8-quinolinol is described. Interference from all the commonly encountered metals and elements with the exception of magnesium and strontium can be eliminated by preliminary carbamate–chloroform and cupferron–chloroform solvent extractions. The proposed method is adapted to the determination of calcium in battery lead.

RÉSUMÉ

On décrit un dosage spectrophotométrique du calcium, au moyen d'hydroxy-8-quinoléine. Les interférences de tous les métaux et éléments généralement rencontrés, à l'exception du magnésium et du strontium, peuvent être supprimées par extractions préliminaires à l'aide des mélanges carbamate–chloroforme et cupferron–chloroforme. La méthode proposée est appliquée au dosage du calcium dans le plomb de batteries.

ZUSAMMENFASSUNG

Die spektralphotometrische Bestimmung von Calcium mit 8-Oxychinolin wird beschrieben. Störungen durch die am häufigsten auftretenden Metalle und Elemente mit Ausnahme des Magnesiums und Strontiums können eliminiert werden durch vorhergehende Extraktionen mit Carbamat–Chloroform und Kupferron–Chloroform. Die vorgeschlagene Methode ist auf die Bestimmung von Calcium in Batterieblei abgestimmt worden.

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Anal. Chim. Acta, 32 (1965) 221–226

THE DETERMINATION OF GLYCEROL

PART II. ABSORPTIOMETRIC DETERMINATION AS THE COPPER COMPLEX

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In the first part of this series[1] the problems relating to the determination of glycerol were discussed and earlier methods involving oxidation procedures[2,3] and chromatographic separation of impurities[4] were mentioned. Early attempts by BERTRAM AND RUTGERS[5,6] to determine glycerol by means of the copper–glycerol complex were briefly described. A method was developed for the determination of 40–400 mg of glycerol using this complex, with iodimetric titration of copper(II).

The above method appeared fully satisfactory for glycerol in the higher concentration ranges and for the assay of commercial and B.P. glycerol, but its relative insensitivity made it impracticable for application to the determination of small quantities of glycerol in industrial solutions and pharmaceutical preparations. However, it was considered that the light absorption of the blue copper–glycerol complex might be used as the basis for a colorimetric method in the lower concentration ranges.

Methods for glycerol employing measurement of the absorption of the copper complex have been described by WHYTE[7] and SPAGNOLO[8]. These methods, however, have some disadvantages in lack of conformity with Beer's law and the necessity for the presence of excess amounts of copper(II) chloride to achieve stability. It appeared that, by the use of the innovations described previously[1], these problems could be overcome and high sensitivity achieved in an absorptiometric method.

Preliminary experiments

The method described in Part I[1] was used as a basis for the initial experiments. These were designed to provide information on the spectral characteristics of the copper–glycerol complex.

A series of solutions was prepared as follows. A known volume (x ml) of M glycerol solution was mixed with ethanol and 10 ml of 7.5 M sodium hydroxide in a 100-ml graduated flask. A volume (y ml) of M copper(II) chloride was then added in small amounts with vigorous shaking after each addition. The solution was then made up to volume with ethanol. The volumes of y were chosen to give definite x/y ratios ($\frac{1}{2}$, 1, 2, etc.) and this volume of copper(II) chloride was increased until a permanent precipitate of copper(II) hydroxide remained. The total amount of ethanol added was such that the final solution was approximately 90% alcohol.

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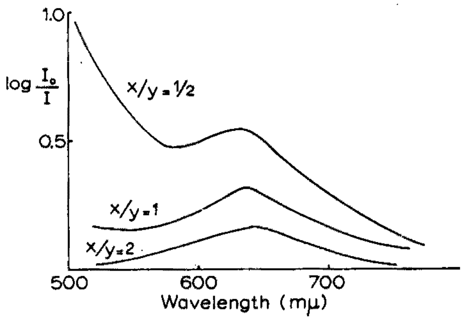
The absorption spectrum of each solution was measured. Typical results are given in Fig. 1. These showed that there was an absorption peak in the region of 630 mμ which increased as the concentration of copper chloride became larger (*i.e.* the rates of x to y became smaller). In addition a sharply rising absorption below 600 mμ developed at the higher copper concentrations. The experiments were therefore repeated using similar solutions, but in the absence of glycerol; it was found (Fig. 2) that the absorption below 600 mμ was again present. Filtration through glass-fibre filters removed the absorption below 600 mμ (Fig. 2). A series of solutions containing glycerol was therefore prepared as before, but filtration was carried out before the spectrophotometric determination. No interference from absorptions below 600 mμ then occurred and a clearly defined absorption peak at 635 mμ was obtained (Fig. 3). The magnitude of this peak, for a given concentration of glycerol reached its maximum when the glycerol–copper chloride ratio became 1 : 1 and was not further increased by additional copper chloride.



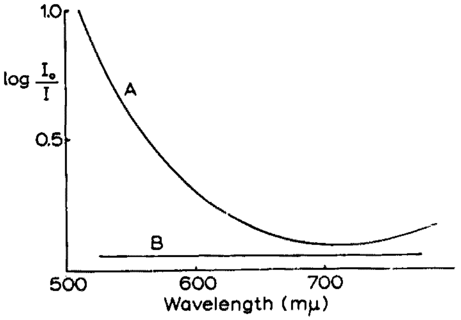


Fig. 1. Spectra of glycerol (x) –copper(II) chloride (y) mixtures in various ratios. In 90% alcohol and 0.75 *M* sodium hydroxide (unfiltered).

Fig. 2. Spectra of copper(II) chloride in 90% alcohol and 0.75 *M* sodium hydroxide (glycerol absent): (A) unfiltered; (B) filtered.

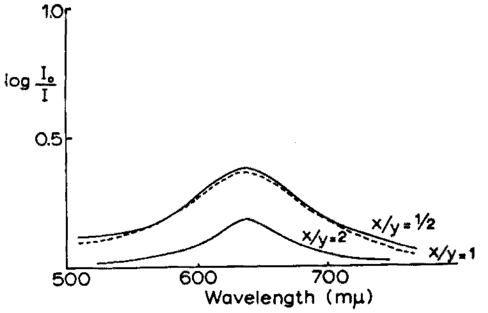


Fig. 3. Spectra of glycerol (x) –copper(II) chloride (y) mixtures in various ratios. In 90% alcohol and 0.75 *M* sodium hydroxide (filtered).

Constitution of the copper–glycerol complex

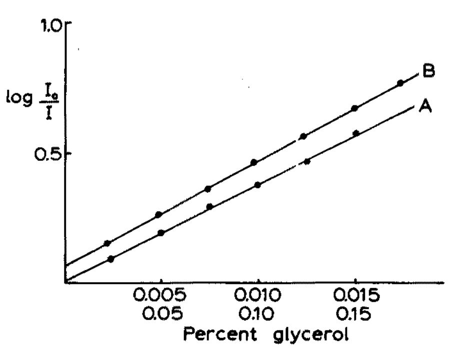
In order to establish that the absorption peak at 635 $m\mu$ was due to a single complex, and to ascertain the copper–glycerol combining ratio, Job's method of continuous variation[9], combined with the method of Vosburgh and Cooper[10] (see also ref. 11, 12), was employed. A series of solutions containing various ratios of M glycerol and M copper(II) chloride was prepared and treated as already described. Their absorptions were measured in each case at several wavelengths within the range 500 to 700 $m\mu$. The resulting curves all showed clearly a combining ratio of 1 : 1. It was therefore concluded that only one complex was formed.

Stability of the complex

A series of solutions containing various concentrations of the copper–glycerol complex was prepared as before, but with just sufficient copper(II) chloride to form a permanent turbidity. Some of these solutions were then filtered. Both the filtered and the unfiltered solutions were allowed to stand at room temperature (20 ± 2°) for 5 h in daylight. In no case was any change observed in the absorption measured at 635 $m\mu$. The solutions were then allowed to stand overnight for a further 16 h. After this time all those unfiltered showed a darkening of the precipitate and a change in its colour from green to brown; this was accompanied by some loss in absorption after filtration. In the case of the filtered solutions those containing higher concentrations (equivalent 0.06% glycerol) also showed some loss of absorption and the formation of white crystalline needles was observed.

Relation between absorption and concentration

A series of solutions containing glycerol in the range 0.08 to 8.0% (w/v) was prepared by accurate dilution, and treated by the method already described. After filtration the absorption of each solution at 635 $m\mu$ was measured. The results for solutions containing 0.003 to 0.3% glycerol are presented in Fig. 4; those in the range 0.3 to 8.0% glycerol are shown in Fig. 5. In the latter series quantitative dilution with 90% ethanol was necessary before the absorption was measured. In all cases the results showed good agreement with Beer's law.



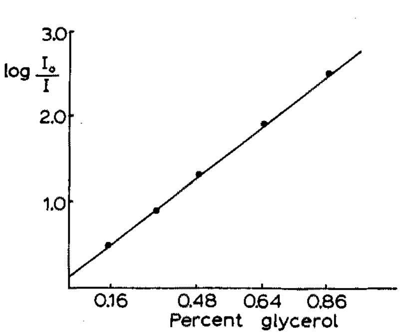


Fig. 4. Calibration curves. (A) low concentration range; (B) medium concentration range.

Fig. 5. Calibration curve. High concentration range.

Effect of sodium hydroxide and ethanol concentrations

A series of solutions, each containing the same amount of glycerol (approximately 0.05%) was treated as before with copper(II) chloride, but the sodium hydroxide concentration was varied over the range 0.1 to 7.0 *M*. The results showed that this change in concentration had little effect on the absorption of the complex at 635 mμ.

The above experiment was repeated using 0.75 *M* sodium hydroxide, but with the final concentration of ethanol varied from 90 to 40%. The absorptions of the solutions were measured over a period of 5 h. The results (Table I) show that appreciable hydrolysis occurs at the lower alcohol concentrations, but that the stability of the complex in 90% alcohol is high.

TABLE I

EFFECT OF ALCOHOL

Per cent	*Absorption*			
ethanol	*After 30 min*	*After 1 h*	*After 3 h*	*After 5 h*
90	0.310	0.310	0.310	0.300
80	0.300	0.299	0.299	0.290
60	0.270	0.260	0.240	0.240
40	0.265	0.260	0.220	0.200

Effect of traces of colloidal or unfiltered copper(II) hydroxide

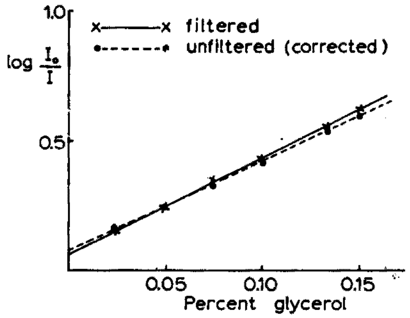
In view of the effect of unfiltered copper(II) hydroxide (Figs. 1–3) comparative determinations, with and without filtration, were made. FOG[13] has shown that the logarithms of the extinction of sols and suspensions have a linear relationship to the logarithm of the wavelength. It is therefore possible to obtain a value for absorption due to turbidity at a specific wavelength from measurements made at two other wavelengths using the same solution. These observations were confirmed by re-plotting the blank values in Fig. 3 as log values against the log of the wavelength; a straight line was obtained. It appeared therefore that the method of FOG provided a means of correcting for the effect of unfiltered copper(II) hydroxide by making measurements at wavelengths on either side of that used to determine the concentration of the complex, provided that these wavelengths were chosen so that the contribution due to the complex itself was negligible.

A series of solutions containing various concentrations of glycerol was treated by the usual method, an amount of copper(II) chloride just sufficient to give a permanent turbidity being added in each case; after filtration the absorptions were measured at 635 mμ. The experiment was then repeated but without filtration; in this case, after vigorous shaking, the absorptions were measured at 440, 635 and 800 mμ (in that order). The solutions were then subjected to further shaking and the readings repeated at 800, 635 and 440 mμ. The means of the pairs of readings were calculated and used to correct the values for the absorption of the complex at 635 mμ.

Results obtained with both filtered and unfiltered solutions are compared in Fig. 6. Since the two curves were almost coincident it is considered that the validity of this method of correction has been demonstrated.

Effect of interfering substances

In order to examine the specificity of this method for glycerol other polyhydric organic compounds having hydroxyl groups in adjacent positions were studied. Ethylene glycol and polyethylene glycol were found to give soluble copper complexes. Their absorption curves, compared with that from a similar concentration of glycerol, are shown in Fig. 7. It is evident from these results that the extinction of the glycerol complex is more than 4 times as large as those of the others. Both the new complexes obeyed Beer's law.



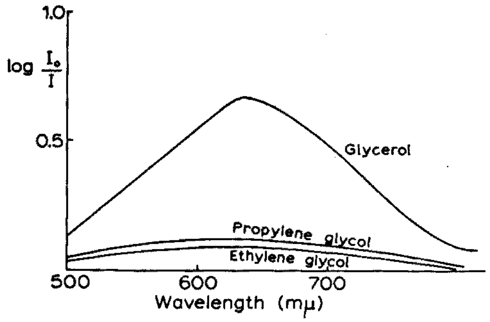


Fig. 6. Comparison of corrected results from unfiltered solutions with those from filtered solutions.

Fig. 7. Comparison of absorptions.

Other compounds studied were trimethylene glycol, sucrose, lactose, mannitol and tartaric acid. These gave negligible absorptions at 635 mμ. Ammonium salts and the salts of sulphurous acid were found to interfere and must be absent.

RECOMMENDED METHOD

Place a 5-ml aliquot of a solution of the sample (adjusted to have a glycerol content in the range 0.5 to 40 mg) in a 250-ml stoppered flask and add 7.5 ml of 10 *M* sodium hydroxide and 50 ml of ethanol. Run in, successively, small volumes of *M* copper(II) chloride solution, stoppering and shaking the flask for 1 min after each addition. Continue until a slight permanent precipitate of copper(II) hydroxide remains. Add 10 ml of ethanol, stopper the flask and shake again for 1 min. If the precipitate dissolves, add more copper(II) chloride and shake again.

Filter under light suction through a Buchner funnel fitted with a Whatman GF/A glass-fibre filter disc. Transfer the filtrate to a 100-ml graduated flask. Rinse out the conical flask and wash the residue with three 5-ml portions of 0.75 *M* sodium hydroxide in ethanol; the wash solution must not contain more than 10% of water.

Use the washings to complete the quantitative transfer of the original filtrate from the Buchner flask to the 100-ml graduated flask. Make up to volume with ethanol. Measure the absorption at 635 mμ using a suitable spectrophotometer (a Unicam S.P. 600 was used) in 1-cm or 4-cm cells (according to the glycerol concentration) against water.

Determine the glycerol concentration by reference to a calibration curve after correction has been made for the reagent blank.

Carry out a blank determination exactly as described above, but without addition of glycerol. Filtration should be carried out without delay[1]. Apply any necessary correction to the absorption of the sample solution measured at 635 mμ.

Calibration

Prepare a series of solutions by dilution of a solution of pure glycerol to give concentrations within the range 0.05–4.0 mg per ml. Treat 10-ml aliquots of these solutions exactly as described in the method. Plot a calibration curve of absorption at 635 mμ against glycerol.

TRIALS OF THE METHOD

In order to test the reproducibility of the method a number of determinations were made with "unknown" solutions of glycerol. These were prepared by dilution of a solution of B.P. quality glycerol, the content of which had been determined by the volumetric procedure[1].

The results obtained in replicate determinations are presented in Table II.

TABLE II

REPRODUCIBILITY OF METHOD

Solution	*Glycerol taken (mg)*	*Content found (mg)*	*Solution*	*Glycerol taken (mg)*	*Content found (mg)*
A	34	33.4	D	1.4	1.2
A	34	33.6	D	1.4	1.4
A	34	33.6	D	1.4	1.5
B	12.5	12.4	E	0.6	0.5
B	12.5	12.4	E	0.6	0.5
B	12.5	12.65	E	0.6	0.65
C	4.6	4.35			
C	4.6	4.4			
C	4.6	4.4			

DISCUSSION

The presence of precipitated copper(II) hydroxide gives rise to an unwanted absorption in the region of 600 mμ, but this may be removed by filtration through glass-fibre filter discs. The filtration greatly simplifies the determination and avoids the addition of excess copper(II) chloride[8]. Under these conditions the copper–glycerol complex has great stability and, contrary to previous experience[7,8], the agreement with Beer's law is close over a wide range of concentration. In agreement with previous studies, only one complex is formed and this has a copper–glycerol ratio of 1 : 1. No attempt was made to confirm previous work relating to the structure or empirical formula of this complex[5,14].

In the investigations of the effect of colloidal or precipitated copper(II) hydroxide on the results, it was shown that a correction can be applied by means of the method of FOG[13], in which the linear relationship between log concentration and log wavelength is utilised. This correction could be employed as an alternative to filtration, but exhaustive studies of such a procedure were not made.

The results obtained show that the method is capable of a high degree of accuracy and reproducibility over the recommended concentration range (0.5–40 mg glycerol). As noted in the previous paper[1], "blank" solutions produced in the absence of glycerol undergo very rapid darkening of the copper(II) hydroxide precipitate. The reason for this is not fully understood, but for practical purposes it may be overcome by filtration without delay.

Studies of the interference of polyhydroxy substances showed that in most cases examined no interference occurs. Ethylene glycol and polyethylene glycol form soluble copper complexes, but their absorption at 635 mμ is small so that interference is not great.

It is considered that the method developed and described in this paper is capable of application to the rapid and accurate determination of small quantities of glycerol in a wide variety of materials.

SUMMARY

Spectrophotometric studies of the copper–glycerol complex are reported. A single 1 : 1 complex is formed under the experimental conditions employed. The interference of precipitated or colloidal copper(II) hydroxide can be overcome by filtration through glass-fibre discs or by application of a correction factor. Filtered solutions of the complex in 90% ethanol obey Beer's law over a wide range of concentration. The stability of the complex and the effects of variation in alcohol and alkali concentration have been studied.

An absorptiometric method for the determination of 0.5–40 mg of glycerol is proposed and the effect of possible interferences is considered.

RÉSUMÉ

Les auteurs ont effectué une étude spectrophotométrique du complexe cuivre–glycérol (1 : 1) et ils proposent une méthode absorptiométrique pour le dosage du glycérol (0.5–40 mg). L'influence gênante du cuivre précipité ou colloïdal peut être évitée par filtration à travers disques filtrants en fibre de verre, ou par application d'un facteur de correction.

ZUSAMMENFASSUNG

Über spektralphotometrische Untersuchungen des Kupfer–Glycerin-Komplexes wird berichtet. Es wird bei den angegebenen experimentellen Bedingungen ein

1 : 1-Komplex gebildet. Die Störung durch das gefällte oder kolloidale Kupfer(II)-hydroxyd kann durch Filtration über Glasfiberfilterscheiben oder durch Anwendung eines Korrektionsfaktors vermieden werden. Die gefilterte Lösung des Komplexes in 90% Äthanol gehorcht dem Beerschen Gesetz über einen weiten Konzentrationsbereich. Die Stabilität des Komplexes und der Einfluss wechselnder Alkohol- und Alkalikonzentrationen wurden untersucht. Eine absorptiometrische Methode für die Bestimmung von 0.5–40 mg Glyzerin wird vorgeschlagen und der Einfluss möglicher Störungen diskutiert.

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INVESTIGATION OF THE IRON(II) COMPLEX OF BIS-3,3'-(5,6-DIMETHYL-1,2,4-TRIAZINE)

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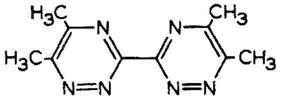
Organic chelates containing the ferroin grouping, –N=C—C=N–, have found widespread application in the spectrophotometric determination of transition metal elements. In particular, the bipyridines and phenanthrolines have become standard colorimetric reagents for iron and copper. Certain substituted triazines and bipyrimidines also contain ferroin groupings or multiple linkages. The unsymmetrical triazine, bis-3,3'-(5,6-dimethyl-1,2,4-triazine) (BDMT), has been prepared and characterized. This compound, containing opposing ferroin linkages, is quite analogous structurally to 2,2'-bipyrimidine, which has recently been proposed as a reagent for iron[1].



Bis-3,3'-(5,6-dimethyl-1,2,4-triazine)

Although there is only one reference to bis-3,3'-(5,6-dimethyl-1,2,4-triazine) in the literature[2], the compound has interesting possibilities as an analytical reagent. The multiplicity of nitrogen atoms in positions suitable for metal ion coordination is readily recognizable. It will be shown in this work that this compound fulfils every expectation as a chelating ligand for iron.

EXPERIMENTAL

Apparatus

All absorbance measurements were made with a Cary Model 14 recording spectrophotometer. Matched silica cells, 1.00 cm, were used for all measurements. A Varian A-60 Nuclear Magnetic Resonance Spectrometer was used for N.M.R. studies. A Beckman Zeromatic pH meter equipped with a saturated calomel electrode and a glass electrode was used for all pH measurements.

Reagents

Preparation of BDMT. BDMT was prepared by the method described by

DEDICHEN[2]. A slurry of 40 g (0.375 mole) of dithiooxamide in 800 ml of 20% ethanol was placed in a 1-l beaker. Hydrazine hydrate was added dropwise with stirring until all the dithiooxamide had reacted. At this point, the suspension had changed in color from orange to tan with no detection of solid orange dithiooxamide. The solid reaction product, oxalhydrazidine, was collected by filtration and washed with cold 20% alcohol. Into a 250-ml beaker in an ice bath, was placed 19.2 g (0.224 mole) of 2,3-butanedione. To this cold solution, 13 g (0.112 mole) of oxylhydrazidine was added slowly with vigorous stirring. The solid reaction product was recovered from the beaker and washed with cold water. The reagent was recrystallized twice from water using Norite decolorizing charcoal and dried in a vacuum desiccator for one day. The product had a melting point of 166–167° (lit. 166°). Overall yields of approximately 50%, based on dithiooxamide, were realized by this procedure. Analysis calculated for $C_{10}H_{12}N_6$: C, 55.53; H, 5.60; N, 38.87. Found: C, 55.66; H, 5.43; N, 38.71.

The hydrochloride of BDMT was prepared by passing dry hydrogen chloride through a solution of *ca.* 1 g of the reagent in 50 ml of acetone. The precipitate was filtered through a sintered glass crucible, washed with acetone, and dried in a vacuum desiccator for 3 h.

Standard Iron(II) solution. 40 g of iron(II) ammonium sulfate were dissolved in water and diluted to 1 l. Aliquots of this solution were titrated with standard sulfatocerate solution. The concentration of iron was found to be 0.0990 mole/l. Solutions of the reagent, *ca.* $1 \cdot 10^{-2}$ *M*, were prepared by dissolving accurately weighed samples (*ca.* 0.5000 g) of the reagent in water, and diluting to volume in a 250-ml volumetric flask.

Other reagents. A buffer solution was prepared 1 *M* in sodium acetate and 0.5 *M* in acetic acid. The reducing agent was prepared by dissolving 50 g of hydroxylamine hydrochloride in 500 ml of deionized water.

Stock solutions of diverse ions were prepared at concentrations such that a fiftyfold dilution would equal the concentrations shown in Table VI.

All other reagents were analytical grade and were used as received.

Investigation of the reagent

The solubility of the reagent was determined in a variety of common organic solvents.

Three accurately weighed samples of the hydrochloride of the reagent were dissolved in water and titrated potentiometrically with standard sodium hydroxide. The equivalent weight was calculated and compared to theoretical values.

