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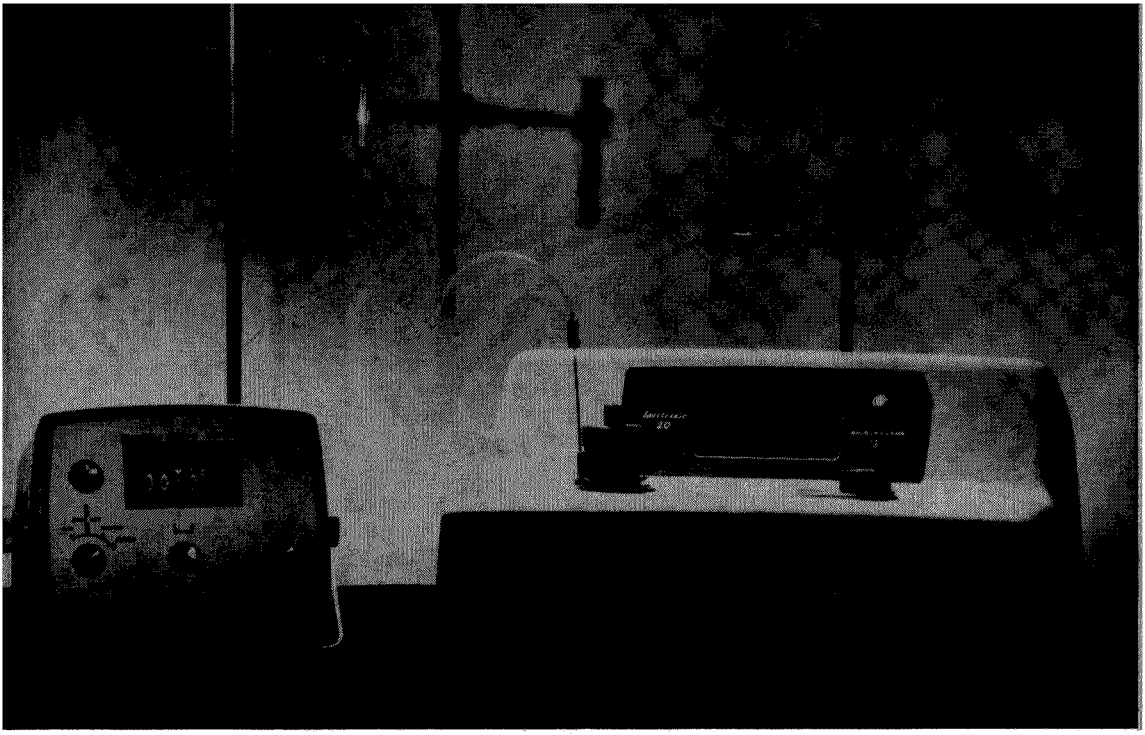

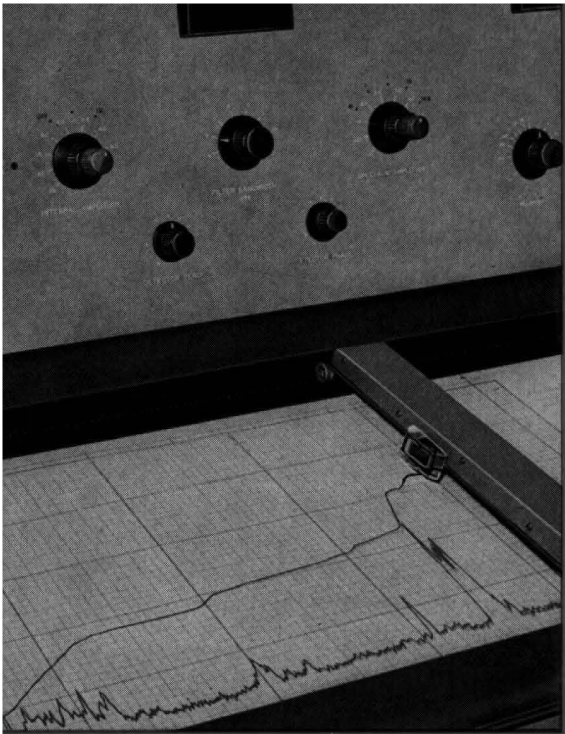

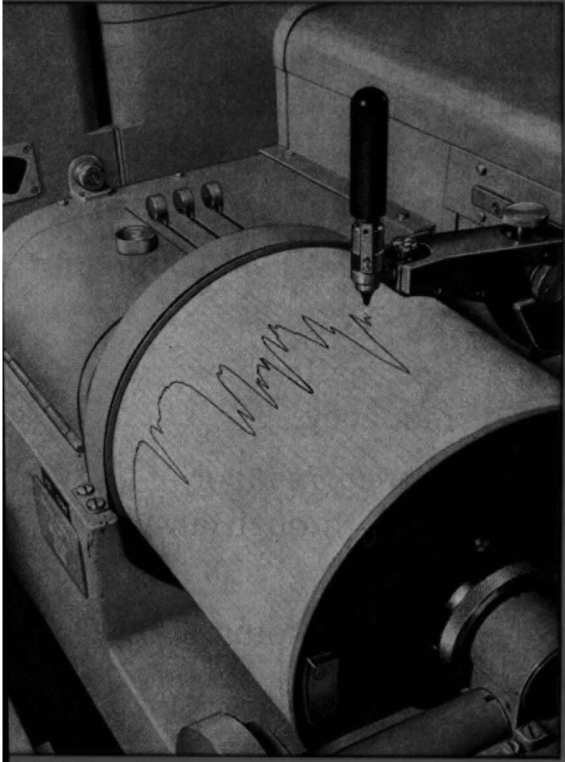

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 36, No. 3, November 1966

AN INVESTIGATION OF SOME EXPERIMENTAL PARAMETERS IN ATOMIC FLUORESCENCE SPECTROPHOTOMETRY

Atomic fluorescence in flames is measured by an adaptation of a commercially available flame spectrophotometer. A study is reported of the effect of background radiation and source scattering on 3 flames, air–propane, air–hydrogen and air–acetylene, and of the effects of variation of fuel gas pressure, zone of measurement in the flame, analysing monochromator slit-width and wavelength of measurement. The air–propane flame appears to offer several advantages. The atomic fluorescence of 10 metals is described; those of Co, Fe and Mn have not been previously reported. Excitation of spectra is achieved by means of an a.c. xenon arc lamp or individual discharge lamps.

R. M. Dagnall, K. C. Thompson and T. S. West,
Anal. Chim. Acta, 36 (1966) 269–277

A STUDY OF SOME INTERFERENCES IN THE ATOMIC ABSORPTION SPECTROPHOTOMETRY OF MAGNESIUM

The effects of some cations, anions and complexing agents on the absorbance of magnesium in the air–propane flame are investigated in detail. The results have enabled the mechanisms of magnesium atom production in this flame to be deduced, and have clarified the nature of the interferences.

D. J. Halls and A. Townshend,
Anal. Chim. Acta, 36 (1966) 278–285

SOME ASPECTS OF N-BENZOYLPHENYLHYDROXYLAMINE AND CUPFERRON REACTIONS WITH TIN, ANTIMONY AND OTHER SELECTED ELEMENTS

N-Benzoyl-N-phenylhydroxylamine (BPHA) and cupferron are compared in the liquid–liquid extraction of tin and antimony. As in their precipitation reactions tin(II) and tin(IV) behave similarly with BPHA and differently with cupferron. Both reagents behave similarly in extraction of antimony(III), except at high acidity when cupferron or its decomposition products prevent extraction which otherwise occurs into chloroform alone. Separations of Sn, Sb, As and Bi are discussed for extractions from hydrochloric and perchloric acid systems with BPHA. The tin product extracted with BPHA from dilute hydrochloric acid appears to be identical with that precipitated in gravimetric analysis; infrared spectral evidence shows the latter to contain tin(IV). Other precipitation reactions of BPHA in the presence of anions other than chloride and some solubility measurements are also reported.

S. J. Lyle and A. D. Shendrikar,
Anal. Chim. Acta, 36 (1966) 286–297

SOME SPECTROFLUORIMETRIC APPLICATIONS OF THE CERIUM(IV)–CERIUM(III) SYSTEM

Cerium(III) ions in dilute sulphuric acid medium exhibit a characteristic fluorescence which has its excitation maximum at 260 nm and its fluorescence emission maximum at 350 nm. By utilising the osmium-catalysed redox reaction between cerium(IV) and arsenic(III), microgram amounts of arsenic (7.5–37.5 µg) may be determined by spectrofluorimetric measurement of the cerium(III) produced. The principle may be applied to the determination of several other ions which cannot yet be determined by direct spectrofluorimetry, *e.g.* Fe(II) (5.6–28 µg), oxalate (8.8–44 µg). Osmium(VIII) (0.05–0.2 µg) and iodide (0.6–2.5 µg) may be determined by their catalytic action.

G. F. KIRKBRIGHT, T. S. WEST AND C. WOODWARD,
Anal. Chim. Acta, 36 (1966) 298–303

DETERMINATION OF CARBONYL COMPOUNDS VIA POLAROGRAPHY OF THEIR SEMICARBAZONE DERIVATIVES

The polarographic behaviour of a range of aldehyde and ketone semicarbazones has been studied and a method for the determination of carbonyl compounds developed. The carbonyl compound is added to an acetate buffer containing 0.1 *M* semicarbazide hydrochloride and 50% ethanol and the polarographic reduction wave of the semicarbazone derivative measured. The similar values of the diffusion current constant *I* for all compounds studied indicate the applicability of this method to functional group analysis.

B. FLEET,
Anal. Chim. Acta, 36 (1966) 304–311

DISSOCIATION AND IONIZATION EFFECTS IN ATOMIC ABSORPTION SPECTROCHEMICAL ANALYSIS

Use of a nitrous oxide–acetylene flame in atomic absorption spectrophotometry reduces or eliminates certain chemical interferences that have been observed in cooler flames. However, ionization increases with temperature, and is significant for some elements in the nitrous oxide–acetylene flame. Ionization can be reduced by adding an easily ionized metal (*e.g.* alkali metal) to the solution. Elements likely to be determined using the nitrous oxide–acetylene flame which will be significantly ionized are: Al, Ba, Ti, V, Zr, Hf, Nb, Sc, Y, the lanthanides and the actinides. The ionization of an element in the nitrous oxide–acetylene flame can be readily calculated by taking absorption readings, provided that relatively sensitive atom and ion resonance lines are available. This technique possibly could be used to establish ionization potentials or partition functions of those lanthanide elements that are not now well known.

D. C. MANNING AND L. CAPACHO-DELGADO,
Anal. Chim. Acta, 36 (1966) 312–318

THE DETERMINATION OF TRACE QUANTITIES OF MOLYBDENUM BY ATOMIC ABSORPTION SPECTROSCOPY

A procedure is described for the determination of trace quantities of molybdenum by atomic absorption spectroscopy. Molybdenum is complexed with ammonium pyrollidine dithiocarbamate or 8-hydroxyquinoline and extracted into *n*-amyl methyl ketone. Molybdenum is then determined by atomic absorption spectroscopy. Interferences have been eliminated and detection limits of 0.002 p.p.m. for water samples, 0.1 p.p.m. for samples of dried plant material and 1 p.p.m. for silicate rock samples have been obtained.

L. R. P. BUTLER AND P. M. MATHEWS,
Anal. Chim. Acta, 36 (1966) 319–327

THE USE OF COMPUTER TECHNIQUES IN EMISSION AND ATOMIC ABSORPTION FLAME PHOTOMETRY

The utilization of flame methods, especially in atomic absorption work, can be enhanced by the application of computer techniques for rapid and accurate reduction of experimental data. Modern computational techniques are described for the analysis of large numbers of solutions; their inherent advantages in time saving and reduction of calculating errors are discussed. Several typical problems have been automated and are explained in some detail; pertinent descriptions of the computer program and the resulting output from sample calculations are included.

J. RAMÍREZ-MUÑOZ, J. L. MALAKOFF AND C. P. AIME,
Anal. Chim. Acta, 36 (1966) 328–338

MICRODETERMINATION OF CHLORINE OR BROMINE IN HIGHLY HALOGENATED ORGANIC COMPOUNDS

The microdetermination of chlorine or bromine in highly halogenated compounds is described. The oxygen flask is used for aromatic, aliphatic and liquid samples with high halogen contents. A microfusion method for some of these compounds is also discussed. As many compounds as possible covering different structures were analysed. Satisfactory results were obtained.

W. I. AWAD, Y. A. GAWARGIOUS, S. S. M. HASSAN AND N. E. MILAD,
Anal. Chim. Acta, 36 (1966) 339–345

THE SPECTROPHOTOMETRIC AND TITRIMETRIC DETERMINATION OF GOLD WITH FERROIN AS REAGENT

A spectrophotometric and a photometric titration method in a two-phase system for the determination of gold with ferroin is reported. Both methods are rapid and reproducible with an accuracy of ±1%. In the spectrophotometric determination Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+} and Cr^{3+} do not interfere with the determination of gold and Pt^{4+}, Pd^{2+}, Hg^{2+}, Ir^{4+} and Os^{4+} can be tolerated up to a ratio of 1:1. The titrations can also be carried out in the presence of a number of diverse ions, *e.g.*, Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Zn^{2+}, Cr^{3+}, Mn^{2+}, without interference; the platinum metals and Hg^{2+} cause interference but, by the use of the spectrophotometric procedure, this can be reduced.

F. G. NASOURI, S. A. F. SHAHINE AND R. J. MAGEE,
Anal. Chim. Acta, 36 (1966) 346–351

A PHOSPHORIMETRIC INVESTIGATION OF SEVERAL SULFONAMIDE DRUGS: A RAPID DIRECT PROCEDURE FOR THE DETERMINATION OF DRUG LEVELS IN POOLED HUMAN SERUM WITH SPECIFIC APPLICATION TO SULFADIAZINE, SULFAMETHAZINE, SULFAMERAZINE AND SULFACETAMIDE

Phosphorescence excitation and emission spectral peaks, lifetimes, and limits of detection of several sulfonamide drugs of pharmacological importance in rigid (77°K) ethanolic solution are given. A direct method for the determination of trace amounts of 4 of these drugs in serum is presented. The method should be generally applicable to many phosphorescent compounds in biological fluids.

H. C. HOLLIFIELD AND J. D. WINEFORDNER,
Anal. Chim. Acta, 36 (1966) 352–359

DIRECT FLUORIMETRIC DETERMINATION OF TRACE BORON IN STEELS WITH 2-HYDROXY-4-METHOXY-4′-CHLOROBENZOPHENONE

(in French)

A simple and rapid method for the direct determination of traces of boron in mild steels, using 2-hydroxy-4-methoxy-4′-chlorobenzophenone (HMCB) as the fluorimetric reagent for boron is proposed.

D. Monnier and M. Marcantonatos,
Anal. Chim. Acta, 36 (1966) 360–365

THERMAL ANALYSIS OF SOME METAL BENZOHYDROXAMATES

The preparation and thermal analysis of metal chelates of benzohydroxamic acid (BHA) with Al(III), Cd(II), Co(II), Cu(II) (two compounds), Fe(III), La(III), Pb(II), Mn(II), Ni(II), U(VI) and Zn(II) is discussed. The Al(III), La(III), Pb(II) and Mn(II) chelates are new compounds. DTA and TGA curves of the chelates and of BHA are presented, and the heats of decomposition of the chelates are estimated.

L. N. Lapatnick, J. F. Hazel and W. M. McNabb,

Anal. Chim. Acta, 36 (1966) 366–371

THIOTHENOYLTRIFLUOROACETONE: A NEW CHELON

The thioderivative of 2-thenoyltrifluoroacetone, 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (STTA) was prepared. NMR and infrared spectra confirmed the previously suggested structure[1,2]. The sulfur is attached to the carbon adjacent to the thienyl group and exists almost entirely in the thioenolic form. The chelates of STTA with Ni(II), Cu(II), Pb(II), Zn(II), Co(II), Cd(II), Pd(II) and Hg(II) were prepared in a neutral to slightly basic medium, and characterized by analysis, NMR, infrared, visible and ultraviolet spectra, DTA, TGA and fractional sublimation. The chelates are relatively stable, insoluble in water, soluble in non-polar and some polar organic solvents, sublimable, and intensely colored compared to their normal diketone analogs. The selectivity of the reagent has not been completely established but divalent ions chelate more readily than trivalent ions; Fe(III), Al(III), Cr(III) apparently do not chelate. The new chelon may be useful as a color developing reagent for the colorimetric analysis of such ions as Zn(II), Cd(II), Hg(II) and Pb(II). The molar extinction coefficients are given for the chelon and the chelates investigated.

E. W. Berg and K. P. Reed,
Anal. Chim. Acta, 36 (1966) 372–382

A MODIFIED AND A NEW STRAIGHT-LINE METHOD FOR DETERMINING THE COMPOSITION OF WEAK COMPLEXES OF THE FORM A_mB_n

A modified ASMUS method and a new method are described for determining the composition and stability of weak complexes of the form A_mB_n. The modified method is applicable to polynuclear complexes and is not based on the approximation necessary originally. The second method is based on variation of the concentration of the reactant being maintained in excess. The method gives a straight line for the correct quotient of n/m and the stability constant can easily be calculated from data extracted from the diagram. The main advantage is that, in combination with the original straight-line method, this method permits the determination of both coefficients (m and n) in the presence of an excess of one of the reactants.

A. HOLME AND F. J. LANGMYHR,
Anal. Chim. Acta, 36 (1966) 383–391

CHROMATOGRAPHIC SEPARATION OF METALS BY ELUTION WITH AMMONIUM SULPHATE. DETERMINATION OF MAGNESIUM, CALCIUM AND STRONTIUM IN WATERS

(in German)

The chromatographic separation of Mg, Ca, Sr, Ba, Fe(II, III) and Mn(II) by elution with ammonium sulphate solution from Dowex 50-X10 was studied. The optimum conditions for the separation of the alkaline earths from each other were established. The method was applied for the separation of Mg, Ca and Sr in salt waters; Mg and Ca were determined by EDTA titration and Sr spectrographically, the coefficient of variation being 1.9% for Mg and 1.4% for Ca.

R. CHRISTOVA AND A. KRUSCHEVSKA,
Anal. Chim. Acta, 36 (1966) 392–398

INTERNAL ELECTROLYSIS FOR THE SEPARATION OF IONS. PART II. DETERMINATION OF ANTIMONY AND LEAD IN PRESENCE OF OTHER IONS. SEPARATION AND DETERMINATION OF Ag, Bi, Cu, Pb, Cd AND Sb

(Short Communication)

A. K. MAJUMDAR AND SM. GOURI BHOWAL,
Anal. Chim. Acta, 36 (1966) 399–402

AUTOMATIC SPECTROGRAPHIC DETERMINATION OF GASES IN METALS ETC.

(Short Communication)

M. S. W. WEBB AND R. J. WEBB,
Anal. Chim. Acta, 36 (1966) 403–406

GAS CHROMATOGRAPHIC ANALYSIS OF A MIXTURE OF HYDROGEN AND OXYGEN WITH A MODIFIED SAMPLING DEVICE

(Short Communication)

Y. S. SU,
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147E

AN INVESTIGATION OF SOME EXPERIMENTAL PARAMETERS IN ATOMIC FLUORESCENCE SPECTROPHOTOMETRY*

R. M. DAGNALL, K. C. THOMPSON AND T. S. WEST
Chemistry Department, Imperial College, London S.W. 7 (Great Britain)
(Received April 16th, 1966)

Studies of theoretical considerations and of some experimental parameters relating to the excitation and measurement of atomic fluorescence in flames have been published recently by WINEFORDNER *et al.*[1-4]. For this purpose they designed their own apparatus and used a total-consumption integral-burner with acetylene or hydrogen as fuel gas. A previous publication from this laboratory reported some preliminary findings on the modification and use of a commercially available atomic-absorption/thermal-emission flame spectrophotometer (the Unicam SP.900A) for the measurement of atomic fluorescence[5]. The present paper reports *inter alia* a critical assessment of the use of the fuel gases propane, hydrogen and acetylene in relation to background radiation and sensitivity of measurement under various experimental conditions. The use of a continuous source, *i.e.* a high pressure a.c. xenon arc lamp, has also been investigated as an alternative to individual discharge lamps for each element.

EXPERIMENTAL

Apparatus

The apparatus used consisted of an Unicam SP.900A atomic-absorption/thermal-emission flame spectrophotometer. The stainless steel burner-head was of the Meker type in which the fuel gas and air/sample mixture is burned above a series of concentric rings of holes giving a flame with a maximum diameter of *ca.* 1.5 cm. A concentric jet nebuliser was used consisting of a metal capillary (80% Pt and 20% Ir) mounted in a Perspex cylinder. The resultant spray spins in an expansion chamber in such a manner that larger droplets are removed by centrifugal force and only a fine homogeneous mist reaches the flame. The normal EMI 9529B photomultiplier supplied with the instrument was replaced by an EMI 9601B photomultiplier, which is particularly sensitive in the ultraviolet region, where most of the lines used in atomic fluorescence spectrophotometry occur.

Simple modification to the burner housing allowed the necessary irradiation of the flame, via an adjustable slit mechanism, from the source. The source itself was mounted so that it subtended a right angle with the entrance slit of the spectrophotometer at the flame.

With the "emission" mode of the SP.900A, light from the flame is chopped at

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* This paper was read at the 2nd Reunion Symposium of the Birmingham University Research School of Analytical Chemistry, held at Birmingham on April 28–29th, 1966.

100 c/s after entering the monochromator and hence both the analytical signal and the background radiation are amplified by the a.c. system, and are recorded. With the "absorption" mode of operation, the monochromator chopper is held in the open position and the background, which is continuous, is not recorded. A chopper is provided to give an a.c. signal from a d.c. hollow-cathode lamp used in atomic absorption spectrophotometry, but in the experiments described in this paper this chopper assembly was not used because it would have required re-positioning of the burner. Hence a.c.-operated sources were used for atomic fluorescence measurements with the "absorption" mode of operation and with the excitation source at the side of the flame opposite to that at which the hollow-cathode lamps are normally situated for atomic-absorption work. The analytical signal recorded under these conditions consists of the fluorescence signal, source scattering and phased fluctuations in the background radiation at the wavelength of measurement. In general, the larger the background, the larger the fluctuations. Scattering with the SP.900A is kept to a minimum by the centrifugal expansion chamber which allows only the smaller droplets through into the flame. WINEFORDNER reports much larger light scattering than was observed in our studies, probably because of his use of a total consumption aspirator-burner which introduces much larger droplets into the flame.

Although the continuous flame background radiation is not recorded in the fluorescence measurements, the d.c. photomultiplier receives both the analytical signal and the background. A large background emission is undesirable because flooding of the photomultiplier with an "indifferent" light signal may cause temporary fatigue of the detector and non-linear response towards the a.c. signal.

Background parameters

Measurements were made with the "emission" mode of operation and with distilled water aspirating through the flame to reduce flame temperature[6]. This was found to decrease all background readings by about 15%. The flame was not irradiated in these studies.

Fuel gases. The burner is supplied with heads and jets suitable for air–propane and air–acetylene flames. In addition to these, an air–hydrogen flame may be maintained using the propane jet and the acetylene head. The propane and acetylene pressures were measured on the manometer supplied, but the much larger hydrogen pressure was measured on an external gauge. The air pressure used in all instances was 15 p.s.i., unless otherwise stated.

The 5 principal flame conditions used are shown in Table I.

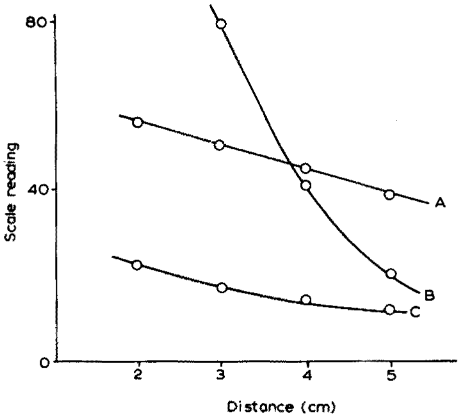
TABLE I

TYPES OF FLAME

Acetylene pressure (cm)[a]	*Propane pressure (cm)*[a]	*Hydrogen pressure (p.s.i.)*	*Flame*
3	7	1.0	Strikes back
4.5	10	1.5	Lean
6–7	12	2.0–2.5	Normal
8	16	3.5	Fuel rich
10	18	5.0	Very fuel rich

[a] Manometer liquid consisted of a red dye solution in dibutyl phthalate.

Position of measurement in flame. Figure 1 shows the background variation in different sections of the normal air–propane, air–acetylene and air–hydrogen flames at 2750 Å. This wavelength was chosen as being intermediate in the range used in atomic fluorescence studies. The distances shown are measured from the top of the burner to a position corresponding to the centre of the analysing monochromator slit.



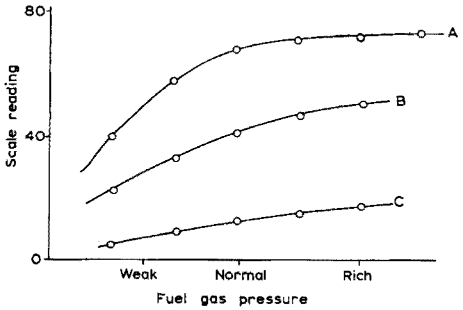


Fig. 1. Background radiation *vs.* burner height. Measurements made at 2750 Å with normal flame conditions and analysing monochromator slit 0.1 mm. The "distances" were measured from the top of the burner to the centre of the analysing monochromator slit. (A) Air–acetylene (multiply ordinate by 16 to compare with curves B and C); (B) air–propane; (C) air–hydrogen.

Fig. 2. Background radiation *vs.* fuel gas pressure. Measurements made at 2500 Å with analysing monochromator slit 0.2 mm and a burner height of 3 cm. Gas pressures used are shown in Table I. (A) Air–acetylene (multiply ordinate by 5 to compare with curves B and C); (B) air–propane; (C) air–hydrogen.

The background radiation could be virtually eliminated in the air–propane and air–hydrogen flames by taking measurements as high as possible in the flame. However, readings tended to fluctuate in the upper flame regions and a distance 3 cm above the top of the burner was chosen as being the most suitable for subsequent measurements. This corresponded to a position just above the tips of the blue luminous cones.

Fuel gas pressure. The background radiation was found to increase with increasing fuel gas pressure for all 3 flames (Fig. 2). This dependence varied with the position of measurement in the flame; for example, in the upper flame regions it was virtually independent of fuel gas pressure.

Wavelength of measurement. The dependence of background upon wavelength for the air–propane and air–hydrogen flames, maintained under normal conditions (*i.e.* "normal" fuel gas pressures and taking measurements 3 cm above the top of the burner), is shown in Fig. 3.

The air–acetylene flame had a very much higher background radiation at all wavelengths (*cf.* Fig. 1 and 2) and for convenience is omitted here.

The air–hydrogen flame exhibited a lower background radiation than the air–propane flame at all wavelengths except between 2810 Å and 2850 Å and over the OH band emission region (3060–3200 Å).

Analysing monochromator slit-width. The background radiation from the normal air–propane and air–hydrogen flames was very dependent on slit-width at all wavelengths. In general, doubling the slit-width quadrupled the background radiation from the both flames. On the other hand, the fluorescence signal was directly proportional to slit-width. Thus, the signal: background ratio decreased with increasing slit-width.

The air–acetylene flame was not investigated for the reasons given above.

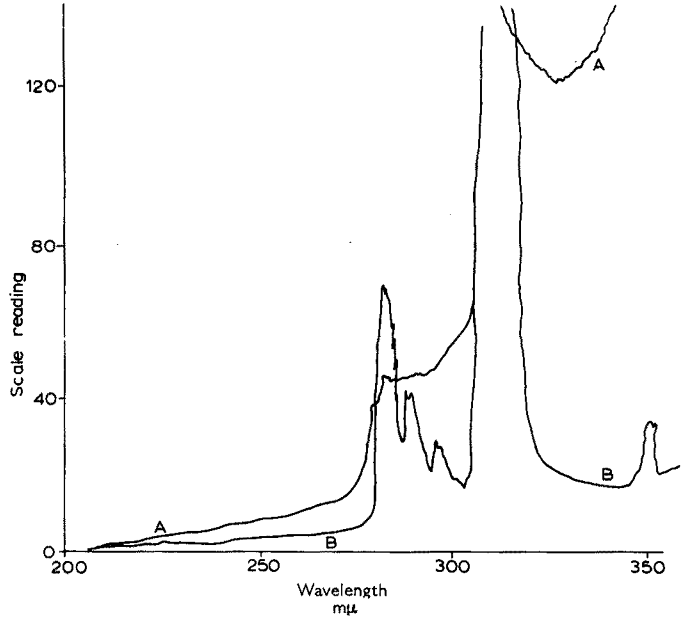


Fig. 3. Background radiation *vs.* wavelength of measurement. Measurements made with normal flame conditions with an analysing monochromator slit 0.1 mm and a burner height of 3 cm. (A) Air–propane; (B) air–hydrogen.

RESULTS AND DISCUSSION

It can be concluded that, chiefly because of its background emission, the air–acetylene flame is the least suitable amongst those examined for the measurement of atomic fluorescence. In addition, the air–acetylene flame was found to produce considerably greater scattering under irradiation from the source. The inferiority of the air–acetylene flame was verified by measuring the fluorescence signal produced by spraying cadmium solutions through the 3 different flames under irradiation from a cadmium discharge lamp. Even at the 100-p.p.m. cadmium level, only the resonance fluorescence at 2288 Å could be detected with the air–acetylene flame[5]. However, a fluorescence signal at both 2288 and 3261 Å could be detected with the other 2 flames.

In general, the air–propane flame was considered to be the most suitable for fluorescence measurements in the ultraviolet region (*ca.* 2000–3200 Å). Its background emission was only slightly greater over most of this region than that from the air–hydrogen flame and, between 3060 and 3200 Å, it was much less. The use of an air–hydrogen flame would be an advantage above *ca.* 3200 Å, but the rate of consumption of hydrogen was rather great and the vast majority of atomic fluorescence measurements are made in the ultraviolet region below this wavelength. In addition, with our equipment, air–propane mixtures gave steadier flames than those obtained with air–hydrogen mixtures.

Preliminary fluorescence measurements with cadmium and zinc (at 2288 and 2139 Å respectively) showed that the fluorescence signal was independent of the propane gas pressure, but was dependent on the hydrogen gas pressure; the fluorescence signal decreased with increasing hydrogen pressure. This may be due to the much faster solution flow rate through the flame because of the comparatively large hydrogen gas pressures. The fluorescence signals were independent of the height of measurement in both flames.

For all these reasons, the air–propane flame was selected as being more suitable than those flames previously described by WINEFORDNER[1–4] and ourselves[5].

Measurement of zinc atomic fluorescence

Optimum operating conditions. Flame irradiation was obtained from a 20-W d.c. Osram zinc vapour discharge lamp operated at 1.5 A via a ballast unit. A window was cut in the outer glass envelope to permit passage of the UV radiation. The source entrance-slit and analysing monochromator slit were set at 2.00 mm and 0.5 mm, respectively. The air pressure was controlled at 15 p.s.i. and the propane pressure at 12 cm, thus giving a translucent flame below the level of luminosity. Measurements were made at a position in the flame corresponding to a distance of 3 cm from the top of the burner to the centre of the monochromator slit. The "absorption" mode of operation of the SP.900A was used.

A 10^{-3} *M* stock solution of zinc was prepared by dissolving 0.2876 g of analytical grade $ZnSO_4 \cdot 7H_2O$ in 1 litre of distilled water. 10^{-5}–10^{-9} *M* solutions were prepared by appropriate dilution immediately before measurement. Because of adsorption on glass surfaces, it was considered unwise to store solutions more dilute than 10^{-4} *M*. The wavelength of measurement was that of the 2139 Å resonance line corresponding to the $4'S_0 \rightarrow 5'P_1$ transition. This line was found by irradiating the flame with the zinc discharge lamp (situated *ca.* 7 cm from the burner) and, whilst aspirating a 10^{-5} *M* zinc solution, scanning the UV region of the spectrum. No other fluorescence emission peaks were obtained for zinc in this study.

With these settings, a linear calibration curve was obtained over the range 10^{-6}–10^{-5} *M* Zn^{2+} (0.06–0.60 p.p.m.). For more dilute solutions, $5 \cdot 10^{-8}$–10^{-6} *M* Zn^{2+} (0.003–0.06 p.p.m.), the analysing slit was opened out to 1.00 mm, and a linear calibration curve was again obtained.

The percentage standard deviation at both 10^{-5} and 10^{-6} *M* concentrations was obtained from the analyses of a set of 12 solutions at the concentrations and was found to be 0.7% and 3.0% respectively.

The effects of 100-fold molar excesses of 41 cations and 18 anions over 10^{-5} *M* Zn^{2+} were examined, *viz.* NH_4^+, Ag, Al, As(III), Au(III), Ba, Be, Bi, Ca, Ce(IV), Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Ga, Hg(II), In, K, Li, Mg, Mn(II), Mo(VI), Na, Ni, Pb, Sb(III), Sc, Se(IV), Sn(IV), Sr, Te(IV), Th, Tl(I), Ti(IV), U(VI), V(V), W(VI), Y, Zn, Zr, acetate, $B_4O_7^{2-}$, Br^-, CO_3^{2-}, Cl^-, citrate, ClO_4^-, CN^-, F^-, I^-, NO_3^-, oxalate, PO_4^{3-}, SCN^-, SiO_3^{2-}, SO_3^{2-}, SO_4^{2-} and tartrate. Hydrolysis was prevented where necessary by the addition of sufficient acid to maintain a clear solution. None of these ions caused more than ±5% variation in the expected fluorescence signal, thus indicating that for most practical purposes the method is free from interference.

Atomic fluorescence using organic solvents

The extraction of zinc diethyldithiocarbamate[7] into methyl isobutyl ketone was investigated as a means of increasing the sensitivity of determination by increased sample concentration and a more favourable rate of aspiration.

To 25 ml of 10^{-6} M Zn^{2+} were added 5 ml of 20% ammonium acetate to give a near-neutral solution and 1 ml of an aqueous 1% solution of sodium diethyldithiocarbamate. The solution was then extracted with 25 ml of methyl isobutyl ketone. Both the aqueous and organic phases were then sprayed into the flame under the usual conditions. With the organic extract, the propane pressure was, however, reduced so that the usual type of non-luminous flame was obtained.

The ketone extract gave a scale reading *ca.* 4.5 times greater than that obtained with an aqueous solution of the same concentration of zinc. The aqueous phase remaining after the extraction gave no detectable fluorescence signal, thus indicating virtually complete extraction.

The increase in fluorescence intensity obtained on spraying the organic extract can be attributed almost entirely to the enhanced rate of aspiration into the flame. The rate of aspiration for an aqueous solution under the usual conditions (*i.e.* air pressure of 15 p.s.i.) was found to be 2.0 ml/min. Of this, only 0.17 ml/min was found to reach the flame. The rate of aspiration with methyl isobutyl ketone was 2.5 ml/min, of which 0.85 ml/min reached the flame. Thus, the amount of ketone reaching the flame was about 5 times that obtained with an aqueous solution.

The limits of detection, corresponding to a signal: noise ratio of 1:1, were found to be *ca.* 10^{-8} M Zn^{2+} for aqueous solutions and *ca.* $2 \cdot 10^{-9}$ M Zn^{2+} for ketone solutions.

These sensitivities could not be improved by the use of quartz lenses to focus the light from the discharge lamp or the fluorescence from the flame. This was because the source had to be moved away from the flame, which in turn had to be moved away from the monochromator slit, in order to accommodate the lenses used which had a rather long focal length (*ca.* 6 cm). However, it would appear that the use of more suitable lenses of shorter focal length which does not allow the inverse square law to operate so effectively would achieve some increase in sensitivity.

Continuous sources

In atomic absorption spectrophotometry the incident light must have a very narrow spectral profile, because of the narrow band-width of the absorption bands. As a consequence, continuous sources can only be used with very high resolution monochromators[8]. On the other hand, in atomic fluorescence spectrophotometry the detector does not receive radiation directly from the source, and the monochromator is only used to isolate the fluorescence radiation of interest. Thus, continuous unreversed sources can be used without the need for additional instrumental modification. Such sources are of considerable interest and utility because of the present limited number of spectral discharge lamps available. In addition, such a source should permit rapid sequential elemental analyses. WINEFORDNER *et al.*[9] have recently described the use of a d.c.-operated 150-W xenon arc lamp. These workers examined 13 elements with an oxy–hydrogen flame and a total consumption integral-burner. The use of a d.c. source and detector results in high background readings and for this reason an a.c. source, at a frequency keyed to that of the amplification system, was used in this examination.

Table II shows the limits of detection for 10 elements obtained in the present study in both air–propane and air–hydrogen flames with an a.c.-operated 150-W xenon arc lamp as source under the usual conditions. The lamp was placed *ca.* 15 cm from the flame and its radiation was focussed by a quartz lens to a point *ca.* 1 cm behind the flame and *ca.* 3 cm above the top of the burner.

TABLE II

ATOMIC FLUORESCENCE WITH A 150-W XENON ARC LAMP

Element	*Wave length (Å)*	*Slit-width (mm)*	*Detection limit (p.p.m.) A.F.S.*			*Detection limit (p.p.m.)*[c] *using air–acetylene*	
			Air–propane[a]	*Air–hydrogen*[a]	*Oxy–hydrogen*[b]	*F.E.*[d]	*A.A.S.*[e]
Zn	2139	2.0	0.6	0.6	0.6	–	0.04
Cd	2288	2.0	0.25	0.25	0.08	11	0.05
Co	2407	1.0	1.5	1.0	–	0.5	0.5
Fe	2483	0.8	5.0	5.0	–	0.4	0.5
Mn	2794	0.25	0.3	0.15	–	0.02	0.2
Pb	2833	0.3	20	10	–	12	1.0
Mg	2852	0.2	2.0	2.0	0.2	0.1	0.02
Cu	3248	0.2	1.0	0.4	0.35	0.1	0.15
Ag	3281	0.4	0.35	0.15	0.08	0.1	0.13
	3383	0.4	0.2	0.10	–	–	–
Tl	3776	0.1	1.0	0.5	0.55	0.2	5.0

[a] A.F.S. denotes atomic fluorescence spectrophotometry.

[b] Data from WINEFORDNER *et al.*[9].

[c] Data from operating manual for SP.900A (Unicam Instruments Ltd., Cambridge, England).

[d] F.E. denotes flame emission.

[e] A.A.S. denotes atomic absorption.

In contrast to WINEFORDNER *et al.*[9], who reported fluorescence for Ag, Au, Ba, Bi, Ca, Cd, Cu, Ga, Mg, Ni, Pb, Tl and Zn, we were not able to detect a fluorescence signal for Ga, and Ni or Pb at 4058 Å. However, a fluorescence signal was obtained for Pb at 2833 Å. This is the resonance line used in atomic-absorption measurements, whereas the 4058 Å line used by WINEFORDNER is usually used for thermal-emission studies. WINEFORDNER's signals could be due, at least in part, to light scattering by droplets or particles in the flame. This is supported by the fact that the limits of detection given for these 3 elements are very high and about 10 times those of any other element.

Fluorescence signals for Co, Fe and Mn were obtained under the above conditions. This appears to be the first time that atomic fluorescence signals have been obtained for these elements. However, fluorescence signals were not obtained from aqueous solutions of Al, Be, Hg(II), Ga, Ni, Pd(II), Sn(IV) and Zr in the air–propane or air–hydrogen flames under irradiation from the 150-W xenon arc lamp. This is attributed to the fact that these elements, except perhaps Ga and Hg(II), only exist as free atoms to a limited extent in these flames. The other elements examined by WINEFORDNER, *viz.* Au, Ba, Bi and Ca, were not investigated.

Table II shows the limits of detection obtained with the same apparatus by thermal-emission and atomic-absorption spectrophotometry. In view of the fact that the intensity of radiation from a 150-W xenon arc lamp at any one wavelength in the UV region is very low, it is somewhat surprising to find such low limits of detection by atomic fluorescence spectrophotometry. These sensitivities are comparable with those obtained by WINEFORDNER *et al.*[9] who used specially designed apparatus.

One of us (K.C.T.) wishes to thank the S.R.C. for the provision of a Research Studentship. We are also grateful to I.C.I. Ltd., for the provision of a grant for the purchase of the SP.900A flame spectrophotometer, and to Mr. R. GOULDEN, Shell Research Centre, Sittingbourne, for the loan of a Beckman DU flame photometer which enabled us to initiate this research.

SUMMARY

Atomic fluorescence in flames is measured by an adaptation of a commercially available flame spectrophotometer. A study is reported of the effect of background radiation and source scattering on 3 flames, air–propane, air–hydrogen and air–acetylene, and of the effects of variation of fuel gas pressure, zone of measurement in the flame, analysing monochromator slit-width and wavelength of measurement. The air–propane flame appears to offer several advantages. The atomic fluorescence of 10 metals is described; those of Co, Fe and Mn have not been previously reported. Excitation of spectra is achieved by means of an a.c. xenon arc lamp or individual discharge lamps.

RÉSUMÉ

Les auteurs ont effectué une étude sur divers paramètres expérimentaux en spectrophotométrie de fluorescence atomique, avec 3 flammes: air–propane, air–hydrogène et air–acétylène. Ils ont examiné l'influence de la pression du gaz combustible, de la zone de mesure dans la flamme, de la largeur de fente du monochromateur et de la longueur d'onde de la mesure. Il semble que la flamme air–propane offre quelques avantages. On décrit la fluorescence atomique de 10 métaux. L'excitation du spectre est réalisée à l'aide d'une lampe à arc xenon ou de lampes à décharge individuelle.

ZUSAMMENFASSUNG

Die Atomfluoreszenz in Flammen wird durch Anpassung an ein kommerziell verfügbares Flammenspektrometer gemessen. Es wird über Untersuchungen berichtet, die den Einfluss der Untergrundstrahlung und Streuquelle von 3 Flammen: Luft–Propan, Luft–Wasserstoff und Luft–Azetylen, beschreiben; ferner die Einflüsse verschiedener Brennstoffgasdrucke, die Messzone der Flamme, die Spaltbreite des Monochromators und die Messung der Wellenlänge. Die Luft–Propan-Flamme scheint verschiedene Vorteile zu bieten. Die Atomfluoreszenz von 10 Metallen wird beschrieben, davon ist über Co, Fe und Mn bisher noch nicht berichtet worden. Die Anregung der Spektren geschieht mit einer Wechselstrom-Xenon-Bogenlampe oder besonderen Entladungslampen.

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A STUDY OF SOME INTERFERENCES IN THE ATOMIC ABSORPTION SPECTROPHOTOMETRY OF MAGNESIUM*

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Atomic absorption spectrophotometry provides a rapid method for the determination of trace amounts of magnesium. Its popularity in this respect can be traced to the small number of interferences and the ease with which they can be eliminated. For example, phosphate is one of the common anions that interfere in this determination, but this effect is counteracted merely by adding a large concentration of strontium or lanthanum to the test solution. Yet little is known of the mechanisms of these interferences and their prevention. As these interference effects are more marked in relatively cool flames, we have investigated the effect of a number of cations, anions and complexing agents on the absorbance of magnesium in an air–propane flame. The results have made it possible to postulate mechanisms for the production of magnesium atoms in this flame, but have not enabled the cation enhancement effects to be fully understood.

EXPERIMENTAL

Apparatus

Hilger and Watts Uvispek with atomic absorption attachment, and fitted with an EEL atomiser.

Magnesium or magnesium–aluminium hollow-cathode lamps. The alloy lamp was only used for the cation interferences.

Air compressor, fitted with a large stabilising tank, and attached through 2 regulators to the atomiser.

Propane flow meter, based on the Venturi principle.

Burner height indicator on outside of burner house, to indicate the position of the light beam in the flame.

Instrumental conditions

The conditions shown below were chosen for flame and instrumental stability, and were kept constant throughout the series of experiments.

Lamp	*Wavelength*	*Slit-width*	*Lamp current*	*Air pressure*
Mg	2852 Å	0.10 mm	32 mA	14 p.s.i.
Mg–Al		0.25 mm	37 mA	

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* This paper was read at the 2nd Reunion Symposium of the Birmingham University Research School of Analytical Chemistry, held at Birmingham on April 28-29th, 1966.

Each recorded point is the mean of 3 or 5 absorbance readings (anion and cation interferences, respectively). Distilled water was sprayed between readings. At least 30 min were allowed for the lamp and burner to stabilise under the working conditions.

The marked dependence of magnesium absorbance on propane flow rate (Fig. 1) emphasizes the care that must be taken to ensure a constant, reproducible propane flow. This was achieved in the anion experiments. There were slight day-to-day variations in the cation experiments; these are recorded (as cm of water) in the text.

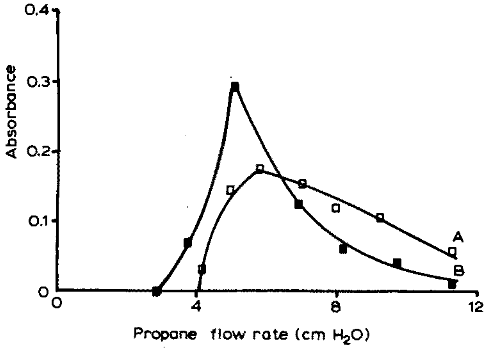


Fig. 1. The effect of propane flow rate on magnesium absorbance with the burner (A) fully lowered, (B) fully raised. Solution: 2.5 p.p.m. Mg in 0.1 *N* HCl.

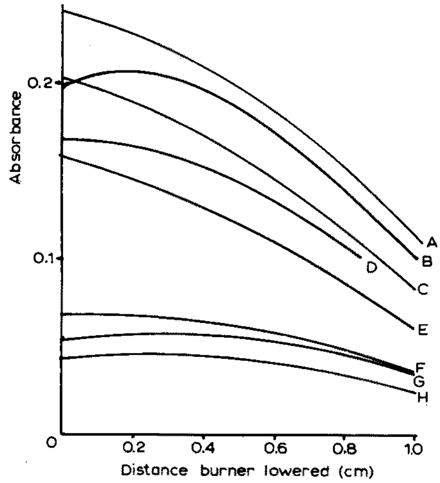


Fig. 2. The effect of anions and complexing agents on magnesium absorbance. Solutions: 2.5 p.p.m. Mg in presence of (A) 8-hydroxyquinoline, (B) HCl, (C) EDTA, (D) HNO_3, (E) EDTA/HCl, (F) H_3PO_4, (G) oxalic acid and (H) H_2SO_4.

The fuel-lean flame was 10 cm long and 2–3 cm in visual height above the burner top. When viewed along the length of the burner top, the flame was colorless when distilled water was sprayed; when a magnesium solution was sprayed, the inner orange zone was bordered by a thin violet zone and the outer mantle remained colorless. When the burner was fully raised, its top was 1.0 cm above its fully lowered position and obscured about half the light beam. The burner is designed so that the lowest 3 mm of the flame is obscured from the light beam.

Investigation of interferences

Anion and complexing agent interferences. The absorbances of aqueous solutions of 2.5 p.p.m. of magnesium (added as the chloride) containing large excesses of the following anions were measured at various heights in the flame: chloride (0.1 *N* hydrochloric acid), sulphate (0.1 *N* sulphuric acid), phosphate (0.1 *N* phosphoric acid), oxalate (0.1 *N* oxalic acid), nitrate (0.1 *N* nitric acid), EDTA (10^{-3} *M* Na_2EDTA, with 0.1 *N* hydrochloric acid also present in one set of experiments), 8-hydroxyquinoline (0.004 *M* in 0.2 *M* acetic acid).

Cation interferences. The following effects of cations (added as their chlorides) on the absorbance of magnesium (also added as its chloride) in 0.1 *N* hydrochloric acid, with the burner fully raised, were measured: (*a*) 0–3000 p.p.m. of calcium on 0.5 and 5.0 p.p.m. of magnesium, (*b*) 0–150 p.p.m. of calcium on 0.5, 2.5 and 5.0 p.p.m. of magnesium, (*c*) 0–75 p.p.m. of strontium, barium, sodium and iron(III) on 0.5 p.p.m. of magnesium.

In addition, the experiments with chloride, sulphate, phosphate and 8-hydroxyquinoline were repeated in the presence of 30 p.p.m. of calcium added as its chloride.

Chemicals

All were A.R. grade except calcium carbonate, which was Specpure (Johnson, Matthey & Co., Ltd.). Calcium and barium chloride solutions were prepared from their carbonates.

RESULTS AND DISCUSSION

Anion interferences

The absorbances at various heights in the flame when the different anions and complexing agents were present in solution are shown in Fig. 2. It allows the anions to be grouped into 2 classes:

(*1*) those that cause low absorbances: sulphate, phosphate, oxalate,

(*2*) those that cause high absorbances: chloride, nitrate, EDTA, 8-hydroxyquinoline.

The enhancing or depressing effect of some of these anions has been noted previously in emission studies[1,2]. The suppressive effects of sulphate and phosphate (and silicate and aluminate) on absorption measurements are also well-known[3]. The EDTA was added as its disodium salt, so it was possible that the effect was that of sodium. Experiments showed, however, that the effect of sodium under these conditions was very small (see Fig. 6); the effects are therefore due to EDTA.

As the absorbance at 2852 Å is directly related to the magnesium atom concentration in the part of the flame under examination, Fig. 2 shows the change in magnesium atom concentration with height in the flame—a one-dimensional flame profile. This Figure therefore compares the flame profiles of magnesium when different anions are present in the solution sprayed into the flame. Thus class (*1*) anions reduce considerably the formation of magnesium atoms compared with those in class (*2*). The reasons for this can be explained by considering what happens to the aerosol in the flame on the basis of the known high-temperature reactions of the compounds involved and the chemical constitution of the flame.