Ultraviolet spectra of the reagent in solutions of pH 0.90 to 12.00 were obtained; 1-ml portions of $1.059 \cdot 10^{-2}M$ BDMT were mixed with small portions of 1 *M* sodium hydroxide or 1 *M* hydrochloric acid to obtain the desired pH.

An absorptiometric study of the reactivity of BDMT toward transition metal ions was performed. Solutions approximately 0.1 *M* in nickel(II) and cobalt(II) ion were prepared by the dissolution of weighed amounts of hydrated nickel and cobalt perchlorate salts and standardized by electrodeposition. A $2 \cdot 10^{-2}$ *M* solution of ruthenium(III) chloride was prepared by dissolving a weighed amount of ruthenium chloride in 15% hydrochloric acid. The standard iron solution was used for the iron system. Absorption spectra in the visible region of the spectrum were recorded.

The iron(II)–bis-3,3′-(5,6-dimethyl-1,2,4-triazine) system

Optimum conditions for the formation of the iron(II) complex in aqueous solution were determined on solutions containing iron(II) hydroxylamine hydrochloride, the reagent, and varying amounts of dilute sodium hydroxide and hydrochloric acid. The pH values varied from 1.60 to 10.30 in the presence of a fiftyfold excess of reagent to metal ion.

The methods of continuous variations[3] and mole ratio[4] were used to determine the composition of the iron(II) complex in aqueous solution. The mole ratio study was carried out on a series of solutions containing 10 ml of $3.960 \cdot 10^{-4}$ M iron, 2 ml of 10% hydroxylamine hydrochloride, 5 ml of acetate buffer, and varying amounts of $9.911 \cdot 10^{-3}$ M reagent solutions. The final concentrations of reagent varied from $4.05 \cdot 10^{-5}$ to $198 \cdot 10^{-5} M$. The combining ratio of BDMT and iron(II) was determined by the method of continuous variations on a series of solutions prepared from $6.002 \cdot 10^{-3} M$ reagent and $5.940 \cdot 10^{-3} M$ iron stock solutions. The solutions were combined in amounts to vary the iron: reagent ratio from 0.1 to 0.9. Two ml of 10% hydroxylamine hydrochloride and 3 ml of acetate buffer were added to each solution. Data were recorded from the measurement of the absorption spectrum of each solution.

The iodide salt of the iron(II) complex of BDMT was prepared for N.M.R. analysis by adding an excess of solid potassium iodide to an aqueous solution of the complex. The iodide salt precipitated as a red powder and was filtered on a sintered glass crucible, washed with water and ethanol and dried in a drying pistol. The N.M.R. spectra of a pyridine solution of BDMT (100 g/ml), the iron(II) complex (100 mg/ml), and a mixture of the two were obtained. Tetramethylsilane was used as a reference.

The conformance of the system to Beer's law was determined over the concentration range of $7.92 \cdot 10^{-6}$ to $1.19 \cdot 10^{-4} M$. Solutions containing a 40:1 ratio of reagent to metal ion were prepared at pH 5.0. Each solution contained one ml of 10% hydroxylamine hydrochloride and 2 ml of acetate buffer. The absorbance values for these solutions were obtained at 493 mμ.

To determine the effect of time on the stability of the iron complex, a solution containing a constant concentration of iron, $3.960 \cdot 10^{-5} M$, was prepared by adding a fiftyfold excess of reagent and the required amount of reducing agent and buffer. The absorbances of these solutions were obtained over a marked period of time.

In the presence of perchlorate ion, the tris-[bis-3,3′-(5,6-dimethyl-1,2,4-triazine)]-iron(II) complex was extracted from aqueous solution into nitrobenzene. Solutions containing varying concentrations of iron, reducing agent, buffer, and perchlorate ion, were extracted with two 10-ml volumes of nitrobenzene. The combined extracts were filtered through cotton into a 50-ml volumetric flask and diluted to volume with additional solvent. Absorbance values were recorded against corresponding solvent reference solutions.

The effects of diverse ions on the iron(II) system were investigated by the addition of varying amounts of diverse ion to the complex system containing 3.10 p.p.m. of iron(II). Into separate 50-ml volumetric flasks containing one ml of the ion to be tested, 7 ml of $3.960 \cdot 10^{-4} M$ standard iron solution, 1 ml of 10% hydroxylamine hydrochloride, 10 ml of $1.056 \cdot 10^{-2} M$ BDMT, and 4 ml of acetate buffer were mixed together.

RESULTS AND DISCUSSION

The reagent, BDMT, is soluble in acetone, benzene, chloroform, diethyl ether, ethanol, methanol, nitrobenzene, pyridine and water.

The hydrochloride salt of BDMT was found to be unstable in contact with air; decomposition with a color change from tan through gray to black occurred. It was found that two equivalents of base were required for each equivalent of salt. The equivalent weight calculated from potentiometric data on 3 samples of the salt were: 148.3, 146.0, 145.3 (average: 146.5). The theoretical equivalent weight for the dihydrochloride salt is 144.6. It is assumed, therefore, that the dihydrochloride was formed in the reaction described above.

Bis-3,3'-(5,6-dimethyl-1,2,4-triazine) as a free base (pH 11) exhibits a wavelength of maximum absorption at 241 mμ (ε = 11,500), with a diminished peak at 345 mμ (ε = 562). As the pH of the aqueous solution of BDMT is decreased, the 345 mμ peak gradually disappears and the 241 mμ peak undergoes a bathochromic shift to 253 mμ.

The ligand under consideration forms colored coordination compounds with divalent cobalt, nickel, iron and ruthenium, and with copper(I). Absorptiometric data on the various metal systems are summarized in Table I.

It was apparent that the iron and copper complexes were worthy of further investigation. These metal complexes are more intensely colored than those formed with 2,2'-bipyridine, 2,2'-bipyrimidine or 1,10-phenanthroline. The copper system is the subject of another investigation. Although the ruthenium complex appeared to merit investigation, color development was very sensitive to pH and required prolonged heating. The cobalt complex appeared colored to the eye, but the absorption spectrum showed only a gradual rise from 400 to 580 mμ with no definite peak.

The effect of pH on the iron complex was ascertained. The data (Table II) show that color formation is essentially constant over a pH range of 3.8 to 7.4. It was found that the acetate buffer, at pH 5.0, was adequate for all determinations.

Results of the mole ratio study are presented in Table III. It is apparent that a fortyfold excess of reagent is required to obtain maximum and reproducible color formation.

TABLE I

ABSORPTIOMETRIC DATA ON METAL ION COMPLEXES

(pH = 5.0)

Metal ion	λ_{max}	ε
Co(II)	—[a]	—
Cu(I)	444	9,700
Fe(II)	408	12,200
	493	15,000
Ni(II)	410	15
Ru(II)[b]	412	13,200

[a] No absorption maximum observed

[b] pH = 3.7.

TABLE II

EFFECT OF pH ON THE IRON COMPLEX

(Concn. Fe = $3.960 \cdot 10^{-5}M$, concn. BDMT = $1.982 \cdot 10^{-3}M$)

pH	$A_{408\ m\mu}$	$A_{493\ m\mu}$
1.60	0.455	0.562
2.70	0.455	0.560
3.87	0.446	0.547
5.40	0.444	0.545
7.45	0.443	0.545
10.30	0.278	0.318

TABLE III

MOLE RATIO STUDY OF IRON(II)–BDMT SYSTEM

(Concn. Fe = $7.920 \cdot 10^{-5}M$, pH = 5.0)

Ratio of ligand to iron(II)	$A_{493\ m\mu}$
2.8	0.039
5.7	0.165
17.0	0.554
28.4	0.583
39.7	0.592
51.1	0.595

The formula of the iron(II) complex was determined by the method of continuous variations. The results (Fig. 1) show the existence in solution of one complex with a composition of one mole of iron(II) and three moles of BDMT.

In an attempt to describe more accurately the type of complex between BDMT and iron, the technique of nuclear magnetic resonance was employed. The method of continuous variations indicated a 3:1 ratio of BDMT to iron(II). By assuming that the coordination occurs through a ferroin-type linkage, three possible structures for the complex can be proposed.

Structure I can be ruled out since the methyl groups in the 5,5′-positions would hinder the formation of an iron complex. The analogous compound, 6,6′-dimethyl-2,2′-bipyridine, likewise, gives no color with iron(II)[5]. Structure II and III are then the remaining possible conformations.

The N.M.R. spectrum of BDMT in pyridine showed two peaks of equal area at 1.86 p.p.m. and 2.00 p.p.m. relative to tetramethylsilane (Fig. 2, Curve 1). The

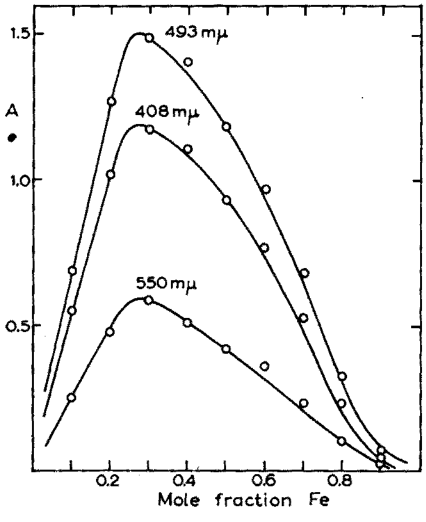
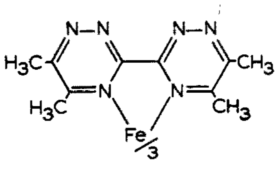


Fig. 1. Continuous variations study of iron(II) complex.



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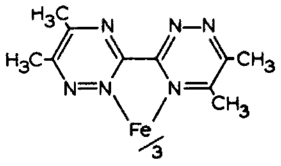

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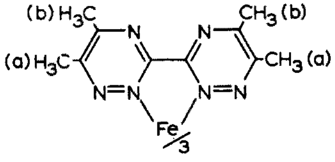

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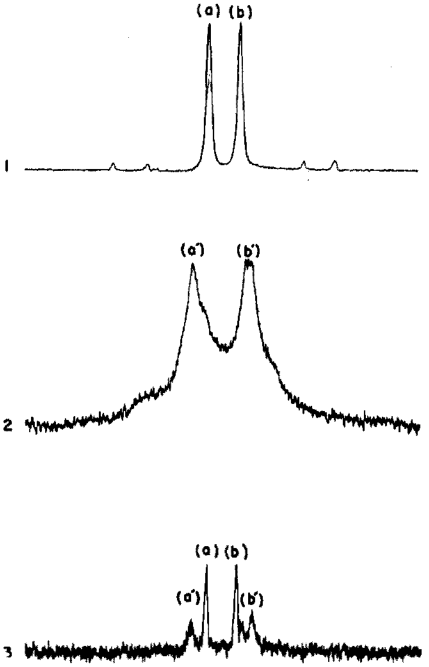

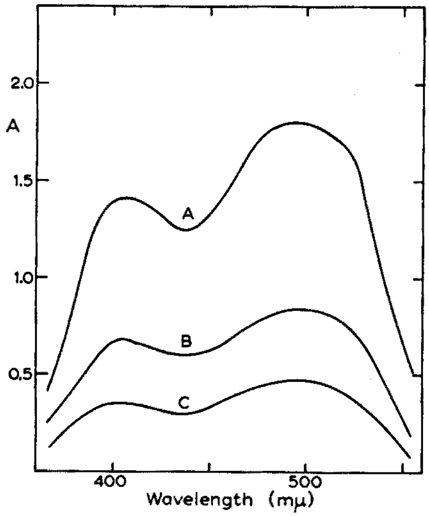

Fig. 2. Proton magnetic resonance spectra. Curve 1, BDMT; Curve 2, Fe(BDMT)$_3$I$_2$; Curve 3, BDMT and Fe(BDMT)$_3$I$_2$.

Fig. 3. Absorbance of iron(II) complex. A, 118.8 · $10^{-6}M$; B, 55.44 · $10^{-6}M$; C, 31.68 · $10^{-6}M$.

iodide salt of the complex, which was only slightly soluble in pyridine, also exhibited two peaks of equal area at 1.86 p.p.m. and 2.10 p.p.m. (Fig. 2, Curve 2). A mixture of the two compounds in pyridine gave 4 peaks, all of equal area (Fig. 2, Curve 3).

The symmetrical ligand yielded 2 proton resonance peaks as expected. The resonance spectrum of the iron complex showed a shift in the resonance peak of the 6,6'-methyl protons. This shift clearly indicates the effect of coordination of the ligand with the metal ion. Since no shift and no splitting of the 5,5'-methyl proton peak was observed in the spectrum of the complex, it can be assumed that coordination takes place between the 2,2'-nitrogen atoms and the metal ion. The structure of the complex is therefore represented by III above.

The iron(II)–bis-3,3′-(5,6-dimethyl-1,2,4-triazine) complex was found to obey Beer's law over a concentration range of $7.920 \cdot 10^{-6}$ to $118.8 \cdot 10^{-6}M$ iron(II) (Table IV). The visible spectra of the iron(II) complex are shown in Fig. 3. The best values for the molar absorptivity were 15,000 at 493 mμ, and 12,200 at 408 mμ.

TABLE IV

DATA FOR BEER'S LAW STUDY

(Concn. BDMT = $3.745 \cdot 10^{-3}M$, pH = 5.0)

Concentration of iron present ($M = 10^6$)	$A_{408\ m\mu}$	$A_{493\ m\mu}$
7.920	0.095	0.111
31.68	0.389	0.478
55.44	0.676	0.835
87.12	1.063	1.315
118.8	1.451	1.809

The stability constant for the reaction:

$$3\ \text{BDMT} + \text{Fe}^{2+} = \text{Fe(BDMT)}_3{}^{2+}$$

can be described as:

$$K = k_1 k_2 k_3 = \frac{[\text{Fe(BDMT)}_3{}^{2+}]}{[\text{Fe}^{2+}][\text{BDMT}]^3}$$

Assuming that the value obtained above for the molar absorptivity is accurate, that there is only one colored species absorbing at the measured wavelengths, that the absorbing species is a 3 : 1 complex, and that there are no competing reactions between the ligand and the hydrogen ion, then the calculation of the stability constant is relatively simple. (These assumptions are valid in view of the observations described in the preceding discussion.)

Table V contains all data used in the calculation of the stability constant from the continuous variations data. The log K value obtained for the tris-[bis-3,3′-(5,6-dimethyl-1,2,4-triazine)]–iron(II) complex was 9.6 ± 0.5. This value is comparable[1,6] to the log K values reported for tris-(2,2′-bipyrimidine)–iron(II), 7.5; tris-(2,2′-bipyridine)–iron(II), 16; and tris-(1,10-phenanthroline)–iron(II), 21.

In the presence of a large excess of reagent (40 : 1), the color intensity of the complex was found to be essentially constant over at least a period of 4 h. Maximum color was developed with a lower ratio of reagent, but this color intensity decreased in a much shorter period of time.

The perchlorate salt of the iron(II)–BDMT complex was extractable from

TABLE V

DATA FOR THE STABILITY CONSTANT CALCULATIONS

Mole fraction Fe	$A(\varepsilon_{493}) \cdot 10^5$	$A(\varepsilon_{408}) \cdot 10^5$	$[Fe]_t \cdot 10^4$	$[BDMT]_t \cdot 10^4$	*Log K 493; 408*
0.1	4.567	4.508	1.188	10.08	10.9; 10.9
0.2	8.473	8.320	2.376	9.630	9.2; 9.2
0.3	9.893	9.623	3.564	8.403	9.4; 9.4
0.4	9.373	9.082	4.752	7.202	9.5; 9.4
0.5	7.847	7.639	5.940	6.002	9.5; 9.5
0.6	6.460	6.270	7.128	4.802	9.6; 9.6
0.7	4.540	4.344	8.316	3.601	9.7; 9.7
0.8	2.167	1.926	9.504	2.401	9.6; 9.5
0.9	0.480	0.287	10.69	1.200	9.6; 9.3

TABLE VI

EFFECT OF VARIOUS IONS ON COLOR FORMATION

(Concn. of iron = 3.10 p.p.m.)

Ion	*Concentration (p.p.m.)*	*Source*	*Relative error(%)*
Cu^+	100	$Cu(NO_3)_2$	Very large
Ni^{2+}	100	$NiCl_2$	Very large
Co^{2+}	104	$Co(NO_3)_2$	−0.3
Mn^{2+}	102	$MnSO_4$	−1.0
Cr^{3+}	108	$CrCl_3$	+2.6
Zn^{2+}	101	$ZnCl_2$	0.0
Al^{3+}	87	$AlCl_3$	+0.3
Mg^{2+}	101	$MgCl_2$	−0.6
Ca^{2+}	99	$CaCl_2$	−0.3
V(V)	62	Na_3VO_4	+0.3
PO_4^{3-}	102	K_2HPO_4	0.0
$C_6H_5O_7^{3-}$	99	$Na_3C_6H_5O_7$	−0.3
F^-	98	KF	+0.3
$S_2O_3^{2-}$	101	$Na_2S_2O_3$	+2.9
SCN^-	96	KSCN	−0.3
SO_4^{2-}	100	K_2SO_4	−0.3

aqueous solution into nitrobenzene. The molar absorptivity of the iron(II) complex in nitrobenzene was 17,000 at the wavelength of maximum absorption of 494 mμ.

Bis-3,3′-(5,6-dimethyl-1,2,4-triazine) reacts as a nonselective reagent towards transition metal ions. Copper, nickel, ruthenium and chromium interfere with the determination of iron(II) due to colored compounds which are formed. Phosphate and thiocyanate ions, which cause considerable error in some iron determinations, can be tolerated with this reagent. The thiosulfate ion was the only anion tested that caused any interference, as shown in Table VI. The method of calculating relative error is essentially the same as that proposed by Fortune and Mellon[7].

CONCLUSIONS

From the data and observations described above, the following conclusions can be formulated.

The ligand, bis-3,3′-(5,6-dimethyl-1,2,4-triazine), is readily soluble in water and most common organic solvents. The compound forms the dihydrochloride salt, and the ultraviolet spectrum of the compound in 50% sulfuric acid shows an absorption maximum at 253 mμ. Absorption maxima at 241 mμ and 345 mμ were observed for the compound in solutions of pH greater than 4.7.

The ligand forms colored reaction products with divalent iron, cobalt, nickel, and ruthenium, and with monovalent copper.

The tris-[bis-3,3′-(5,6-dimethyl-1,2,4-triazine)]-iron(II) complex exhibits wavelengths of maximum absorption at 493 mμ and 408 mμ, with molar absorptivities of 15,000 and 12,200 in aqueous solution of pH 4.0 to 7.0. Beer's law for these systems is obeyed over the concentration range of $7.9–119 \cdot 10^{-6}M$.

The iron(II) forms the complex through the 2,2′-nitrogens in the ring as shown by nuclear magnetic resonance. The log K for the iron(II) complex was observed to be 9.6.

The iron(II)-bis-3,3′-(5,6-dimethyl-1,2,4-triazine) complex could be extracted as the perchlorate salt from aqueous solutions into nitrobenzene. The complex in nitrobenzene exhibited a wavelength of maximum absorption at 494 mμ and a molar absorptivity of 17,000.

A spectrophotometric method for iron based upon the color formed between the reagent and iron(II) was both accurate and precise.

RECOMMENDED PROCEDURE

Dissolve the sample containing iron by appropriate means. Adjust the pH of the solution to *ca.* 4. To a 5-ml aliquot containing from 0.40 to 7.0 p.p.m. of iron(II) in a 50-ml volumetric flask, add 2 ml of 10% hydroxylamine hydrochloride, 5 ml of acetate buffer, and at least a fortyfold excess of BDMT. Measure the absorbance of the solution in 1-cm cells with an appropriate spectrophotometer at a wavelength of 493 mμ. From a previously prepared calibration curve, determine the amount of iron in the unknown sample. Typical results are shown in Table VII.

TABLE VII

SUMMARY OF IRON DETERMINATIONS

Sample	*Iron present (p.p.m.)*	*Iron found (p.p.m.)*
S_1	0.44	0.41
		0.43
S_2	1.77	1.78
		1.78
S_3	3.10	3.11
		3.09
S_4	4.87	4.90
		4.87

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SUMMARY

The reagent, bis-3,3′-(5,6-dimethyl-1,2,4-triazine) (BDMT), forms intensely colored complexes with selected transition metal ions. The reagent is water-soluble and easily prepared. An intense orange complex, $Fe(BDMT)_3^{2+}$, is formed on reaction of iron(II) with the reagent in aqueous solution at pH 4.0–7.0. Nuclear magnetic resonance data show that chelation occurs between the 2,2′-nitrogens of the reagent. The complex exhibits absorption maxima at 408 mμ and 493 mμ, with molar absorptivities of 12,200 and 15,000 respectively. The perchlorate salt of the complex is readily extracted into nitrobenzene. A proposed spectrophotometric method for the determination of iron is both accurate and precise.

RÉSUMÉ

La bis-3,3′-(5,6-diméthyl-1,2,4-triazine) (BDMT) donne avec des métaux de transition des complexes fortement colorés. Ce réactif est soluble dans l'eau et sa synthèse est facile. Avec le fer(II), il forme un complexe orange ($Fe(BDMT)_3^{2+}$), entre le pH 4 et le pH 7. Maximum d'absorption à 408 et 493 mμ; coefficients d'extinction molaire 12,000 et 15,000. Le perchlorate de ce complexe peut s'extraire facilement dans le nitrobenzène. Les auteurs proposent une méthode spectrophotométrique pour le dosage du fer.

ZUSAMMENFASSUNG

Bis-3,3′-(5,6-dimethyl-1,2,4-triazin) (BDMT) bildet intensiv gefärbte Komplexe mit den Ionen ausgewählter Übergangsmetalle. Das Reagenz ist wasserlöslich und leicht herstellbar. Bei der Reaktion mit Eisen(II) in wässriger Lösung beim pH-Bereich von 4.0–7.0 wird ein intensiver orange gefärbter Komplex, $Fe(BDMT)_3^{2+}$, gebildet. Ergebnisse der magnetischen Kernresonanz zeigen, dass die Chelatbildung mit den in 2,2-Stellung gebundenen Stickstoffatomen des Reagenzes erfolgt. Der Komplex besitzt Absorptionsmaxima bei 408 mμ und 493 mμ mit einer molaren Extinktion von 12200 bzw. 15000. Das Perchloratsalz des Komplexes wird leicht mit Nitrobenzol extrahiert. Es wird eine spektralphotometrische Methode zur Bestimmung des Eisens vorgeschlagen, die genaue und richtige Ergebnisse liefert.

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VAPOR PRESSURE–TEMPERATURE DATA FOR VARIOUS METAL β-DIKETONE CHELATES

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A unique and somewhat unexpected property of the metal β-diketone chelates is their volatility, which is quite pronounced. For example, the vapor pressure of aluminum acetyltrifluoroacetonate is 100 mm of mercury at 205° while the vapor pressure of beryllium acetylacetonate is 431 mm of mercury at 264°. The vapor pressure of beryllium acetyltrifluoroacetonate is 656 mm of mercury at 231° while the vapor pressure of copper acetyltrifluoroacetonate is 7 mm of mercury at 185°. The chemical literature contains a number of reports which mention the volatile character of some metal chelates but by far the most extensive study is that of TRUEMPER[1] and BERG *et al.*[2,3]. Vapor pressure–temperature curves were determined for the chelates prepared from 6 different ligands and 9 metal ions. An evaluation of the data indicates that molecular symmetry and polarity are determinative with regard to the magnitude of the molar heats of sublimation but these factors cannot be sharply divided according to the nature of the metal and the structure of the ligand.

Further analysis of the data clearly indicates that it should be possible to separate various mixtures of the metal chelates by fractional sublimation or gas chromatography. It is abundantly clear from previous work[4–9] that many of these metal chelates can be successfully chromatographed in the vapor state.

The purpose of this paper is to present the vapor pressure–temperature data collected in the earlier study[1] and use it as the basis for the development of a fractional sublimation scheme for the separation of various metal β-diketone chelates. It seems likely that these data also can be used to explain some of the unexpected

TABLE I

β-DIKETONES INVESTIGATED

Common name	*IUPAC name*	*Abbreviation*
Acetylacetone	2,4-Pentanedione	AA
Acetyltrifluoroacetone	1,1,1-Trifluoro-2,4-pentanedione	ATA
Benzoylacetone	1-Phenyl-1,3-butanedione	BA
Benzoyltrifluoroacetone	1-Phenyl-4,4,4-trifluoro-1,3-butanedione	BTA
2-Furoyltrifluoroacetone	1-(2-Furoyl)-4,4,4-trifluoro-1,3-butanedione	FTA
2-Thenoyltrifluoroacetone	1-(2-Thenoyl)-4,4,4-trifluoro-1,3-butanedione	TTA

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failures in the attempted gas chromatographic separations of various metal β-diketone chelate mixtures.

The ligands used in this study are listed along with convenient abbreviations in Table I. The central metal atoms were Be(II), Al(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II).

EXPERIMENTAL

Source of β-diketone

Acetylacetone, benzoylacetone and 2-thenoyltrifluoroacetone were commercially available but were purified before use by distillation, recrystallization and sublimation, respectively. Acetyltrifluoroacetone, benzoyltrifluoroacetone and 2-furoyltrifluoroacetone were prepared by the method of REID AND CALVIN[10].

Preparation of metal chelates

The following general procedure was used for the preparation of the chelates. The nitrate salt (except for beryllium as sulfate) of the metal was made up as a 5 weight % solution and buffered immediately before use by adding 5 g of sodium acetate for every 100 ml of solution. The buffered metal ion solution was shaken with an alcoholic solution of the ligand until reaction appeared complete. The chelate was collected by filtration, washed, recrystallized from an appropriate solvent and dried. The exact procedure for the preparation and the description of the chelates is given by BERG AND TRUEMPER[1,2].

The various chelates studied are listed in Table II.

Vapor pressure–temperature measurements

Vapor pressure–temperature data were obtained by utilizing an isotenoscopic technique described by SMITH AND MENZIES[11] and modified by BOOTH AND HALBEDEL[12]. Samples showing a temperature hysteresis were discarded and fresh runs were made at a lower maximum temperature until no hysteresis was observed. Thermal decomposition thus limited the upper temperatures studied.

A check of the method for measuring vapor pressure at various temperatures was made by measuring the vapor pressure of mercury and of benzoic acid. For pressures below 4 mm an error of ±0.05 mm was observed, whereas for pressures up to 600 mm an error of ±1 mm was estimated. The precision for the range of pressures covered with the cathetometer was ±0.02 mm. The precision for the range of pressures over which the manometer was used was ±1 mm. The data were plotted as the logarithm of the vapor pressure *vs.* $1/T$ and are presented in Figs. 1–7.

Sublimation temperature measurements

A vertical vacuum sublimator was constructed of Pyrex glass. It consisted of a water-cooled cold finger inserted into a vacuum jacket. The tip of the cold finger had a flat surface at an angle of 45° to the vertical. The tip of the cold finger was filled with mercury to provide a mirror background for the flat surface. The apparatus was placed in a hand-stirred oil bath and the temperature raised at a rate of 0.5 degree per min. The flat surface of the cold finger was observed through the oil bath with a low power microscope. The cold finger was maintained at 20° by circulating water. The temperature at which sublimate was first observed on the flat surface of the cold finger is recorded as the sublimation temperature in Table II. The pressure in the sublimation apparatus was maintained at 0.25 mm of mercury and the sample was 5 mm from the surface of the cold finger. Sublimation temperatures are not physical constants such as melting points for they are dependent on the pressure, and the geometry of the sublimator.

TABLE II

PHYSICAL PROPERTIES OF THE VARIOUS METAL CHELATES STUDIED[a]

Chelate	*Color*	*M.p. (°)*	*Molar heat of sublimation (kcal)*	*Sublimation temperature (°)*
$Be(AA)_2$	White	108	8.51	37
$Al(AA)_3$	White	112	4.58	74
$Mn(AA)_2$	White	d. < 290		(91)
$Fe(AA)_3$	Red	179	4.67	69
$Co(AA)_2$	Red	Sublimes 120°, 0.2 mm	15.0	(100)
$Ni(AA)_2$	Green	d. 230	16.5	(185)
$Cu(AA)_2$	Blue	d. 230		(72)
$Be(ATA)_2$	White	112	7.28	38
$Al(ATA)_3$	White	117	9.56	48
$Fe(ATA)_3$	Red	115	20.8	48
$Ni(ATA)_2$	Green	Sublimes 150°, 0.5 mm	8.14	(111)
$Cu(ATA)_2$	Blue	200	12.1	55
$Be(BA)_2$	White	213	4.71	105
$Al(BA)_3$	White	224–225	~ 4.90	(152)
$Mn(BA)_2$	Yellow	d. > 140		(95)
$Fe(BA)_3$	Red	222–224	~ 2.68	(125)
$Co(BA)_2$	Red	181	22.9	(162)
$Cu(BA)_2$	Blue	197		(135)
$Be(BTA)_2$	White	143–144	~ 3.93	78
$Al(BTA)_3$	White	173–174	13.2	88
$Mn(BTA)_2$	Yellow	129–130	14.3	
$Fe(BTA)_3$	Red	128–129	8.56	(89)
$Co(BTA)_2$	Yellow	158		55
$Ni(BTA)_2$	Green	223–224	0.915	98
$Cu(BTA)_2$	Green	241		(130)
$Be(FTA)_2$	White	169–170	7.78	71
$Al(FTA)_3$	White	204–205		95
$Mn(FTA)_2$	Yellow	146–149	15.8	
$Fe(FTA)_3$	Red	207–208	~ 14.3	(95)
$Co(FTA)_2$	Yellow	215–220		63
$Ni(FTA)_2$	Yellow	293–296	4.51	65
$Cu(FTA)_2$	Green	227–228	3.53	105
$Be(TTA)_2$	White	169–170		(73)
$Al(TTA)_3$	White	203–205	11.1	125
$Mn(TTA)_2$	Yellow-orange	177–179	4.62	
$Fe(TTA)_3$	Red	159–160	11.1	135
$Co(TTA)_2$	Yellow	215	~ 4.24	69
$Ni(TTA)_2$	Yellow	291–295	5.95	70
$Cu(TTA)_2$	Green	242–243		(112)

[a] Temperatures enclosed in parentheses are temperatures at which sublimation was apparently accompanied by decomposition.

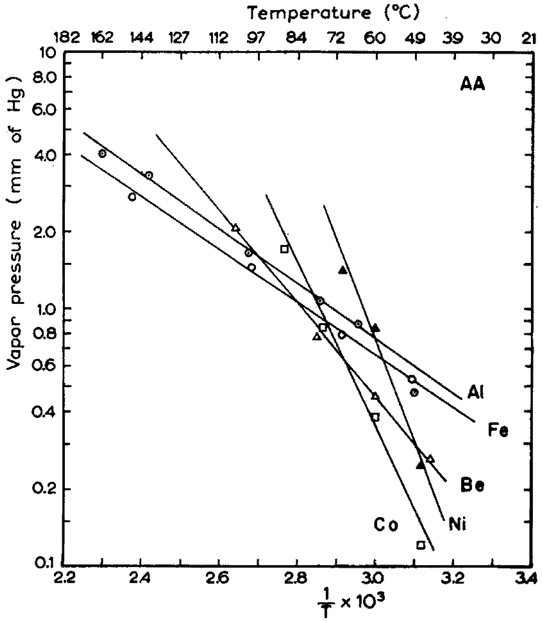

Fig. 1. Vapor pressure–temperature data for various metal chelates of acetylacetone.

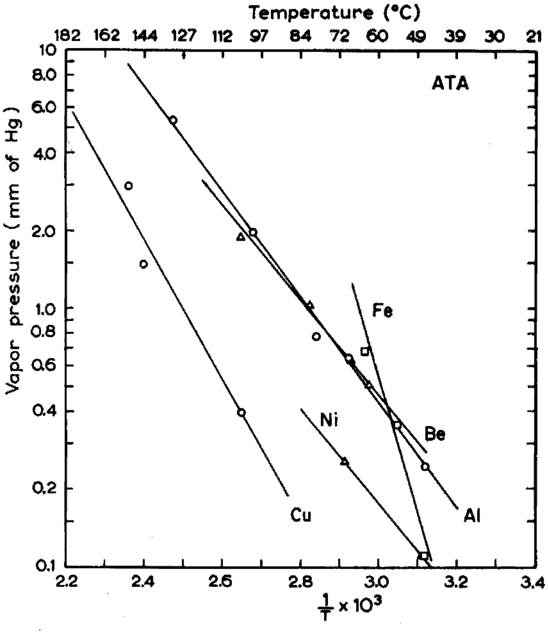

Fig. 2. Vapor pressure–temperature data for various metal chelates of acetyltrifluoroacetone.

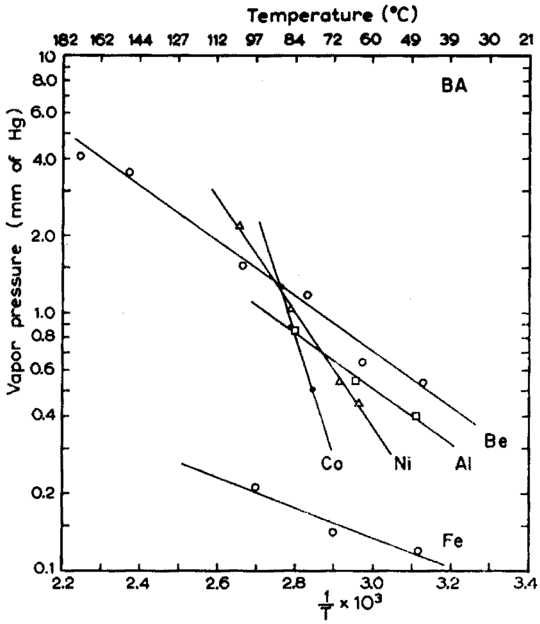

Fig. 3. Vapor pressure–temperature data for various metal chelates of benzoylacetone.

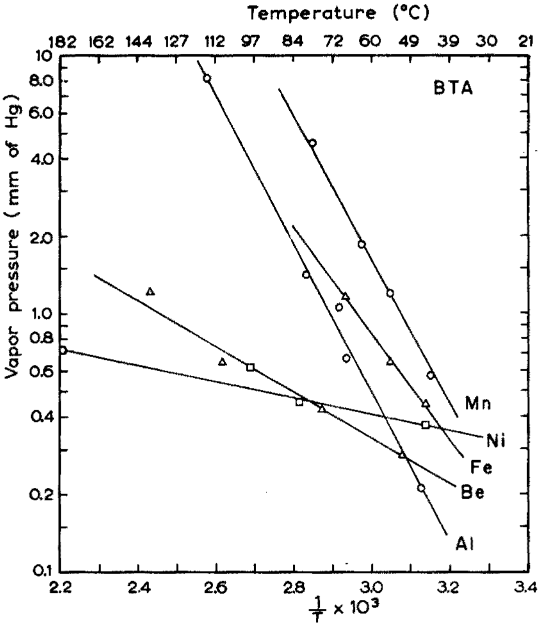

Fig. 4. Vapor pressure–temperature data for various metal chelates of benzoyltrifluoroacetone.

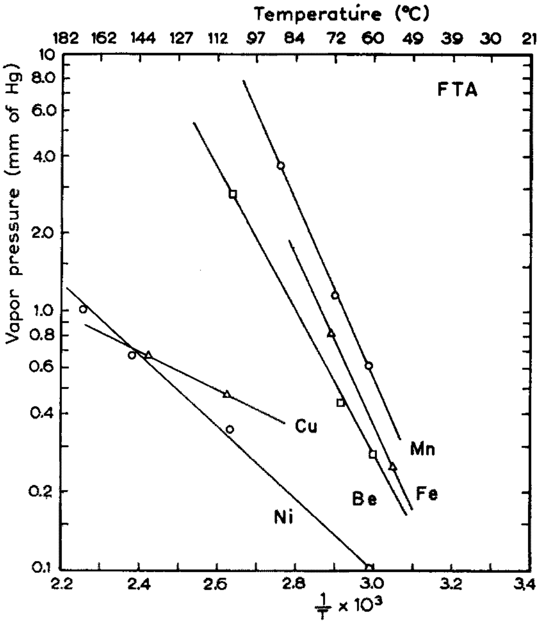

Fig. 5. Vapor pressure–temperature data for various metal chelates of 2-furoyltrifluoroacetone.

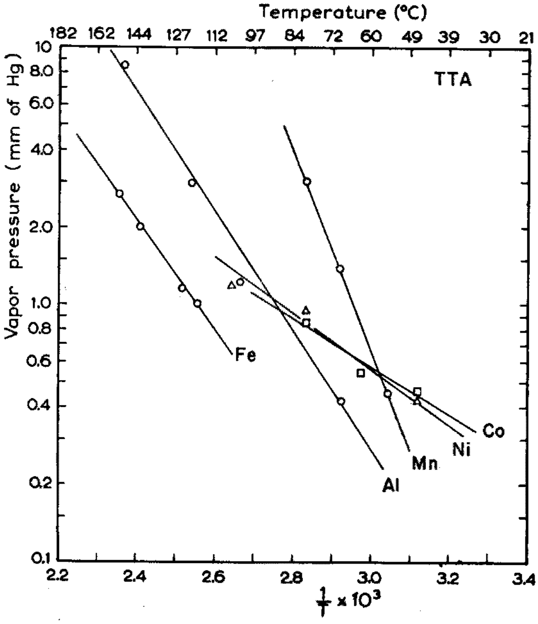

Fig. 6. Vapor pressure–temperature data for various metal chelates of 2-thenoyltrifluoroacetone.

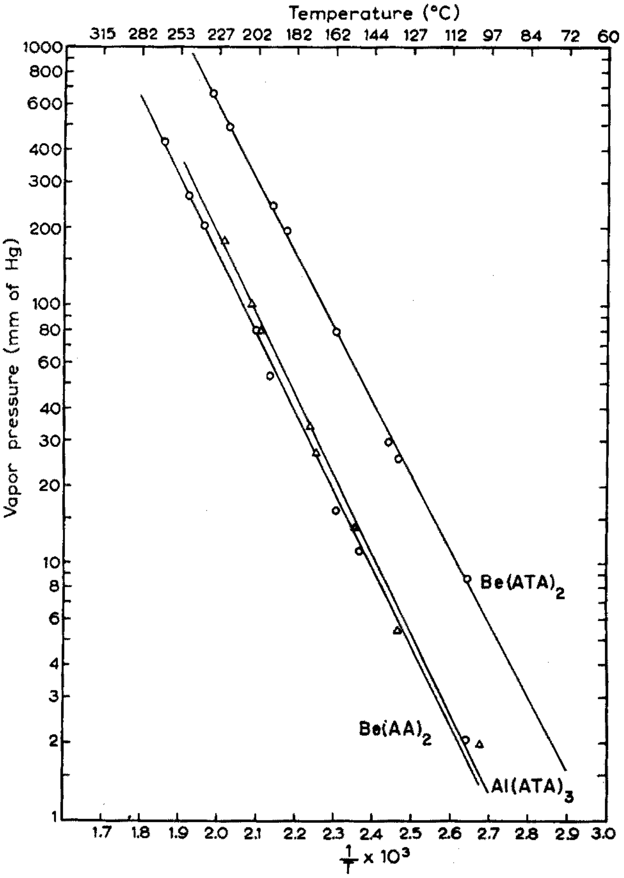

Fig. 7. Extended vapor pressure–temperature curves for various chelates of Be(II) and Al(III).

DISCUSSION

It is apparent from a scrutiny of the vapor pressure–temperature data that there are relatively large differences in volatility among the various metal chelates of a given ligand. It seems likely, therefore, that various mixtures of metals can be separated by the fractional sublimation of the chelates. Attempts to effect such separations will be reported in subsequent papers.

A disconcerting feature of these data is that one cannot correlate the measured vapor pressure to sublimation temperature for a series of chelates involving the same ligand with the molar heat of vaporization of the respective chelates. Neither is there any regularity noted in the magnitude of the volatility exhibited by a series of chelates of one metal with different ligands. The substitution of a trifluoromethyl group for a methyl group in the ligand increases the volatility of some metal chelates while a decrease in volatility is noted with others.

It appears, thus, that the relationships which exist between volatility, molecular structure, heats of vaporization, and sublimation temperatures are rather complex and that any attempt to predict a fractional sublimation scheme from the vapor pressure–temperature data will be unsuccessful. Nonetheless, the noted difference in volatilities among a group of chelates of the same ligand is great enough to allow a separation.

SUMMARY

Vapor pressure–temperature data, molar heats of sublimation, and sublimation temperatures are given for 29 metal β-diketone chelates. The chelates studied were those of Be(II), Al(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with acetylacetone, acetyltrifluoroacetone, benzoylacetone, benzoyltrifluoroacetone, 2-furoyltrifluoroacetone, and 2-thenoyltrifluoroacetone. The observed difference in volatilities of the various metal chelates of a given ligand is the basis for a suggestion that various mixtures of metal ions can be resolved by a fractional sublimation scheme.

RÉSUMÉ

Les tensions de vapeur, températures et chaleurs molaires de sublimation sont données pour 29 chélates métalliques de β-dicétones. On a examiné les chélates de Be(II), Al(III), Mn(II), Fe(III), Co(II), Ni(II) et Cu(II) avec l'acétylacétone, l'acétyltrifluoroacétone, la benzoylacétone, la benzoyltrifluoroacétone, la 2-furoyltrifluoroacétone et la 2-thénoyltrifluoroacétone. Les différences de volatilité observées permettent d'envisager une sublimation fractionnée lors de divers mélanges d'ions métalliques.

ZUSAMMENFASSUNG

Dampfdruckdaten, molare Sublimationswärmen und Sublimationstemperaturen werden für 29 Metall-β-Diketonchelate angegeben. Es wurden folgende Chelate untersucht: Be(II), Al(III), Mn(II), Fe(III), Co(II), Ni(II) und Cu(II) mit Acetylaceton, Acetyltrifluoroaceton, Benzoylaceton, Benzoyltrifluoroaceton, 2-Furoyltrifluoroaceton und 2-Thenoyltrifluoroaceton. Die beobachteten Unterschiede in den Flüchtigkeiten der verschiedenen Metallchelate eines gegebenen Liganden lassen vermuten, dass Trennungen durch fraktionierte Sublimation möglich sind.

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SOME CAUSES OF BENDING OF ANALYTICAL CURVES IN ATOMIC ABSORPTION SPECTROSCOPY

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Since 1955, when the first papers on atomic absorption spectroscopy were published, this method has become widely used, but little attention has been paid to some of the fundamental laws on which it is based. Light sources emitting narrow lines are normally used and it is generally supposed that the widths of the emitted lines are small compared with the widths of the absorbing lines and may therefore be neglected. In this case, the resulting absorption coefficient is given by its value in the maximum of the absorption line and if the profile of the absorption line does not change, the analytical curve should be linear within an almost unlimited concentration interval. This, however, seems to be rather the exception than the rule.

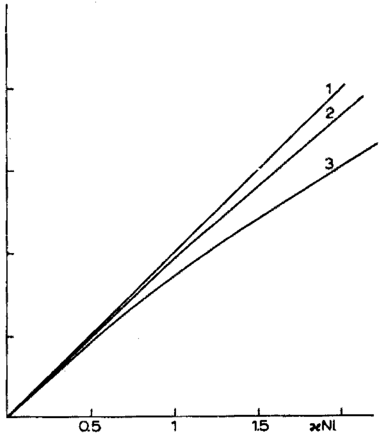
If all the processes which disturb the proportionality between the concentration of an element in the sample and its concentration in the absorbing medium (flame, hollow cathode[1,2], graphite tube[3] or absorption cell with flame gases[4]) are neglected, the factors which cause bending of analytical curves may be roughly classified in two groups. The first includes factors given by faults in the apparatus, *e.g.* if some of the light emitted by the lamp and falling on the detector is not absorbed by the absorbing medium, or if an DC measuring device is used and the emission of the absorbing medium influences the signal measured. This case has been dealt with quantitatively by SHIMAZU AND HASHIMOTO[5]. Any inhomogeneities of temperature and space distribution of the absorbing atoms in the absorbing medium may also be considered as apparatus faults.

The second group includes factors related to properties of the particular spectral line itself. It is this second group which is discussed in the present paper. The following factors must be considered:

(1) the hyperfine structure of the line,
(2) the ratio of the absorption and emission line widths,
(3) the resonance line broadening and line shift in the absorbing medium.

The hyperfine structure

LVOV[6] examined the ideal case of a spectral line with two h.f.s. components of equal intensity separated by a certain fraction of the width of the absorption line. He assumed resonance profiles for both components and found that the effective absorption coefficient differs from the theoretical value for a one-component line and that the difference increases with increasing separation of both components and with increasing optical depth. The calculated analytical curves for different ratios of h.f.s. component separation to half-widths are given in Fig. 1. To avoid non-linear analytical curves, Lvov raised the pressure in the absorbing medium, and succeeded



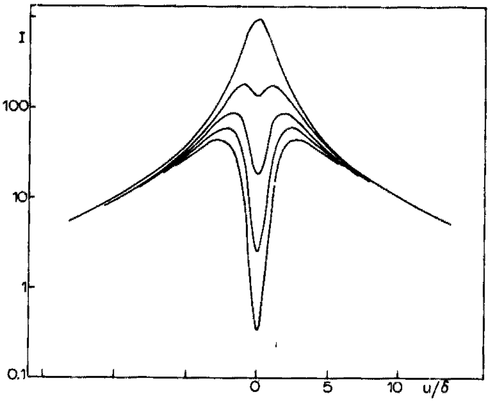
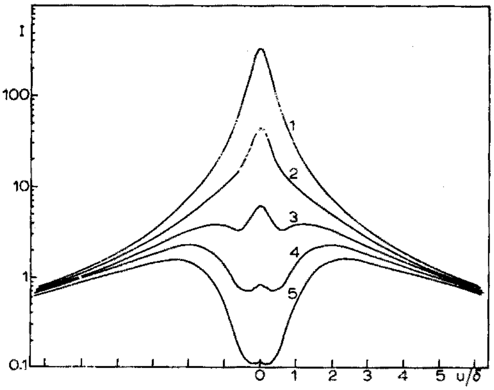


Fig. 1. Analytical curves for different h.f.s. component separation. 1, $\Delta\nu_{\mathrm{hfs}} = 0$; 2, $\Delta\nu_{\mathrm{hfs}} = \frac{1}{2}\delta_L$; 3, $\Delta\nu_{\mathrm{hfs}} = \delta_L$.