When a salt-containing aerosol is sprayed into a flame, the solvent evaporates rapidly, leaving minute particles. It has been suggested[4,5] that the particles then disintegrate, at least partially, into atoms, when the hotter part of the flame is reached. These atoms are oxidised in the reaction zone of the flame, and equilibrium is reached in its outer mantle[5]. The direct dissociation of many inorganic magnesium salts to give magnesium atoms, however, is not a realistic concept. For instance, magnesium sulphate decomposes, without volatilising, at 890° into magnesium oxide and sulphur oxides[6]. There can be no question of direct dissociation to magnesium atoms at this temperature. Thus the magnesium atoms must arise entirely from the magnesium oxide particles in the hot region of the flame. The mechanism of this latter reaction has not been established. However, as the sublimation point of magnesium oxide is 2770°, at which temperature monomeric magnesium oxide molecules are the vaporising species[7], it would seem unlikely that sublimation would contribute significantly to the production of magnesium species in the vapour phase at the temperature of the air–propane flame ($T_{\max} \simeq 1925°$). A more acceptable mechanism is the interaction of hydrogen atoms with the surface of the magnesium oxide particles:

$$\mathrm{MgO\ (s) + H\cdot(g) \rightleftharpoons Mg\ (g) + OH\cdot\ (g)} \qquad (1)$$

The existence of hydrogen atoms in flames is well known, and they are found in concentrations much in excess of those expected from thermodynamic equilibrium, especially between 1330 and 2130°[8]; they persist for several milliseconds after primary combustion[8]. As the reaction is essentially a surface reaction, and as the particles traverse the flame rapidly, reaction (1) would not be completed before the oxide particle leaves the flame. Thus there is a lower magnesium atom concentration in the flame, especially in the lower regions, than if all the magnesium compounds had been in the gas phase. Magnesium phosphate and oxalate, which also decompose to the oxide, have similar flame profiles.

The class (*2*) magnesium salts must be able to produce magnesium species in the vapour phase by a reaction other than (1). Magnesium chloride is a typical example. Magnesium chloride hexahydrate loses water at 160° to form the monohydrate[9]. This then reacts further in one of two ways:

$$\mathrm{MgCl_2\cdot H_2O\ (s) \rightleftharpoons MgCl_2\ (s) + H_2O\ (g)} \qquad (2)$$

$$\mathrm{MgCl_2\cdot H_2O\ (s) \rightleftharpoons MgO\ (s) + 2\ HCl\ (g)} \qquad (3)$$

Anhydrous magnesium chloride boils at 1412°[6] to give $MgCl_2$ in the vapour phase[7]. Thus, in addition to the formation of magnesium oxide by reaction (3) and the subsequent production of magnesium atoms as described above, the gaseous magnesium chloride provides another source of magnesium atoms. In this instance direct decomposition to the elements may contribute to the production of magnesium atoms, but it is more likely to occur via hydrolysis to the oxide, with the subsequent production of magnesium atoms by the reaction of hydrogen atoms with magnesium oxide molecules that are produced in the gas phase:

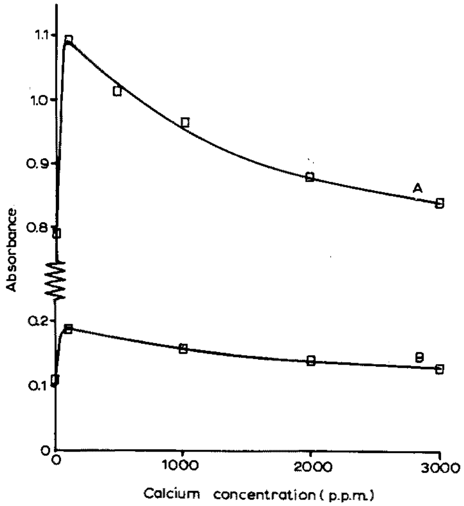
$$\mathrm{MgO\ (g) + H\cdot(g) \rightleftharpoons Mg\ (g) + OH\cdot(g)} \qquad (4)$$

It should be noted that this additional source of magnesium atoms only enhances the production of magnesium atoms when reaction (1) is incomplete. If the temperature is high enough to allow reaction (1) to occur with the whole magnesium oxide particle before it leaves the reaction zone of the flame, the final magnesium atom concentration in the gas phase should be independent of the means by which the magnesium atoms are produced. Numerous reports, such as that of ALLAN[10], that the depressive action of sulphate and phosphate is reduced or eliminated by the use of the air–acetylene flame, confirm that at higher temperatures, the concentration of magnesium atoms in the gas phase is independent of the mechanism by which they were formed. Magnesium nitrate decomposes to the oxide at 321°[11]. However, magnesium nitrate melts before decomposing if heating is sufficiently rapid[12], thus some volatilisation might occur during the very rapid heating in the flame.

Magnesium chloride, and, to a lesser extent, magnesium nitrate, produce the highest concentration of magnesium atoms somewhat above the flame base, as do the class (*1*) anion salts. This position of highest concentration has been noted previously[13], and is to be expected if reaction (4) reaches equilibrium rapidly, so that the greatest magnesium atom concentration occurs in the hottest region of the flame. The organic ligands, however, produce most atoms at the flame base, with the atom concentration decreasing as equilibrium is established. This indicates that a proportion of the magnesium atoms probably arises by direct decomposition at relatively low temperatures. DEBRAS-GUÉDON AND VOINOVITCH[14] and WALLACE[15] have found that aluminium atoms are similarly released from the aluminium–8-hydroxyquinoline complex.

Cation interferences

Calcium. The effects of calcium on the absorbance of 0.5 and 5 p.p.m. of magnesium are shown in Fig. 3. The considerable initial enhancement was examined in detail for 3 different magnesium concentrations (Fig. 4). The marked enhancement, even by equivalent amounts of calcium, is very striking. There seems to be some correspondence between the calcium–magnesium ratios required to produce the peaks in the enhancement curves. These peaks are especially prominent for 5 p.p.m. of magnesium.



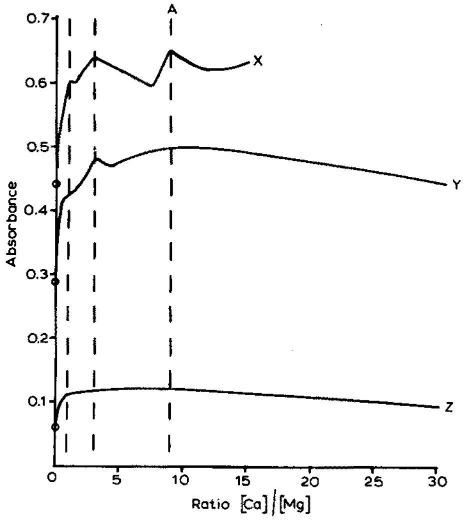


Fig. 3. The effect of calcium on the absorbance of (A) 5.0 p.p.m., (B) 0.5 p.p.m. of magnesium. Propane flow rate: 10 cm H_2O. Burner fully raised.

Fig. 4. The variation in absorbance of magnesium with ratio by weight of calcium to magnesium: (X) 5.0, (Y) 2.5, (Z) 0.5 p.p.m. Mg. Propane flow rates: (X) 5.4, (Y) 5.6, (Z) 5.0 cm H_2O. Burner fully raised.

The flame profile of the calcium enhancement of the absorbance of 2.5 p.p.m. of magnesium was measured in the presence of chloride, sulphate, phosphate and 8-hydroxyquinoline in order to obtain further information about the enhancement process. The results are given in Fig. 5. The calcium concentration used (30 p.p.m.) was that which gave peak A in Fig. 4. As the absorption enhancement is the difference between the absorbances in the presence and absence of calcium, Fig. 5 gives a flame profile of the enhancement (*i.e.* the increase in magnesium atom concentration), arising from the addition of calcium, in the initial presence of the various anions. Although these profiles qualitatively resemble those of magnesium in the absence of calcium, they correspond in profile and relative magnitude to the expected flame profiles of calcium alone under the same conditions. It is well-known that phosphate seriously suppresses calcium atom production in the air–propane flame, whereas sulphate has less effect. Thus phosphate not only suppresses magnesium atom production, but likewise prevents the formation of calcium atoms, and thus prevents the enhancing effect of calcium. It would seem, therefore, that the enhancement is related to the production of calcium atoms, and could arise from an overall reaction similar to reaction (5)

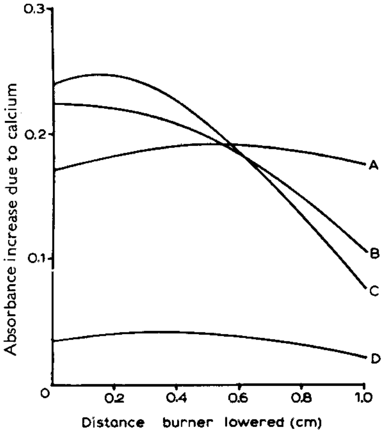


Fig. 5. The effect of anions and complexing agents on the enhancement by calcium of magnesium absorbance. Solutions: 2.5 p.p.m. Mg, 30 p.p.m. Ca, in presence of (A) H_2SO_4, (B) 8-hydroxyquinoline, (C) HCl, (D) H_3PO_4. Propane flow rates: (A, B) 5.7, (C,D) 5.6 cm H_2O.

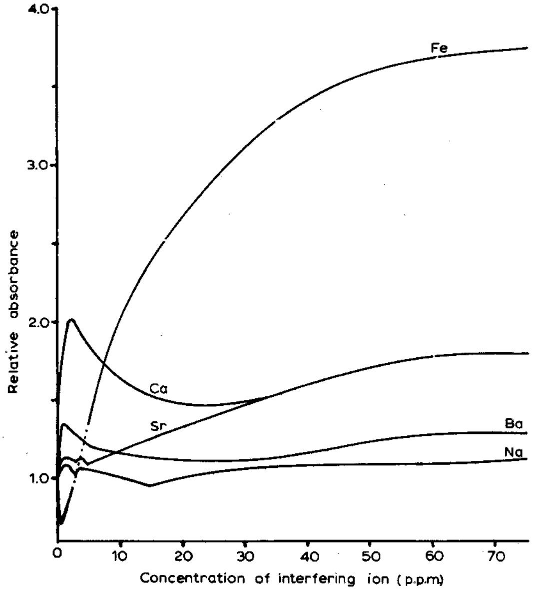


Fig. 6. The effect of some cations on the absorbance of 0.5 p.p.m. of magnesium. Propane flow rates: Fe, 5.3; Ca, 5.0; Sr, 5.3; Ba, 5.5; Na, 5.7 cm H_2O. Burner fully raised.

$$\mathrm{Ca\ (g) + MgO \rightleftharpoons CaO + Mg\ (g)} \tag{5}$$

The reason for the peaks is not clear; possibly they are due to eutectic mixtures of increased volatility. The eventual decrease in magnesium absorbance in the presence of large concentrations of calcium salts (Fig. 3) could be due to the formation of large particles in the flame, in which the surface concentration of magnesium oxide is low; this would inhibit reaction (1).

Other cations. Other metals are known to interfere in the production of magnesium atoms in a flame[16]. In Fig. 6, the effects of calcium, strontium, barium, sodium and iron (all initially present as their chlorides) on the absorbance of 0.5 p.p.m. of magnesium are compared. In all cases, there was a rapid initial change in absorbance which quickly diminished and gave way to a further enhancement as the concentration of the interfering ion increased.

There is a considerable difference between the magnitudes of the enhancements by the various metals. The magnitude of the initial peak decreases in the order Ca> Ba> Sr> Na (>Fe). The reason for this initial enhancement by the alkaline earth metals is not known, but the fact that the enhancement reaches a maximum when the concentrations of magnesium and the other metal are commensurate suggests the formation of more volatile, mixed-element compounds. The second enhancement decreases in magnitude in the order Fe > Ca > Sr > Ba > Na. The conclusion that this effect is due to the production of atoms of interfering metal and the subsequent reaction of these atoms with magnesium oxide is supported by the fact that the only elements that give such an enhancement are those that (*a*) produce significant concentrations of their atoms in the air–propane flame, and (*b*) have oxides that are more, or not much less, stable than magnesium oxide.

The initial depressive effect of iron is similar to that of aluminium[3]. The mixed oxides $MgFe_2O_4$ and $MgAl_2O_4$ are probably produced, which are more stable than, and therefore more resistant to radical attack than magnesium oxide. As the aluminate is more stable than the ferrite, the depressive effect of aluminium is greater than that of iron. The considerable enhancement that results from the addition of larger concentrations of iron can be ascribed to the production of iron atoms from the iron not involved in mixed oxide formation, and their subsequent reaction. It is worth noting that aluminium compounds, unlike those of iron, normally produced very few aluminium atoms in relatively cool flames, and would thus not be expected to show this enhancing effect. Indeed, ALLAN[10] did not find such an enhancement, and MENZIES[4] found only a small effect under slightly different conditions.

ELWELL AND GIDLEY[3] found that the depressive effect of aluminium on magnesium absorbance was much increased by sulphuric and nitric acids, and slightly decreased by hydrochloric acid. Aluminium interferes by mixed oxide formation, which must arise from reactions (6) or (7).

$$MgXO_n + Al_2O_3 \rightleftharpoons MgAl_2O_4 + XO_{n-1} \quad (X = N, P, S) \tag{6}$$

$$MgO \quad + Al_2O_3 \rightleftharpoons MgAl_2O_4 \tag{7}$$

The effect of sulphuric acid, therefore, is both to reduce the production of magnesium chloride vapour, and to increase the concentration of species susceptible to the suppressive reaction (6) or (7). Nitric acid has a similar effect. Aluminium nitrate decomposes to the oxide at 150°[6], so that reaction (6) could take place before any magnesium nitrate volatilises.Hydrochloric acid would enhance the production of magnesium chloride vapour, and thus decrease the depressive effect of aluminium. WALLACE[15] reported that 8-hydroxyquinoline markedly reduced the effect of aluminium. This is because, as already mentioned, 8-hydroxyquinoline allows the production of appreciable amounts of both metals in the vapour phase without involving preliminary oxide formation, so that mixed oxide formation is avoided.

The addition of large amounts of strontium is reported to overcome the depressive effects of aluminate, silicate and phosphate in a hydrochloric acid solution[17]. This occurs because the strontium, present in such large amounts, competes successfully with magnesium in the formation of stable mixed oxides, and is also able to enhance the production of magnesium atoms by a reaction similar to (5). Calcium has been found to have a similar effect[18].

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SUMMARY

The effects of some cations, anions and complexing agents on the absorbance of magnesium in the air–propane flame are investigated in detail. The results have enabled the mechanisms of magnesium atom production in this flame to be deduced, and have clarified the nature of the interferences.

RÉSUMÉ

On a examiné en détails l'influence de quelques cations, anions et agents complexants sur l'absorption du magnésium dans une flamme air–propane. Les résultats obtenus ont permis de trouver le mécanisme de la production d'atomes de magnésium et d'éclaircir la nature des interférences.

ZUSAMMENFASSUNG

Die Einflüsse einiger Kationen, Anionen und komplexbildenden Reagentien auf die Absorption des Magnesiums in der Luft–Propan-Flamme wurden im einzelnen untersucht. Die Ergebnisse ermöglichten es, den Mechanismus für die Atombildung des Magnesiums in dieser Flamme abzuleiten und die Ursache der Störungen zu erklären.

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SOME ASPECTS OF N-BENZOYLPHENYLHYDROXYLAMINE AND CUPFERRON REACTIONS WITH TIN, ANTIMONY AND OTHER SELECTED ELEMENTS*

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RYAN AND LUTWICK[1] found that tin(II) and tin(IV) in dilute hydrochloric acid solution were precipitated by N-benzoyl-N-phenylhydroxylamine (BPHA) giving a common product of the composition $Sn(C_{13}H_{11}O_2N)_2Cl_2$ (I) or $Sn(C_{13}H_{10}O_2N)_2Cl_2$ (II). Whether the precipitate consists of I or II depends on the valency state of the tin in the substance and at first it was thought that the BPHA reduced tin(IV) to tin(II) which then reacted with further BPHA to give I. In a later paper[2] the same authors were less certain of this conclusion and tended to favour formula II on the basis of the oxidation potentials for the tin(II)–tin(IV) and phenylhydroxylamine–aniline couples. Since then the substance, which is a useful gravimetric weighing form for tin, has variously been referred to as containing tin in either the (II) or (IV) oxidation state.

While N-nitrosophenylhydroxylamine (commonly used as the ammonium salt, "cupferron") normally reacts with the same elements in the same valency states under fairly similar conditions of acidity as does BPHA, tin reactions are different. Cupferron gives 2 distinct tin derivatives[3,4] depending on whether tin(II) or tin(IV) reacts.

Available information on the behaviour of antimony with BPHA is confined to a limited study of its extraction into chloroform containing the reagent[5]. With cupferron, antimony(III) is precipitated almost completely from weakly acidic solution and it is also extracted into chloroform[6]. Antimony(V) and arsenic(III) and -(V) are not precipitated or extracted with cupferron under any conditions[6]; published data are not available relating to BPHA. Bismuth(III) is extracted into chloroform from weakly acidic solutions in the presence of either BPHA[7] or cupferron[6].

In the present work the behaviour of both organic reagents was compared in the liquid–liquid extraction of tin and antimony from hydrochloric acid solution; this led to an attempt to identify the main products of decomposition of cupferron by strong acid. In addition, extraction data relating to BPHA were obtained for arsenic and bismuth under comparable experimental conditions. Potential separations are discussed for extractions employing BPHA for aqueous hydrochloric and perchloric acid systems.

A more detailed examination of the efficiency of extraction of tin into chloroform as a function of BPHA, chloride and hydrogen ion concentrations coupled with a study of infrared spectra was carried out to provide information on the nature of the

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* This paper was read at the 2nd Reunion Symposium of the Birmingham University Research School of Analytical Chemistry, held at Birmingham on April 28–29th, 1966.

extracted tin species and to enable a distinction to be made between formulation I and II for the precipitate.

Other precipitation reactions, in particular of tin by BPHA in the presence of anions other than chloride, and some solubility measurements are also reported.

EXPERIMENTAL

Isotopes

Arsenic-74 as sodium arsenate solution of high specific activity was obtained from the Radiochemical Centre, Amersham, England.

Bismuth-210 (radium E) in admixture with *lead-210* (radium D) and *polonium-210* (radium F) was also obtained from the Radiochemical Centre.

Antimony-124 and tin-113 were obtained by neutron irradiation of Sb_2O_3 and Sn respectively in BEPO, Harwell. Shorter-lived induced activity was allowed to decay before use.

Arsenic, bismuth and antimony samples were counted in an annular type Geiger-Muller counter (Twentieth Century Electronics, type M6H). Since in the radium D, E, F decay system only radium E is counted in this way, a separation from lead and polonium was not needed. The tin-113 was determined through its indium daughter as described previously[8].

Reagents

These were of analytical-reagent grade unless otherwise stated.

Standard solutions of arsenic, antimony, bismuth and tin containing about 5 mg of each element per ml were prepared in hydrochloric acid from the appropriate element or its oxide.

Cupferron was supplied by Messrs. Hopkin and Williams Ltd., Chadwell Heath, Essex, England.

Other reagents, *e.g.* BPHA, were discussed in a previous paper[8].

Extraction studies and separations

The procedure followed in arriving at suitable extraction conditions for each element in the appropriate valency state has already been outlined[8]. In all the experiments described equal volumes of the 2 phases were equilibrated. Reduction with nickel powder was employed where necessary to ensure the valency states tin(II), arsenic(III) below 4 M in hydrochloric acid, antimony(III) and bismuth(III)[9]. In hydrochloric acid, bromine gave the higher oxidation states of all but arsenic for which hydrogen peroxide was used[9].

In the cupferron studies, the solid water-soluble reagent was added to the aqueous phase. (The acid concentrations recorded in presenting the results are those obtaining before addition of the cupferron which amounts to a 0.32 M solution; the true acid concentration in such systems may therefore be lower by as much as 0.32 M.)

The separation of pairs of elements was checked using radioisotopes and decontamination factors calculated[8].

In the studies to determine the nature of the extracting tin species, aqueous phases of constant ionic strength were used. Components reacting with the tin except that whose effect was being studied were maintained constant.

BPHA dependence. The aqueous phase was 0.80 M in hydrochloric acid and initially $1.3 \cdot 10^{-3}$ M in tin(IV). The BPHA concentration in the chloroform was varied over the range $4.6 \cdot 10^{-3}$ to $4.6 \cdot 10^{-2}$ M (0.10–1.0%). For the investigation in a perchloric acid medium, the ionic strength was 4.0, the initial tin concentration 10^{-3} M and the BPHA range $2.3 \cdot 10^{-4}$ to $3.2 \cdot 10^{-2}$ M (0.050 to 0.70%).

Chloride dependence. An aqueous phase of ionic strength 0.28 in perchloric acid was chosen for this investigation and the chloride concentration varied using hydrochloric acid from $1.5 \cdot 10^{-3}$ to $8.0 \cdot 10^{-3}$ M. The chloroform phase was 1% in BPHA. Extraction of tin from the perchloric acid alone is appreciable (31.8%) thus reducing the range of chloride concentrations which might otherwise be covered.

Hydrogen ion dependence. The following sets of conditions were employed in an attempt to check the hydrogen ion dependence.

Run	*Tin concentration (M)*	*Hydrogen ion range (M)*	*Ionic strength*	*BPHA (%)*
1	$1.3 \cdot 10^{-3}$	$(4 \text{ to } 1.2) \cdot 10^{-2}$	1.0	1.0
2	$7.1 \cdot 10^{-3}$	0.2 to 0.8	1.1	0.30
3	$1.4 \cdot 10^{-2}$	0.49 to 4	6.0	0.50

The ionic strength was maintained using lithium chloride and equal volumes of the phases were equilibrated.

Acid-induced decomposition of cupferron

A Pye series 104 gas–liquid chromatography apparatus with a flame ionisation detector was used with a column packing of SE-30 (a methyl silicone gum), nitrogen as the carrier gas (flow rate 40 ml/min) and a column temperature of 150±5°.

Ten percent solutions of cupferron in 1–11.4 M hydrochloric acid were shaken with equal volumes of benzene for 15 min. The benzene layer was separated and dried over sodium sulphate and 0.25 ml injected into the chromatographic column. Various known substances were chromatographed for comparison purposes.

Infrared spectra

Spectra from mulls in perfluorokerosene or nujol were obtained using a Grubb-Parsons GS-2A double-beam grating spectrophotometer, and those from chloroform-d solution by means of a Unicam-200 with a sodium chloride monochromator. Chloroform-d ($CDCl_3$) was obtained with a minimum purity of 99% from E. Merck AG, Darmstadt, Germany. Deuterium oxide (99.5% D_2O) was supplied by Koch-Light Laboratories Ltd., Colnbrook, Bucks, England.

Deuterium was substituted for the hydroxyl hydrogen of BPHA by following the general method of HARP AND EFFERT[10]. The BPHA (0.1 g) in dry ether (3 ml) was shaken with deuterium oxide (2 ml) for 30 min. The aqueous layer was replaced by fresh deuterium oxide (2 ml) and the shaking continued for 15 min. The ether phase was finally shaken with a third portion of deuterium oxide for 15 min and then separated and the ether removed by evaporation under vacuum.

The $Sn(C_{13}H_{10}O_2N)_2Cl_2$ was prepared by the method of RYAN AND LUTWICK[1].

Tin and antimony precipitation reactions

The precipitation of tin by BPHA was examined from solutions 0.5 to 1 *M* in hydrobromic, hydriodic, nitric and sulphuric acids essentially following the method recommended previously for the precipitation from hydrochloric acid[1]. Antimony(III) was precipitated from 1 *M* hydrochloric acid using a slight excess of BPHA assuming that the latter reacts as a monobasic acid giving a neutral salt.

Solubility measurements

Tin(IV) chloride or bromide labelled with tin-113 was used to prepare[1] $Sn(C_{13}H_{10}O_2N)_2Cl_2$ or $Sn(C_{13}H_{10}O_2N)_2Br_2$. Samples of the precipitate were sealed in polythene capsules with 10-ml portions of the chosen solvent or solution and agitated in a thermostatted water-bath maintained at 25°. After equilibration the excess solid was separated by centrifugation (preferably) or filtration and 5 ml of the solution counted in a γ-scintillation counter.

A weighed portion of each dry labelled tin substance was dissolved in 5 ml of a 1:1 (v/v) alcohol:water mixture and counted. Separate experiments showed that the change in solvent medium had little effect on the counting efficiency. The solubility, *S*, in mg/100 ml of solution was calculated from the relation

$$S = \frac{WY}{X} 20$$

where *W* is the weight of substance (in mg) dissolved in the ethanol/water and *X* its count rate; *Y* is the count rate of the solution equilibrated with solid substance.