Fig. 2. The shape of a resonance-profiled line at increasing optical depths for $\delta = \delta'$. $\varkappa_0 Nl = 0$, 2, 4, 6, and 8.



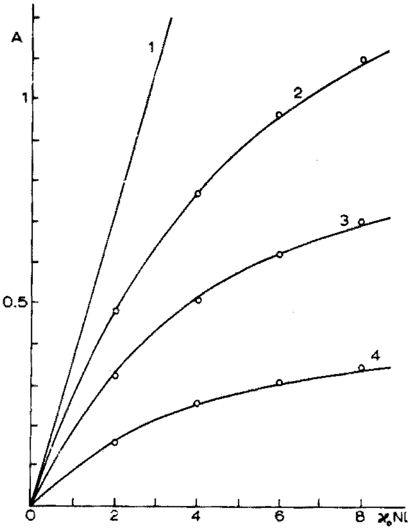


Fig. 3. The shape of a resonance-profiled line at increasing optical depths. 1, $\varkappa_0 Nl = 0$; 2, $\varkappa_0 Nl = 2$; 3, $\varkappa_0 Nl = 4$; 4, $\varkappa_0 Nl = 6$; 5, $\varkappa_0 Nl = 8$. $\delta = 3\delta'$.

Fig. 4. Calculated analytical curves for resonance-shaped lines and different emission and absorption line half-widths. 1, $\delta' = 0$, $\delta = 5$; 2, $\delta' = 1.5$, $\delta = 5$; 3, $\delta' = \delta = 5$; 4, $\delta' = 15$, $\delta = 5$. The points were calculated using the empirical relation (11).

in straightening the analytical curves for cadmium when the pressure was raised from 1 to 10 atm. This, however, is hardly feasible when a flame is used as the absorbing medium.

The ratio of line widths

In many cases, and especially when hollow-cathode lamps with low intensity currents are not used, the width of the emission line cannot be neglected in comparison with the width of the absorption line. This too causes bending of the analytical curves as SHIMAZU AND HASHIMOTO[5] have pointed out. This case will be dealt with in more detail in the present paper.

In further calculations we shall use the atomic absorption coefficient related to a single atom. The advantage of such a definition is that the concentration of atoms, N, appears explicitly in the Beer–Lambert law independently of the actual shape of the absorption line. The Beer–Lambert law may then be written as:

$$-\frac{\mathrm{d}I_\nu}{\mathrm{d}l} = \varkappa_\nu N I_\nu \tag{1}$$

or for a homogeneous layer, as:

$$I_{\nu,l} = I_{\nu,0} \exp\left[-\varkappa_\nu N l\right]$$

where $I_{\nu,l}$ is the intensity of radiation of frequency ν which penetrates a layer of thickness l with a concentration of atoms N, and $I_{\nu,0}$ is the intensity of the incident radiation. The analytical curve for this ideal monochromatic light is given by the simple equation:

$$A = \log I_{\nu,0}/I_{\nu,l} = \varkappa_\nu N l \tag{2}$$

where A is the absorbancy.

However, in practice, the profile of the emission line as well as that of the absorption line must be considered. Let us express[7] the line profiles with normalised functions $\mathrm{P}(u)$, assuming that the lines are symmetrical. The function $\mathrm{P}(u)$ may be a Gaussian function if the Doppler effect determines the line shape, or a resonance function in case of impact line broadening, or a Voigt function resulting from a combination of the former two. We shall consider the two extreme cases, *i.e.* a Gaussian function:

$$\mathrm{P}(u) = (\sqrt{\ln 2/\pi}/\delta_\mathrm{D}) \exp\left[-u^2 \ln 2/\delta_\mathrm{D}{}^2\right] \tag{3a}$$

and a resonance function:

$$\mathrm{P}(u) = \delta_\mathrm{L}/(u^2 + \delta_\mathrm{L}{}^2) \tag{3b}$$

In these equations $u = \nu - \nu_0$ is the distance from the line centre ν_0, and δ_D and δ_L are the line half-widths caused by the Doppler effect and impact broadening, respectively. Because the functions $\mathrm{P}(u)$ are normalised

$$\int_{-\infty}^{+\infty} \mathrm{P}(u)\,\mathrm{d}u = 1$$

the profile of the absorption line may be expressed as:

$$\varkappa(u) = \varkappa_0 \mathrm{P}(u) \tag{4}$$

and that of the emission line as:

$$I(u) = I_0 \mathrm{P}'(u) \tag{5}$$

where $\varkappa_0$ and I_0 are the integral absorption coefficient and the integral line intensity, respectively.

Substituting eqns. (4) and (5) into the Beer–Lambert equation, we obtain

$$\frac{\mathrm{d}I(u)}{\mathrm{d}l} = \varkappa(u)I(u)N = \varkappa_0 I_0 \mathrm{P}(u)\mathrm{P}'(u)N \tag{6}$$

This equation is valid for radiation in the frequency range $(u, u + \Delta u)$ assuming that $\varkappa(u)$ in this interval is constant. However, in atomic absorption spectrophotometry all radiation is measured after passing through the absorbing medium in the spectral band-width of the monochromator. Because this band-width is usually much greater than the width of the emission line, eqn. (6) can be integrated over the whole line profile, *i.e.* from $-\infty$ to $+\infty$.

$$\frac{\mathrm{d}I_0}{\mathrm{d}l} = -\varkappa_0 I_0 \int_{-\infty}^{+\infty} \mathrm{P}(u)\mathrm{P}'(u)\mathrm{d}u \tag{7}$$

This differential equation cannot be easily integrated over the path length l, because the line profile of the emitted line $\mathrm{P}'(u)$ is changed by absorption. This may be seen in Figs. 2 and 3, where the profiles of resonance-shaped lines in different depths of the absorbing medium are given. These were calculated on the assumption that both the emission and the absorption lines are resonance-shaped with different half-widths.

If both half-widths are identical, a minimum appears in the centre. With increasing absorption the minimum becomes deeper and the two side maxima draw apart. This behaviour is well known from line reversal in different light sources, *e.g.* with arcs. If the absorbing line is narrower than the emitted line the minimum is also narrower but the minimum value is not changed. However, for atomic absorption the opposite case with a broader absorption line is more common; in this case, side maxima appear next to the maximum in the line centre, as shown in Fig. 3.

Returning to eqn. (7), we may evaluate a "limiting value" of the absorption coefficient for a layer of very small optical depth. This limiting absorption coefficient determines the slope of the analytical curve and therefore also the sensitivity of detection. When resonance functions are substituted for both $\mathrm{P}(u)$ and $\mathrm{P}'(u)$, and eqn. (7) is integrated with respect to u, we obtain:

$$\frac{\mathrm{d}I_0}{\mathrm{d}l} = \varkappa_0 I_0 N/\pi(\delta_\mathrm{L} + \delta_\mathrm{L}')$$

When this equation is compared with eqn. (1), it follows that the limiting absorption coefficient is given by

$$\varkappa_\mathrm{lim} = \varkappa_0/\pi(\delta_\mathrm{L} + \delta_\mathrm{L}') \tag{8a}$$

Similarly, when Gaussian functions are substituted for both profiles, we obtain:

$$\varkappa_{\text{lim}} = \varkappa_0 \sqrt{\ln 2/\pi(\delta_D^2 + \delta_D'^2)} \tag{8b}$$

From eqns. (8a) and (8b) it follows that to attain maximum sensitivity, the half-widths of both lines must be kept as small as possible. If the emitted line width δ' is negligible in comparison with the absorption line width δ, eqns. (8a) and (8b) become the relations derived for monochromatic light at the maximum of the absorption line.

$$\varkappa_{\text{max}} = \varkappa_0/\pi\delta_L \tag{9a}$$

$$\varkappa_{\text{max}} = \varkappa_0\sqrt{\ln 2/\delta_D^2\pi} \tag{9b}$$

It is also evident that for Gaussian profiles the emitted line width may be more easily neglected than for resonance profiles because squares of the line widths are compared.

According to eqn. (7) the profiles P(u) and P′(u) are interchangeable, *i.e.* the slope of the analytical curve does not depend on whether the absorption line or the emission line is broader. Equations (8a) and (8b) may also be used for continuous light sources, so long as the apparatus function may be approximated by resonance or Gaussian functions[8]. GIBSON, GROSSMAN AND COOKE[9] calculated numerically the decrease of absorbance with a continuous source for resonance-shaped absorption lines and a Gaussian apparatus function. According to their results, when a monochromator with a spectral band width of 0.16 Å is used, the absorbance decrease is between 20% for potassium and 90% for copper. They did not consider the dependence on the optical depth, however.

To evaluate this, eqn. (7) must be integrated along the path length, l:

$$I_{0,l} = I_{0,0} \int_{-\infty}^{+\infty} \mathrm{P}'(u) \exp\left[-\mathrm{P}(u)Nl\right] \mathrm{d}u \tag{10}$$

This equation has been solved in connection with investigations on resonance lamp radiation. LADENBURG AND LEVY[10] present a formula for Gaussian profiles with equal line widths. For resonance profiles with equal line widths the solution may be expressed as:

$$I_{0,l} = I_{0,0}\delta_L[1 + \sum_{k=1}^{\infty} (-1)^k a^k (2k-1)!/2^k(k!)^2]$$

where $a = \varkappa_0 Nl/\pi\delta_L$.

MITCHELL AND ZEMANSKY[11] have tabulated values of the total absorption, $1 - T = 1 - I_{0,l}/I_{0,0}$, for Gaussian profiles with different line-width ratios and for different optical depths. For resonance profiles we solved eqn. (10) numerically; in Fig. 4 the shapes of analytical curves for different half-width ratios are given. It can be seen that the bending of the analytical curves increases as the half-width of the emission line increases. Their shape may be expressed by the following empirical relationship:

$$A = \varkappa_0\varkappa_{\text{lim}} Nl/(1 + c\varkappa_0 Nl/\delta_L) \tag{11}$$

where $\varkappa_{\text{lim}}$ is the limiting absorption coefficient given by eqn. (9a) and c is a constant whose numerical value is 0.058. The agreement with the exact value may be seen from Fig. 4.

The resonance broadening

From eqns. (9a) and (9b) it can be seen that even when the width of the emission line is negligible in comparison with the width of the absorption line, *i.e.* in the case of the so-called peak absorption, the analytical curves may bend if the half-width of the absorption line increases with increasing concentration of the element. This can occur only because of resonance broadening, for which the following formula holds

$$2\delta = RC_3N \qquad (12)$$

where $C_3 = e^2f/2mv$. For the constant R, different values are given by the several existing theories of resonance broadening. According to the Weisskopf theory, the value is $1/\pi$; according to Lindholm, $\frac{1}{2}$; according to Furssow and Wlassow, $4/3\pi$; and according to the statistical theory[12], $\frac{1}{3}$. However, these values differ only insignificantly.

Let us further consider the flame as an absorbing medium. The concentration of free atoms depends on the concentration of the particular element in the solution sprayed, on the atomiser yield, on the composition of the flame gases and on the formation and dissociation of molecules in the flame. For sodium, the following relationships connecting the concentrations in the solution and in the flame have been found experimentally:

$N = 6.2 \cdot 10^{14}C$ (ref. 13); $N = 7.4 \cdot 10^{13}C$ (ref. 14);
and $N = 2.2 \cdot 10^{14}C$ (ref. 15)

where C is the molar concentration of sodium in the sprayed solution. These equations indicate the upper limit, because sodium has no tendency to form compounds in the flame. We shall therefore use the relationship:

$$N = 10^{14}C \qquad (13)$$

Expressing the resonance line width, according to Weisskopf, as wavelength and substituting in eqn. (13), we obtain:

$$\Delta\lambda = 4.484 \cdot 10^{-14}\lambda^3 fN = 4.484\lambda^3 fC$$

This means that when molar solutions are atomized the corresponding resonance line

TABLE I

HALF-WIDTHS OF SOME LINES IN AN ACETYLENE–AIR FLAME[16]

Wavelength (Å)	*Half-width (Å)*
Na 5890	0.0425
Li 6707	0.066
Tl 5350	0.0255
Ca 4227	0.0255

width should be of the order of 10^{-4} Å. This value is several orders smaller than the width caused by a Doppler effect and collision broadening due to Van der Waals forces (see Table I[16]). Resonance broadening therefore should not influence the width of the absorption line and could not cause bending of the analytical curves.

However, it seems that these theoretical line widths differ greatly from those found experimentally. In earlier work the width of there sonance line was derived from measurements of the total absorption, resonance-shaped line profiles being assumed. The experimental values found were approximately one order higher than the theoretical values. In more recent work in which the line width was measured directly the difference is about three to four orders. This may be clearly seen from Table II which is taken from the work of MOSER AND SCHULZ[17].

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED RESONANCE BROADENING

Line	*Reference*	*Line width*	*(cm)*
		Measured	*Calculated*
Na 5896	18	$0.8 \cdot 10^{-26}N$	$3.0 \cdot 10^{-27}N$
5890		$1.3 \cdot 10^{-26}N$	$6.2 \cdot 10^{-27}N$
K 7700	19	$6.3 \cdot 10^{-26}N$	$7.1 \cdot 10^{-27}N$
7665		$6.2 \cdot 10^{-26}N$	$14.2 \cdot 10^{-27}N$
Rb 7948	20	$1.3 \cdot 10^{-26}N$	$7.4 \cdot 10^{-27}N$
7800		$2.0 \cdot 10^{-26}N$	$14.6 \cdot 10^{-27}N$
Cs 8943	21	$2.2 \cdot 10^{-26}$	$10.6 \cdot 10^{-27}N$
8521		$3.5 \cdot 10^{-26}N$	$18.7 \cdot 10^{-27}N$
Na 5896	22	$1.7 \cdot 10^{-24}N$	$3.0 \cdot 10^{-27}N$
5890		$2.2 \cdot 10^{-24}N$	$6.2 \cdot 10^{-27}N$
K 7700	23	$7.7 \cdot 10^{-24}N$	$7.1 \cdot 10^{-27}N$
7665		$6.0 \cdot 10^{-24}N$	$14.2 \cdot 10^{-27}N$
Rb 7948	24	$1.0 \cdot 10^{-24}N$	$7.4 \cdot 10^{-27}N$
Cs 4555	17	$1.8 \cdot 10^{-24}N$	$5.1 \cdot 10^{-29}N$

The experimental material so far published is too scarce to allow definite conclusions. However, if the experimental values are correct, resonance broadening should appear when 0.1—0.01 *M* solutions are sprayed and this is already in the working range of atomic absorption analysis. The effects of resonance broadening on the shapes of analytical curves may differ. If the width of the absorption line is fully determined by resonance broadening and if the width of the emission line is negligible, the analytical curves should be parallel to the concentration axis; this becomes evident when eqn. (12) is substituted in the analytical curve equation for monochromatic light (eqn. 2). If, however, the width of the emission line is not negligible compared with that of the absorption line, resonance broadening may actually straighten the analytical curves.

The line shift

An increasing concentration of atoms in the flame also causes a proportional shift of the line maximum. Let us consider the change of the absorption coefficient in the case of an ideally monochromatic emission line. When a shift $\Delta\lambda_{\max}$ is substituted in the resonance profile, *e.g.*

$$\varkappa = \frac{\varkappa_0}{\pi} \frac{\delta_L}{\Delta\lambda^2_{\max} + \delta_L{}^2}$$

it may be seen that the lowering is considerably only when the shift is commensurable with the line half-width δ_L.

Experimental data, so far, are very rare. MOSER AND SCHÜLZ[17] studied resonance broadening of the Cs 4555 Å line and found a shift of the maximum, given by the relationship:

$$\Delta\lambda_{\max} = + 10^{-24}N$$

where $\Delta\lambda_{\max}$ is a shift in centimeters.

SHIMAZU AND HASHIMOTO[5] reported a shift when registering profiles of the absorbed Na 5896 Å line with a Fabry–Perot interferometer. On the assumption that the approximate relationship (13) holds under their working conditions, the following equation may be derived from their results:

$$\Delta\lambda_{\max} = + 10^{-22}N$$

From eqn. (13) and from the line half-width given in Table I, it is evident that the resonance line shift should cause bending of working curves when 0.01 M or less solutions are sprayed.

CONCLUSIONS

From all these considerations, it follows that the bending of analytical curves in atomic absorption spectroscopy may be caused by several factors: resonance broadening and resonance shift of the absorption line, the ratio of the line widths as well as their hyperfine structure all play a part. Which of these factors will prevail depends on the particular conditions and may be estimated. However, for exact evaluation, a more precise knowledge of the line widths, resonance broadening constants and resonance line shift constants is necessary.

SUMMARY

Some factors affecting the shape of analytical curves in atomic absorption spectroscopy are considered and the influence of the emission and absorption line profiles is discussed in detail. An empirical equation expressing the analytical curves for different ratios of emission line width to absorption line width is given. The possible influence of resonance line broadening and resonance line shift in atomic absorption flame photometry is also discussed.

RÉSUMÉ

Les auteurs ont examiné certains facteurs pouvant modifier les courbes analytiques de spectroscopie d'absorption atomique. Une équation semi-empirique est proposée, exprimant les courbes analytiques pour différents rapports entre largeur des raies d'émission et largeur des raies d'absorption.

ZUSAMMENFASSUNG

Einige Faktoren, die die Gestalt von analytischen Kurven bei der atomaren Absorptionsspektroskopie beeinflussen, werden betrachtet und der Einfluss des Emissions- und Absorptions-Linienprofils im einzelnen diskutiert. Es wird eine halbempirische Gleichung für die analytischen Kurven für verschiedene Verhältnisse der Emissions- zu Absorptionslinienweite angegeben. Der mögliche Einfluss einer Verbreiterung und Verschiebung der Resonanzlinie bei der atomaren Absorptionsflammenphotometrie wird ebenfalls diskutiert.

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THE NATURE OF LIGHT

PART I. A PHYSICAL MODEL OF THE PHOTON

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The object of this paper is to describe a model of light which can be interpreted physically. It is intended that this concept will fit the mathematical models described in wave mechanics. It is hoped that it also explains why light sometimes behaves like a particle, and at other times like a wave.

IS LIGHT A WAVE OR A PARTICLE?

A number of classical experiments have been described which give contradictory results. Some suggest that light is a wave form of energy. Such experiments include the observation of interference fringes, the polarization of light, and diffraction of X-rays and visible light. But equally conclusive experiments indicate that light is particulate. These experiments include Compton scattering, Einstein's photoelectric effect and Raleigh's detection of weak gamma emission over long distances.

The conclusions drawn from the results of these experiments seem to be completely contradictory. We are faced with an energy form which appears to become both a wave and a particle almost at will. Although the mathematical treatment can ignore this wantonness, it is also inescapable that there must be a physical explanation for these results.

An attempt to do this is made with the following model. This depicts a photon which would have properties which could be interpreted as wave-like and particle-like and plausibly explains many of the apparent contradictions in the properties of light.

THE PROPOSED PHYSICAL MODEL OF A PHOTON

It has long been assumed that the photon has zero electrical charge and zero mass. However certain considerations, such as the electromagnetic character, and the Compton effect, indicate that it has both charge and mass.

The model may therefore be envisioned as in Fig. 1. It must be emphasized that Fig. 1 is not intended to portray the actual physical shape of the photon, only the arrangement of the component parts.

It is made up of one − and one + charge, each charge equal to half the charge of an electron and a positron respectively. The charges rotate around the locus of the center of mass, each producing a magnetic field. The locus of either of these charges will describe a distorted sine wave. This produces a "wavelength" which is equivalent to the distance travelled by the center of mass during a complete revolution of the particle and a wavenumber, which is the number of revolutions per unit-time. The energy of this particle has two forms, *i.e.*, translational and rotational.

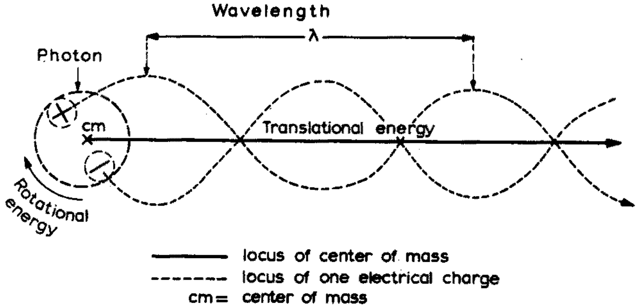

Fig. 1. Proposed model of a moving photon.

Translational energy

The velocity of the particle is equal to the speed of light. Collisions between photons and other particles are elastic, causing transfer of translational energy to be fairly uncommon. The momentum and velocity of the particle therefore rarely changes during reflection or simple collision.

The elastic collisions enable the particle to maintain a constant velocity in spite of collisions with atoms, etc. However its electrical charges should allow some interaction with its environment causing a change in velocity in different transparent media. We can conclude therefore that its velocity is a function of its environment. Also, unless other interaction takes place, it should be a function of its velocity at the point of origin.

Rotational energy

This is the energy involved in the electrical charges and gravitational forces rotating around the center of mass. The quantity of energy involved is defined by quantum mechanics as $E = h\nu$. It will be noted that when $\nu = 1$ then $E = h$, and Planks constant is the rotational energy of the photon at unit-wavenumber. This is of course a fundamental physical constant and would explain the importance and widespread application of Planks constant.

Transfer of rotational energy is common between the photon and other interacting bodies. The energy involved is governed by the standard equation $E = h(\nu_1 - \nu_2)$, where ν_1 and ν_2 are the wavenumbers before and after absorption. After absorption, the photon may be re-emitted as radiant energy giving rise to fluorescence, phosphorescence or infrared radiation. Any residual transferred rotational energy which is not re-emitted as spectral energy probably emerges ultimately as heat. If the photon falls into the nucleus of the absorbing atom, its translational energy may also be transferred to the absorbing atom and emerge as heat.

It is also proposed that I.R., visible, UV, gamma rays and X-rays are all similar particles differing only in their rotational energy. The physical properties of these different light-forms, such as penetrating power, is a function of how easily their energy is transferred (absorbed) to the surrounding medium. This would be a function of the wavelength of the photon which must be sympathetic to the absorbing material before absorption can take place. As can be seen from the model, the wavelength and the rotational energy of the photon are inversely related. Hence these energy forms, I.R., UV, etc., which differ only in wavelength can be interpreted as being the same particle with different rotational energies.

If a medium does not absorb light at certain wavelengths, it is transparent to that light. The wavelength range of the light absorbed is governed by the difference in energy levels of absorbing molecules or atoms. For example, vibrational or rotational energies are low and absorbed light with low rotational energy, *i.e.*, infrared. Electronic energies are higher and light of higher energy is absorbed, *i.e.*, ultraviolet. Inner shell electrons require even more energy to become excited and can therefore only absorb light with high rotational energy such as X-ray.

WAVE MOTION OF THE MODEL

There have been observed in light studies, properties ascribed to wave motion. These phenomena include X-ray diffraction, interference fringes and polarization. The behavior of the proposed model in these phenomena is described below.

X-ray diffraction

The standard proof of the Bragg formula $n\lambda + 2d\ Sine\ \theta$ is indicated below.

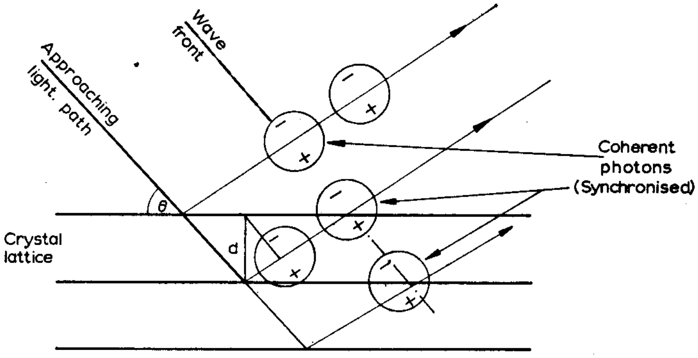

Fig. 2

A coherent wave front occurs when the photons reinforce each other, *i.e.* when their charges are synchronized or in phase. Using the standard Bragg proof, this occurs when $n\lambda = 2d\ Sine\ \theta$, where θ is the wavelength of the X-rays, but is interpreted here as the distance travelled during one complete revolution of the photon. When $n\lambda = 2d\ Sine\ \theta$, then the photons which would constitute the wave front would be out of phase. They would repel each other, and no reinforcement would take place, *i.e.*, we would observe the absence of photons — or darkness.

Interference fringes

It has been stated that "each photon then interferes only with itself. Interference between different photons never occurs"[1]. Although this concept fits the mathematics of the phenomenon, it is hard to conceive the physical interpretation.

Recently a significant contribution was made to the understanding of this phenomenon. Interference fringes were produced by superimposing two independent maser light beams, polarized to be parallel to each other[2]. This result supports a classical interpretation of interference fringes, *i.e.* by the interaction of the independent light beams, but seem to refute the idea of such fringes being caused by the interaction of photons with themselves since this type of interaction should require only one light beam to be present. It would not be expected that two independent light beams would interact. What takes place to produce interference fringes is not yet clearly understood, but the interaction of magnetic fields associated with photons would explain much of the observed data.

In order to explain the occurrence of interference fringes it is proposed that a light beam is composed of groups of photons, coherent within each group, but incoherent with other groups — even of the same wavelength. When such a group of photons reaches a beam splitter, the group is divided into two paths in the conventional way and later recombined. With light in wave motion, interference fringes are observed under these conditions: reinforcement takes place when the path length difference is $n\lambda$, but interference (or dark rings) occurs when the path difference is $(n + \frac{1}{2})\lambda$. In the model, it can be seen that when the path length difference is $n\lambda$, then the photons come together in phase and attract each other producing a light fringe. When the path length difference is $(n + \frac{1}{2})\lambda$ the photons are out of phase and repel each other. The absence of photons produces a dark ring. This is illustrated in Fig. 3.

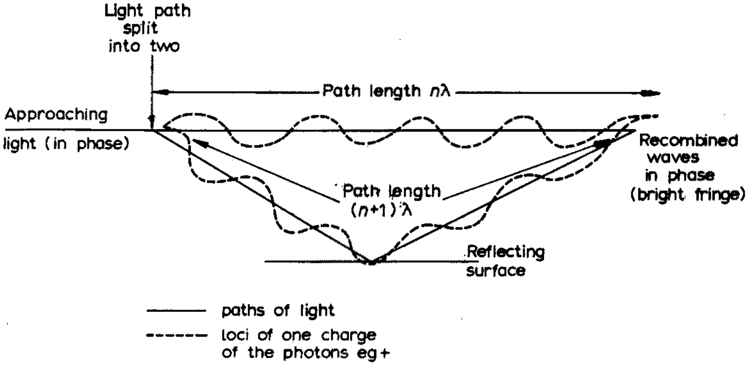

Fig. 3. Interference fringes.

It will be noted in the production of interference fringes using superimposed laser beams that these beams were polarized parallel to each other. The necessity of this step could have been predicted from the model described in this article, because this model requires that the charges be correctly oriented in three dimensions before interaction takes place. Further, information could be obtained on the degree of interaction between the photons by decreasing the synonymity of the polarization between the two beams until no further interference was noted. This would indicate how much out of phase the photons must be before interference (repulsion) is noted.

Polarization

Polarized light can be produced under numerous conditions, *e.g.* using various crystals, Nicol prisms, double refraction, light-scattering and reflection. For this phenomenon the classical pictorial representation is of light waves vibrating at right angles to the director of propagation. Polarization takes place when the light is separated into two beams, the vibrations of which are in planes which are mutually perpendicular.

With the proposed model we can conceive of a similar situation. The direction of propagation of the light is the direction of translational motion of the center of mass. The vibration noted in the classical model is reproduced by the rotating charges of the photon. As with classical polarization vibrations, the direction of the rotation of the electrical charges on the proposed model is not specified, but can be resolved into two directions mutually perpendicular to each other and to the direction of translational motion of the center of mass. The properties of polarized light can be interpreted in terms of the proposed model by substituting this model for the classical vibrating light wave used in current interpretations.

PARTICLE MOTION OF THE PROPOSED MODEL

The most convincing evidence of the existence of light as a particle includes Compton scattering, Einstein's photoelectric effect and Raleigh's work with γ-rays. The behavior of the proposed model under these conditions is given below.

Compton scattering

It was observed by Compton that collisions took place between light particles and electrons.

From the angles of scatter of the photon and the electron, Compton calculated that the energy of the photon was $h\nu + h\nu/c$ where $h\nu/c$ was the momentum of the photon. It is important to note that Compton had to include a term for the momentum of the photon in his calculations. Substituted in the proposed model for the photon, it can be seen that $h\nu$ is the rotational energy of the photon and $h\nu/c$ is its momentum.

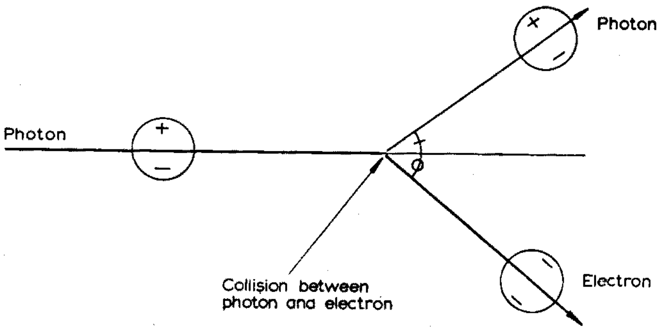

Fig. 4. Compton scattering.

Further, if the momentum is considered in classical terms, it is mc where m is the mass of the photon and c is its speed.

Comparing this with Compton's calculations,

$$\frac{h\nu}{c} = mc$$

$$\text{or } h\nu = mc^2$$

$$\text{or } E = mc^2$$

As indicated, this relationship develops into Einstein's mass and energy relation. It also indicates that the mass is proportional to ν, the wavenumber. This shows the particle has variable mass. However, it may only indicate that the forces used to measure mass vary under different electrical environments. This difficulty emphasises our lack of understanding of the real significance of mass and energy.

Photoelectric effect

It was observed by Einstein that if a metal surface is negatively charged, then irradiated with UV light, that electrons are emitted. The required wavelength of the light is a function of the metal used for the surface. Einstein proved the relationship $h\nu_0 = \phi_e = \cdot Kb_0$ where ν_0 is the minimum wavelength of the light and ϕ is the work function to release the electron. According to wave theory the excess energy of the emitted electrons should be a function of I_0, the intensity of the UV light. It was found, however, that the rate of emission of electrons was proportional to I_0, but that their K.E. was a function of the wavelength of the light, as $\frac{1}{2}mv^2 = Ve = h(\nu - \nu_0)$.

If $h\nu > h\nu_0$ emission takes place. This was considered proof of the particulate form of light, since if it was a wave form it would dissipate its energy with increasing distance from the source and would be dependent on I_0. This photoelectric effect has also been observed with X-rays and γ-rays.

If we substitute our model for the photon, we see that its rotational energy is involved. When this energy is in excess of the threshold energy of the electrons, emission takes place. Unless prior absorption takes place, it is independent of the distance travelled by the photon from its source. Also we see that the excess rotational energy of the photon is translated into kinetic energy of the electron, and the equation $\frac{1}{2}mv^2 = Ve = h(\nu - \nu_0)$ still applies.

Further, when I_0 is increased, the number of photons making up the light beam is increased. This in turn would liberate more electrons from the metal surface per unit-time but would not change the energy of each electron. This interpretation fits in with the observed experimental evidence.

Rutherford's observations

Further amplification of the photoelectric effect was made by Rutherford. He calculated that the energy emitted as γ-rays from 1 g of radium is about $4.7 \cdot 10^4$ ergs. At a distance of 100 m, it should require 10^{15} sec to build up sufficient energy to be detected, according to wave theory. However these rays were in fact observed immediately. His evidence strongly supports the contention that light is particulate and not a wave form, since light in a wave form would have dissipated most of its energy over this distance.

Interpretation in terms of the proposed model is as follows. Its energy would remain constant until some interaction with another body took place. This would be independent of the distance travelled. Hence the energy of individual photons would remain constant, however, it must be remembered that a beam of such photons would spread out with increasing distance from the source. The total energy per unit cross-sectional area of the light would diminish with this distance and would follow the laws governing wave motion. Hence, although the total energy per unit cross-sectional area diminishes according to wave form energy, the energy in each particle remains constant until interaction takes place.

CONCLUSION

The model of a photon presented in this thesis provides a starting point for understanding the conflicting properties of light. Part II of this discourse will describe the relationship between protons and electrons. It is hoped that this will show a close relationship between photons and the other fundamental particles of matter.

SUMMARY

The dualistic behavior of light has always presented a problem to scientists in general, and spectroscopists in particular.

A model of a photon has been proposed which has mass, and a matched positive and negative charge. The properties of the proposed particle would be expected to behave as a particle usually behaves, but under certain circumstances a group of such particles would exhibit wave-like properties. Several classical phenomena are examined and interpreted in terms of the proposed model.

RÉSUMÉ

Le comportement dualistique de la lumière a toujours posé un problème pour les savants en général, et pour les spectroscopistes en particulier. Un modèle de photon a été proposé, avec une masse et une charge positive et négative. Plusieurs phénomènes classiques ont été examinés et interprétés selon le modèle proposé.

ZUSAMMENFASSUNG

Das dualistische Verhalten des Lichts ist schon immer ein Problem für Wissenschaftler im allgemeinen und für Spektroskopiker im besonderen gewesen. Es wird ein Modell des Photons vorgeschlagen, das eine Masse und eine positive und negative Ladung besitzt. Die Eigenschaften der vorgeschlagenen Teilchen sind so, wie es normalerweise der Fall ist; aber unter gewissen Umständen kann eine Gruppe solcher Teilchen Welleneigenschaften herausstellen. Verschiedene klassische Phänomene werden geprüft und im Hinblick auf das vorgeschlagene Modell interpretiert.

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THE USE OF POORLY RESOLVED GAS CHROMATOGRAPHIC CURVES FOR THE ANALYSIS OF BINARY MIXTURES OF PETROLEUM FRACTIONS

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Chromatographic analyses are used to great advantage in quantitatively determining lower boiling components of petroleum for which reasonably good resolution is possible. For petroleum fractions of broader range many devices have been used to allow a quantitative analysis. Examples are the use of subtractive techniques, pre-fractionation and detection of back-flushed fractions, etc. Qualitative characterization of these broad-range fractions has been accomplished by chromatographically simulating the true boiling point curve and by other similar approaches.

The success of all of these techniques poses the question whether there is enough information in simple, single chromatograms of broad-range petroleum fractions to characterize the fractions both qualitatively and quantitatively. No work designed specifically to explore this question seems to have been reported. In this paper we have taken the simplest case, the quantitative resolution of a binary petroleum blend into its constituent fractions, and shown the practicality of such an approach.

The simple case is explored first not only because it represents a fundamental starting point but also because many common analyses fit these conditions and the solution may be applied with a minimum of calibration and calculation and can serve as a useful field method. The more complex analyses would require machine calculation.

THEORETICAL CONSIDERATIONS

The shape of the peaks obtained in a usual chromatographic analysis may be described with varying degrees of exactitude by any of several distribution functions. One such is given by PORTER *et al.*[1]:

$$C_i = (N^{\frac{1}{2}}/V_{Ri^\circ})\,(w_i/\sqrt{2\pi})\,\exp\left[-(N/2)\,(1-V_0/V_{Ri^\circ})^2\right] \tag{1}$$

in which C_i = concentration of constituent i entering detector, N = number of theoretical plates in column, V_{Ri° = retention volume of constituent i, V_0 = volume passed through column, and w_i = initial weight of constituent i.

The derivation of this equation from the binomial theorem has been described in detail by DAL NOGARE AND JUVET[2]. This particular equation was chosen because there is no need to reproduce its derivation, because it contains the term w_i, which is usually of fundamental significance to analytical chemists, and because the following discussion, while equally applicable to any of the other possible distribution functions, follows most simply from it.

When N and V_{Ri° are constant and the sample composition is fixed, eqn. (1) may be rewritten in the form:

$$C_i = QW_s[\mathrm{f}(V_0)] \tag{2}$$

where W_s = sample weight and $\mathrm{f}(V_0) = \exp[a(1 - V_0/b)^2]$, where a and b are constants. The area under any segment of this curve is:

$$A_i = \int_{V_{0_1}}^{V_{0_2}} C_i \mathrm{d}V_0 = QW_s \int_{V_{0_1}}^{V_{0_2}} \mathrm{f}(V_0)\mathrm{d}V_0 = K_i W_s \tag{3}$$

Whenever a sample is composed of several fractions the resulting elution curve will be given by the sum of the individual curves:

$$C_T = C_1 + C_2 + \ldots + C_j$$

and the area under any segment of the resulting curve will be given by:

$$A_j = K_1 W_{s_1} + K_2 W_{s_2} + \ldots + K_n W_{s_n} \tag{4}$$

The weight (W_s) of each fraction in the blend is given by the product of the sample weight of the blend (W) and the fractional contribution of each fraction (F), so that eqn. (4) may be rewritten:

$$A_j = W(K_1 F_1 + K_2 F_2 + \ldots + K_n F_n) \tag{5}$$

For a blend of two fractions $F_1 + F_2 = 1$ and this equation, together with an equation of the form of (5) whose constants have been determined experimentally, will serve to determine F_1 and F_2.

The derivations just given seem trivial but they will serve the further discussion by demonstrating that, for any particular sample, when N and V_{Ri° are constant, the area under the chromatographic elution curve *for the same interval* of V_0 is directly proportional to the weight of the sample no matter what the degree of resolution of individual components. Thus, our need is to always treat an invariant interval of V_0 although previous experience might suggest the methods of PECSOK[3] or BARTLETT AND SMITH[4] .These latter devices are designed to assign a proper area to a single peak which, in our case, is not necessary. It is obvious that one may be entirely arbitrary in selecting the interval of V_0 and this interval may be taken infinitesimally small (a line) or sufficiently large to include several peaks. Selection of a proper interval will be discussed presently.

Equation (5) contains the weight of injected sample. This value is not always easy to assess and it is usually more convenient to eliminate the necessity for its use. For a binary blend we can do this by measuring the areas of two intervals of V_0 and utilizing their ratio in the further calculations.

$$R = \frac{A_a}{A_b} = \frac{(K_{a_1} F_1 + K_{a_2} F_2)}{(K_{b_1} F_1 + K_{b_2} F_2)} \tag{6}$$

This equation may be expanded to give:

$$R = \frac{[\bar{R}(R_1 - R_0)\bar{F}_1 + R_1(R_0 - \bar{R})]F_1 + R_0(\bar{R} - R_1)\bar{F}_1}{[(R_1 - R_{10})\bar{F} + (R_0 - \bar{R})]F_1 + (\bar{R} - R_1)\bar{F}_1} \tag{7}$$

where $R_0 = R$ at $F_1 = 0$ (pure fraction 2), $R_1 = R$ at $F_1 = 1$ (pure fraction 1), and $\bar{R} = R$ at $F_1 = \bar{F}_1$ (a blend of 1 and 2).

In this equation R is seen to be a function of F_1 (or F_2) and independent of sample size. Since this is the case, the composition of any blend may be determined from a measurement of R for that blend, either through the use of eqn. (7) or by means of a working curve constructed from measurements made on several blends of known composition. It should be realized that eqn. (7) involves the minimum number of points theoretically needed to establish the curve and does not guarantee the reliability of the curve should there be error in determining the points. Error cannot very well be excluded from experimental measurement and so it is much better to construct a curve from many points. This may be done from a statistical treatment of eqn. (7) using several experimental values of R for each point. Such a treatment ignores error introduced in making the standard blend but ordinarily its composition can be accurately determined to 4 or 5 significant figures. Further refinement may be had by choosing a standard blend in the anticipated concentration range of subsequent samples. The form of the curves obtained by these procedures is shown later.

In the foregoing discussion it has been tacitly assumed that eqn. (1) properly describes the elution curve and that N and $V_{Rt}{}^{\circ}$ can be conveniently held constant throughout a series of calibrations and analyses. Of course, these conditions are not achieved without some attention to detail and to the particular system. Many of those factors which influence N and $V_R{}^{\circ}$ are capable of close control. A discussion of the detector and column variables involved is given by DAL NOGARE AND JUVET[2]. A more concise statement of detector parameters is available[5] which will aid those who have occasion to use detectors of more than one type. In addition, if the areas are measured from a strip-chart recording, then recorder sensitivity, response time and chart speed must also be properly controlled. Practically, all of these conditions may be readily satisfied with reasonable care and constitute no serious drawback.

A more insidious difficulty can be present. The partition coefficient is dependent upon the activity coefficient of the solute in the partitioning liquid. For any constituent the activity coefficient may vary with concentration and for unresolved constituents the activity coefficients of both may vary with the concentration of either one. Since the relative concentration of any particular constituent is determined entirely by the composition of the blend, concentrations may be controlled only indirectly by regulating the quantity of injected material. Although it is a demonstrable fact that in many cases retention volumes can be changed by varying concentration or by introducing an adjacent, poorly resolved constituent, experiment has shown that this is not the case when small samples of petroleum fractions are analyzed. However, any attempt to apply these techniques to other systems would have to be preceded by a demonstration that N and $V_{Rt}{}^{\circ}$ did indeed remain constant for all compositions of those systems. Finally, the applicability of eqn. (1) and variation of N and $V_{Rt}{}^{\circ}$ may be influenced by the amount and rate of vaporization of the sample in the injection port and by the presence and linearity of flow splitters associated with these ports. These effects have been discussed by PORTER *et al.*[1], KIESELBACH[6] and others whose findings are summarized by DAL NOGARE AND JUVET[2]. Injection port effects may be highly variable even for different weights of identical samples and they must be minimized for individual systems. Again, in the case of petroleum fractions, experiment indicates that with reasonable care good results can be obtained with a wide variety of injection port geometry.

As indicated in the derivation, the choice of a proper interval of V_0 is entirely arbitrary. Further examination of requirements indicates that this is not quite true. Areas must be chosen in such a way that differences between the constituent fractions are emphasized. However, this may be accomplished in a variety of arbitrary ways. In conventional analyses the interval of V_0 is either chosen as a point (peak height measurements), as an interval just large enough to contain the peak or such an interval as described in the procedure of PECSOK[3]. Experience would suggest one of these assignments. However, as emphasized, we are not limited to measurements of single peaks and so may use other criteria for a choice of interval. In those cases where there is little base-line noise and where very good reproducibility of $V_R°$ and N can be achieved it is best to measure the curve height at some point, V_0, for this will allow maximum variation of R or maximum differences among the constants of eqn. (7). On the other hand, for certain cases where good reproducibility of conditions is not assured (*e.g.* when programming temperature) it is more advisable to choose intervals of V_0 which contain a large area of several peaks bounded by pronounced and relatively wide minima. In these cases the entire curve may be displaced slightly along the V_0 (time) axis and such a choice of interval will produce area variations which are but a small fraction of the total area and will consequently result in minimum error. This latter measurement will also prove more accurate whenever $V_R°$, N and eqn. (1) are affected by those uncontrollable factors previously discussed. Again, care should be taken in choosing areas so that the constants or the values of R are sufficiently different to give over-all sensitivity to the method.

EXPERIMENTAL

To check the applicability of the mathematical conclusions, various measurements of area and height were made for several mixtures of 2 synthetic blends. The blends were mixtures of *n*-octane, *n*-nonane and mixed *n*-octenes. Since the purity of these compounds did not affect any subsequent calculations, it was not determined. The compositions of the blends and mixtures are given in Table I.

TABLE I

COMPOSITION OF STANDARD BLENDS AND TEST MIXTURES (wt. %)

	n-Octane	*n-Nonane*	*n-Octene*	*Blend 1*	*Blend 2*
Blend 1	11.49	64.75	23.76		
Blend 2	72.99	15.23	11.78		
Mixture 1				23.06	76.94
Mixture 2				30.13	69.87
Mixture 3				65.75	34.25
Mixture 4				74.71	25.29

The measurements were made with a Wilkens Model 600, Hy-Fi, flame-ionization chromatograph (Wilkens Instrument and Research, Inc., Walnut Creek, California). The column was 12′ × 0.09″, packed with 10% Carbowax 20M supported on 80–100 mesh G-Cel. The column was maintained at a constant temperature of 135°. The carrier gas was helium at a rate of 3 ml/min. The hydrogen was provided from a Wilkens hydrogen generator at a rate of 25 ml/min. Samples were introduced by means of a 1-μl Hamilton syringe. Under these conditions, complete resolution of the components was not achieved.

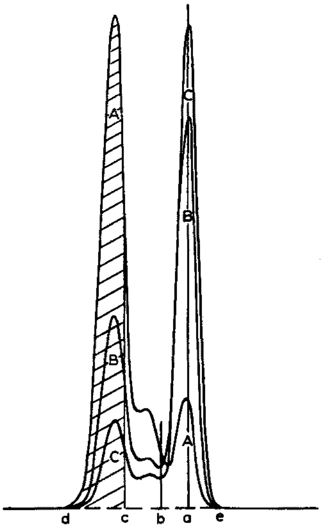

Fig. 1. Vertical axis, recorder response; horizontal axis, retention volume; caption, actual elution curves for the system: (A) Blend 1, (B) Mixture 2, (C) Blend 2.

Figure 1 shows the peaks produced by Blends 1 and 2 and Mixture 2. In order to use the ratio of two heights, measurements of curve height were made at points *a* and *b*. Two areas were produced by dividing the area under the entire curve along the line *c*. The position of this latter line was chosen so that neither interval of V_0 would correspond to any ordinarily encountered in conventional analyses. In so doing, all normal considerations for choice of area were violated and minimum error could not be expected to result. These measurements produced the following ratios.

$$R_h = \frac{\text{curve height at point } a}{\text{curve height at point } b}$$

$$R_a = \frac{\text{area from point } c \text{ to point } e}{\text{area from point } d \text{ to point } c}$$

From the values of R_h and R_a obtained with Blends 1 and 2 and Mixture 2, curves of R *vs.* weight fraction of Blend 1 (F_1) were made (Fig. 2). From the equation relating R and F_1 and measurements of R obtained with Mixtures 1, 3 and 4, the values of F_1 for these mixtures were calculated (Table II).