RESULTS AND DISCUSSION

The extraction of the various elements of interest into a 1% solution of BPHA in chloroform is recorded in Fig. 1. It was found that arsenic extraction was not enhanced more than 1 or 2% by the presence of BPHA in the chloroform; the results presented are in fair agreement with those of BRINK *et al.*[11]. All the data with the exception of antimony(V) in perchloric acid were obtained for hydrochloric acid

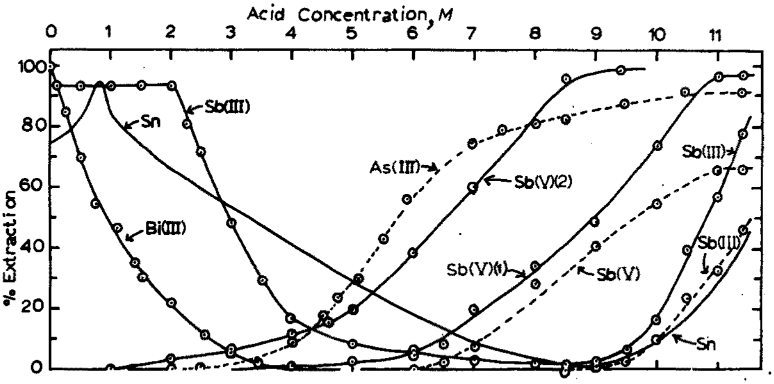


Fig. 1. Extraction data for concentrations of 1–3 · 10^{-3} *M* metal ions from hydrochloric acid (except Sb(V), curve 2, which is for a perchloric acid medium) into (*a*) 1% BPHA in chloroform (full lines) and (*b*) into chloroform alone (broken lines).

systems. In general, extraction first decreases with increasing acid concentration and then again increases at high acidity depending on the element and its valency state. The increase is clearly partly due to extraction by chloroform alone in the case of antimony but for tin the presence of BPHA had little or no effect on the extraction at acidity greater than 9 *M*. Bismuth(III) was not extracted from hydrochloric acid greater than 4 *M*. Arsenic(V) was found to give around 5% extraction over the whole concentration range of this acid. Hydrogen peroxide was used as oxidant but independent experiments using nitric acid and cerium(IV) where effective gave similar results. As with arsenic(III) the presence of BPHA in the chloroform did not affect this extraction. Bismuth(V) was not extracted into BPHA in chloroform from solutions 0.1 to 11.4 *M* in hydrochloric acid.

Antimony(V) extracted well from perchloric acid into BPHA but not into chloroform alone; extraction occurred less readily from hydrochloric acid. A previous study showed that tin extracts well into BPHA in chloroform from perchloric acid[8].

Data relating to the extraction of antimony(III), tin(II) and -(IV) from hydrochloric acid to which cupferron had been added are presented in Fig. 2. The range of maximum extraction of antimony(III) in the direction of higher acidity was appreciably shorter than that for BPHA. Unlike BPHA, tin extraction with cupferron depended on the valency state; neither state however gave a distribution curve similar to that obtained with BPHA (Fig. 1). For tin(II) and -(IV) extraction decreased with increase in acidity and after passing through minima again increased due to chloroform extraction alone for aqueous phases above 8 and 5 *M* respectively in hydrochloric acid. Antimony(III) did not show this behaviour; extraction became negligible in the presence of added cupferron above 8 *M* in hydrochloric acid although extraction of both antimony(III) and -(V) (Fig. 1) into chloroform occurred in its absence. The cupferron or one or more of its decomposition products must therefore inhibit antimony extraction into chloroform. The extraction of arsenic(III) into chloroform is also inhibited; a 10% solution of cupferron gave only 10% and 17% extraction from 5 *M* and 11.4 *M* hydrochloric acid respectively. Antimony(V) was not extracted into chloroform from hydrochloric acid solutions to which cupferron had been added.

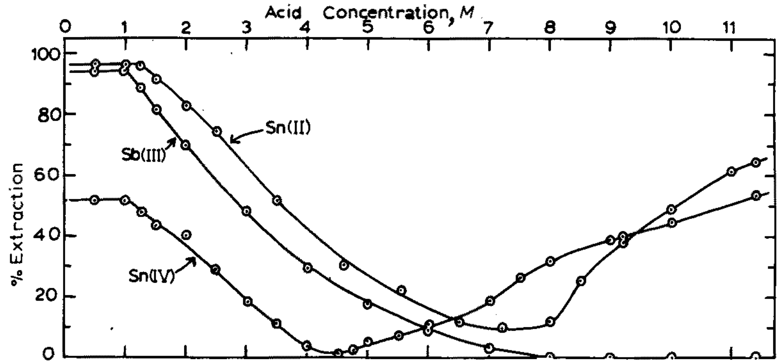


Fig. 2. Extraction of 1–3 · 10^{-3} *M* metal ions from hydrochloric acid 5% in cupferron into chloroform.

The acid decomposition of cupferron

It has long been known that N-nitrosophenylhydroxylamine is unstable in aqueous mineral acid and various decomposition products have been reported[12]. In the course of the present work it was found in preliminary experiments that the substance or substances causing inhibition of extraction of arsenic and antimony were extracted into chloroform or benzene since the aqueous phase from which they were thus removed gave the expected distribution of these elements on shaking up with fresh chloroform. An attempt was therefore made to identify the extractable decomposition products of the reagent by the method outlined in the experimental section.

For aqueous phases up to about 6–8 *M* in hydrochloric acid the main decomposition product was found to be nitrosobenzene which increases in yield with increasing acidity. At higher acid concentrations the main product, which may amount to about 80% of the total volatile decomposition products, is different; nitrosobenzene is present only in relatively small amount. This product has not been identified; it is not, however, phenol, nitrobenzene, phenylhydroxylamine, azoxybenzene or aniline. Nitrosobenzene is not responsible for inhibiting the extraction of antimony.

Separations

Table I contains collected data (obtained by the method previously outlined[8]) relating to sets of optimum conditions for the extractions. In all cases except tin(IV) a single extraction with cupferron removes over 90% of the element from the aqueous phase. From the Table, Fig. 1 and extraction data obtained previously for tin from perchloric acid[8], a number of separations are possible.

TABLE I

OPTIMUM SETS OF CONDITIONS FOR THE EXTRACTION OF VARIOUS ELEMENTS

Element	*Aqueous phase*	*Chloroform phase*[a]	*Optimum equilibration time (min)*	*Maximum metal concn. (mg/10 ml)*	% *Extracted*[b]
Sn(IV)	0.8 *M* HCl	1% B	10	10	94.4[c]
	4 *M* $HClO_4$	1% B	10	10	96.1
Sb(III)	1 *M* HCl	0.5% B	10	10	93.1
Sb(V)	9.4 *M* $HClO_4$	0.9% B	15	8	98.3
Bi(III)	0.1 *M* HCl	0.6% B	10	8	99.4
Sn(IV)	0.5 *M* HCl[d]	6% C	6	10	51.8
Sn(II)	1 *M* HCl	6% C	6	10	96.4
Sb(III)	1 *M* HCl	2% C	12	5	94.2
As(III)	11.4 *M* HCl	$CHCl_3$	7	12.5	91.2

[a] B = BPHA; C = cupferron.
[b] In a single extraction with equal phase volumes.
[c] From ref. 8.
[d] For cupferron systems the acidity recorded does not take account of acid consumed by the reagent.

(*1*) Extraction of tin from 0.8 *M* hydrochloric acid into BPHA in chloroform gives a reasonable separation from antimony(V).

(*2*) Arsenic(III) is separated from bismuth(III) by partitioning the former into chloroform alone from concentrated hydrochloric acid.

(*3*) Bismuth is removed from tin(IV) by extracting the latter from 4 *M* perchloric acid into BPHA in chloroform.

(*4*) Solutions 9 *M* or more in perchloric acid permit the extraction of antimony(V) into BPHA in chloroform leaving bismuth in the aqueous phase.

(*5*) Bismuth is separated from tin(IV) and antimony(V) by extracting the last 2 mentioned from 9 *M* perchloric acid, 0.1 *M* in oxalic acid. Separation of tin and antimony is then achieved by procedure *1* above, without interference from the oxalic acid.

TABLE II

SEPARATION FACTORS FOR PAIRS OF ELEMENTS

Element A separated from B	*Method of measuring*	*Phases*	*Separation factor*[a]
Sn(IV) from Sb(V)	Active Sb	0.8 *M* HCl/1%B	$1 \cdot 10^2$
As(III) from Bi(III) or (V)	Active Bi	conc. $HCl/CHCl_3$	$2 \cdot 10^3$
Sn(IV) from Bi(III) or (V)	Active Bi	4 *M* $HClO_4$/1%B	$9 \cdot 10^2$
Sb(V) from Bi(III) or (V)	Active Bi	9 *M* $HClO_4$/1%B	$7 \cdot 10^2$
Sn(IV) and Sb(V) from Bi(III) or (V)	Active Bi	9 *M* $HClO_4$/1%B	$7 \cdot 10^2$

[a] The ratio of the amount of B present initially in A + B to the amount of B present in the separated A.

These various separations were performed by the procedure given previously[8] and separation factors for pairs of elements are recorded in Table II. In determining the separation factor, the aqueous phase was extracted twice with equal volumes of the chloroform phase (Table II) and then washed with 2 successive portions of chloroform alone before counting.

The nature of the tin, BPHA, chloride interaction

Partition studies. The equilibrium distribution of tin between chloroform containing BPHA and hydrochloric acid (Fig. 1) is independent of the initial oxidation state of the tin. Therefore, depending on the valency state of the tin to which the BPHA attaches itself one or other of the equations:

$$Sn(II) + 2\,HB + 2\,Cl^- \rightleftharpoons Sn(HB)_2Cl_2 \qquad (1)$$

or

$$Sn(IV) + 2\,HB + 2\,Cl^- \rightleftharpoons SnB_2Cl_2 + 2\,H^+ \qquad (2)$$

may be postulated to lead to the product which extracts into chloroform (HB represents benzoylphenylhydroxylamine). If K_1 and K_2 are the equilibrium constants for reaction (1) and (2) respectively and if it can be assumed that only tin in the form of the BPHA complex extracts then the ratio, *E*, of tin in the chloroform to tin in the aqueous phase would be $K_1\,[HB]^2[Cl^-]^2$ for reaction (1) and $K_2[HB]^2[Cl^-]^2/[H^+]^2$ for reaction (2). An examination of the dependence of *E* on [HB], $[Cl^-]$ and $[H^+]$ should therefore throw some light on the product extracted into chloroform.

With the systems outlined under EXPERIMENTAL, a direct dependence on the square of the BPHA and the chloride concentrations was observed (Fig. 3) under conditions relating to tin extraction at low acid concentrations (Fig. 1).

The hydrogen ion dependence studies all showed that E decreased with increase in hydrogen ion concentration. The inverse square relation (eqn. (2)) although not observed was approached as the hydrogen ion concentration was increased; the first set of conditions gave E approximately proportional to $1/[H^+]^{0.5}$ and the last set to $1/[H^+]$. Thus, while it is likely that at least at low acid concentrations (<1 or 2 M) BPHA has a proton replaced by tin in the extraction, the expected dependence is obscured. This could follow from competing tin extraction by formation of ion-association complexes. Such a process would result from protonation of the BPHA in the chloroform; experiment showed that negligible proton transfer occurred from aqueous phases up to 1 or 2 M in hydrochloric acid, but at higher acidity (5 M) about 20% of the BPHA was transformed.

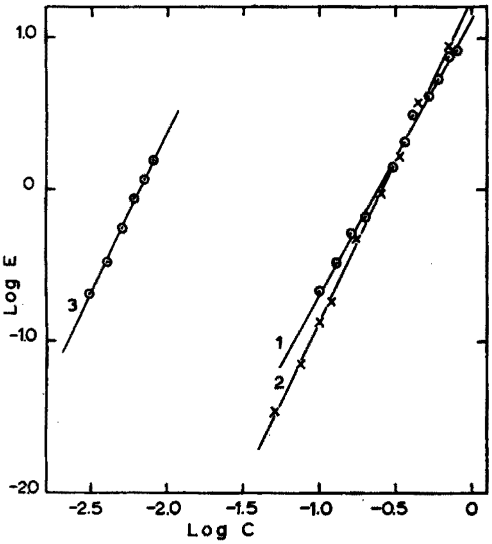


Fig. 3. Log E as a function of log C, the concentration of BPHA (curve 1 from a hydrochloric acid medium, curve 2 from perchloric acid) and of chloride (curve 3). The slopes by the least squares method were 1.85, 2.13 and 2.08 in that order.

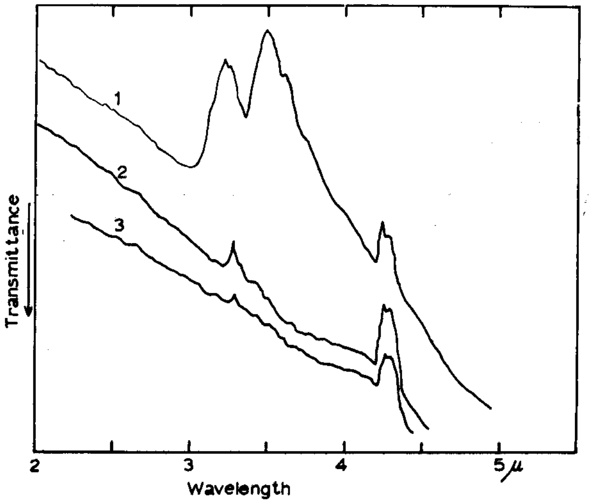
It is therefore more likely that partial hydrolysis of tin occurs under the experimental conditions at lower acidity. Data on hydrolysis of tin(IV) are scanty[13] but EVEREST AND HARRISON[14] found indirect evidence for some hydrolysis below 1 M in hydrochloric acid from ion-exchange studies. The presence of a basic tin ion would change the hydrogen ion dependence in the observed way without altering the product extracted as the equation

$$SnOH^{3+} + 2\,HB + 2\,Cl^- \rightleftharpoons SnB_2Cl_2 + H^+ + H_2O,$$

shows. The product extracted has been identified with that given by this equation by examining the spectrum of the extract in chloroform-d in the 4000 to 1400 cm^{-1} region, and by removal of chloroform from a sample by evaporation and comparison (after triturating with water to remove a slight excess of BPHA) of melting and mixed melting points with the substance prepared by precipitation[1]. In these experiments the tin was shaken up with rather less than the stoichiometrically required amount of BPHA.

Infrared spectra. The substance precipitating in the gravimetric method of analysis was shown to contain tin(IV) by an examination of infrared spectra and thus to have the same composition as that which was extracted at moderate acid concentrations.

The spectrum of BPHA as a mull (Fig. 4) showed peaks at 3.23 and 3.50 μ (3085 and 2890 cm^{-1}) which may be ascribed[15] to the stretching modes for "free" and hydrogen bonded –O–H. Corresponding spectra for the tin–BPHA compounds precipitated from chloride and bromide solutions only showed a relatively weak peak at 3.27 μ (3090 cm^{-1}) attributable to the aromatic –C–H stretch[15]. (The peaks appearing around 4.25 μ (2350 cm^{-1}) are due to carbon dioxide.)



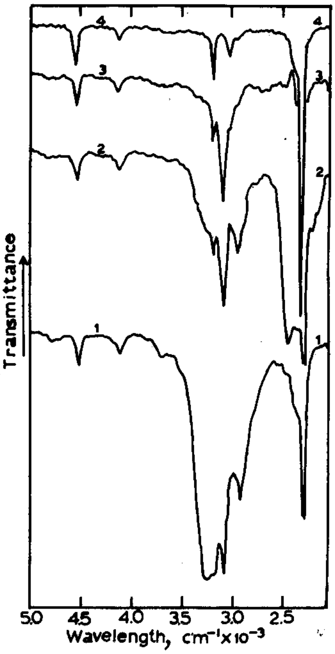


Fig. 4. Infrared spectra of (*1*) BPHA, (*2*) $Sn(C_{13}H_{10}O_2N)_2Cl_2$, and (*3*) $Sn(C_{13}H_{10}O_2N)_2Br_2$ from perfluorokerosene mulls.

Fig. 5. Infrared spectra of (*1*) 1 *M* BPHA, (*2*) 1 *M* deuterated BPHA, and (*3*) 0.5 *M* $Sn(C_{13}H_{10}O_2N)_2Cl_2$ solutions in chloroform-d (curve 4).

Spectra obtained from chloroform-d ($CDCl_3$) solutions are recorded in Fig. 5. A comparison of absorption in the 3000 to 3500 cm^{-1} region for the solvent (curve 4), 1 *M* BPHA (curve 1) and 1 *M* deuterated BPHA (curve 2) shows that the middle peak (at 3080 cm^{-1}) is due to the aromatic –C–H stretching mode. The spectrum of the tin–BPHA substance precipitated from a chloride solution only shows (curve 3) this peak at 3080 cm^{-1}, as would be expected if hydroxyl hydrogen is substituted by tin.

However, if the hydroxyl oxygen is bonded to the tin through a lone pair of electrons and still retains the hydrogen, the –O–H stretching frequency would be altered (probably reduced) and the absorption peak(s) due to it shifted. From spectra obtained using mulls in perfluorokerosene and nujol, evidence was not obtained in the region 4000 to 1400 cm^{-1} for an absorption peak ascribable to such a group. It may therefore be concluded that the hydroxyl hydrogen is lost on precipitation of tin by BPHA.

The absorption peak (stretching mode) due to the carbonyl group in BPHA was located at 6.15 μ (1625 cm^{-1}) and at about 6.6 μ (1510 cm^{-1}) in $Sn(C_{13}H_{10}O_2N)_2Cl_2$ (from nujol mulls), a shift which is comparable to those observed in acetylacetone on metal complex formation[16]. The carbonyl oxygen is thus bonded to the tin.

Precipitation reactions and solubility measurements

Antimony(III) is precipitated quantitatively from 1 *M* hydrochloric acid as a white substance, melting at 149°. It is readily soluble in organic solvents like acetone, benzene, chloroform and alcohol. Analysis: found C, 61.2%; H, 3.94%. $Sb(C_{13}H_{10}O_2N)_3$ requires C, 61.7%; H, 3.99%. This reaction is therefore comparable to that observed for cupferron which gives the substance $Sb(C_6H_5O_2N)_3$[3,17]. Antimony(V) does not give a precipitate with BPHA at any concentration of hydrochloric acid sufficient to prevent its hydrolysis.

Tin gives a white substance stable in air and melting at 155° when precipitated by BPHA from solutions containing bromide. Analysis has shown it to be $Sn(C_{13}H_{10}O_2N)_2Br_2$. (Found C, 44.3%; H, 2.89%; Br, 22.8%; required, C, 44.4%; H, 2.87%; Br, 22.7%.) The precipitates obtained with BPHA from iodide or nitrate solutions of tin were yellow in colour when produced but decomposed slowly on standing. Precipitation was slow from 1 *M* sulphuric acid giving a small yield of white substance; a white substance not examined further was also obtained from 9 *M* perchloric acid.

The solubilities of $Sn(C_{13}H_{10}O_2N)_2Cl_2$ (II) and $Sn(C_{13}H_{10}O_2N)_2Br_2$ (III) were measured in various solvents and solutions at 25°; the results are recorded in Table III.

TABLE III

SOLUBILITY DATA AT 25°

Substance	*Solvent or solution*	*No. of measurements*	*Mean solubility (mg/100 ml)*
II	Water	4	2.2
III	Water	3	2.9
II	1 *M* NaCl	3	1.6
II	1 *M* KBr	2	2.0
II	0.5 *M* HCl	2	1.3
II	0.8 *M* HCl	2	1.4

The solubility was thus appreciable in all the aqueous systems examined at 25° although the presence of chloride ion reduced it somewhat compared to water. As recommended by RYAN AND LUTWICK[1] it is nevertheless advisable to cool the system in ice-water before separating the tin precipitate in a gravimetric analysis.

We are grateful to Mr. G. COLLIER of Durham University and Mr. A. FASSAM of this University for the spectroscopic measurements and to Mr. T. F. HOLMES of the former University for the C, H and Br analyses. One of us (A.D.S.) gratefully acknowledges receipt of a postgraduate studentship from this University.

SUMMARY

N-Benzoyl-N-phenylhydroxylamine (BPHA) and cupferron are compared in the liquid–liquid extraction of tin and antimony. As in their precipitation reactions tin(II) and tin(IV) behave similarly with BPHA and differently with cupferron. Both reagents behave similarly in extraction of antimony(III), except at high acidity when cupferron or its decomposition products prevent extraction which otherwise occurs into chloroform alone. Separations of Sn, Sb, As and Bi are discussed for extractions from hydrochloric and perchloric acid systems with BPHA. The tin product extracted with BPHA from dilute hydrochloric acid appears to be identical with that precipitated in gravimetric analysis; infrared spectral evidence shows the latter to contain tin(IV). Other precipitation reactions of BPHA in the presence of anions other than chloride and some solubility measurements are also reported.

RÉSUMÉ

La N-benzoyl-N-phénylhydroxylamine (BPHA) et le cupferron sont comparés pour l'extraction liquide–liquide de l'étain et de l'antimoine. De même que pour leurs réactions de précipitation, l'étain(II) et l'étain(IV) se comportent de la manière identique avec BPHA et différemment avec le cupferron. Avec l'antimoine(III), ces deux réactifs se comportent de la même façon sauf en milieu très acide. On examine les séparations Sn, Sb, As et Bi par extraction au moyen de BPHA en milieu acide chlorhydrique–acide perchlorique.

ZUSAMMENFASSUNG

N-Benzoyl-N-phenylhydroxylamin (BPHA) und Kupferron werden bei der Flüsssigextraktion von Zinn und Antimon verglichen. Zinn(II) und Zinn(IV) verhalten sich bei der Fällungsreaktionen mit BPHA ähnlich, jedoch unterschiedlich bei denen mit Kupferron. Beide Reagentien verhalten sich ähnlich bei der Extraktion von Antimon(III) ausser bei hoher Acidität, weil dann Kupferron oder seine Zersetzungsprodukte vorzugsweise extrahiert werden. Es werden die Trennungen von Sn, Sb, As und Bi durch Extraktion aus Salzsäure- und Perchlorsäuresystemen mit BPHA diskutiert. Das aus verdünnter Salzsäure mit BPHA extrahierte Zinnprodukt scheint mit dem identisch zu sein, welches bei der gravimetrischen Analyse gefällt wird. Infrarotspektroskopisch konnte gezeigt werden, dass das letztere Zinn(IV) enthält. Über andere Fällungsreaktionen von BPHA in Gegenwart anderer Anionen als Chlorid und einige Löslichkeitsmessungen wird ebenfalls berichtet.

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SOME SPECTROFLUORIMETRIC APPLICATIONS OF THE CERIUM(IV)–CERIUM(III) SYSTEM*

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As an analytical trace technique solution spectrofluorimetry has the basic advantage of considerably greater sensitivity than absorption spectrophotometry. This, to a large extent, compensates for the number of interferences which are encountered in the few spectrofluorimetric methods that are presently available. These methods have recently been reviewed by WEISSLER AND WHITE[1].

The determination of metals with empty, completely filled or particularly stable partly-filled "d" orbitals such as aluminium, beryllium and zinc, which readily form fluorescent complexes with organic reagents, has already been investigated fairly thoroughly and there is only limited room for further improvements in selectivity and sensitivity in these particular determinations. There is, however, a need for methods of determination of those elements which do not fall into these categories. This communication describes some work on one multipurpose system which is useful for the indirect determination of several inorganic species.

In previous work on the determination of thallium(I) in a hydrochloric acid–potassium chloride medium[2], it was noted that cerium(III) was one of the few ions to produce a fluorescence under these conditions. Furthermore, in a dilute sulphuric acid solution, cerium(III) ions exhibit a characteristic fluorescence[3], which has its excitation maximum at 260 nm (with a secondary peak at 295 nm) and fluorescence emission maximum at 350 nm (Fig. 1). For the concentrations of cerium examined, it was shown in the present work that this fluorescence is unaffected by change in sulphuric acid concentration between 0.02 and 1 *M* or by a high concentration of electrolyte and provides a method for determination of cerium(III) at concentrations down to *ca.* 0.1 p.p.m. The behaviour of several other rare earths, *viz.* La, Pr, Nd, Sm, Gd, Dy, Er and Yb, was studied under these conditions without any increase in the cerium(III) fluorescence being observed. Hence this fluorescence reaction is selective for cerium(III) even within the lanthanide series. In the previous communication[2], the fluorescence of cerium(III), copper(I), lead, tin(II) and thallium(I) in a chloride medium was reported. In sulphuric acid medium only cerium(III) shows fluorescence.