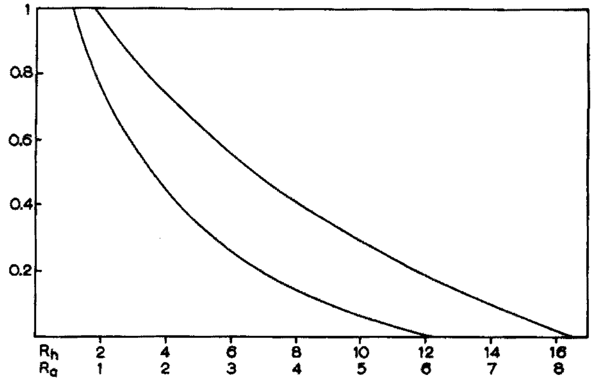

Fig. 2. Vertical axis, weight fraction of component 1 (F_1); horizontal axis, response ratio; caption, height and area response ratios as a function of F_1 for mixtures of Blends 1 and 2.

TABLE II

WEIGHT FRACTION OF BLEND 1 (F_1)

	Blended	*Calculated from R_h*	*Calculated from R_a*
Mixture 1	0.23	0.22	0.21
Mixture 3	0.66	0.67	0.59
Mixture 4	0.75	0.78	0.72
Average error		3.3%	7.5%

The constancy of the ratios R_h and R_a for samples of varying size was checked by injecting replicate samples of Mixture 3 of 0.05, 0.1, 0.15, 0.2 and 0.25 µl volume. Variation of R_h was $\pm 1.4\%$ while that of R_a was $\pm$ 0.85%.

DISCUSSION

Figure 3 shows chromatograms obtained in a typical practical application. Samples of oil were recovered from a well core. The oil was known to be either Mid-Cypress or Upper-Cypress crude contaminated with an unknown amount of diesel oil which had invaded the core from the drilling mud. During recovery from the core considerable light ends were lost from the oil sample, and although comparison standards were available for the two crudes and the diesel oil, it was not expected that they were any longer representative of the core sample in the light-end region. The problem was to find what proportion of the recovered sample was actually crude oil.

Although the problem involved 3 components it was possible to select areas of the 2 crudes which gave identical ratios so that for subsequent purposes the crudes could be considered identical. These areas were chosen in the boiling point range where loss was considered unlikely, a region impossible to resolve chromatographically. Figure 3 shows this region for the crude, the diesel oil and the mixture. The chosen interval of V_0 is indicated. An exact quantitative analysis was possible. The accuracy cannot be judged in the absence of standards but the results were verified in a semi-quantitative way by comparison with fluorescent spot tests and X-ray fluorescence determinations of the sulfur content and were used to make subsequent drilling decisions. The chromatographic results were available within a few hours.

Such an application typifies the unique position of the chromatographic method. Only a restricted fraction of the sample was unchanged, so that ordinary physical data would be misleading. Chromatography could rapidly provide information on this particular portion of the sample. The large number of possible measurements in this region allowed the convenience of choosing those measurements which rendered 2 components indistinguishable, normally an uncommon requirement but quite necessary in this instance. These measurements, although not considered "ideal" by the standards of conventional gas chromatography, provided more than enough information for a solution of the problem. The only suitable alternative method (X-ray fluorescence) required expensive equipment, was restricted to the laboratory and was of dubious applicability owing to insufficient knowledge of the effect of sample treatment on sulfur content.

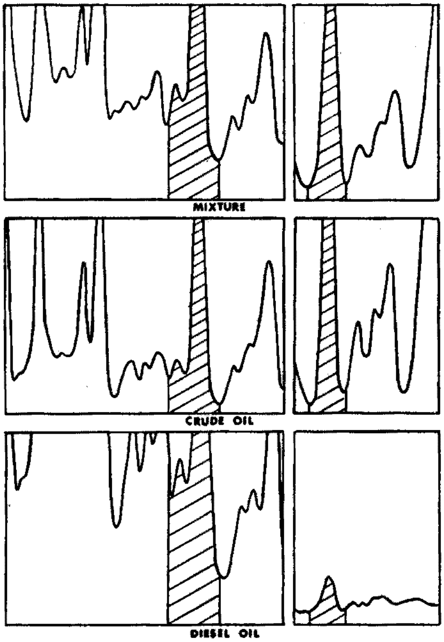

Fig. 3. Vertical axis, recorder response; horizontal axis, retention volume; caption, analysis of oil mixture recovered from a well core. Upper curve, elution curve for sample; middle curve, elution curve for crude associated with formation; lower curve, elution curve for oil associated with drilling mud.

One would suppose that, ordinarily, binary systems can be treated in many ways and this is true. In most laboratories this is done even for complex crudes by simple measurements of density, aromatic content, vanadium or sulfur content, etc.

But none of these measurements are generally applicable to all samples. Furthermore, they very often require expensive equipment and usually cannot be applied outside the laboratory. On the other hand, a chromatographic technique is entirely general, involves little time, requires simple apparatus, does not demand highly trained operators and lends itself readily to outlying operations.

If one accepts that the chromatographic method is desirable, the question immediately arises whether application can be made to mixtures of more than two components. It follows from the mathematics that, when the necessary conditions maintain, the number of components is unrestricted except by the number of independent equations available. The limiting factor becomes the tolerable error and this depends upon the particular system. In the case of petroleum fractions it is likely that the error would be too great for blends of more than a very few fractions. Furthermore, the simple dependence of the ratio of two areas on the concentration of one constituent no longer holds and, if this device is to be used to circumvent the need for a sample weight, more areas must be involved in the ultimate ratio. The constancy of V_{Rt° and N is very important and must be checked experimentally for each system.

The concept of a reproducible but incompletely resolved chromatogram as a spectrum of properties of a system is a useful one. Much could be done with complex systems from a statistical treatment of the information available in such a chromatogram. However, much information concerning sample-partitioning agent interactions must still be accumulated before general reproducibility of chromatograms can be achieved.

SUMMARY

Blends of petroleum products are usually made from fractions which contain preponderantly the same compounds. Only the relative abundances vary. A calculation of the contribution of each blended fraction is theoretically possible with the aid of the gas chromatographic elution curve even though resolution is uniformly poor in such complex systems. An elementary mathematical analysis is made to show what conditions must maintain. Experimental evidence is presented to indicate that the necessary conditions can be realized for petroleum blends. Binary mixtures of complex fractions may be analyzed with an accuracy of better than 10% and only normal attention to detail need be observed.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'analyse de mélanges binaires de pétrole; il est possible théoriquement de calculer la répartition de chaque fraction à l'aide de courbes d'élution de chromatographie gazeuse. Une analyse mathématique élémentaire est faite pour déterminer les conditions. Des mélanges binaires de fractions complexes peuvent être analysés avec une exactitude d'au moins 10%.

ZUSAMMENFASSUNG

Mischungen von Petroleumprodukten werden gewöhnlich aus Fraktionen hergestellt, die überwiegend dieselben Verbindungen enthalten, bei denen jedoch der relative Anteil variiert. Eine Berechnung der Zusammensetzung jeder gemischten Fraktion ist theoretisch mit Hilfe der Gaschromatographieelutionskurve möglich, sogar wenn die Auflösung in solchen Systemen schlecht ist. Es wird eine elementare mathematische Analyse durchgeführt, um zu zeigen, welche Bedingungen eingehalten werden müssen. Die Übereinstimmung mit dem Experiment zeigt, dass die notwendigen Bedingungen für Petroleummischungen realisiert werden können. Binäre Mischungen von komplexen Fraktionen können mit einer Genauigkeit von besser als 10% analysiert werden.

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THE APPLICATION OF THIN-LAYER CHROMATOGRAPHY AND PHOSPHORIMETRY FOR THE RAPID DETERMINATION OF NICOTINE, NORNICOTINE, AND ANABASINE IN TOBACCO

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Numerous methods have been reported for the analysis of tobacco alkaloids. Methods vary from the complete and lengthy procedure of Jeffrey and Tso[1] to the nonspecific and rapid method of Bowen and Barthel[2]. Several papers have dealt with the specific analysis of nornicotine in the presence of other alkaloids[3-6] while other papers have been primarily concerned with the nonspecific analysis of total alkaloids in tobacco[7-9]. In this paper, a method is presented for the specific, rapid and accurate analysis of each of the 3 major alkaloids present in cigarette, cigar and pipe tobaccos. The method utilizes the method of phosphorimetry[10,11] for the final measurement. Because of the sensitivity and selectivity of phosphorimetry, only small amounts of samples are necessary for measurement. Therefore, it is possible to use thin-layer chromatography (TLC) as a rapid means of separation of small amounts of the alkaloids from each other and from other impurities in the tobacco, to remove the spots with a suitable solvent and to measure the resultant extract phosphorimetrically. The entire procedure requires less than 90 min which is considerably less than the time for any other technique.

Paper chromatography has long been favored for the separation and identification of alkaloids in tobaccos[1,12], but this method presents a number of difficulties when quantitative measurements are made. For example, the background absorption from the paper is high, the amount of sample which can be applied is small and the development step is slow. A gas-chromatographic method devised by Quin and Pappas[13] requires frequent replotting of analytical curves, high concentrations of alkaloids in the tobacco leaves and high concentrations of alkaloids in the extracts. However, if the concentrations of nicotine were too high this resulted in so-called "fouling-up of the column". A column elution method[3] required considerable time, was intricate and resulted only in the separation of nicotine and nornicotine.

Several workers[14-18] have shown the applicability of TLC for the quantitative separation prior to measurement. Bird and co-workers[19] have shown that TLC should be sufficiently accurate and precise to allow its use in control laboratories. Millett, Moore and Saeman[20] developed efficient collecting and spotting techniques which are significant improvements on the techniques listed by Ritter and Meyer[21]. Two comprehensive monographs concerning TLC have recently been written[22,23]. Both of these books gave some discussion on the application of TLC to quantitative analysis.

EXPERIMENTAL

Instrumentation and apparatus

All phosphorimetric measurements were obtained with an Aminco spectrofluorimeter with phosphoroscope attachment (American Instrument Co., Inc., Silver Springs, Md.). All spectra were recorded with a Moseley Autograf Model 135A X-Y recorder (F. L. Moseley Co., Pasadena, Calif.). All phosphorimetric measurements were carried out with the following slit program: A — 3 mm, B — 4 mm, C — 4 mm, D — 3 mm, E — 3 mm. The phosphorescence decay times (the time for the intensity to drop from a given value to 1/e of that value) were obtained using the Moseley Autograf X-Y recorder and a manual shutter arrangement inserted in place of the fixed slit holder in front of the xenon excitation source. Upon closing the shutter the X-Y recorder was activated, and the phosphorescence decay was observed.

The thin-layer chromatographic equipment consisted of a rectangular Desaga developing tank and a model S-4 thin-layer applicator (Brinkman Instruments, Inc., Great Neck, N.Y.). Tobacco extracts were applied by means of a cemented needle 100-μl Hamilton syringe. The tip of the hypodermic needle had a short length of polyethylene tubing positioned so as to hold a piece of white cotton thread (number 50). The thread extended about 0.5 mm below the point of the needle. A sample was then applied by placing the needle just above the layer until the thread just touched this surface. The syringe was held in place by an ordinary laboratory clamp and ring stand. This procedure allowed samples to be spotted slowly without damage to the thin-layer surface by the hypodermic needle. A Chaney adapter was also fitted on the syringe.

Reagents and chemicals

Chloroform used in the extraction of the alkaloids and methanol used in the elution step were both spectrograde solvents. Brinkman aluminum oxide type G was used as the thin-layer substrate. All phosphorimetric analyses were carried out with ethanol which had been distilled using a 5-ft. vacuum-jacketed and silvered column. The column had a 1-in. inside diameter and was packed with glass helices (Labglass, Inc., Vineland, N.J.). With a reflux ratio of 15 to 1, only the center fraction was collected and checked for phosphorescence background. The tobacco alkaloids were obtained from several chemical companies (nicotine and nornicotine from K and K Laboratories, Jamaica 33, N.Y. and anabasine from Aldrich Chemical Co., Inc., Milwaukee 10, Wis.). All other reagents and chemicals were of reagent grade quality. Celite was used as an analytical filter aid in the extraction procedure.

Stock solutions in ethanol of nicotine, nornicotine and anabasine were prepared. Solutions used to determine the analytical curves were prepared from the stock solutions of each of the above alkaloids. These solutions were stored in a refrigerator maintained at 0°.

A stock solution containing exactly 220 mg of anabasine in 10 ml of chloroform was prepared. Accurate volumes of this solution were added to several of the dry, ground tobacco samples. These solutions were used to study the recovery of anabasine and to increase the total amount of anabasine so as to be on the linear region of the analytical curves.

A stock solution of toluene in ethanol (0.2 ml of toluene in 100 ml of ethanol) was prepared. This solution was used daily to check the sensitivity of the spectrophosphorimeter. If any change in the meter reading occurred, the fine sensitivity adjustment of the photometer circuit was changed to give the same meter reading as previously obtained. In this way, the sensitivity of the instrument could be checked each day and also the analytical curves of each of the alkaloids were found never to vary more than the accuracy of measurement. The toluene solution was stored at 0° in a refrigerator.

Procedure

Extraction of tobacco. The method used was similar to that described by CUNDIFF AND MARKUNAS[24]. In this method the free alkaloids are nearly quantitatively extracted into chloroform from strongly basic aqueous solution. Five grams of the dry tobacco were ground to a coarse powder with a rotary grinder and were then placed into a phosphorimetrically[11] clean 250-ml Erlenmeyer flask. To the ground tobacco sample 1 ml of the anabasine stock solution was added while shaking the flask. A stream of dry air was passed through the tobacco to evaporate the chloroform, and then 10 ml of 1 M hydrochloric acid was added with swirling. The resultant mixture was allowed to stand for 3 min to ensure complete wetting; 10 ml of 36% sodium hydroxide solution were then added while the solution in the flask was swirled. After adding 60 ml of chloroform, the flask was capped with a chloroform-rinsed cork and was then clamped onto a platform shaker and shaken for 20 min.

About 100 ml of dried Celite was added to the flask which was shaken for another 3 min. The sample was filtered into a 100-ml volumetric flask through a 125-ml medium-grade, sintered-glass funnel and washed with enough chloroform to bring the volume up to exactly 100 ml.

Thin-layer preparation and sample spotting. A thin layer of aluminum oxide G (5 cm × 20 cm × 1 mm thick) was applied to a number of glass plates. The slurry of aluminum oxide used for spreading was prepared and applied as described by the manufacturer. After spreading the aluminum oxide, the plates were dried overnight at room temperature and then activated at 130° for 30 min. They were then stored at room temperature without desiccating or reactivating before use. It was found convenient to prepare 20–30 plates at one time. A 100-μl aliquot of one of the tobacco extracts was applied to the thin layer 1 cm from one side and 2 cm from the bottom of the plate. A similar 100-μl aliquot of the same extract was applied on the opposite lower corner of the plate, 1 cm from the side and 2 cm from the bottom of the plate. The tobacco extracts were applied to the thin layer as previously described. The application of the tobacco extracts was performed with care to maintain the smallest possible spots (3 mm diameter or less). It was convenient to have a stream of warm air focussed on the point of application to allow a more rapid application of the sample.

Spot development. The sample plates were then placed in a tank containing the solvent (100 ml of chloroform and 1.5 ml of methanol) and were developed for 30 min; after 30 min, the solvent front had moved about 10 cm. The plates were then removed and dried after marking the solvent front.

Spot detection. One-half of each thin layer was covered while the other half was sprayed using Dragendorff's reagent. The alkaloids showed up as orange spots on a yellow background. An area corresponding to the location and size of each spot on the sprayed side was scraped from the unsprayed side into a polyethylene capped vial.

Spot analysis. Five ml of ethanol were added to each vial along with 4 drops of diethylamine. Each vial was vigorously hand-shaken and decanted into a test tube. After centrifuging, the clear supernatant liquid was decanted into a clean vial containing 0.1 ml of concentrated sulfuric acid. The vial was shaken and a small volume of this solution was used to clean and fill the lower end of a sample tube used in the Aminco instrument. The excitation monochromator was set at 270 mμ and the emission monochromator at 390 mμ. The phosphoroscope speed was set to approximately one-third maximum speed, and liquid nitrogen was added to the Dewar flask[11]. The reading on the photometer meter was then recorded. In addition, a solvent blank (5 ml of ethanol with 0.1 ml of concentrated sulfuric acid) was measured in the same manner as the sample. The meter reading for the blank was then subtracted from the meter reading for the sample. The blank reading never exceeded 10% on the most sensitive scale (0.001) when the fine sensitivity was adjusted to one-half of its maximum value. In most cases the phosphorescence signal due to the sample was nearly 100 times the signal due to the blank. Therefore, the accuracy of the blank signal did not greatly influence the accuracy of the sample measurement. The fluctuation in the meter reading due to the bubbling of liquid nitrogen resulted in the greatest uncertainty in the final meter reading (± 2% of full-scale). A series of standard solutions of each of the alkaloids in ethanol were also measured as described above. These results were used to obtain the analytical curves, relative intensity of meter reading *vs.* concentration in mole/l for each of the alkaloids.

Instrument calibration. At the beginning of a series of determinations, the photometer circuit of the phosphorimeter was adjusted to have exactly the same sensitivity as on previous days. This was done by placing an Aminco sample tube containing the standard toluene solution in the phosphorimeter. The excitation and emission monochromators were set at 270 mμ and 385 mμ, respectively, and the fine sensitivity knob on the photometer was adjusted to give a meter reading of 43 on the 0.3 coarse sensitivity setting. The shutter speed was the same as described above. This procedure allowed one analytical curve for each alkaloid to be usable over a period of months.

Calculation of weight per cent of alkaloid in tobacco. The per cent by weight of each alkaloid in the tobacco was found with the equation:

$$\% \text{ Alkaloid} = \frac{C \cdot M_W \cdot F \cdot V}{W} 100\% ,$$

where C is the concentration in mole/l corresponding to the meter reading as read off the analytical curve, M_W is the molecular weight of the alkaloid in concern, F is the factor to account for the dilution of the sample (in this case 1000 because only 0.1 ml of the 100-ml extract is separated), V is the volume in l of ethanol used to remove the alkaloid from the thin layer (in this case 0.005 l) and W is the weight of tobacco sample being analyzed (in this case 5 g). Therefore, for the procedure used in this manuscript the above equation can be simplified to

$$\% \text{ Alkaloid} = C \cdot M_W \cdot 100\% .$$

RESULTS AND DISCUSSION

The experimentally measured phosphorescence excitation and emission spectra for the nicotine, nornicotine and anabasine were found to be identical within experimental error, and so only one excitation and one emission spectrum is shown in Fig. 1. The phosphorescence decay times were also found to be nearly the same. The decay times for nicotine, nornicotine and anabasine were found to be 5.2, 5.3 and 6.2 sec, respectively. Because of these spectral similarities, it was necessary to use a physical means of separating the alkaloids. Thin-layer chromatography was used for the reasons discussed below. The analytical curves for nicotine, nornicotine and anabasine in the ethanol–sulfuric acid solvent are given in Fig. 2.

Thin-layer chromatography required only 30 min for complete separation, was capable of handling fairly large loads, gave no detectable phosphorescence background even at the highest instrumental sensitivity and provided a relatively simple means of removal of the spot. Silica gel G with a variety of solvents was found to give a poor separation under all conditions tested. The aluminum oxide G with the chloroform–methanol solvent resulted in a nearly perfect separation. The three major

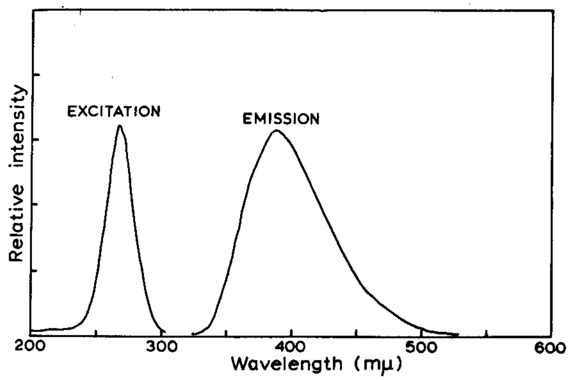

Fig. 1. Phosphorescence excitation and emission spectra of nornicotine ($2.84 \cdot 10^{-4}$ M nornicotine in ethanol–sulfuric acid solution with coarse sensitivity set on 0.3).

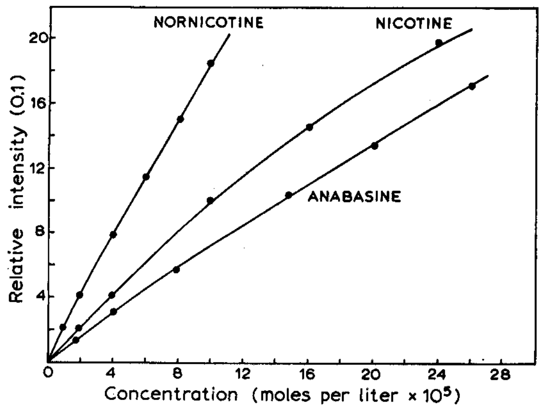

Fig. 2. Analytical curves for nicotine, nornicotine and anabasine.

alkaloids in tobacco (nicotine, nornicotine and anabasine) were nearly equally distributed over the solvent path. Recoveries from the thin layer for standard solutions of each of the 3 tobacco alkaloids were found to be quite good as can be seen from the data in Table I. Over 50 different solvents were tried for removing the alkaloid spots from the thin layer. Of these, the solution containing 5 ml of ethanol and 4 drops of diethylamine gave the most complete recovery of all the alkaloids.

The method of applying the tobacco extract to the thin layer was fast and simple. By means of touching the fiber to the thin layer rather than the hypodermic needle tip, the thin layer surface was never damaged.

Six lesser known brands of tobacco were analyzed in the hope of finding a brand containing more nornicotine than nicotine. As can be seen from the data in Table II, this was not the case. Sample 1 is an American tobacco mixture. Samples 2 and 3 are tobaccos obtained from Turkish cirgarettes. Samples 4, 5 and 6 are tobaccos obtained from American non-filter cigarettes. The R_F values of nicotine, nornicotine and anabasine are given in Table I. In addition to the thin-layer spots due to the above alkaloids, 3 other spots with R_F values of 0.87, 0.65 and 0.00 were also found when the tobacco extracts were separated. These spots were visible before color development and so were attributed to three pigments present in the tobaccos. If very large amounts of tobacco extracts were applied, two other alkaloids with R_F values of 0.59 and 0.65 could be barely detected. One of these was probably due to myosmine although the spot was so weak that its exact identification was impossible.

TABLE I

RECOVERIES OF ALKALOIDS FROM ALUMINUM OXIDE G[a]

Alkaloid	*Quantity added (μg)*	*Quantity recovered (μg)*	*% Recovery*	*R_F value*
Nicotine	42.1	42.5	101	0.80
Nornicotine	67.6	60.9	90	0.26
Anabasine	81.0	78.6	97	0.48

[a] The values listed are averages of 6 separate and complete analyses in which the standard solutions were applied to the thin layer, separated and phosphorimetrically analyzed. The relative standard deviations for nicotine, nornicotine and anabasine are 5.9%, 2.2% and 5.4%, respectively.

TABLE II

ANALYSIS OF TOBACCO SAMPLES FOR NICOTINE, NORNICOTINE AND ANABASINE

Sample number	*Weight % found*		
	Nicotine	*Nornicotine*	*Anabasine*[a]
1	4.96	0.033	0.63
2	1.46	0.016	0.49[b]
3	0.89	0.015	0.41
4	1.05	0.036	0.41
5	1.83	0.061	0.41
6	1.36	0.036	0.37

[a] 0.41% anabasine was added to each 5-g sample.

[b] Complete determination was repeated 6 times with a relative standard deviation of 6.0%. All other results in the above Table are averages of triplicates.

The value for nicotine in sample number 1 in Table II appears abnormally high. However, this value was checked a number of times and found to be as listed. Sample 2 was analyzed 6 times for anabasine, and the relative standard deviation was found to be 6.0%. Each of the 6 analyses involved the entire procedure consisting of extraction of the alkaloids from the tobacco, thin-layer chromatographic separation, dissolution of the spot with ethanol and phosphorimetric measurement. All other results in Table II are the averages of triplicate determinations. Addition of known amounts of nicotine and nornicotine to several of the tobacco samples resulted in recoveries similar to those listed in Table II for anabasine.

Each of the measured solutions contained a small volume (0.1 ml of concentrated sulfuric acid and 5.0 ml of ethanol) of sulfuric acid. It was found that a ten-fold increase in phosphorimetric sensitivity resulted when the sulfuric acid solution of ethanol was used. The reason for this is not known. Ethanol and ethanol mixtures were previously[25] shown to be good solvents for phosphorimetric measurements.

To check for the possibility of an interfering species coinciding with an alkaloid spot, several tobacco samples had their spots measured in the phosphorimeter without, and then with, sulfuric acid in the ethanol. In all cases, there was at least a ten-fold increase in intensity. Because this is characteristic of the pure alkaloids, it appears indicative that the intensities were due to the alkaloids alone.

Once analytical curves have been established for each of the 3 alkaloids, an entire analysis of a dry tobacco sample for nicotine, nornicotine and anabasine can be completed in less than 90 min. It should be stressed that the analytical curves were completely reproducible over a period of 4 months as long as the sensitivity of the photometer was adjusted according to the method presented in this manuscript. The time for the analysis is considerably shorter than any previously described method in which each of the 3 alkaloids were analyzed. The sensitivity of analysis is greater than any absorption spectrophotometric method for the pure alkaloids. Some visible absorption spectrophotometric methods utilizing color reactions result in comparable sensitivities. However, such methods require even more tedious steps and chemical reagents and therefore are subject to even larger errors. In addition, these methods have normally employed paper chromatography as the means of separation which is slow, utilizes only low spot loads and requires large background corrections. In addition, the sample cells used in absorption spectrophotometry normally require 5–10 times more solution than those used in phosphorimetry. The method presented appears to be the fastest, simplest method for the simultaneous analysis of nicotine, nornicotine and anabasine in tobacco samples.

In order to apply the method presented here to the analysis of the less concentrated alkaloids, it would have been necessary for the extract of the tobacco samples in concern to be further concentrated. In all samples analyzed the alkaloids other than nicotine, nornicotine and anabasine were over 10 times less concentrated than the most dilute of the 3 alkaloids analyzed. However, if any other alkaloids were present in appreciable concentration, it should be quite simple to perform a quantitative analysis according to the procedures outlined above.

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SUMMARY

Tobacco is ground and extracted with chloroform, and thin-layer chromatography is used to separate the 3 major tobacco alkaloids—nicotine, nornicotine and anabasine. Each of the alkaloids is quantitatively removed by scraping the spot into a container and dissolving in ethanol–sulfuric acid. A small volume of the ethanol solution is then measured phosphorimetrically. Excellent recoveries of each of the tobacco alkaloids were obtained; the relative standard deviation of analysis was 6% or less for all analyses. The total time for analysis of the 3 alkaloids was less than 90 min. This method is considerably faster and more accurate than previous methods.

RÉSUMÉ

Les auteurs ont mis au point une méthode pour le dosage rapide des trois principaux alcaloïdes du tabac: nicotine, nornicotine et anabasine. On procède par extraction dans le chloroforme et séparation par chromatographie sur couche mince. Chaque alcaloïde est ensuite dosé par phosphorimétrie. Ce procédé est plus rapide (moins de 90 min pour doser les 3 alcaloïdes) et donne des résultats plus précis que les méthodes précédemment utilisées.

ZUSAMMENFASSUNG

Die Dünnschichtchromatographie wird zur Trennung der 3 Haupttabakalkaloide—Nikotin, Nornikotin und Anabasin—benutzt. Dazu wird der Tabak vorher zerrieben und mit Chloroform extrahiert. Jedes der Alkaloide wird quantitativ zurückgewonnen, indem der Fleck abgeschabt und in einem Gemisch aus Äthanol und Schwefelsäure gelöst wird. Ein kleines Volumen dieser Lösung wird dann phosphorimetrisch gemessen. Die Wiedergewinnung jedes der Tabakalkaloide ist ausgezeichnet. Die relative Standardabweichung der Analyse beträgt höchstens 6%. Die Gesamtzeit für die Analyse der 3 Alkaloide beträgt weniger als 90 Min. Diese Methode ist beträchtlich schneller und genauer als die bisherigen.

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Short Communications

A new neocuproine–carbamate spectrophotometric determination of copper

The 3 best spectrophotometric methods for the determination of copper are the carbamate, dithizone and neocuproine methods[1]. The latter has the advantage of complete specificity but is not as sensitive as the other methods[2]. It seemed that it might be possible to develop a combination method of high selectivity and high sensitivity by adding dithizone or diethylammonium diethyldithiocarbamate (DDC) to the chloroform–ethanol extract of the copper–neocuproine chelate in order to form a more strongly colored copper chelate. In order for such a method to work, the added reagent would have to form a stronger copper chelate than copper–neocuproine. Tests showed that dithizone will not displace copper from its neocuproine chelate in chloroform–ethanol solution but that carbamate does so readily. By measuring the color of the resulting copper–carbamate chelate at 435 mμ, the sensitivity of the neocuproine method can be virtually doubled.

To prove that the proposed new method was valid, it was necessary to show that Beer's law holds and that high specificity is still retained, *i.e.*, that the chloroform–ethanol extract does not contain traces of metals that react with DCC to form a colored solution. To be safe in the latter respect, and in order to save labor in the specificity work, composite mixtures of 20 μg of copper plus 100 μg of each of 6 metals or elements, chosen at random, were analyzed. Preliminary results obtained by neutralizing the solutions to pH 4 using congo red paper[2] were insufficiently reproducible; this difficulty was overcome by the use of a pH 4 acetate buffer. Surprisingly, however, it was noted that when the buffer was used, low recoveries of copper were obtained in the presence of zirconium or hafnium. These low values for copper are not found when the solutions are neutralized to pH 4 with congo red paper. It is probable that some unknown complex of copper and zirconium or hafnium is formed in the presence of the buffer, since similar phenomena involving copper have been observed[3,4]. Fortunately, it was found that the low recoveries of copper could be eliminated by heating the solution after the addition of the neocuproine reagent. The preparation of the calibration graph and the analysis of the composite solutions were done as outlined below.

Procedure

Obtain the copper or copper plus other metals, as perchlorate, plus 0.5 ml of perchloric acid in 35 ml of water. Add 1 ml of 10% (w/v) hydroxyammonium hydrochloride solution and 1 ml of 30% (w/v) sodium citrate solution[2]. Neutralize with ammonium hydroxide (1 : 1) just to the yellow color of *m*-cresol purple indicator and then add 10 ml of pH 4 buffer solution (143 ml of glacial acetic acid plus 36.9 g of anhydrous sodium acetate made up to 1 l). Add 2 ml of neocuproine solution[2]. Unless zirconium or hafnium are known to be absent, heat the solution nearly to boiling and then cool. Transfer to a separating funnel, add 10.0 ml of chloroform and extract for 30 sec. Drain all of the lower layer through a triply folded Whatman No. 40 filter paper. Add 0.1 g of DDC (recrystallized from ether) to the filtrate, swirl and measure spectrophotometrically at 435 mμ in a 1-cm absorption cell using chloroform as the reference liquid.

With this method, it was found that Beer's law was followed over the range tested, *i.e.*, 0–40 μg of copper. In the analysis of the composite solutions no high results were obtained, showing that no interfering metals had accompanied the copper into the chloroform–ethanol layer. Typical results in the analysis of composite solutions are shown in Table I.

TABLE I

SPECIFICITY OF THE METHOD

Metals added (100 μg)	*Copper added (μg)*	*Copper found (μg)*
Ta, Sa, La, Re, Ge, Fe	20.0	20.2
W, Th, Au, Sn, Ga, Ba	20.0	20.0
Nb, U, Sc, Sb, Mg, V	20.0	20.0
Be, Ce, Pt, Hg, Tl, Sr	20.0	20.0
K, Os, Y, Al, Se, As	20.0	20.0
Cr, In, Cd, Ag, Pd, Ca	20.0	20.4
Ni, Co, Mn, Ti, Nd, Cs	20.0	20.0
Bi, Pb, Mo, Te, Zn, Rb	20.0	20.3
Li, S, P, Rh, Zr, Hf, Si	20.0	20.0

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The direct gravimetric determination of calcium in silicates

Since the first work by MEADE[1], many procedures have been proposed for the direct determination of calcium in silicate and phosphate rocks, in which calcium is precipitated as the oxalate from a weakly acid solution containing oxalic and acetic, citric, or salicylic acids. Manganese interferes in all these procedures, and magnesium probably also interferes if present in amounts of the order of 60 mg or more; in some, titanium causes difficulty. Further purification of the calcium oxalate precipitate is necessary to assure accurate results[2].

Experiments with 8-hydroxyquinoline-5-sulfonic acid in connection with another problem indicated this reagent might prove to be an effective masking agent in the direct determination of calcium. The reagent prevents the precipitation of titanium, iron and aluminum from neutral and basic solutions, and also forms more stable complexes with manganese and magnesium than with calcium[3].

Reagents and solutions

Calcium standards. Calcium solutions were prepared from calcium carbonate and standardized gravimetrically with oxalate. The first standard contained 10.12 mg of calcium oxide per ml. A second standard, containing 9.81 mg of calcium oxide per ml, was also prepared. Calcium standards, containing approximately 1 mg of calcium oxide per ml, were prepared by diluting 10-ml aliquots of the above solutions to 100 ml with water.

8-Hydroxyquinoline-5-sulfonic acid, 5% solution. Weighed amounts of the reagent were dissolved in 1:30 ammonia solution, filtered, and diluted to the appropriate volume.

Solutions of iron (10 mg of Fe_2O_3 per ml), aluminum (10 mg of Al_2O_3 per ml), magnesium (10 mg of MgO per ml), manganese (0.45 mg of MnO per ml) and titanium (1 mg of TiO_2 per ml), all as the chlorides, were used to prepare synthetic samples.

Reagent-grade chemicals were used. Ammonia solution (s.g. 0.90) was prepared by dissolving gaseous ammonia in chilled, distilled water. The concentration of solutions prepared from solids are weight/volume per cent.

Experimental

Tests of the effectiveness of 8-hydroxyquinoline-5-sulfonic acid as a masking agent in the direct determination of calcium were made with solutions containing known amounts of calcium and various amounts of potentially interfering substances. All solutions contained 8 ml of 1:1 sulfuric acid, the amount used in the dissolution of the silicate samples which were analyzed. The solutions had a final volume of 200–300 ml, and contained 3 g of 8-hydroxyquinoline-5-sulfonic acid and 5 g of ammonium oxalate, except as noted below.

Initially, calcium was precipitated from a hot, acidic solution by the dropwise addition of ammonia to approximately pH 7. Quantitative separations from iron, titanium and aluminum were obtained, but significant amounts of manganese and magnesium contaminated the calcium oxalate. When ammonium oxalate was slowly added to a hot, ammoniacal solution (approximately pH 9) containing calcium, 8-hydroxyquinoline-5-sulfonic acid, and various metal ions, the amount of contaminants in the precipitate was much less. Presumably the increased effectiveness of 8-hydroxyquinoline-5-sulfonic acid as a masking agent for manganese and magnesium in alkaline solution is due to the greater degree of complex formation by these metals at the time the calcium is precipitated.

The calcium oxalate was initially very fine, but digestion for 2 h at 80–100° produced a precipitate coarse enough to filter. After the digestion, the pH of the solution must be lowered to prevent a solubility loss of calcium. A final pH of 6 was arbitrarily selected in the early stages of the work and was found to be satisfactory, although values as high as 8 were subsequently found to be permissible. Iron forms a colored complex with 8-hydroxyquinoline-5-sulfonic acid which prevents the use of pH indicators in solution. The final pH, after the 2-h digestion period, was adjusted to 6 with the aid of a pH meter.

Precipitation of small amounts of calcium oxide (1–5 mg) with 5 g of ammonium oxalate was very incomplete, even if the solutions were set aside for 2 days before filtration. Addition of a larger amount of oxalate improved the results.

Procedure

Weigh accurately *ca.* 1 g of the silicate powder and transfer to a platinum crucible. Dissolve the sample with 10 ml of hydrofluoric acid and 8 ml of 1:1 sulfuric acid, and evaporate to dense fumes of sulfuric acid to remove fluoride ions. Cool the crucible, add water, and digest to dissolve soluble sulfates. Filter the solution and collect the filtrate in a 400-ml beaker. Rinse the crucible several times with hot 1:19 hydrochloric acid to complete the transfer, and wash the paper well with the same solution. If barium sulfate is present, a certain amount dissolves in the wash solution. The use of dilute sulfuric acid would prevent this.

Add 60 ml of a 5% solution of 8-hydroxyquinoline-5-sulfonic acid (or up to 120 ml for certain minerals and meteorites) and heat to near boiling. Add concentrated ammonia solution until a slight odor is detected, then 5 ml in excess. Add slowly, and with constant stirring, 100 ml of a 5% solution of ammonium oxalate. If it is known or suspected that the amount of calcium oxide is less than 5 mg, add 200 ml of a 5% solution of ammonium oxalate or 10 g of ammonium oxalate. The final volume should be 200–300 ml. Cover the beaker and digest at 80–100° for 2 h. Stir the solution occasionally. Add 1:1 hydrochloric acid until only a slight odor of ammonia is detected, then a few drops in excess. When cool, adjust the pH of the solution to 6.0 with the aid of a pH meter. Set the solution aside overnight.

Approximately 24 h after the addition of the oxalate solution, collect the precipitate on a 9-cm retentive paper. Wash the precipitate with small portions of a 0.1% solution of ammonium oxalate until the washings are colorless. A purple stain may persist on the paper in spite of continued washing, but it is of no consequence, presumably being organic material that is combusted with the paper.

Transfer the paper with the precipitate to a tared platinum crucible, and burn the paper in a muffle furnace. Then heat the crucible at the full heat of a Meker burner for 20 min, cool in a desiccator and weigh. Repeat to constant weight.

Results and discussion

Some typical results are recorded in Table I (synthetic samples) and Table II (silicate samples). The "conventional procedure" referred to in Table II indicates procedures in which calcium is separated from a number of interfering ions before the final determination, and in the main indicates procedures based on the classical methods of silicate analysis. The bulk compositions of the silicates are shown in part in Table III.

Most of the precipitates from the synthetic samples were analyzed spectrographically. Some were dissolved and tested chemically for sulfate, phosphate or manganese. Amounts of contaminants equal to or greater than 0.1 mg are recorded in Table I.

After the analysis of the silicates as above, the precipitates were dissolved, checked for the presence of the ammonia group, and reprecipitated as the oxalate. The final precipitates, after ignition to constant weight, were analyzed spectrographically. These tests showed that strontium accompanied calcium in the procedure

TABLE I

DETERMINATION OF CALCIUM OXIDE IN THE PRESENCE OF VARIOUS IONS

Sample no.	*Weight of calcium oxide*		*Contaminants*	*Foreign ions present*[a]
	Taken (mg)	*Found (mg)*		
1	0.0	0.0[b]	—	
2	1.0	0.6[b]	—	Samples no. 1 to 8 contained
3	2.0	1.7[b]	—	100 mg Fe_2O_3 150 mg Al_2O_3
4	2.9	3.1[b]	—	100 mg MgO 9 mg MnO
5	4.9	4.8[b]	—	10 mg TiO_2
6	10.1	10.1	—	
7	50.6	50.7	—	
8	98.1	97.8	—	
9	50.6	50.9	0.4 mg P_2O_5	1000 mg P_2O_5
10	50.6	51.3	0.3 mg P_2O_5 0.2 mg MgO	100 mg MgO; 9 mg MnO 10 mg TiO_2; 1000 mg P_2O_5
11	10.1	10.3	0.1 mg MgO	250 mg MgO
12	10.1	9.9	—	250 mg MgO
13	60.7	60.8	—	45 mg MnO

[a] All samples contained 8 ml of 1:1 sulfuric acid.
[b] Calcium precipitated with 10 g of ammonium oxalate.

TABLE II

COMPARISON OF CALCIUM VALUES

Sample	*Concentration of calcium oxide*		*Reprecipitation*
	Conventional procedure	*This procedure*	
G-1	1.39	1.36	1.33
W-1	10.96	10.94	10.94
Andesitic Tuff	2.56	2.53	2.55
Granitic Gneiss	0.40	0.41[a]	0.37
Garnet	6.00	6.08[b]	5.95
Meteorite (Bruderheim)	1.78	1.78[c]	1.80

[a] Calcium precipitated with 10 g of ammonium oxalate.
[b] Calcium precipitated in the presence of 4.5 g of 8-hydroxyquinoline-5-sulfonic acid. 1.3 mg of the ammonia group found in this precipitate.
[c] Calcium precipitated in the presence of 6 g of 8-hydroxyquinoline-5-sulfonic acid.

outlined above, as it does in the conventional procedure. The calcium precipitate from the garnet in the presence of 8-hydroxyquinoline-5-sulfonic acid contained 1.3 mg of the ammonia group, chiefly aluminum oxide. No evidence of contamination was observed in the other precipitates.

TABLE III

BULK COMPOSITION OF THE SILICATE SAMPLES

	G-1[a]	*W-1*[a]	*Andesitic*[b] *Tuff*	*Granitic Gneiss*[b]	*Garnet*[b]	*Meteorite*[c] *(Bruderheim)*
CaO	1.39	10.96	2.56	0.40	6.00	1.78
Total iron as Fe_2O_3	1.96	11.12	9.54	2.43	32.23	31.87
TiO_2	0.26	1.07	1.09	0.20	0.18	0.12
Al_2O_3	14.27	15.03	12.78	13.60	20.81	2.15
MnO	0.03	0.16	0.11	0.03	4.17	0.32
MgO	0.41	6.62	4.61	0.49	1.29	24.69
Na_2O	3.32	2.07	3.67	2.21	0.07	0.99
K_2O	5.45	0.64	0.14	5.94	0.09	0.12
P_2O_5	0.09	0.14	0.25	0.13	0.14	0.28

[a] M. FLEISCHER AND R. E. STEVENS, *Geochim. Cosmochim. Acta*, 26 (1962) 525.
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In applying this procedure to minerals containing large amounts of complexable ions, such as garnets, the amount of 8-hydroxyquinoline-5-sulfonic acid necessary to prevent contamination must be established. The result obtained in the analysis of the meteorite Bruderheim shows that as much as 6 g may be used.

The results obtained with synthetic samples 9 and 10 indicate that the procedure is applicable to the determination of calcium in phosphates. Analyzed material was not available to confirm this.

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The successive compleximetric determination of thorium and uranium in nitrate solution

A compleximetric titration of uranium was recently described[1]; essentially the same method was independently developed in this laboratory for production control, which required the determination of thorium and uranium in nitrate solutions as well as in sintered products (UO_2–ThO_2 mixed crystals). No authoritative translation of the original paper[1] is available, but it appears that our experience confirms the published results; the present paper also includes useful extensions of the earlier work.

Recommended procedure

Dilute a suitable aliquot of the solution until the metal concentration is about 0.001 *M*. Adjust to pH 3.5 using a pH meter, add 6 drops of xylenol orange indicator and titrate with standard EDTA solution (*e.g.* 0.05 *M*) to the colour change from red to yellow. Add a roughly 100% excess of EDTA with respect to the uranium. Add *ca.* 10 drops of 35% formaldehyde solution and roughly 100 mg of solid sodium dithionite. Wait for a change of colour from brown to green. Add another 6 drops of indicator solution, adjust the pH to 3.5–4.0 using a pH meter for precise work. Then titrate with standard thorium solution to the colour change from yellow to red. The titration can be done in contact with the air.

The method is reasonably precise and sufficiently rapid for use as a routine control method.

Notes

(1) EDTA should be present before the reduction is carried out. The order of addition of dithionite and formaldehyde is immaterial.

(2) The pH can be 2–4 if a precision of 1–2% is satisfactory. For results within 1% the pH limits given in the procedure should be adhered to, when xylenol orange is used as indicator. With some experience the attainment of the right pH may be judged from the colour of the metal indicator. (This also holds when arsenazo is used as the indicator, see below.)

(3) In the successive determination of thorium and uranium, any error in the first titration naturally affects the value subsequently found for uranium; the effect can become important if the thorium is present in large amounts, *e.g.* in the case of the ThO_2–UO_2 product containing 15 at.% UO_2 discussed below.

Applications

The method was also used to determine uranium(IV) in uranium(VI) solutions reduced by other reagents, or containing chloride or acetate as anion.

Since plutonium can be titrated with EDTA[2], a suitably modified procedure should serve for the analysis of mixed plutonium and uranium solutions.

A drawback of the method is the interference by phosphate and sulfate. The concentration limits above which the indicator change tends to become unsatisfactory are not sharply marked and depend somewhat on the experience of the observer. An amount of sulfate 2–3 times the molar amounts of the metal ions can be tolerated. Larger amounts of these ions can be tolerated when arsenazo is used as the indicator;

amounts of sulfate 3–8 times the amount of metal can then be present. The optimum pH for the arsenazo titration is 1.8 for both thorium and uranium.

From the limits given for the sulfate interference it follows that there is no interference in the analysis of uranium and thorium sulfates if these materials can be dissolved in nitric or hydrochloric acid. An example is the analysis of a basic uranyl sulfate[3]: found 64.26, 64.26%, while heating to U_3O_8 gave 64.22 and 64.18% U (also present: 14.29% SO_4^{2-} and 3.15% NH_3).

Very large amounts of sulfate are present when sintered thorium oxide or thorium–uranium oxides are brought into solution by fusion with potassium bisulfate. Uranium and thorium must then be precipitated together with carbonate-free sodium hydroxide. The precipitate is filtered, washed at once with hot 2% ammonium nitrate solution and then dissolved in a small amount of nitric acid. Titration with arsenazo as the indicator then gives satisfactory results.

Table I shows the analyses of an 85:15 at.% ThO_2–UO_2 mixed crystal product. In Table II analyses of solutions with different Th:U ratios are presented.

Summarizing, it can be said that the described procedures give rapid and reasonably accurate results with very simple apparatus.