Because cerium(IV) is non-fluorescent under the same conditions and is easily reduced, it seemed probable that this system might offer a method for the indirect spectrofluorimetric determination of several other ions which cannot as yet

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be determined directly by spectrofluorimetry. For example, the reaction:

$$2\ \mathrm{Ce(IV)} + \mathrm{As(III)} \rightarrow 2\ \mathrm{Ce(III)} + \mathrm{As(V)}$$

is catalysed by osmium tetroxide[4], and it should, therefore, be possible to determine arsenic(III) indirectly by measurement of the fluorescence of the cerium(III) produced. It will be noted that one mole of arsenic(III) produces 2 moles of cerium(III) so that there is effectively a two-fold molar amplification of arsenic(III) in this reaction. The variation in the fluorescence intensity produced by a varying amount of cerium(IV) with a constant amount of arsenic(III) is shown in Fig. 2. This curve shows the 2:1 stoichiometry of the reaction. The decrease in fluorescence after the equivalence point is caused by the inner-filter effect of the excess cerium(IV) on the fluorescence of cerium(III) at 350 nm due to its absorption of radiation at this wavelength.

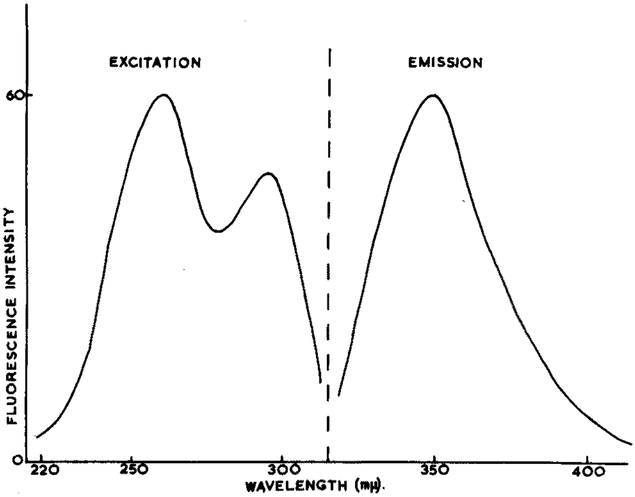
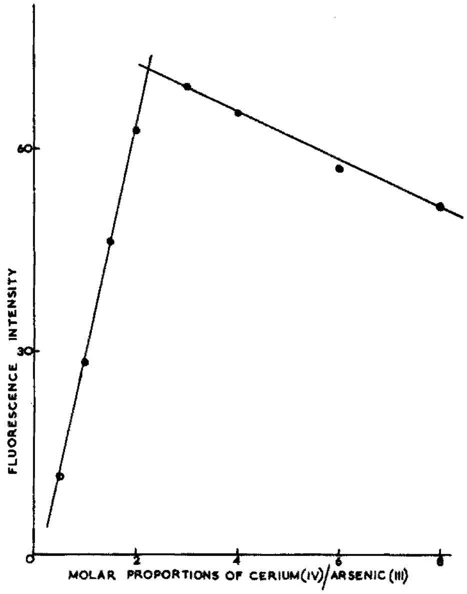


Fig. 1. Excitation and emission spectra (uncorrected) for cerium(III) in dilute sulphuric acid. Excitation spectrum plotted with emission measured at 350 nm; fluorescence emission spectrum plotted with excitation wavelength set at 260 nm.

In 0.05 *M* sulphuric acid and with a two-fold equivalent excess of cerium(IV) relative to the maximum arsenic(III) concentration, the measured fluorescence intensity at 260/350 nm is directly proportional to the arsenic(III) present (0.07–0.40 p.p.m.). The experimental procedure used is described later. Many cations, including Al, Be, Ca, Cd, Cu(II), K, Mg, Na, NH_4, Ni, Sr, Zn and the other rare earths, do not interfere with this system at room temperature when present in 200-fold molar excess, but interference is caused by ions which have oxidising or reducing properties under these conditions and by ions which absorb at either 260 nm or 350 nm, *e.g.* nitrate, iron(III), etc. The presence of organic complexing agents (citrate, tartrate, EDTA, etc.) causes high results by partial reduction of the excess of cerium(IV) present.

It is also possible to determine iron(II) (5.6–28 μg) or oxalate (8.8–44 μg) by measurement of the cerium(III) fluorescence produced by their reduction of cerium(IV). The precision in the determination of arsenic(III), iron(II) and oxalate in the range stated is good, and the standard deviation obtained in the determinations of these amounts is *ca.* 2% of the fluorescence signal in each case. It is probable that cations such as mercury(I), tin(II), titanium(III) and vanadium(IV) could be determined similarly by using their redox reactions with cerium(IV).



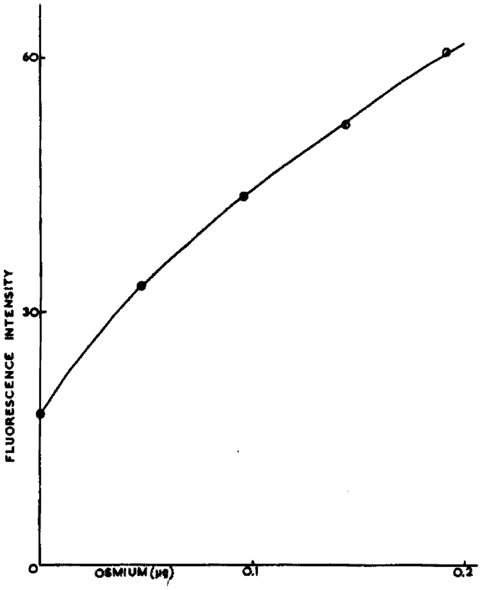


Fig. 2. Effect of varying excess of cerium(IV) on fluorescence, 0.05 *M* sulphuric acid, 5 ml of 10^{-4} *M* arsenic(III) solution.

Fig. 3. Calibration graph of fluorescence intensity against weight of osmium (0.05–0.2 µg) in 100 ml of solution.

The system is, of course, applicable to the determination of cerium, either as cerium(III) or indirectly as cerium(IV). If an excess of arsenic(III) solution is added to an unknown cerium(IV) solution, the intensity of the cerium(III) fluorescence generated is proportional to the cerium content. The determination of cerium(III) in the presence of cerium(IV) is also possible provided that the concentration of the latter is not too high.

SAUERBRUNN AND SANDELL[5] have applied this particular reaction to the determination of trace amounts of osmium by a kinetic spectrophotometric method. A straight line calibration graph was obtained by measuring the time taken for the transmittance of the solution at 340 nm to reach a given value and then plotting the osmium concentration against the reciprocal of the time. In the present work this principle was modified and applied spectrofluorimetrically by measuring the fluorescence intensity of the solution (260/350 nm) at a rigidly controlled time (10 min) after addition of osmium to a cerium(IV)–arsenic(III) mixture. The experimental procedure used is described later and the resultant curve is given in Fig. 3.

The catalysed reaction presents a nearly linear relationship between fluorescence signal and osmium concentration over the range examined. The extension of the calibration curve does not pass through the origin because of the extent to which cerium(IV) is reduced by arsenic(III) during the reaction time in the absence of the osmium(VIII) catalyst. The intercept on the axis at zero concentration of osmium does not, therefore, constitute a "true blank" representing traces of osmium in the reagents or fluorescent impurities. It will be seen that 0.002 p.p.m. of osmium produces a signal more than 3 times that which would have been obtained in its absence. Iodide, which also catalyses the cerium(IV)–arsenic(III) reaction, may be determined similarly in the range 0.006 to 0.025 p.p.m.

The cerium(IV)–arsenic(III) reaction is known[6] also to be catalysed by ruthenium, so that a similar determination of trace amounts of this element should be possible.

Obviously, if one of these systems were to be applied to the determination of trace elements in technical materials, as with any catalytic method, prior isolation of the element to be determined would be necessary. However, the systems have considerable interest as examples of the spectrofluorimetric determination of elements which are not themselves fluorescent and which show no positive fluorescence reactions with organic reagents.

EXPERIMENTAL

Apparatus

Farrand spectrofluorimeter as previously described[2].

Reagents

Arsenic(III) solution. Dissolve 0.989 g of AnalaR arsenic trioxide in 600 ml of water containing a minimum of sodium hydroxide. Add 50 ml of concentrated hydrochloric acid and dilute to 1 l with water. This solution is 10^{-2} M in arsenic(III) and should be diluted to 10^{-3} M or 10^{-4} M as required (1 ml of 10^{-4} M solution $\equiv$ 7.5 μg As).

Osmium(VIII) solution. Dissolve 0.5 g of osmium tetroxide in 100 ml of 6% sulphuric acid solution. This stock solution may be diluted as required using 6% sulphuric acid (1 ml of 10^{-6} M solution $\equiv$ 0.19 μg Os). Solutions should be standardised by KLOBBIE's iodometric method[7], *i.e.* treatment of the solution with 6 M sulphuric acid and 2 g of potassium iodide followed by titration of the liberated iodine with sodium thiosulphate solution using starch.

Cerium(IV) solution. Dissolve 5.483 g of AnalaR ammonium ceric nitrate in 600 ml of water containing 10 ml of concentrated sulphuric acid and dilute to 1 l with water. This solution is *ca.* 10^{-2} M in cerium(IV) and should be standardised by titration with the standard arsenic(III) solution and then diluted as required (1 ml of 10^{-4} M solution $\equiv$ 14 μg Ce).

Iron(II) solution. Dissolve 1.39 g of AnalaR iron(II) sulphate heptahydrate in 500 ml of water containing 14 ml of concentrated sulphuric acid. The solution is *ca.* 10^{-2} M in iron(II) and should be standardised by any of the standard titrimetric procedures for iron(II), and then diluted as required (1 ml of 10^{-2} M solution $\equiv$ 5.6 μg Fe).

Oxalate solution. Dissolve 1.421 g of AnalaR ammonium oxalate monohydrate in 1 l of water. This solution is 10^{-2} M in oxalate and should be diluted as required

(11 ml of 10^{-4} *M* solution ≡ 8.8 μg oxalate). Solutions should be standardised by titration with standard cerium(IV) solution.

Construction of calibration curves for arsenic(III), iron(II) or oxalate

To 100-ml flasks containing 50 ml of water, add 10 drops of concentrated sulphuric acid (AnalaR), 2 ml of 10^{-3} *M* cerium(IV) solution and one drop of 0.05% osmium tetroxide solution. Now add 1–5 ml aliquots of 10^{-4} *M* arsenic(III) solution (7.5–37.5 μg As), or 10^{-4} *M* iron(II) solution (5.6–27.9 μg Fe) or 10^{-4} *M* oxalate solution (8.8–44.0 μg oxalate), dilute to volume with water and measure the fluorescence intensity after 15 min at 260/350 nm. The calibration curves obtained are straight lines which, after subtraction of the blank, pass through the origin. Unknown test samples in the above concentration ranges should be treated similarly.

Calibration curve for osmium or iodide

To 100-ml flasks containing 50 ml of water add 10 drops of concentrated sulphuric acid, 1 ml of 10^{-3} *M* cerium(IV) solution and 2 ml of 10^{-3} *M* arsenic(III) solution. Then add 0.25–1 ml aliquots of 10^{-6} *M* osmium(VIII) solution (0.05–0.2 μg Os), or 0.5–2 ml aliquots of 10^{-5} *M* iodide solution (0.6–2.5 μg I), mix well and dilute to volume. Measure the fluorescence intensity of each solution at 260/350 nm exactly 10 min after addition of the osmium or iodide. A typical curve obtained (0.0005–0.002 p.p.m. Os) is shown in Fig. 3.

These experiments were conducted at room temperature without rigid control (23 ±3°). The standard deviation obtained in the replicate analysis of solutions containing 0.2 μg of osmium (0.002 p.p.m.) was 5%. The catalytic (Os) method would be particularly susceptible to temperature changes and should, therefore, be operated under thermostatted conditions where better reproducibility is required.

We are grateful to the Science Research Council for the provision of a Research Studentship for one of us (C.W.) and for a special grant (to T.S.W.) for the purchase of the spectrofluorimeter.

SUMMARY

Cerium(III) ions in dilute sulphuric acid medium exhibit a characteristic fluorescence which has its excitation maximum at 260 nm and its fluorescence emission maximum at 350 nm. By utilising the osmium-catalysed redox reaction between cerium(IV) and arsenic(III), microgram amounts of arsenic (7.5–37.5 μg) may be determined by spectrofluorimetric measurement of the cerium(III) produced. The principle may be applied to the determination of several other ions which cannot yet be determined by direct spectrofluorimetry, *e.g.* Fe(II) (5.6–28 μg), oxalate (8.8–44 μg). Osmium(VIII) (0.05–0.2 μg) and iodide (0.6–2.5 μg) may be determined by their catalytic action.

RÉSUMÉ

Le cérium(III) en milieu acide sulfurique dilué présente une fluorescence caractéristique. Une méthode, basée sur la réaction redox entre cérium(IV) et arsenic(III), catalysée par l'osmium, permet de doser des teneurs en arsenic de 7.5 à 37.5 µg par mesure spectrofluorimétrique du cérium(III). Le principe de ce procédé peut être appliqué au dosage de plusieurs autres ions ne pouvant pas être dosés directement par spectrofluorimétrie. On peut doser aussi osmium(VIII) et iodure grâce à leur action catalytique.

ZUSAMMENFASSUNG

In verdünntem schwefelsauren Medium zeigen Cer(III)-Ionen eine charakteristische Fluoreszenz mit einem Anregungsmaximum bei 260 nm und einem Fluoreszenzemissionsmaximum bei 350 nm. Verwendet man die durch Osmium katalysierte Redox-Reaktion zwischen Cer(IV) und Arsen(III), so können Mikrogramme Arsen (7.5–37.5 µg) durch spektralfluorimetrische Messungen des Cer(III) bestimmt werden. Dieses Prinzip kann auch zur Bestimmung verschiedener anderer Ionen, welche nicht direkt spektralfluorimetrisch bestimmt werden können, verwendet werden. So können z.B. Fe(II) (5.6–28 µg), Oxalat (8.8–44 µg), Osmium(VIII) (0.05–0.2 µg) und Jodid (0.6–2.5 µg) durch ihre katalytische Wirkung bestimmt werden.

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DETERMINATION OF CARBONYL COMPOUNDS VIA POLAROGRAPHY OF THEIR SEMICARBAZONE DERIVATIVES*

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The reaction of carbonyl compounds with semicarbazide hydrochloride is widely used for the separation and characterization of carbonyl compounds but the analytical utility of this reaction has been little exploited. The reason for this is, in part, the relatively weak nucleophilic power of semicarbazide (pK_A for $XH^+ = 3.7$)[1] in comparison with the much more commonly used hydroxylamine (p$K_A = 6.0$)[2] and also the greater ease of hydrolysis of semicarbazones when compared with the corresponding oximes.

These two disadvantages seriously limit the application of titrimetric methods based on titration of the carbonyl compound with semicarbazide, because large excesses of the reagent are necessary to ensure complete conversion to the semicarbazone and also to minimise hydrolysis. Even with similar methods using the more reactive hydroxylamine, impossibly long reaction times are required for the less reactive ketones.

The polarographic method, however, is capable of overcoming both of these disadvantages, because the semicarbazone is polarographically reducible whilst the semicarbazide hydrochloride does not give a cathodic wave. This enables very large excesses of reagent to be used.

Polarographic behaviour of semicarbazones[3]

Semicarbazones are reduced in acidic media giving a polarographic wave, the height of which is pH-independent over a limited pH range. Beyond this region the wave-height decreases with increasing pH in the form of a dissociation curve (Fig. 1); the pH value at which this decrease begins depends on the nature of the carbonyl component. Several papers have described the analytical applications of the polarography of semicarbazones[4-6], but the proposed mechanisms of the reduction process are often contradictory. Although most of the evidence points to a 4-electron reduction in acidic media[3,7,8], a 2-electron process has been postulated[9,10] and an intermediate number of electrons has also been found[11]. Obviously, the utility of a method based on the polarographic reduction of this functional grouping would be very limited if the nature of the electrode process were influenced by structural effects.

ZUMAN *et al.*, during a study of substituent effects on polarographic behaviour, investigated a wide range of aldehyde and ketone semicarbazones[3]. One of the primary problems of the study was to ascertain whether semicarbazones of re-

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* This paper was read at the 2nd Reunion Symposium of the Birmingham University Research School of Analytical Chemistry, held at Birmingham on April 28–29th, 1966.

presentatively selected types behaved in a similar manner. In acidic media containing 50% ethanol, the total height of the polarographic wave observed was the same for all compounds studied; for acetaldehyde, heptaldehyde, 4-pyridinealdehyde, and less markedly for cyclohexanone derivatives, this wave was split into two. All the aliphatic derivatives and acetophenone showed extensive hydrolysis in acidic media but hydrolysis was completely repressed at pH 4.4. The value of the diffusion current at this pH value varied between 90 and 95% of the value of the limiting diffusion current at lower pH values.

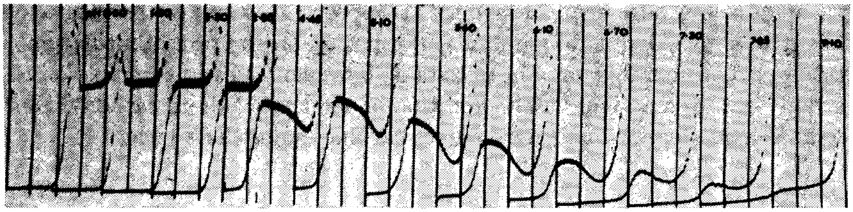

Fig. 1. pH-Dependence of reduction waves of $(C_6H_5)_2C{=}N{-}NHCO{-}NH_2$. $1 \cdot 10^{-4}$ *M* depolariser. Sulphuric acid, acetate and phosphate buffers in 50% ethanol. pH given on polarogram. Curves starting at: 1–4, −0.2 V; 4–11, 0.6 V *vs.* S.C.E.; 200 mV/abs.; *h* = 80 cm; full scale sensitivity 1.5 μA.

Comparison of the wave-heights of various semicarbazone derivatives with the wave-heights for compounds for which the number of electrons involved was known, indicated that a 4-electron process was involved. Microcoulometric measurements generally supported this conclusion, although hydrolysis during the 3-h electrolysis period presented some difficulties. The values for the number of electrons involved obtained[3] by this procedure were in the range 3.6–3.9.

Thus with one or two isolated exceptions, the polarographic reduction of aldehyde and ketone semicarbazones occurs by an essentially 4-electron process:

$$R^1R^2C{=}N{-}NHCONH_2 + 2\,e + 2\,H^+ \xrightarrow[E_1]{} R^1R^2C{=}NH^+ + H_2NCONH_2$$

$$R^1R^2C{=}NH^+ + 2\,e + 2\,H^+ \xrightarrow[E_2]{} R^1R^2CHNH_2$$

When R^1 is C_6H_5, the potentials E_1 and E_2 are so close together that only one 4-electron wave is observed. This reduction scheme was confirmed by the products obtained from controlled potential electrolysis.

The essentially analogous mechanism of the electrode process proves that the determination of carbonyl compounds in the presence of semicarbazide is possible, while the information obtained from the polarographic behaviour indicates the optimum conditions for carrying out this determination.

The optimum pH conditions for the measurement of the semicarbazide waves can be defined as a narrow pH region bounded at the upper limit by the pH value where the limiting current of the compound with the lowest p*K*′ value* (benzophenone semicarbazone) is equal or almost equal to the limiting diffusion current. The lower end of this region is marked by the pH value at which the most easily hydrolysed semicarbazone (cyclohexanone, acetone and acetaldehyde) shows no decrease in

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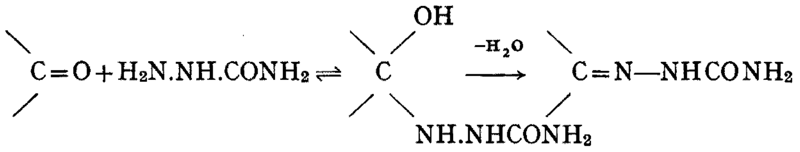
* The polarographic p*K*′ value is defined as the pH value at which the current of a kinetically controlled wave is equal to one-half of the value of the limiting diffusion current.

wave-height during the period of the measurement. The available pH region then is slightly more than one pH unit, from about pH 2.8 to 4.0. Sugar semicarbazones were excluded from this study as HAAS *et al.*[5] reported pK' values for the semicarbazone derivatives of pentoses and hexoses from 1.5 to 3.5.

In the study of the polarographic behaviour of semicarbazones all measurements were made using pure semicarbazones as opposed to forming the derivative *in situ*. Thus it was not possible to gain any information on the rate of formation of semicarbazones. A considerable amount of data is, however, already available on the rates of carbonyl group reactions[12]. The addition of semicarbazide to carbonyl compounds occurs in two steps via an intermediate carbinolamine derivative.



$$\mathrm{>C{=}O + H_2N.NH.CONH_2 \rightleftharpoons >C(OH)(NH.NHCONH_2) \xrightarrow{-H_2O} >C{=}N{-}NHCONH_2}$$

The major requirement that the attacking nucleophilic reagent must have a free electron pair to attack the carbonyl group has long been realized. General acid catalysis also plays an important role, particularly in view of the relatively weak nucleophilic power of semicarbazide. The dependence of reaction rate on pH shows the well-known[12] bell-shaped curve with a maximum at about pH 4.8. A change in the rate-determining step at the pH maximum is responsible for this type of curve. The two steps on either side of the maximum show widely different sensitivities to general acid catalysis; on the alkaline side of the maximum the reaction is influenced by general acid catalysis whereas on the acid side it is unaffected. These factors will influence the composition of the buffer medium used to carry out the measurement.

Thus the formation of semicarbazones in an acetate buffer containing semicarbazide hydrochloride was studied over the pH range 3.5–4.0.

EXPERIMENTAL

Apparatus

The polarographic curves were recorded on a Metrimpex Polarograph Model OH 102. A Kalousek vessel with a separated reference electrode (saturated calomel electrode) was used.

The capillary used had the following characteristics: outflow velocity $m = 2.00$ mg/sec, drop time $t = 4.20$ sec, at the potential of the S.C.E. Mercury pressure $h = 50$ cm. Separate values of m and t were calculated for the calculation of diffusion current constants.

Half-wave potentials were measured using a three-electrode cell[3] with the potential of the dropping mercury electrode measured potentiometrically against a reference S.C.E. in an auxiliary circuit.

Substances

The substances studied are listed in Tables I and II. Standard solutions (10^{-2} M) of the carbonyl compound in absolute ethanol were prepared. Benzaldehyde, hexaldehyde, heptaldehyde, 4-methoxybenzaldehyde and methyl isobutyl ketone were redistilled. Formaldehyde solution was prepared from "AnalaR" aqueous 36% formaldehyde solution. The purity was checked by comparison with the waves of the pure semicarbazones[3].

TABLE I

REDUCTION WAVES OF SUBSTITUTED BENZALDEHYDE SEMICARBAZONE DERIVATIVES

Substituent	*Diffusion current constant I* $= i/cm^{2/3}\,t^{1/6}$	$E_{\frac{1}{2}}$	*pK'*
H	4.26±0.10	−1.058	6.60
4-Methyl	4.25±0.10	−1.105	6.8
2,4,6-Trimethyl	4.40±0.15	−1.112	7.0
3-Methoxy	4.33±0.10	−1.100	6.8
4-Methoxy	4.20±0.10	−1.252	7.5
4-Bromo	4.14±0.10	−0.948	6.8
3,4-Dihydroxy	4.20±0.15	−0.979	6.8
4-Nitrilo	3.55	−0.902	3.9[a]

[a] Second wave.

TABLE II

REDUCTION WAVES OF SEMICARBAZONES OF KETONES AND ALKYL ALDEHYDES

Carbonyl compound	*Diffusion current constant I* $= i/cm^{2/3}\,t^{1/6}$	$E_{\frac{1}{2}}$	*pK'*
Formaldehyde	3.75±0.20	−1.081	7.9
Acetaldehyde	4.18±0.20	−1.141	7.4
Hexaldehyde	3.95±0.20	−1.120	7.2
Heptaldehyde	4.02±0.20	−1.170	7.2
Acetone	4.36±0.32	−1.249	7.4
Methyl isopropyl ketone	3.99±0.28	−1.200	—
Methyl isobutyl ketone	2.86±0.30	−1.268	—
Acetophenone	4.16±0.12	−1.119	6.8
Benzophenone	4.28±0.10	−1.125	6.35
Cyclohexanone	4.23±0.20	−1.144	7.6

Reagents

Glacial acetic acid. "AnalaR" glacial acetic acid (1 l) was refluxed over 5 g of chromic oxide for 3 h, to oxidise any traces of carbonyl compounds, and then redistilled twice.

Ethanol. Absolute ethanol (2 l) was refluxed for 1 h over 3 g of semicarbazide hydrochloride and then redistilled twice.

Semicarbazide hydrochloride. "AnalaR" reagent was recrystallised from 9:1 water/ethanol after filtering through active carbon.