TABLE I

ANALYSES OF ThO_2–UO_2 MIXED OXIDE PRODUCT

	ThO_2 (wt. %)	*UO_2 (wt. %)*	*Total (%)*
	86.04	13.80	99.84
	86.04	13.88	99.92
	85.70	14.12	99.82
	86.01	14.00	100.01
Mean	85.95	13.95	

TABLE II

ANALYSES OF PURE SOLUTIONS OF THORIUM AND URANYL NITRATES

Moles/5 ml		*Moles/1 ml*		*Moles/2 ml*	
Th	*U*	*Th*	*U*	*Th*	*U*
0.245	0.160	0.039	0.108	0.191	0.199
0.244	0.162	0.041	0.113	0.190	0.200
0.246	0.159	0.040	0.110	0.191	0.201
0.245	0.158	0.040	0.110	0.191	0.201

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Semiquantitative measurement of small amounts of solid substances

In qualitative or quantitative analysis when the addition of some drops of a reagent solution is prescribed, the volume and thus the quantity of the reagent is rather well defined. In contrast, the directions for taking a solid sample in qualitative micro-analysis or for the addition of solid reagents contain only vague indications of the quantity, *e.g.* a pin's head, tip of knife blade, a spatula tip, a few mg, a crystal, etc.; see for instance the monographs of FEIGL on spot tests[1]. Too high or too low an amount of reagent can readily have a detrimental influence on the result of the experiment. An example is the oxidation of antimony(III) to antimony(V) by means of sodium nitrite, an excess of which interferes with the subsequent detection of antimony(V) with rhodamine B. Large amounts of masking agents lower the sensitivity of many reactions, etc. For semiquantitative estimates of materials a more or less constant measurement is desirable.

A simple method for a less subjective measurement seems not to have been proposed. In this paper the idea of "a tip of a spatula" is elaborated and extended to a series of scoops, called "measuring spatulae". These consist of a ribbon of stainless steel, sharply bent at an angle of 60 degrees (see Fig. 1). The horizontal part measures 1.0 × 1.0 mm, 2.0 × 2.0 mm, 4.0 × 4.0 mm and 8.0 × 8.0 mm for the numbers 1, 2, 4 and 8 respectively.

When the spatula is plunged into the substance and then raised with the square plane kept horizontal, a pyramid of material is left on the square; the top of the pyramid is limited by the inclined part of the ribbon and the free sides by the natural angle of repose. Various model substances with differing physical properties and grain size were chosen and the quantity taken up by each spatula was determined ten times. In Table I, the mean weight X, the standard deviation σ and the mean volume V taken up, calculated from the apparent specific weight (asw) of the loosely cast material. are given. The reproducibility appears to be satisfactory for the purpose, the extreme quantities seldom differing by more than 50% from the mean. The reproducibility is particularly good for finely divided materials such as sodium chloride (fine), sodium carbonate and zinc dust. As can be seen the volumes are then similar. The pyramids of sodium chloride (coarser) were low, those of carbo vegetabilis sometimes very high.

These easily made and simply handled measuring spatulae* are thus capable of

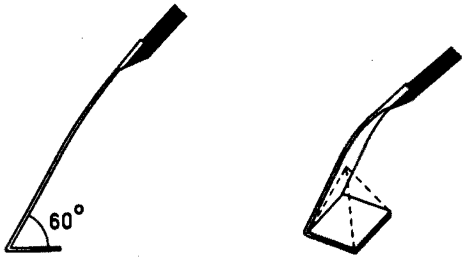

Fig. 1

TABLE I

AMOUNTS OF DIFFERENT SUBSTANCES MEASURED

	No.	X (mg)	σ (mg)	V (μl)		No.	X (mg)	σ (mg)	V (μl)
Sodium									
chloride	1	0.70	0.18	0.68	Zinc dust	1	1.7	0.48	0.69
(fine)	2	6.5	1.3	6.3	0.003–0.03 mm	2	14	2.6	5.9
0.10–0.35 mm	4	35	4.2	34	(+ agglom.)	4	68	11.2	28
asw 1.03	8	236	24.3	229	asw 2.45	8	569	87	232
Sodium	1	0.51	0.11	0.39	Carbo vegetabilis	1	0.21	0.07	1.31
chloride	2	3.0	0.42	2.4	0.002–0.05 mm	2	1.8	0.48	12.5
(coarser)	4	19	2.2	15	(+ agglom.)	4	11.6	3.7	73
0.30–0.50 mm	8	125	7.4	98	asw 0.16	8	65	14.4	406
asw 1.27									
Sodium	1	0.68	0.16	0.71	Oxalic acid	1	0.36	0.10	0.40
carbonate	2	5.1	0.7	5.3	0.05–3 mm	2	3.2	0.86	3.6
0.01–0.5 mm	4	31	2.6	32	asw 0.90	4	18	2.6	20
asw 0.96	8	208	17.2	217		8	143	14	159
Sodium	1	0.42	0.10	0.47	Phenol	1	0.34	0.12	0.5
acetate	2	2.9	0.90	3.2	0.05–3 mm	2	2.1	0.64	3.45
0.10–2 mm	4	17	3.8	19	asw 0.62	4	16	3.2	26
asw 0.90	8	127	14.1	141		8	107	18	173

addition of easily estimated amounts of powdered materials. Moreover, when reactions on a spot plate are carried out, needless dilution by a solvent can be avoided. This will increase the sensitivity of the reaction, which may be a reason for considering a more general application of reagents in the solid state.

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G. DE VRIES

1 F. FEIGL, *Spot Tests in Organic Analysis*, Elsevier, Amsterdam, 1956; *Spot Tests in Inorganic Analysis*, Elsevier, Amsterdam, 1958.

(Received September 25th, 1964)

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* Also obtainable from VECA Instrumentenfabriek, O. Bennekomseweg 58, Wageningen, The Netherlands.

Anal. Chim. Acta, 32 (1965) 294–295

Book Reviews

PETR ZUMAN, *Organic Polarographic Analysis*, International Series of Monographs on Analytical Chemistry, Vol. 12, Pergamon Press, Oxford, 1964, x + 313 pp., price 50 s.

Le volume 12 de l'"International Series of Monographs on Analytical Chemistry" est consacré à l'analyse polarographique organique. Il est rédigé par le docteur PETR ZUMAN de l'Institut de Polarographie de Prague, un des rares spécialistes de l'analyse polarographique organique.

L'introduction a été écrite à l'intention des chimistes organiciens. Elle n'aborde pas le problème théorique complexe de la diffusion, mais rappelle d'une façon concise l'origine des différents types de vague (vagues de diffusion, vagues cinétiques, vagues catalytiques et vagues d'adsorption), qu'il est indispensable de connaître avant tout travail ou toute recherche systématique.

L'auteur présente ensuite le matériel expérimental puis les techniques propres à la chimie organique. Il établit la liste des principales fonctions électroactives et indique les méthodes utilisées pour transformer une substance non électroactive en substance polarographiable.

Le domaine des applications est divisé en deux grandes rubriques: applications pratiques (pharmacie, médecine et biochimie, chimie de l'agriculture et de l'alimentation, plastiques, explosifs, etc.) et application en recherche fondamentale (cinétique, équilibre et études structurales). Ce volume reste d'ailleurs avant tout un traité d'analyse. On y trouvera décrits de nombreux exemples de dosages pratiques mais l'auteur a évité d'aborder en détail les problèmes théoriques complexes. C'est également à dessein qu'il ne développe pas les tendances qui apparaissent actuellement dans la recherche polarographique en milieu non aqueux.

Le non spécialiste trouvera dans ce traité l'essentiel des connaissances théoriques indispensables, l'analyste pourra l'utiliser directement pour la plupart des dosages courants. Enfin, le polarographiste déjà averti aimera retrouver sous une forme condensée, mais immédiatement utilisable, l'essentiel de nos connaissances actuelles dans ce domaine encore trop ignoré de nombreux organiciens.

J. TIROUFLET (Dijon)

Anal. Chim. Acta, 32 (1965) 295–296

S. SIGGIA, *Quantitative Organic Analysis via Functional Groups*, 3rd Ed., J. Wiley and Sons, Inc., New York, 1963, xii + 697 pp., price 145 s.

Purely physical methods of organic analysis seem unlikely entirely to replace quantitative chemical methods in the foreseeable future, particularly for research purposes; chemical methods are not only more economical for short runs of compounds but are also essential for calibration purposes. Accordingly, this greatly enlarged edition of Dr. SIGGIA's well-known text will be welcomed by all analytical chemists.

The lay-out is similar to that of previous editions; little of the earlier material has been discarded and much has been added. As before, many methods are reprinted in part from the original journals, but generally there are additional discursive sections and illuminating footnotes. The most notable feature of this edition is the increased attention given to spectrophotometric methods for the determination of traces of compounds containing certain functional groups, and to non-aqueous titrimetry. These branches of organic analysis in particular are expanding very rapidly and there have been several worthwhile developments even since this book was written.

Quantitative analysis for functional groups is technically much simpler than elemental analysis but it has disadvantages in dealing with unknown materials because so often the reactivity of a required group is influenced by the presence of other groups in the molecule. Thus is it well-nigh essential to have alternative methods available for a particular group. Fortunately the selection of methods presented here is broad and all the procedures have been checked in the author's

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laboratory. There is no doubt that this edition will confirm the position of 'SIGGIA' as the standard text on funtional group analysis.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 32 (1965) 296–297

O. I. MILNER, *Analysis of Petroleum for Trace Elements*, International Series of Monographs on Analytical Chemistry, Vol. 14, Pergamon Press, Oxford, 1963, viii + 128 pp., price 35 s.

This book gives a good impression of what has been done so far to determine minute concentrations of various elements relevant to the petroleum industry. About one quarter of the book is devoted to information of a general nature such as the effects of non-hydrocarbon material on petroleum technology and products, and general practices used in trace analysis. Eleven chapters provide detailed information on selected elements (arsenic, chlorine/bromine, copper, iron, lead, nickel, nitrogen, phosphorus, sodium/potassium, sulfur, vanadium). Each chapter contains a brief discussion on the significance of the element in question, a critical literature review of applicable chemical and instrumental methods and finally a detailed description of one or two methods recommended by the author. These recommended methods are invariably based on chemical procedures so that they can be carried out even by modestly equipped laboratories. The final (one fifth) part is devoted to a discussion of the chemical analysis of elements which are less often analyzed for at trace level (barium, boron, calcium, cobalt, fluorine, magnesium, manganese, molybdenum, oxygen, silicon, zinc).

The book is well written and organized, though one is not left entirely without questions. For instance, it is not clear why so little uniformity exists in the description of the range of products to which the recommended methods may be applied, *e.g.* "nickel in oil", "chlorine in liquid hydrocarbons", "nitrogen" without any product range indication. One also wonders why an admirable method like the Wickbold oxyhydrogen method is the preferred one for sulfur, but not for chlorine and other elements.

Of course, these are minor criticisms and one should certainly be grateful to the author for presenting such a wealth of information in so few pages. This book should be read by all those who are faced with problems of trace analysis, and certainly not only by those working in the petroleum industry.

P. GOUVERNEUR (Amsterdam)

Anal. Chim. Acta, 32 (1965) 297

J. N. BUTLER, *Ionic Equilibrium — A Mathematical Approach*, Addison-Wesley Publishing Company Inc., Reading, Mass., 1964, xi + 547 pp., price $8.75.

This book provides for the first time a unified rigorous treatment of ionic equilibrium. Of course, specialised texts exist which deal with particular aspects of ionic equilibria, but these are directed towards advanced physico-chemical studies. If one accepts that students of analytical chemistry need to be given a greater insight into the theoretical basis of chemical reactions, then much more than the usual treat-

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ment of the subject which is provided by most textbooks of quantitative chemistry is required. The present book seems admirably suited to bridge the gap between the conventional and the specialised texts.

It deals with all the common types of ionic equilibria — acids and bases, precipitation and solubility, complex formation, redox processes — in a simple and direct mathematical way. Considerable emphasis is given to the use of valid approximations and graphical methods which facilitate the solving of quite complicated problems. A highly original and commendable feature of the book is contained in the reference section concluding each chapter; the author gives there his personal comments on books, articles and references of historical interest which must prove valuable for selecting further reading.

This is an extremely worthwhile book which it is a pleasure to recommend; its refreshing approach to the subject of ionic equilibria should appeal to students and teachers alike.

W. I. STEPHEN (Birmingham)

Anal. Chim. Acta, 32 (1965) 297–298

H. M. EL-BADRY, *Micromanipulators and Micromanipulation*, Monographien aus dem Gebiete der qualitativen Mikroanalyse, Band III, Hrsg. von A. A. BENEDETTI-PICHLER, Springer-Verlag, Wien, 1963, vii + 333 pp., price $12.20.

The tremendous surge of interest in the chemistry of the transuranium elements and in biochemistry during the past two decades has severely taxed the ingenuity of workers who must deal with extremely small amounts of samples. The present monograph is a compilation of the techniques which have been evolved for analysis under the microscope of samples in the microgram to nanogram range. In the first part, microscopes and micromanipulators are considered in detail, as well as all the ancillary apparatus needed for chemical experimentation in the submicrogram range. The second part deals with the general techniques required for sampling and in inorganic and biochemical work. Part III contains an outline of the application of these techniques, ranging from "classical" qualitative analysis through nuclear chemistry, air pollution, metallurgy, engineering, fibre studies, micropalaeontology and archaeology to brain research in entomology. The numerous applications of the techniques are fascinatingly diverse.

The author has done a considerable amount of original research in this area, which enhances the validity of the text. The volume should prove of great value to workers faced with handling minute samples in all branches of chemistry and technology.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 32 (1965) 298

CLEMENT DUVAL, *Inorganic Thermogravimetric Analysis*, 2nd Ed., Elsevier Publishing Company, Amsterdam, 1963, xv + 722 pp., price 120 s (D.fl. 60.—, DM 67.—).

Since the first edition of this book appeared in 1953 much research work on thermogravimetric analysis has been published and many varieties of thermobalance

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have become commercially available. The expansion of the subject is indicated by the fact that the present edition is nearly twice the size of the previous one, despite the removal of virtually all the actual thermograms which appeared previously.

A brief historical review is followed by full descriptions of many deflection-type and null-type thermobalances. The subsequent general chapters on applications and precautions needed in the use of thermobalances contain much of interest and here Professor DUVAL attempts to resolve and explain some of the arguments and inconsistencies that have arisen in the development of thermogravimetric methods. The major part of the text deals with the thermolysis curves of precipitates derived from 77 different elements, and covers the literature up to the end of 1960.

As the protagonist in the development of thermogravimetric analysis, Professor DUVAL has his critics as well as many emulators; that he has not shied away from controversy enlivens the book considerably. This edition is a worthy successor to the first and must be essential reading for all analytical chemists.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 32 (1965) 298–299

F. E. CRITCHFIELD, *Organic Functional Group Analysis*, International Series of Monographs of Analytical Chemistry, Vol. 8, Pergamon Press, Oxford, vii + 187 pp., price 42 s.

The purpose of this book is to provide a collection of reliable chemical procedures for the determination of the more commonly encountered organic functional groups. These are classified in the text under various generalised chapter headings and include the groups present in acids and bases, nitrogen compounds, carbonyl compounds, hydroxyl compounds, unsaturated compounds, 1,2-epoxy compounds, esters, carboxylic acid anhydrides, peroxides, and finally sulphur compounds.

Only the more useful methods are described for any one functional group and considerable emphasis is given to the scope and limitations of each method. This is of considerable value when an assessment of the applicability of a method to a particular problem is required. Chemical methods of organic functional group analysis have undergone considerable development in recent years, because of their suitability not only for routine process control work but also for the analysis of research samples. Their use for calibration of instrumental methods underlines the importance of reliable chemical methods of analysis being available.

The author has obviously tried to cover as wide a range of groups as possible within the limits of the size of this book, and on the whole has succeeded very well. However, one or two quite useful methods have been omitted, notably for the nitro group, and several other methods are given a somewhat superficial treatment. Nevertheless, the book forms a useful addition to the expanding literature of quantitative organic analysis and is to be recommended to all interested in the subject.

W. I. STEPHEN (Birmingham)

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Announcements

VERANSTALTUNGEN DER GESELLSCHAFT DEUTSCHER CHEMIKER 1965

15.–19. März 1965 HEIDELBERG
Vortragstagung *Moderne analytische Methoden in der Lebensmittelchemie und der biologischen Chemie*

31. März–2. April 1965 FRANKFURT (M)
2. Europäisches Symposium *Lebensmittel–Neuzeitliche Entwicklung in der Wärmebehandlung*

26.–30. April 1965 SCHLOSS ELMAU/OBB.
1. EUCHEM-Konferenz *Chemie bei hohen Temperaturen mit besonderer Berücksichtigung gasförmiger und fester Subverbindungen.* Teilnahme an der Konferenz nur auf besondere Einladung möglich.

30. August–2. Sept. 1965 MÜNCHEN
3. Internationales Fluorsymposium

13.–18. September 1965 BONN
GDCh-Hauptversammlung und Kekulé-Feier.
Im Rahmen dieser Hauptversammlung tagen auch folgende Fachgruppen: Fachgruppe *Analytische Chemie.* Thema: Elektroanalyse organischer Substanzen. Fachgruppe *Anstrichstoffe u. Pigmente.* Fachgruppe *Freiberufliche Chemiker.* Fachgruppe *Geschichte der Chemie.* Fachgruppe *Gewerblicher Rechtsschutz.* Fachgruppe *Halbleiterchemie,* zusammen mit der Fachgruppe *Angewandte Elektrochemie.* Thema: Grenzflächenchemie von Halbleitern. Fachgruppe *Kern-, Radio- und Strahlenchemie.* Thema: Chemische Reaktionen im Anschluss an Kernprozesse. Fachgruppe *Kunststoffe und Kautschuk.* Fachgruppe *Lebensmittelchemie und gerichtliche Chemie.*

21.–22. Oktober 1965 FRANKFURT (M)
GDCh-Fachgruppe *Angewandte Elektrochemie.* Vortragstagung *Elektrochemische Stromquellen.*

Auskünfte zu diesen Tagungen erteilt ebenfalls: Gesellschaft Deutscher Chemiker – Geschäftsstelle – 6000 Frankfurt (Main), Postfach 9075.

4TH INTERNATIONAL CONFERENCE ON X-RAY OPTICS AND MICROANALYSIS

Faculté des Sciences, Orsay, Seine-et-Oise, France
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An international Conference on X-ray Optics and Microanalysis will be held from September 8th through September 10th 1965 at the Faculté des Sciences d'Orsay, a centre for higher education and research created by the University of Paris some twelve miles outside the French capital. This conference is a continuation of similar meetings held in Cambridge in 1956, in Stockholm in 1959 and at Stanford University in 1962. It is intended for research workers concerned with new techniques involving X-ray optics or with methods of microanalysis based on X-ray spectrography, electron optics and corpuscular optics. The work of the Conference will be mainly concerned with:

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- New developments in X-ray spectroscopy in the long wave-length field;
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Further details may be obtained from M. P. DESCHAMPS, Département de Physique, Institut de Recherches de la Sidérurgie Française, Saint-Germain-en-Laye (S.-et-O.), France.

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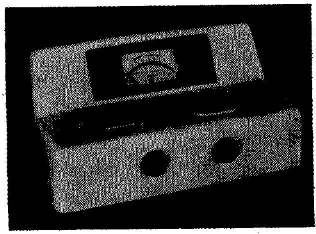

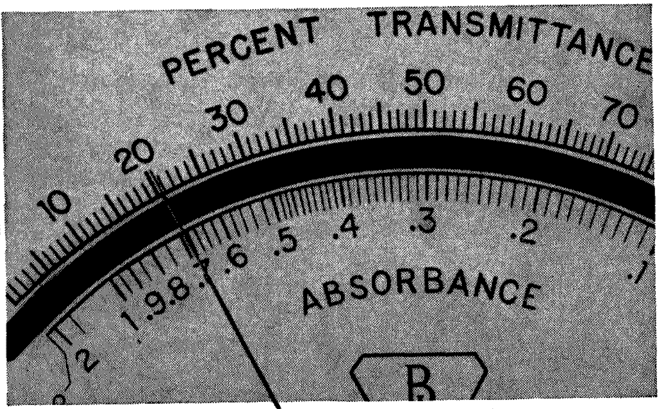
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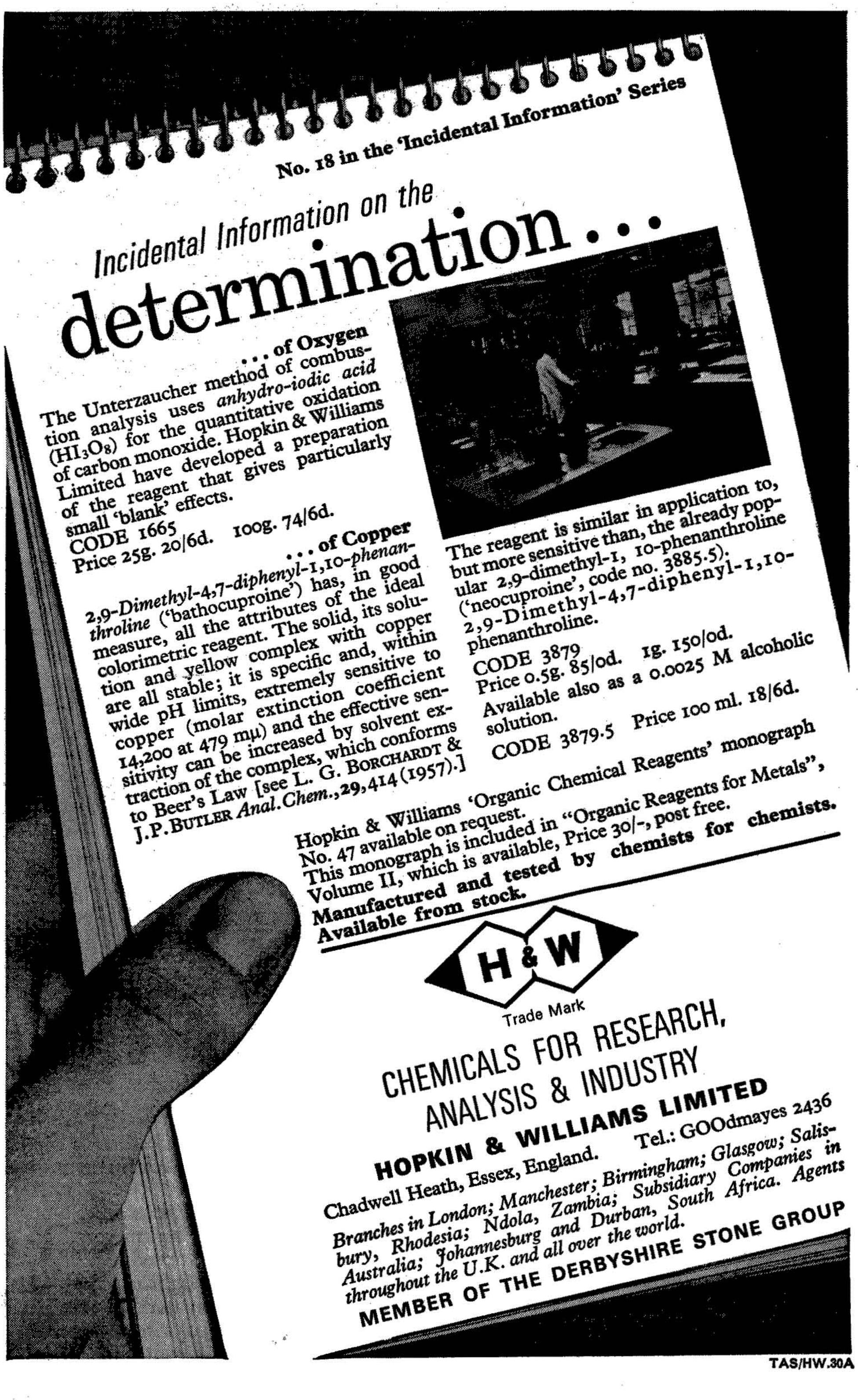

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Chemistry Titles from ELSEVIER

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