Acetate buffer. 10 *M* acetic acid, 1 *M* sodium acetate. This buffer showed a pH value of 3.65; in 50% ethanolic solution, the apparent pH was 4.45, whereas with the addition of 0.1 *M* semicarbazide the apparent pH was 3.85.

Techniques

Sample solutions were prepared in 10-ml volumetric flasks. The standard carbonyl solution was added from an Agla micrometer syringe. The solutions were diluted to volume with 1:1 ethanol/water.

RESULTS AND DISCUSSION

The aim of the present study was to follow the formation of semicarbazones in an acetate buffer containing varying concentrations of semicarbazide hydrochloride by comparison of the height of the polarographic wave with the wave of the pure semicarbazone. Benzophenone, a typical unreactive carbonyl compound, was chosen as a model substance.

An acetate buffer containing 0.1 *M* semicarbazide hydrochloride was first examined. Addition of $2 \cdot 10^{-4}$ *M* benzophenone gave a wave of equal height to the wave obtained from the corresponding amount of pure semicarbazone, thus showing the reaction to have reached completion. The concentration of semicarbazide was next reduced to 0.01 *M* and with $2 \cdot 10^{-4}$ *M* benzophenone the reaction was again found to be quantitative, although the height of the wave was slightly lower than the wave formed in 0.1 *M* semicarbazide solution. This was due to the fact that when the concentration of semicarbazide was lowered from 0.1 to 0.01 *M*, the pH of the solution increased from 3.85 to 4.4. In order to achieve a pH value in the range 3.5 to 4.0 in the presence of 0.01 *M* semicarbazide hydrochloride it would be necessary to use a formate buffer, which is much less convenient to prepare in a carbonyl-free form than the corresponding acetate buffers. Accordingly, 0.1 *M* semicarbazide hydrochloride in a 0.1 *M* acetate buffer was chosen for the present study.

When the carbonyl compound was added to a mixture of 1 *M* semicarbazide hydrochloride and 1 *M* sodium acetate and the pH adjusted by the addition of the acetic acid (10 *M*) and ethanol, the rate of formation and the shape of the wave were the same as those obtained under the above conditions. This procedure should allow lower concentrations of semicarbazide to be used; this would be important for an extension of the method to the 10^{-6} *M* range using linear-sweep cathode ray polarography, where the difficulties of removing traces of carbonyl impurities from reagents would be much greater.

Reaction between $2 \cdot 10^{-4}$ *M* benzophenone and 0.1 *M* semicarbazide hydrochloride in 0.1 *M* acetate buffer containing 50% ethanol (pH 3.8) is complete in less than the 3 min required to remove oxygen from the solution before measurement. Under these conditions, a range of aldehydes and ketones was examined (Tables I and II, Fig. 2) and the values of the diffusion current constant *I* were calculated for each compound.

All the aliphatic and alicyclic compounds examined, with the exception of formaldehyde, exhibited streaming maxima. These maxima could be suppressed by the addition of 0.5 ml of a 0.25% solution of gelatin, but the shape of the wave was very sensitive to the amount of gelatin added. As gelatin affects not only the shape of the wave but also the half-wave potential its addition as a standard practice is not advised. None of the aromatic or mixed aromatic aliphatic compounds examined exhibited maxima (the dip on the limiting current in the case of benzophenone is a minimum that results from the fact that protonation of the semicarbazone occurs partly as a surface reaction).

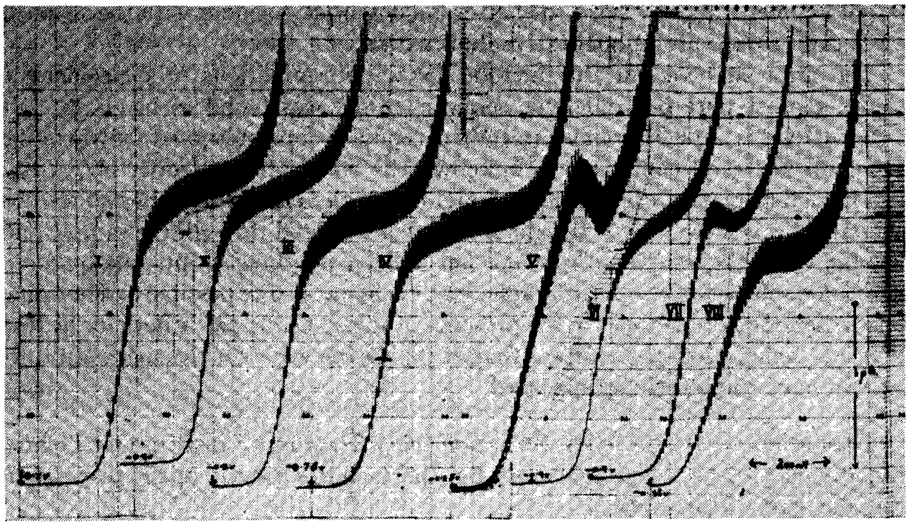


Fig. 2. Reduction waves of semicarbazones in 0.1 M acetate buffer containing 0.1 M semicarbazide hydrochloride. $2 \cdot 10^{-4}$ M depolariser; 50% ethanol; pH 3.85; 50 mV/abs.; h = 50 cm; full scale sensitivity 3 μA. I, Benzaldehyde; II, 4-Methylbenzaldehyde; III, 4-Methoxybenzaldehyde; IV, 4-Bromobenzaldehyde; V, Benzophenone; VI, Hexaldehyde; VII, Cyclohexanone; VIII, Formaldehyde.

It was shown previously[3] that the diffusion current constants for benzaldehyde and 20 substituted benzaldehydes were constant within the limit of experimental error (4.4 ± 0.2). In the present study 8 of these derivatives were chosen so as to cover as wide a range of reactivity as possible. As all of these reacted readily under the conditions used, it can safely be predicted that the method can be applied to any substituted benzaldehyde. A linear correlation between half-wave potential and the Hammett substituent constant σ was found for the unsubstituted, 3- and 4-methoxy, 4-bromo and 4-methyl derivatives, but the value of $\varrho = 0.5$ V did not agree with the value obtained over the pH range 0–2. As it had not been shown that the dependence of half-wave potential on pH was constant over the pH range 3–4, it was not possible to predict half-wave potentials for other benzaldehyde derivatives from the $E_{\frac{1}{2}}$–σ plot.

The half-wave potential for 4-nitrilobenzaldehyde semicarbazone deviated from the $E_{\frac{1}{2}}$–σ plot, but in this case, owing to the low pK' value, the wave-height was no longer at its limiting value. This is clearly shown in the low value of the diffusion current constant, $I = 3.55$, for this derivative.

The only other compound to show a significant variation in the value of the diffusion current constant was methyl isobutyl ketone semicarbazone. It is probable that at pH 3.85 the reduction wave for this derivative is below its limiting value. Attempts to measure this wave over the pH range 2–4 have, as yet, been unsuccessful owing to the very rapid hydrolysis. The addition of large amounts of semicarbazide hydrochloride in order to suppress the hydrolysis caused the wave to become very poorly defined.

The fact that an almost constant value for the diffusion current constant, I, was obtained for all the carbonyl compounds studied indicates the applicability of this method to functional group analysis for a wide range of saturated and aromatic aldehydes and ketones. In many cases the half-wave potential, together with the shape of the wave can provide useful qualitative information.

The error involved in this method for 4 determinations of benzaldehyde (measured against pure benzaldehyde semicarbazone) was found to be ±2%, but when the method is applied simply as a total carbonyl group determination where the nature of the carbonyl compound is unknown the error is of the order of ±10%.

The determination of volatile carbonyl compounds in natural oils can also be carried out by this method[13]. A stream of nitrogen is passed through the sample and the volatile carbonyl compound is swept out and passed directly into the buffered semicarbazide solution in the polarographic cell. It should also be possible to determine aliphatic aldehydes and ketones in the presence of sugars as the pK' values for hexose and pentose[5] semicarbazones indicate that at pH 3.8 the wave for the sugar semicarbazone will have completely disappeared.

The author is grateful to Dr. ZUMAN of the J. Heyrovský Institute for Polarography, Prague, for his suggestions and for the facilities placed at his disposal in carrying out part of this work.

SUMMARY

The polarographic behaviour of a range of aldehyde and ketone semicarbazones has been studied and a method for the determination of carbonyl compounds developed. The carbonyl compound is added to an acetate buffer containing 0.1 *M* semicarbazide hydrochloride and 50% ethanol and the polarographic reduction wave of the semicarbazone derivative measured. The similar values of the diffusion current constant *I* for all compounds studied indicate the applicability of this method to functional group analysis.

RÉSUMÉ

Les auteurs ont examiné le comportement polarographique de nombreux dérivés de la semicarbazone; ils proposent une méthode de dosage des composés carbonyle. Le composé carbonyle est ajouté à un tampon acétique renfermant du chlorhydrate de semicarbazide 0.1 *M* et 50% d'éthanol; on mesure ensuite le polarogramme obtenu avec le dérivé semicarbazone.

ZUSAMMENFASSUNG

Das polarographische Verhalten einer Anzahl von Aldehyd- und Keton-Semicarbazonen wurde untersucht und eine Methode zur Bestimmung von Carbonylverbindungen entwickelt. Die Carbonylverbindung wird zu einem Acetatpuffer gegeben, der 0.1 *M* Semicarbazidhydrochlorid und 50% Äthanol enthält, und die polarographische Reduktionsstufe des Semicarbazonderivats gemessen. Die Untersuchung ähnlicher Werte der Diffusionsstromkonstanten *I* aller dieser Verbindungen zeigt die Anwendbarkeit dieser Methode für die Analyse funktioneller Gruppen.

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DISSOCIATION AND IONIZATION EFFECTS IN ATOMIC ABSORPTION SPECTROCHEMICAL ANALYSIS

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One of the fundamental differences between flame emission spectroscopy and flame atomic absorption spectroscopy is that in the former the signal derives from excited atoms, while in the latter the signal derives from unexcited or ground-state atoms. Atomic excitation is strongly dependent on flame temperature, and therefore relatively small variations in flame temperature cause large variations in the flame-emitted signal. On the other hand, the number of ground-state atoms present is much less dependent on flame temperature[1]. If one could assume that the excitation phenomena were the only ones that must be considered, for all practical purposes the number of atoms in the ground state, and therefore the absorption signal, would be independent of flame temperature. But this is not the case. In flame spectroscopy as commonly practised, in order for an atom to be free, either in the excited or unexcited state, it is necessary that the solvent and sample be vaporized, and the sample be dissociated to free atoms. The completeness of this process depends, among other things, on the flame temperature, the element species present (anion as well as cation), and the concentrations of the elements in the original solution. These variables have been studied primarily in connection with flame emission spectroscopy[2] but the conclusions apply equally well to flame atomic absorption spectroscopy, since the formation of free atoms is required in either case.

In the early work with flame atomic absorption, two observations were made that verified similar experience in flame emission spectroscopy. Firstly, it was noted that solutions of some elements provided no absorption signal when introduced into the flames then commonly used (air with propane, city gas, hydrogen, or acetylene). Secondly, it was noted that the absorption signal produced by a given concentration of certain elements varied, depending on the presence of certain other anions and/or cations. It is fairly well established that the first effect is due to the inability of the flame to dissociate the compounds of those elements not providing absorption signals, and that the second effect is due to different rates of vaporization and dissociation, depending upon the energy required to break apart the particular compounds formed, which in turn depends upon the species present. Early efforts in flame emission spectroscopy to use hotter flames to increase the dissociation were largely unsuccessful until it was realised that it was also necessary to provide a reducing atmosphere (fuel-rich condition) to inhibit oxide and/or hydroxide formation[2-4]. Using a hotter flame ($\sim$3000°) under reducing conditions, various workers have shown that at least partial vaporization and dissociation of the compounds of most if not all metals can be achieved. The hotter flame also greatly reduces or eliminates the effect of vaporization and dissociation with respect to different anion or cation species present[5,6]. Therefore, if the number of free ground-state atoms were a function only of vaporization and dissociation, it would be logical to use the hottest possible flame that is convenient to obtain.

However, there is another factor to consider which is also temperature-dependent: ionization. When one or more electrons are removed from an atom, the ion does not absorb radiation at the same wavelengths which it absorbs as a neutral atom. In an analytical procedure, if one is measuring the radiation absorbed by ground-state atoms, and a certain fraction of these is ionized, the measurement will differ from the condition of no ionization by this amount. If the ionization is not suppressed, or some other compensation is not made, an error will be introduced.

For any given element concentration in solution when aspirated into a flame, there is a corresponding partial pressure of the element in the gas phase. For a given partial pressure the ionization increases with temperature. Figure 1 shows this relationship for calcium at two partial pressures. The data for this graph were taken from GAYDON AND WOLFHARD[7], who made the calculations using the SAHA equation[8]. At low calcium concentrations and high flame temperatures the ionization is significant.

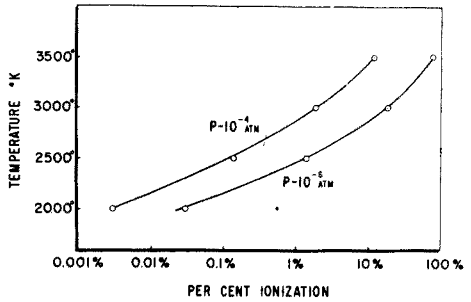


Fig. 1. The increase of calcium ionization with temperature, calculated for two partial pressures. Temperature of an air–acetylene flame is about 2550°K; that of a nitrous oxide–acetylene flame is about 3200°K.

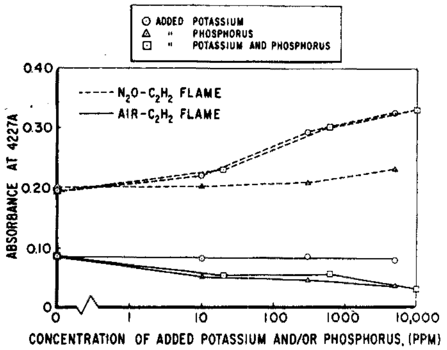


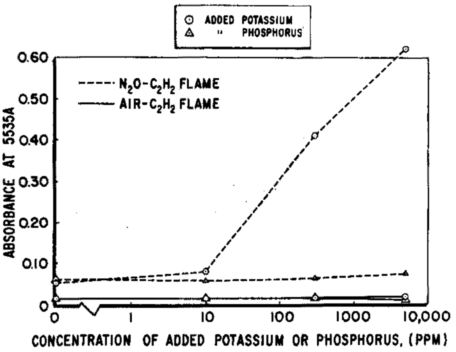
Fig. 2. The effect of added potassium chloride and/or phosphoric acid on the absorption signal of 2 p.p.m. calcium at 4227 Å.

Therefore, we have two requirements (among others) that are contradictory: a flame hot enough to provide adequate volatilization and dissociation, and a flame cool enough to prevent unacceptably large ionization. Fortunately there is a reasonably simple solution to this seeming dilemma, which has been used in emission flame spectroscopy. If one adds a relatively large amount of an easily ionized metal such as one of the alkalis to the sample solution, the electron density in the flame is greatly increased when the solution is atomized. The additional electrons suppress the ionization of the metal of interest, to a level that no longer produces a significant error. It is therefore possible to work with a hot, fuel-rich flame to provide sufficient vaporization and dissociation, and to add a relatively large amount of an easily ionized metal when it is necessary to inhibit the ionization of the element to be determined.

Figure 2 illustrates the effects which have been described. Various amounts of potassium as KCl, phosphorus as H_3PO_4, and a combination of these two were added to a solution of 2 μg of calcium (as the chloride) per ml. Absorption values were obtained with an air–acetylene flame and a nitrous oxide–acetylene flame at the calcium 4227 Å atom resonance line. In the air–acetylene flame there is negligible effect from the added potassium chloride, confirming the calculation (Fig. 1, ~2600°K) of the SAHA equation. The presence of phosphoric acid depresses the signal markedly, as the result of the formation of stable calcium phosphate. This effect has been studied in detail by a number of workers[2,5,9]. When both potassium chloride and phosphoric acid are added, the effect is essentially the same as with phosphoric acid alone, indicating that in this case the potassium chloride has little effect on vaporization and dissociation.

The data from the nitrous oxide–acetylene flame show that calcium sensitivity without added ions is about twice that of the air–acetylene flame. The addition of potassium into this flame evidently causes an increase in the calcium atom population. The natural conclusion is that the increase is due to suppression of ionization. It is possible that the potassium also increases the rate of dissociation[5], which would produce the same effect. However, since it does not increase the dissociation in the lower-temperature air–acetylene flame, as is shown by the curve, it is more likely that the entire enhancement is due to calcium-ion suppression rather than more efficient vaporization and dissociation.

The absorption enhancement of calcium by phosphoric acid in the nitrous oxide flame is very small compared to that caused by potassium chloride, and is apparently due to an increase in the rate of dissociation, since the absorption of calcium measured at the 3934 Å ion resonance line is unaffected by phosphoric acid, up to 5000 p.p.m. When both phosphorus and potassium were added, the effect was almost identical to that obtained with potassium alone. It is interesting to note that, when calcium is determined in the presence of large amounts of phosphorus and potassium the nitrous oxide–acetylene flame is 10 times more sensitive than the air–acetylene flame.



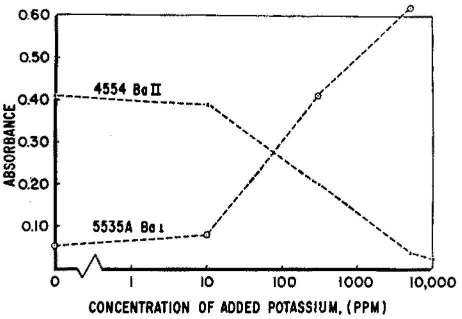


Fig. 3. The effect of added potassium chloride or phosphoric acid on 50 p.p.m. barium absorption at 5535 Å.

Fig. 4. The effect of added potassium chloride on the absorption of barium at the atom and ion lines in the nitrous oxide–acetylene flame.

Figure 3 summarizes similar data taken with barium. The effect of potassium chloride and of phosphoric acid is negligible in the air–acetylene flame. In the nitrous oxide–acetylene flame there is little or no enhancement on addition of phosphoric acid, and a striking enhancement from added potassium chloride. The effect is the same as was seen for calcium; the difference is in degree. The addition of potassium chloride markedly reduces the barium ion concentration as shown by the data in Fig. 4, in which the absorbance of the atom line and the ion line are plotted on the same scale. This is very similar to results observed with strontium in earlier work[10]. This Figure illustrates the increase in sensitivity one can obtain by using the high-temperature flame to achieve improved vaporization and dissociation, along with a large addition of an easily ionized metal to inhibit ionization.

Calculation of the degree of ionization

For those elements such as calcium and barium having a sensitive ion resonance line located within the wavelength region 2000–8000 Å, it is possible to calculate the degree of ionization in a hot flame using absorption readings taken with and without added potassium chloride. Absorption readings are taken at both atom and ion resonance lines. In setting up the calculation, at least two assumptions are made. First, it is assumed that the addition of potassium chloride to the flame does not change the total number of free atoms and ions of the element present in the flame; that is, the degree of vaporization and dissociation is not materially changed. The second assumption is that the Beer–Lambert relationship holds over the absorbance range used for the calculation. To establish this, it is not sufficient to construct a typical absorbance *vs.* concentration curve using plain salt solutions with the nitrous oxide–acetylene flame. It is a well established fact[2,7,8] that the percentage of atoms ionized varies inversely with their concentration in the flame.

To reduce the possible effect of more efficient vaporization and dissociation, one should use as small an amount of potassium chloride as possible that gives a measurable change in ionization. This also reduces any error due to deviation from the Beer–Lambert law, since differences in absorbance produced are less with a small amount of added potassium. The validity of the assumptions can be tested by repeating the experiment using larger concentrations of added potassium chloride.

Two equations can be written involving the absorbance readings obtained

TABLE I

ABSORBANCE FROM FREE ATOMS AND IONS[a]

Element	*Concn. (μg/ml)*	*Absorbance*						
		0 p.p.m. K	*+10 p.p.m. K*		*+300 p.p.m. K*		*+5000 p.p.m. K*	
Barium 5.2 ev								
5535.6 Ba I	50	0.052	0.079	(1.52)	0.409	(7.87)	0.620	(11.9)
4554.0 Ba II	50	0.409	0.387	(0.947)	0.199	(0.487)	0.037	(0.090)
Calcium 6.1 ev								
4226.7 Ca I	2	0.199	0.221	(1.11)	0.297	(1.48)	0.325	(1.63)
3933.7 Ca II	2	0.050	0.040	(0.800)	0.004	(0.088)	0.000	(0)

[a] Numbers in parentheses are ratios of absorbance with added potassium to absorbance without added potassium.

from the free atoms and ions in each of 2 solutions of a given element concentration, one solution also containing potassium as the chloride. In Table I are listed the absorbance readings obtained for solutions of barium and of calcium taken at the most sensitive atom and ion line of each. Potassium as the chloride was added in the amounts: 0, 10, 300, 5000 p.p.m. The numbers in parentheses are the ratios of absorbance with added potassium to no added potassium. Let us use barium as an example. If x equals the fraction of free ground-state neutral atoms, and y equals the fraction of free ground-state neutral ions present in the flame when measuring the absorbance of the barium solution without potassium, we can form 2 independent equations involving x and y for each concentration of potassium. Using the barium values with 10 p.p.m. potassium added:

$$x+y = 1$$

$$1.52\,x+0.947\,y = 1$$

Solving for x and y, we obtain:

$$x = 0.092; \quad y = 0.908$$

Therefore, the barium in the plain solution with the nitrous oxide–acetylene flame is 91% ionized.

Treating the calcium results similarly, with 10 p.p.m. potassium added we obtain:

$$x = 0.644; \quad y = 0.356$$

The calcium in the solution containing no potassium is 36% ionized.

These results can be compared with values calculated using the SAHA equation[8], which may be written in the form:

$$\log\left(\frac{x^2}{1-x^2}\right) = -\log P - \frac{5040v}{T} + 2.5\log T + \log u^+ - \log u^0 - 6.18$$

where x = fraction of the atoms that are ionized, P = total pressure in atmospheres of the electrons and the metal in all forms in the burnt gases, T = absolute flame temperature, v = ionization potential of the element, u^+ = partition function of the ion, u^0 = partition function of the atom.

To evaluate the fraction of atoms ionized (x) we can use established[11] values of v, and calculated values[2] for u^+ and u^0.

	v	u^+	u^0
Calcium	6.11	2.0	1.0
Barium	5.21	2.9	1.3

The absorption measurements of atoms and ions are taken in the nitrous oxide–acetylene flame in the reaction zone close to the burner top. While chemical and thermal equilibrium may not be established in this region[2] for purposes of calculation we can assume a temperature that has been measured for a nitrous oxide–acetylene flame in equilibrium[12], which is 3230°K. Also it is reasonable to assume a pressure P of 10^{-6} atmospheres[2,13]. Using these values in the SAHA equation, we obtain the numbers given in Table II compared to those derived from the experiment. This is the calculated ionization of the calcium and the barium in solution with no added potassium.

TABLE II

APPARENT IONIZATION (%)

	Calcium	*Barium*
Observed		
with 10 p.p.m. K	35.6	90.8
with 300 p.p.m. K	34.6	93.3
with 5000 p.p.m. K	38.6	92.3
Calculated		
From SAHA	41.9	90.5

If the addition of potassium chloride did appreciably increase the vaporization and dissociation, the apparent ionization values calculated from the absorbances of atoms and ions would increase with an increase in added potassium. The difference between the values for various concentrations of potassium shown in Table II appears to be random, indicating that if there is a change in dissociation, it causes an error which is less than other contributing effects.

SUMMARY

Use of a nitrous oxide–acetylene flame in atomic absorption spectrophotometry reduces or eliminates certain chemical interferences that have been observed in cooler flames. However, ionization increases with temperature, and is significant for some elements in the nitrous oxide–acetylene flame. Ionization can be reduced by adding an easily ionized metal (*e.g.* alkali metal) to the solution. Elements likely to be determined using the nitrous oxide–acetylene flame which will be significantly ionized are: Al, Ba, Ti, V, Zr, Hf, Nb, Sc, Y, the lanthanides and the actinides. The ionization of an element in the nitrous oxide–acetylene flame can be readily calculated by taking absorption readings, provided that relatively sensitive atom and ion resonance lines are available. This technique possibly could be used to establish ionization potentials or partition functions of those lanthanide elements that are not now well known.

RÉSUMÉ

L'emploi d'une flamme oxyde nitreux–acétylène en spectrophotométrie par absorption atomique diminue ou élimine certaines interférences chimiques observées dans des flammes plus froides. Cependant, l'ionisation augmente avec la température et est importante pour certains éléments (Al, Ba, Ti, V, Zr, Hf, Nb, Sc, Y, lanthanides et actinides). Elle peut être réduite par addition d'un métal facilement ionisé (ex. métal alcalin) à la solution. Il est possible de déterminer les potentiels d'ionisation encore mal connus de lanthanides.

ZUSAMMENFASSUNG

Die Verwendung einer Distickstoffoxid–Acetylen-Flamme bei der Flammenabsorptionsspektroskopie reduziert oder eliminiert gewisse chemische Störungen, die in kälteren Flammen beobachtet wurden. Die mit der Temperatur steigende Ionisa-

tion ist jedoch bedeutsam für einige Elemente in dieser Flamme. Die Ionisation kann durch Zugabe eines leicht ionisierenden Metalls (z.B. Alkalimetall) zur Lösung reduziert werden. Folgende Elemente, welche wesentlich ionisiert werden, lassen sich gut unter Verwendung dieser Flamme bestimmen: Al, Ba, Ti, V, Zr, Hf, Nb, Sc, Y, die Lanthaniden und die Aktiniden. Die Ionisation eines Elements in der Distickstoffoxid–Acetylen-Flamme kann schnell mittels der Absorption berechnet werden, wenn dafür gesorgt wird, dass relativ empfindliche Atom- und Ionenresonanzlinien verfügbar sind. Mit dieser Technik können möglicherweise noch nicht gut bekannte Ionisationspotentiale oder Verteilungsfunktionen von den Lanthanidelementen festgestellt werden.

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THE DETERMINATION OF TRACE QUANTITIES OF MOLYBDENUM BY ATOMIC ABSORPTION SPECTROSCOPY

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There has recently been an attempt to extend geochemical methods of prospecting to the analysis of water samples from boreholes, springs, and rivers. In view of the low solubility of certain elements such as molybdenum, chromium, and lead, highly sensitive methods, capable of determining concentrations as low as 0.001 p.p.m., and having sufficient accuracy to detect trends and anomalies, are required. An atomic absorption method for the determination of molybdenum in these low concentrations has been developed. Not only is the determination of this element of interest to geochemists in water and rock samples, but also to agricultural chemists in plant and soil samples.

DAVID[1] made a comprehensive study of the factors influencing the determination of molybdenum by atomic absorption spectroscopy and achieved a detection limit of the order of 0.5 p.p.m. in aqueous solutions, when a fuel-rich air–acetylene flame was used. This detection limit is not low enough for the determination of molybdenum in natural waters (0 to 0.005 p.p.m.), silicates and soils (0 to 20 p.p.m.), and plant materials (0 to 10 p.p.m.). There are, moreover, several elements present in these samples, which DAVID found interfered with molybdenum. Liquid–liquid extraction methods were investigated which simultaneously concentrate the molybdenum and eliminate most of the interfering cations. There do not appear to be any previous attempts to combine organic solvent extraction with atomic absorption spectroscopy for the determination of trace quantities of molybdenum.

MALISSA AND SCHÖFFMANN[2] have reported the chelating of many heavy metals, including molybdenum, by ammonium pyrollidine dithiocarbamate (APDC). This extraction technique was, however, found to be unsuitable for samples with high iron content, because of the preferential extraction of this element. MITCHELL AND SCOTT[3] reported the use of 8-hydroxyquinoline as a complexing agent for molybdenum and other metals with subsequent determination by emission spectroscopy. With certain modifications this method was found to be more suitable for silicate materials where iron concentrations are high. WILLIS[4], ALLAN[5,6] and ROBINSON[7] have shown that considerable enhancement in sensitivity may be achieved by spraying an organic solvent containing the analytical element, into the flame. Combinations of these methods, *viz.* liquid–liquid organic extraction with subsequent determination of molybdenum in the organic phase, have satisfactorily been used for the determination of molybdenum.

EXPERIMENTAL

Apparatus

Initially a Zeiss PMQ II spectrophotometer with self-built atomic absorption attachments was used with a flat-topped, water-cooled type of burner[8], the premixed flame and sample aerosol issuing from a number of 1.0-mm diameter holes. DAVID[1] stressed the importance of using only a small region of the air–acetylene flame. For this reason the light beam through the flame was controlled by apertures as is shown in Fig. 1. Under optimum conditions a detection limit of 2 p.p.m. could be achieved, which indicated that this type of burner was not suitable for the determination of low concentrations of molybdenum.

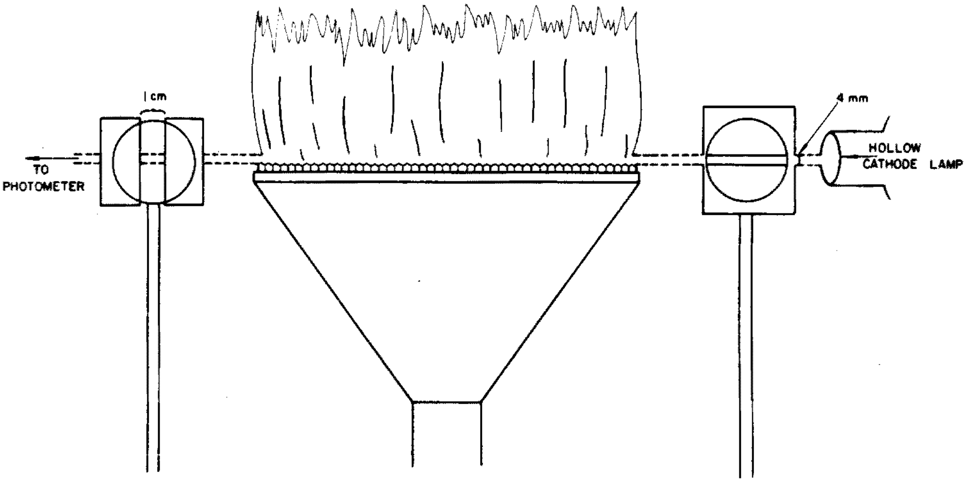

Fig. 1. Position of light beam.

TABLE I

OPTIMUM INSTRUMENTAL PARAMETERS

Spectrometer	Perkin Elmer 303.
Atomizer	EEL at 25 lb/sq. in. air pressure.
Gas	Acetylene at 10.0 on flowmeter. Supplementary air at 7.5 on flowmeter.
Burner	Slit, laminar flow type, gap 0.025 in., length 4.25 in. Height set ± 3 mm below centre of optical axis.
Wavelength	3133 Å.
Slit width	0.3 mm.
Light source	Self-built Mo hollow-cathode lamp run at 15 mA, stabilized D.C. power supply.

At this stage a Perkin Elmer 303 atomic absorption spectrometer was acquired. Optimum conditions using this instrument are shown in Table I. It has a slit-type burner and with a slightly luminous (fuel-rich) flame, a detection limit of 0.1 p.p.m. was obtained for molybdenum with aqueous standards. Figure 2 shows some of the calibration curves obtained with this instrument, using both aqueous solutions and an organic solvent. Also shown is the best curve obtainable with the flat-topped burner.

When spraying a combustible organic solvent, careful adjustment of the supple-

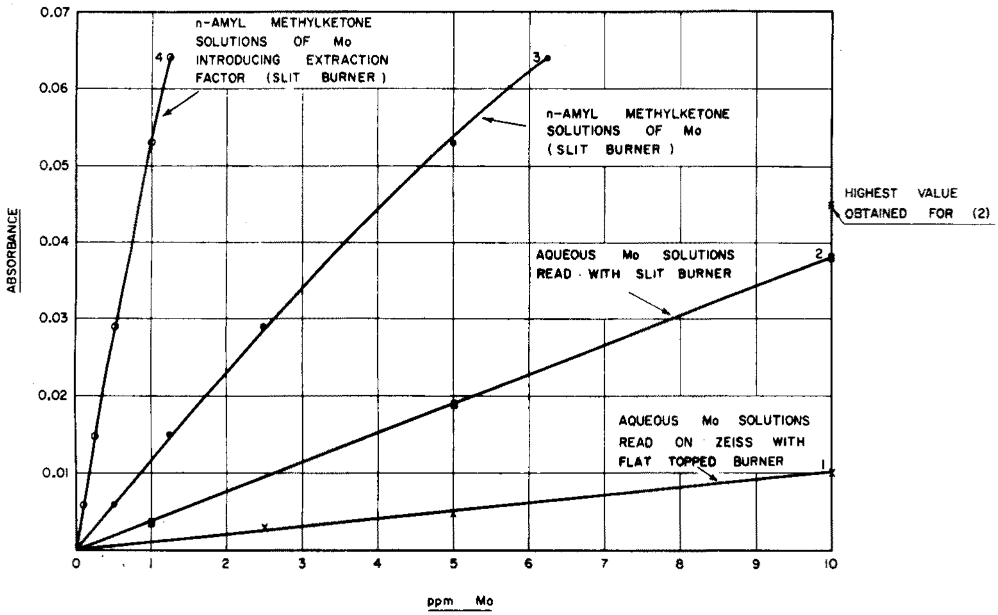

Fig. 2. Calibration graphs.

mentary air supply should be made to obtain optimum combustion. The flame tends to blow off when the ketone is not being sprayed and it is advisable to spray a blank ketone between samples.

Preparation of samples and standards

The samples and standards are prepared as follows.

Water samples. These require little preparation apart from acidifying and partial concentration by evaporation. It was found convenient to evaporate 500 ml to approximately 40 ml and then to add 2 ml of hydrochloric acid to dissolve any precipitate that formed. As iron is present in relatively small quantities in most natural water samples, it can be prevented from interfering by adding 5 ml of a 10% solution of citric acid, which complexes the iron. The pH is adjusted to 2.0 and after transferring the mixture to a separating funnel, 5 ml of a 2% solution of APDC are added. After addition of 10 ml of *n*-amyl methyl ketone, the mixture is shaken and allowed to stand for 5–10 min to allow the two phases to separate. The aqueous phase is discarded and the organic phase containing the molybdenum is transferred to a 10-ml beaker for convenient handling.

Plant samples. After drying and grinding, 5–10 g of plant material are ashed at 500°. The ash is dissolved in as little concentrated hydrochloric acid as possible and diluted to 40 ml with distilled water. It is then treated in the same way as the water samples.

Silicate samples. Finely crushed material (0.5 g of 200 mesh) is fused with 2 g of sodium peroxide and 1.5 g of sodium hydroxide at 470° for 30 min in a platinum crucible[9]. Platinum corrosion may occur if the iron content of the sample exceeds 5%.

This can be prevented by first leaching the sample with hydrochloric acid, filtering, and igniting the filter paper before fusion. The fusion product is dissolved in hydrochloric acid and recombined with the filtrate. As APDC forms preferential complexes with iron, 8-hydroxyquinoline (25 ml of a 4% solution) is added before adjusting the pH to 1.0. The procedure of ketone addition etc. follows as described above.

Standards. Standard ketone solutions are prepared by following the extraction procedure on aqueous standards containing known concentrations of molybdenum. These aqueous standards are prepared by dissolving ammonium molybdate in distilled water and making up the volume to form a stock solution (200 p.p.m. Mo) from which further dilutions are made.

Extraction procedure

Because of the deviation from reported procedures, an investigation was carried out to determine suitable pH extraction ranges and to test interference effects.

Methyl isobutyl ketone has a relatively high solubility in water (1.8 g per 100 ml), which is not desirable when the concentration factor (10 ×) is large. Amyl methyl ketone is less soluble in water (±0.5 g per 100 ml) and separates more easily from the aqueous phase because of lower density. This solvent was therefore selected as being the most suitable for extraction.

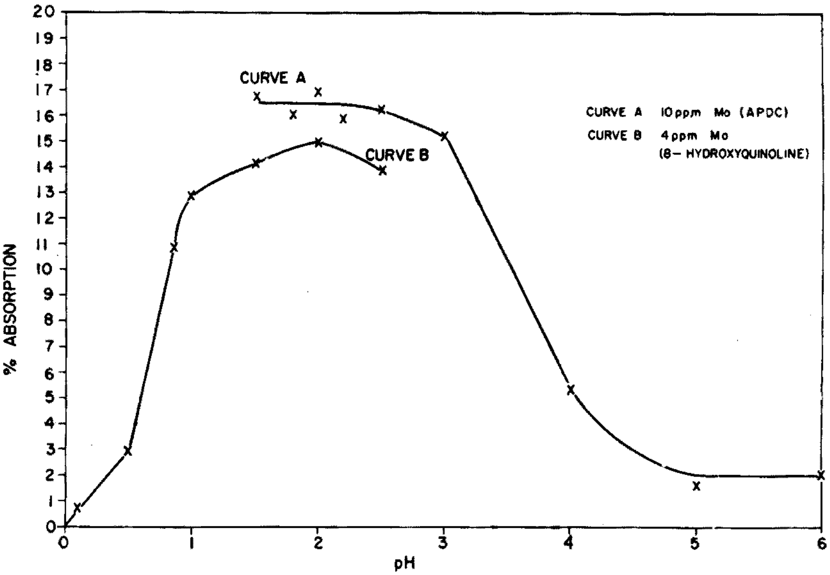

Fig. 3. Extraction efficiency graphs.

The effect of pH was tested by carrying out the extraction procedure with known standards and APDC at pH values varying from 1.5 to 6.0. Graph A in Fig. 3 shows that optimum recovery (94%) takes place between pH values of 1.5 and 2.5.

Similar tests made with 8-hydroxyquinoline (Graph B, Fig. 3) indicate that optimum extraction (99%) takes place at a pH value of 2.0. Unfortunately at this pH value a heavy precipitate forms, probably due to iron in the presence of excess

8-hydroxyquinoline. For this reason extraction is done at a pH value of 1.0, extraction efficiency being 98%.

Interference with the determination of molybdenum, by other elements likely to be present in the sample, was investigated by adding these elements at various concentration levels to known standards and extracting molybdenum using both the APDC and the 8-hydroxyquinoline procedures. The results of the investigations are shown in Tables II and III. It may be seen in Table II that with the APDC extraction, copper, zinc, and lead have no effect; sodium, calcium, and magnesium at high concentrations depress the absorbance slightly. Iron, however, in excess of 0.2 p.p.m. depresses molybdenum absorption markedly, probably because of preferential extraction or complex formation and flame interference. The prior addition of citric acid to complex the iron and thus prevent its extraction was successful for concentrations up to 20 p.p.m. For higher concentrations of iron, 8-hydroxyquinoline was used for extraction at a pH of 1.0. Table III shows that iron, even at a concentration of 5000 p.p.m. in solution, has no effect on the extraction and determination of molybdenum. Other elements, at concentrations most likely to occur in rock samples were also tested for interference. The results are shown in Table III.

TABLE II

THE INFLUENCE OF Cu, Zn, Pb, Na, Mg, Ca AND Fe ON THE EXTRACTION AND ABSORPTION OF MOLYBDENUM USING APDC EXTRACTION

p.p.m. Mo	*Elements added to 50 ml of aq. soln.*	*Mo absorbance after extraction*
2.0	Nil	0.090
	1.0 p.p.m. Cu	0.090
	5.0 p.p.m. Cu	0.088
2.0	Nil	0.089
	0.5 p.p.m. Zn	0.089
	1.0 p.p.m. Zn	0.088
2.0	Nil	0.089
	0.2 p.p.m. Pb	0.089
	0.5 p.p.m. Pb	0.088
2.0	Nil	0.090
	30 p.p.m. Na, 100 p.p.m. Mg, 200 p.p.m. Ca	0.086
	300 p.p.m. Na, 400 p.p.m. Mg, 800 p.p.m. Ca	0.084
2.0	Nil	0.085
	0.10 p.p.m. Fe	0.085
	0.20 p.p.m. Fe	0.082
	0.50 p.p.m. Fe	0.076
	1.0 p.p.m. Fe	0.065
	2.0 p.p.m. Fe	0.059
	5.0 p.p.m. Fe	0.042
2.0	Nil	0.089
	10 p.p.m. Fe + citric acid	0.086
	20 p.p.m. Fe + citric acid	0.086

TABLE III

THE INFLUENCE OF Mg, Ca, K, Al, Cr, Mn, Ni, Co AND Fe ON THE EXTRACTION AND ABSORPTION OF MOLYBDENUM USING 8-HYDROXYQUINOLINE

p.p.m. Mo	*Elements added to 50 ml of aqueous solution*	*Mo absorbance after extraction*
2.0	Nil	0.084
	100 p.p.m. Mg, 100 p.p.m. Ca, 100 p.p.m. K	0.084
	250 p.p.m. Mg, 250 p.p.m. Ca, 250 p.p.m. K	0.084
2.0	Nil	0.084
	100 p.p.m. Al	0.084
	250 p.p.m. Al	0.084
2.0	Nil	0.084
	20 p.p.m. Cr	0.080
2.0	Nil	0.084
	20 p.p.m. Mn	0.083
	50 p.p.m. Mn	0.082
2.0	Nil	0.084
	80 p.p.m. Ni	0.084
	200 p.p.m. Ni	0.084
2.0	Nil	0.084
	20 p.p.m. Co	0.083
	50 p.p.m. Co	0.081
2.0	Nil	0.084
	2000 p.p.m. Fe	0.082
	5000 p.p.m. Fe	0.082

RESULTS

Precision tests were carried out on borehole water samples to which molybdenum had been added, and on 2 geological samples. The results are shown in Table IV.

Recovery tests and chemical analyses were used to determine the accuracy of

TABLE IV

PRECISION TESTS

Type of sample	*No. of samples analysed*	*p.p.m. Mo*	*Average absorbance*	*Coefficient of variation (%)*
Borehole water	22	0.050	0.049	1.9
Silicate rock G1	10	13.0	0.034	4.0
Sulphide ore 1	10	4.0	0.011	10.0

TABLE V

RECOVERY TESTS

Type of sample	*p.p.m. Mo present*	*p.p.m. Mo added*	*p.p.m. Mo recovered*	*Recovery (%)*
Borehole water	0.050	0.010	0.061	102
	0.050	0.025	0.075	100
	0.050	0.050	0.100	100
Sulphide ore 1	4.0	2.0	5.8	98
	4.0	4.0	8.0	100
	4.0	10.0	13.9	99

TABLE VI

COMPARISON OF RESULTS OBTAINED FOR WATER SAMPLES ANALYSED BY ATOMIC ABSORPTION SPECTROSCOPY AND COLORIMETRY

Sample	*p.p.m. Mo*	
	Atomic absorption spectroscopy	*Colorimetry*
I	0.048	0.052
II	0.091	0.091
III	0.010	0.011

TABLE VII

COMPARISON OF RESULTS OBTAINED FOR PLANT SAMPLES ANALYSED BY ATOMIC ABSORPTION SPECTROSCOPY AND OTHER METHODS

Sample	*p.p.m. Mo*		
	Atomic absorption spectroscopy	*Spectrographic*	*Chemical*
Peach leaves 4A	0.33	0.1 0.04 0.05 0.2 0.1 0.13	0.1
Beetroot leaves 4C	1.19	0.85 0.67 0.85 0.74 0.4 0.76	2.7
Lucerne 3	0.27		0.27
Lucerne 4	7.5		6.6
Lucerne 13	1.84		1.0
Lucerne 26	0.18		0.05

the method. The results of the recovery tests are given in Table V. Comparisons of atomic absorption determinations on a variety of samples with those obtained by chemical and spectrochemical methods are given in Tables VI, VII and VIII.

DISCUSSION

If due care is taken, the precision of the method is acceptable. Results obtained for plant and rock samples, however, were less precise than those obtained for water samples. It was felt that this could be explained by non-homogeneity of the sample, as comparatively small weights of material were used. Nevertheless, the precisions obtained on these samples compared favourably with those obtained by other methods.

The results of the recovery tests shown in Table V indicate that the extraction procedure is reliable.

The comparison values of plant samples given in Table VII show the atomic absorption values to be somewhat higher than those of the other methods. The large spread of values obtained by other methods makes it difficult to assess these results

TABLE VIII

COMPARISON OF RESULTS OBTAINED FOR SILICATE ROCKS ANALYSED BY ATOMIC ABSORPTION SPECTROSCOPY AND OTHER METHODS

Sample	*p.p.m. Mo*		
	Atomic absorption spectroscopy	*Spectrographic*[10]	*Chemical*[10]
G1[a]	13.0	6	14
	(±0.7)	6	6.5
		5	6.7
		4	
		11	
		10	
		4	
		9	
		7	
		6	
		7	
		9	
W1	<0.2	5	5
		<4	0.5
			0.4
			0.5
Sulphide ore 1	4.0	10	—
	(±0.6)		

[a] The latest accepted mean value for this standard is 7.0 p.p.m.

conclusively. The sensitivity of the method for plant material is of the order of 0.1 p.p.m. using the weights mentioned previously. There is little doubt that this limit of detection could be improved by increasing the initial sample weight. The detection limit of 0.1 p.p.m., however, is probably sufficient to meet the requirements of most plant chemists.

Table VIII shows the values obtained with 3 standard rock samples. It is interesting to note that relatively few values are available for molybdenum for the much analysed G1 and W1. Comparison values[10] show a marked spread, but atomic absorption values are well within the order of magnitude of values obtained by other methods.

The limit of detection for silicate samples is about 1 p.p.m. This limit could probably also be improved by the use of larger sample weights.

CONCLUSION

The methods developed appear to be satisfactory from the point of view of accuracy and precision. Although the chemical steps are time-consuming, many samples can be analysed daily. The method appears to be at least as rapid and accurate as any other method at present in use.

The authors are indebted to Mrs. D. B. DE VILLIERS for help with the manuscript.

SUMMARY

A procedure is described for the determination of trace quantities of molybdenum by atomic absorption spectroscopy. Molybdenum is complexed with ammonium pyrollidine dithiocarbamate or 8-hydroxyquinoline and extracted into *n*-amyl methyl ketone. Molybdenum is then determined by atomic absorption spectroscopy. Interferences have been eliminated and detection limits of 0.002 p.p.m. for water samples, 0.1 p.p.m. for samples of dried plant material, and 1 p.p.m. for silicate rock samples have been obtained.

RÉSUMÉ

Un procédé est décrit pour le dosage de traces de molybdène par spectroscopie par absorption atomique. Le molybdène est complexé au moyen de pyrollidine dithiocarbamate d'ammonium ou d'hydroxy-8-quinoléine et extrait dans la *n*-amylméthylcétone. On procède ensuite au dosage par spectroscopie par absorption atomique. Limites de détection: 0.002 p.p.m. pour eaux, 0.1 p.p.m. pour des échantillons de plantes séchées et 1 p.p.m. pour des échantillons de silicates.

ZUSAMMENFASSUNG

Es wird ein Verfahren für die Bestimmung von Spuren Molybdän mit der Flammenabsorptionsspektroskopie beschrieben. Das Molybdän wird mit Ammoniumpyrollidindithiocarbamat oder 8-Hydroxychinolin komplexiert und mit N-Amylmethylketon extrahiert. Molybdän wird dann mit der Flammenabsorptionsspektroskopie bestimmt. Störungen konnten eliminiert werden. Es wurden Nachweisgrenzen von 0.002 p.p.m. für Wasserproben, 0.1 p.p.m. in getrocknetem Pflanzenmaterial und 1 p.p.m. in Silikatgesteinen erhalten.

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THE USE OF COMPUTER TECHNIQUES IN EMISSION AND ATOMIC ABSORPTION FLAME PHOTOMETRY

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During evaluation programs of new instruments utilizing atomic absorption flame photometry, and in the development of methods of analysis involving atomic absorption determinations, an enormous number of experimental readings were accumulated in these laboratories. This accumulation of data was a consequence of the relatively short time needed to prepare the sample solutions and to obtain the readings with the instrument (2 of the most outstanding advantages of flame methods). In addition, several flame photometrists were working simultaneously on the above-mentioned projects. The normal progress of the evaluation programs is dependent upon the reduction of certain sets of test data.

The advantages of flame photometry methods in obtaining rapid readings from quickly prepared samples were being eliminated in the common procedures of manually calculating the averages of several readings, transforming the averages to concentration related values, interpolation of working curves, and calculation of sensitivity values. Therefore, in order to maintain an orderly scheduling of tests, rapid evaluation of prior results by computer was necessary. This problem is also found in many laboratories doing routine analysis (metallurgical, agricultural, biological samples) in which hundreds—even thousands—of samples should be analyzed and reported per day.

All these manual calculations are subject to a potential personal error—operator's calculating errors—and conditioned in many cases to manually traced working curves. Plotting of data and drawing curves is frequently necessary in linearity tests and dynamic range tests under different operating conditions.

To minimize the time involved in manual data handling and to diminish the error hazard, it was decided to take advantage of computer techniques: (*a*) for processing the data collected and providing tabulated final results; (*b*) for processing other data and providing plotted points and/or with working curves on graph or vellum paper (working graphs and presentation graphs for reports or slides).

The computer techniques have been used for *emission* and *atomic absorption* flame photometry problems.

EXPERIMENTAL

Instrumentation

For computer and plotting techniques:

(*a*) IBM 1410 computer, 40K memory, 6-tape system.

(*b*) CalComp Digital Plotter, Model 565, off line via CalComp Model 470 tape system.

For flame photometry techniques:

(*a*) Beckman DU® Flame Spectrophotometer equipped with A.C. power supply, SERA and Bristol Recorder (10″).

(*b*) Beckman DU-2 Spectrophotometer equipped with A.C. power supply, SERA, Beckman 5″ Recorder, Model 1300 Atomic Absorption Accessory, Laminar Flow Burner, and Turbulent Flow Burner*.

(*c*) Beckman DB® Spectrophotometer equipped with Beckman 5″ Recorder, Model 1301 Atomic Absorption Accessory, Laminar Flow Burner, and Turbulent Flow Burner*.

Operating conditions for newly developed atomic absorption instruments have been discussed elsewhere[1].

Solutions

Sample solutions. Diluted with distilled water from original (real or synthetic) samples.

Standard solutions. Aqueous solutions obtained by dilution with distilled water (dilution series) from aqueous stock solutions.

Blanks. When possible, distilled water.

PROBLEMS STUDIED

Addition method

The (standard) addition method is widely used in flame photometry[2]. It can be utilized in those analytical systems showing: (*a*) linearity (emission and atomic absorption); (*b*) similar interference effects of the interfering component on the analyte before and after the necessary additions. The application of the addition method to flame analysis (emission and atomic absorption) has been studied in detail[2]. In brief, the method consists of adding to aliquots of the sample solution one or several additions (known volumes of solution containing the analyte in known concentration). The concentration of the sample solution is calculated from the readings obtained for the sample with and without additions (provided that the analytical system still shows linearity after the additions).

The problem can be solved graphically, but it involves: (*a*) transformation of readings into other variables (in emission: instrumental readings into net emissions; in atomic absorption: % of absorption readings into absorbances); (*b*) plotting the values; (*c*) tracing the best straight-line fit corresponding to the actual points while visually compensating for variations; (*d*) extrapolating the working graph for desired concentration. By manual calculation, the operations involved are simple, but take an appreciable time. The calculations, however, are too complicated for manual reduction when there are several additions and/or variations of volumes (that is, not all the aliquots are diluted to the same final volume and/or variable volumes of the additions are used).

There is a source of error, in the case of simple or multiple addition, when the

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* The Laminar Flow Burner (LFB) fed with air and acetylene. The Turbulent Flow Burner (TFB) fed with air and hydrogen.

operator tries to trace the line, using the experimental points. The method of *single addition* is the more convenient because the operator has to prepare fewer solutions and take fewer readings. Thus, special attention has been paid to the case of single addition.

Addition method in atomic absorption. Two solutions are prepared and measured.

Sample solution. The sample solution as it is, or an aliquot diluted to a known volume. Concentration: C_S.

Mixture solution. An aliquot of the sample solution mixed with a known volume of a standard solution of the analyte.

$$\text{Concentration: } C_M = \frac{C_S V_S + C_A V_A}{V_T}$$

where V_S = Volume of the aliquot of sample solution of concentration C_S, V_A = Volume of the standard solution of concentration C_A, $V_T = V_S + V_A$.

Blank. Solution without analyte. The blank is zeroed and the other solutions measured. Absorption percentage readings:

$A^0{}_{T1}$ For the mixture solution
$A^0{}_{T2}$
$A^0{}_{S1}$ For the sample solution
$A^0{}_{S2}$

These readings should be averaged, and the average converted to the absorbances A_T and A_S. Then,

$$C_S = C_A \frac{A_S}{A_T \dfrac{V_T}{V_A} - A_S \dfrac{V_S}{V_A}}$$

For testing new procedures and checking recoveries, the differences are also calculated:

Difference = C_S found − C_S added

Addition method in emission. The laboratory process is the same as described above for atomic absorption. The readings R_{T1}, R_{T2}, R_{S1}, R_{S2}, R_{B1}, and R_{B2} are used to calculate the net emissions ΔE_T and ΔE_S. Then

$$C_S = C_A \frac{\Delta E_S}{\Delta E_T \dfrac{V_T}{V_A} - \Delta E_S \dfrac{V_S}{V_A}}$$

Also, differences are calculated.

Dilution method

The dilution method[3] is a modification of the addition method and has the advantages of needing less laboratory work in the preparation of solutions, of being applicable to analytical systems that present curvature at high concentration levels, and of permitting some compensation of variations of matrix components.

Dilution method in atomic absorption. The operator reads $A^0{}_{A1}$ and $A^0{}_{A2}$ for the mixture solutions instead of $A^0{}_{S1}$ and $A^0{}_{S2}$. Then C_S is calculated with the equation:

$$C_S = C_A \frac{A_T \dfrac{V_T}{V_S} - A_A \dfrac{V_A}{V_S}}{A_A}$$

Dilution method in emission. The operator reads R_A1 and R_A2 instead of R_S1 and R_S2. The equation used is:

$$C_S = C_A \frac{\Delta E_T \dfrac{V_T}{V_S} - \Delta E_A \dfrac{V_A}{V_S}}{\Delta E_A}$$

*Linearity tests and percentual sensitivity**

In flame studies it is fundamental to know if the analytical systems present linear response in the representative *instrumental response* (*i.e.* absorbance value) *vs. concentration.*

The following information is generally derived for atomic absorption: (*a*) slope of the working curve, and if possible, its equation; (*b*) information about the point at which curvature begins; (*c*) qualitative (relative) percentual concentration limit (RPCL or PCL); (*d*) qualitative (relative) percentual sensitivity (RPS or PS).

This information must be derived from the only available data, *i.e.* the percentage absorption values (one to four values), and the known concentration of the solutions (standard solutions).

The percentage absorption values are averaged and converted to absorbances, and these are plotted *vs.* concentration in p.p.m. to obtain working curves. The *slope* is calculated as absorbance per 1 p.p.m. For any concentration (N p.p.m.) giving an absorbance A_N (in the linear region):

$$m = A_N/N$$

The *qualitative* (relative) *percentual concentration limit* is calculated by

$$\mathrm{RPCL} \doteq \frac{0.0044}{m}$$

The qualitative (relative) percentual sensitivity is

$$\mathrm{RPS} = \frac{1}{\mathrm{RPCL}} = \frac{m}{0.0044}$$

Interpolation and extrapolation

Once the working curves have been defined, they are used in analytical determinations to obtain the concentration of sample solutions by reading the corresponding instrumental responses.

Two standard method

This method is widely used in flame photometry and consists in "sandwiching" a sample solution between 2 known standard solutions.

*Fluctuational sensitivity**

In atomic absorption it is necessary to calculate fluctuational sensitivity values besides the already mentioned percentage values.

Three values should be known: (*a*) qualitative (relative) fluctuational con-

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* See ref. 4.

centration limit (RFCL or FCL); (*b*) qualitative (relative) fluctuational sensitivity (RFS or FS); and (*c*) qualitative absolute fluctuational limit (AFL).

To calculate these values the following data are used:

(*a'*) *Solution signals* (% Absorption, generally $<5\%$ Absn.): Triplicate data obtained with a solution of known concentration.

(*b'*) *Blank signals* (% Absorption): Adjusted to 0% absorption, but read whatever they are at that level. Triplicate data.

(*c'*) *Noise level* (In % Absorption units): Peak-to-peak noise (about 4σ; σ being the standard deviation of blank readings). Triplicate data.

All values are averaged, and the net signal is calculated (solution signal minus blank signal). Then for a concentration N p.p.m. of the solution, the *qualitative (relative) fluctuational concentration limit* is given by

$$\text{RFCL} = N \frac{\text{Noise level}}{\text{Net signal}}$$

And the *qualitative (relative) fluctuational sensitivity by*

$$\text{RFS} = \frac{1}{\text{RFCL}}$$

Now, for a given feeding rate (FR) in ml/min, for a given feeding time (t) in sec and knowing the value of the RFCL in p.p.m.*, it is possible to calculate the *qualitative absolute fluctuational limit* (in g) by

$$\text{AFCL} = \text{RFCL} \cdot \frac{t \cdot \text{FR}}{60}$$

(RFCL is also given in g)

Precision studies

For calculation of standard deviation and coefficients of variation, the standard formulae can be applied.

Flame profiles

These are representatives of variations of absorbance with the height of the burner (height of the selected zone in the flame over the top of the burner). Usually A values are plotted on the abscissae.

COMPUTER RESULTS

Automation of a variety of data-handling problems experienced by the flame photometrist was undertaken in order to minimize the time involved in manual data handling, as well as to minimize the potential errors from such handling. In the previous sections of this paper, typical problem descriptions encountered in flame photometry have been discussed. In the following section, samples of computed and plotted results are presented in order to emphasize the efficiency gained through computer utilization.

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* RFCL (in p.p.m.) is converted to RFCL (in g/ml) by multiplying its value by 10^{-6}.

The first 4 experimental problems can be considered together in terms of automating their data-handling requirements. These are: (*a*) addition method in atomic absorption; (*b*) addition method in emission; (*c*) dilution method in atomic absorption; (*d*) dilution method in emission.

Addition method in atomic absorption

For purposes of explanation, the results of the addition method in atomic absorption are presented in Fig. 1. Input for this program includes the following: (*a*) a system identification number; (*b*) concentration and volume of both the standard solution and the sample solution; (*c*) percentage absorption readings for the sample solution and the mixed solution.

```
   TABLE A-1-E     MAGNESIUM - NO.7-164-LF.SEE REP-92-TABLE V      ABSORPTION

SYSTEM          CA         CS         ABT        ABS        AT         AS          CS      DIFFERENCE
                                                                                  FOUND

   1           .0100      .0100      7.0000     3.9000     .0315      .0172      .0121         .0021
   2           .0100      .0100      7.0000     3.7500     .0315      .0165      .0111         .0011

   TABLE A-1-D     MANGANESE - NO.7-123-TF.SEE REP-89-TABLE XV     ABSORPTION

SYSTEM          CA         CS         ABT        ABS        AT         AS          CS      DIFFERENCE
                          ADDED                                                   FOUND

   1           .1000      .1000      3.3000     1.6000     .0145      .0070      .0925        -.0074
   2           .1000      .1000      3.5000     1.8000     .0154      .0078      .1040         .0040

   TABLE A-1-6     COPPER - NO.6-98-TF.    SEE REP-89-TABLE XV-    ABSORPTION

SYSTEM          CA         CS         ABT        ABS        AT         AS          CS      DIFFERENCE
                          ADDED                                                   FOUND

   1           .1000      .1000     10.3000     5.3000     .0472      .0236      .1003         .0003
   2           .3000      .2000     24.1000    10.1000     .1197      .0462      .1886        -.0113
   3           .5000      .5000     42.0000    24.1000     .2365      .1197      .5126         .0126
   4          2.0000     1.0000     78.0000    41.8000     .6575      .2350     1.1127         .1127
```

Fig. 1. Addition method in atomic absorption (direct reproduction of the printed computer output tables).

The program calculates the absorbances A_T and A_S from the average percent absorbance readings and computes the C_S found and the difference from the C_S found and C_S added.

This program is quite simple and eliminates the errors inherent in averaging, taking logs, and solving a complex algebraic equation. The results in Fig. 1 are those returned to the experimenter in a short enough time to be used in determining which way to continue in his testing.

The basic differences between this program and the other 3 are contained in earlier parts of this paper and are simply changes in the algebraic equation solved and a difference in the reading.

Linearity tests and percentual sensitivity

The program to solve this particular problem is more complex than that described above. There is more choice given to the worker in determining both his input and his output. The program allows the worker to utilize from 1 to 4 readings of percent absorption for each level of concentration, within a limit of 15 levels of concentration.

Calculated output for this program includes the slope of the linear portion when plotting absorbances *vs.* concentration, the relative percentual concentration limit, and the relative percentual sensitivity. The linear portion is found by obtaining the best straight-line fit to the lower concentration values, including as many values as possible within error limits set forth. The remaining points are then fitted to the best quadratic form possible. A sample of the tabular output from this program is given in Fig. 2. In addition to the tabular output, Figs. 3, 4, and 5 are examples of the graphic representation of these results, using the computer-generated data.

```
Emitting Elements – Denver Paper – Strontium – Test 27
Element     Wave      Burner +   Oper-    Con-     Slope    RPCL          RPS
            Length    Instru.    ation    dition            PPM
SR          4607      DU-2-T     1B3P     ADJ.     .12202   .32781E-01    .30505E-02
The error limits for this test are 10.00 percent for absorbances of less than .12 and 5.00 percent for
the remaining range.

This Test is Linear Between Concentration Limits of 0.0 and 2.0000
Data
Concentration          Percent Absorption                  Absorbances
              AB1        AB2         AB3        AB4
  .0000        .0000       .0000     .0000      .0000      .0000
  .5000      12.3000     12.3000     .0000      .0000      .0570
 2.0000      43.0000     43.0000     .0000      .0000      .2441
 5.0000      70.0000     70.0000     .0000      .0000      .5228
10.0000      86.7000     86.7000     .0000      .0000      .8761
 1.0000      25.3000     25.3000     .0000      .0000      .1266
 3.0000      52.3000     52.3000     .0000      .0000      .3214
This test fits the following quadratic equations
.030418 +   .112411  X +   —.002783  X**2   Between concentration limits of   2.0000 and 10.0000
```

Fig. 2. Linearity test and percentual sensitivity.

Figure 3 shows an obvious data error, made obvious by the discontinuity in the smoothness of the plotted curve. This error could occur from an incorrect reading or an error in transcribing these data for computer entry. The experimenter, upon seeing this, can check back over his work and determine what the error was. A rerun of these data is shown in Fig. 4, where the program has been told to disregard erroneous points. This figure now shows a smooth curve and valid results for the test. Figure 5 is included as an option of the program which restrains the output such that no curve is plotted, and allows the experimenter to hand-fit a curve of his choice. This is sometimes necessary when quadratic forms do not satisfy the tests.

Fluctuational sensitivity

Figure 6 is a sample of the output from the Fluctuational Sensitivity Program, which takes percent absorption signal values, blank signal values, and zero percent

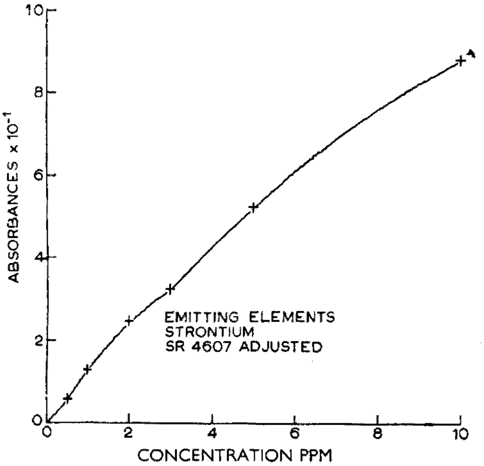

Fig. 3.

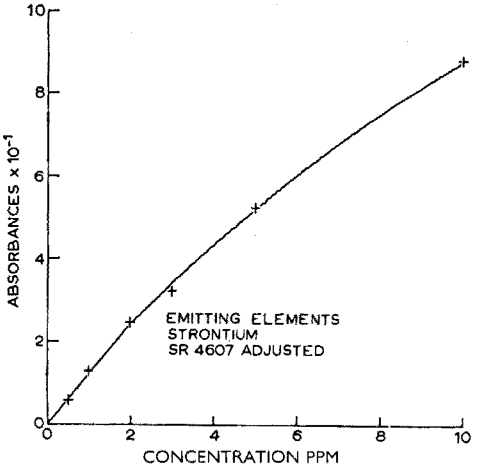

Fig. 4.

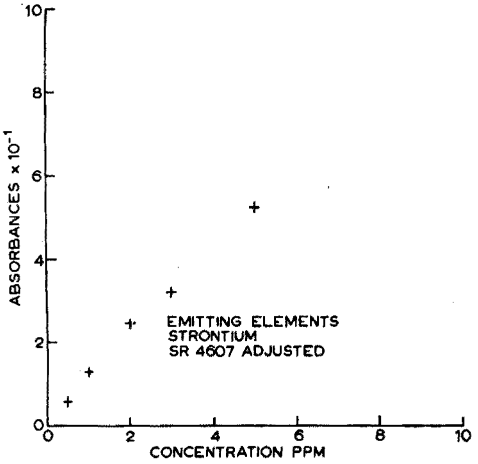

Fig. 5.

Figs. 3–5. Linearity test and percentual sensitivity.

absorption noise values, averages up to 3 readings of each type, and, utilizing known feeding rate, reading time and concentration of the standard, calculates the relative fluctuational concentration limit, the relative fluctuational sensitivity, and the absolute fluctuational concentration limit. Of prime importance in this program is the elimination of routine errors due to algebraic manipulation of data.

Precision studies

Figure 7 is a presentation of output of basic statistical parameters as generated by the computer. This is a standard program for any computer installation, and the equations that are solved can be found in any statistics text.

```
Fluctuational Conc. Limits                               Silver
Ele-  Wave-   Burner + Oper-  Con-    Conc.   Net     Aver.  RFCL  RFS      AFLC
ment  length  Instru.  ation  dition  stand.  Signal  Noise  (PPM)          (G×1OE-6)
AG    3281    L-DU     HOT            .100    3.866   .100   .002  386.666  .002
AG    3383    L-DU     HOT            .100    2.066   .100   .004  206.666  .004
```

Fig. 6. Fluctuational concentration limits.

```
Element         No.  Mean      Sigma  R      Min       Max       Spread  Pct. Spread
Identification
NA              24   199.6750  .3514  .1760  198.8000  200.2000  1.4000   .7011
K               24     9.9191  .0572  .5776    9.8000   10.0300   .2300  2.3187
NA              24   199.7541  .4443  .2224  198.7000  200.5000  1.8000   .9011
K               24    10.0045  .0543  .5428    9.9100   10.1100   .2000  1.9990
NA              10   199.6000  .2932  .1469  199.0000  200.0000  1.0000   .5010
```

Fig. 7. Precision study—standard deviation.

```
FLAME PROFILES
Height       Readings                   Absorbances
in Inches    Percent Absorption
             0. AL 50 BA
 .0000       48.0000       .0000        .2839
1.0000       54.0000       .0000        .3372
2.0000       52.0000       .0000        .3187
3.0000       43.0000       .0000        .2441
4.0000       37.0000       .0000        .2006
5.0000       22.0000       .0000        .1079
6.0000       19.0000       .0000        .0915
7.0000       16.0000       .0000        .0757
8.0000       10.0000       .0000        .0457

Height       Readings                   Absorbances
in Inches    Percent Absorption
             50 AL 50 BA
 .0000       4.6000        .0000        .0204
1.0000       6.5000        .0000        .0291
2.0000       6.5000        .0000        .0291
3.0000       5.9000        .0000        .0264
4.0000       4.3000        .0000        .0190
5.0000       3.5000        .0000        .0154
6.0000       2.7000        .0000        .0118
7.0000       2.0000        .0000        .0087
8.0000       1.5000        .0000        .0065
```

Fig. 8. Flame profiles.

Flame profiles

A program has been developed to calculate the absorbance from percent absorption readings relative to a height within a flame. Figure 8 shows the tabular output of this program. Figure 9 is a graphical representation of this output and shows at a glance the variation of absorbances within flame height expressed in turns of the instrument adjustment with an arbitrary zero taken at the first reading. Under normal circumstances, only the right-hand portion of the plot is given. The mirror image, as an option, is given in this paper purely to present an appreciation for the data-handling capabilities of the computer/plotter combination.

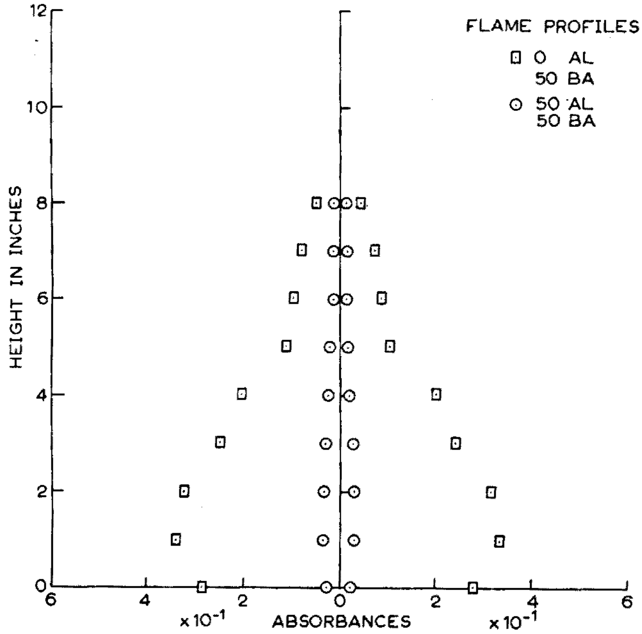

Fig. 9. Flame profiles.

CONCLUSION

The output from selected techniques in emission and atomic absorption flame photometry has been presented. Most computer output shows 4 places to the right of the decimal. This is done as a matter of convenience in formulating the output and does not indicate the number of significant digits, which are a function of the number of significant places in the input. Care has been exercised in the input formulating for the computer programs, such that the worker can code the input forms in the same way as he now records data from his experiments. He is allowed, within limits, to provide his own run identification and also labeling for any of the plotted output. Under normal circumstances, without priority, the experimenter can expect his plotted output and tabular results to be returned to him the morning following his data submission. This time delay can be reduced to a matter of hours for priority operations.

The use of the computer programs has maximized the inherent advantages of flame photometry and has substantially minimized the time required for data handling with the added advantage of error reduction.

SUMMARY

The utilization of flame methods, especially in atomic absorption work, can be enhanced by the application of computer techniques for rapid and accurate reduction of experimental data. Modern computational techniques are described for the analysis of large numbers of solutions; their inherent advantages in time saving and reduction of calculating errors are discussed. Several typical problems have been automated and are explained in some detail; pertinent descriptions of the computer program and the resulting output from sample calculations are included.

RÉSUMÉ

L'utilisation de méthodes de flamme, spécialement pour l'absorption atomique, peut être améliorée par l'application de techniques à "computer". Des techniques modernes sont décrites pour l'analyse de nombreuses solutions; leurs avantages de gain de temps et de réduction des erreurs de calcul sont discutés. Plusieurs problèmes typiques ont été rendus automatiques et expliqués en détails.

ZUSAMMENFASSUNG

Die Verwendung von Flammenmethoden, besonders der Flammenabsorptionsspektroskopie kann durch die Anwendung von Rechnern zur schnellen und genauen Auswertung experimenteller Daten gefördert werden. Moderne Rechnertechniken werden für die Analyse einer grossen Zahl von Lösungen beschrieben; ihre vorteilhaften Zeitersparnisse und die Verminderung von Rechenfehlern werden diskutiert. Verschiedene typische Probleme wurden automatisiert und werden in einigen Details behandelt. Angemessene Beschreibungen des Rechenprogramms und die sich ergebende Ausgabe für einige Probenberechnungen sind eingeschlossen.

REFERENCES

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MICRODETERMINATION OF CHLORINE OR BROMINE IN HIGHLY HALOGENATED ORGANIC COMPOUNDS

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An examination of the literature shows that the determination of chlorine or bromine in highly halogenated organic substances by many of the commonly used methods can lead to difficulties on any scale of working, because of the thermal stability and often the high volatility of such compounds.

In the present work a close examination of the application of micro methods involving magnesium fusion and oxygen-flask combustion was considered to be the most promising approach. SCHÖNIGER[1] has described a magnesium fusion procedure followed by a Volhard titration for the microdetermination of halogens. This finish is not attractive for routine micro work and out of the 5 compounds analysed by SCHÖNIGER, only tribromophenol possessed a high halogen content. However, this method has been modified by BALLESTER AND RIERA[2] for the analysis of highly chlorinated compounds on the semimicro scale but combined with the tedious and very lengthy gravimetric finish; one analysis requires over 5 h.

On applying the well-known oxygen-flask method, BENNEWITZ[3] obtained very erratic results for the highly halogenated organic liquids; the figures reported are invariably low and in some cases as low as 50% of theoretical. Other workers[4] modified the method for the analysis of such compounds by saturating the filter paper wrapper with 2% potassium nitrate before combustion. MÁZOR *et al.*[5] mixed the sample with a three-fold amount of sugar before the combustion and absorbed the halides produced in ammonia solution followed by argentimetric titration using variamine blue indicator. KIRSTEN[6] recommended the use of nitrite as absorbent in the flask for the semimicro determination of halogen in organic compounds, but a potentiometric finish was used and no data were given.

RESULTS AND DISCUSSION

Halogen determination by fusion with magnesium

The semimicro magnesium procedure described for highly chlorinated compounds[2] suffers from the disadvantage that more than 5 h are required for fusion and chloride determination. In the present work this time was reduced to less than half. After fusion with magnesium, the halide ions are leached with 0.05 N nitric acid solution which also adjusts the pH to the required value suitable for the mercurimetric titration[7]. The magnesium nitrate, unavoidably present with the halides, does not interfere even when present in high concentrations (up to 0.5 g Mg). The results

TABLE I

MICRODETERMINATION OF CHLORINE AND BROMINE IN THEIR RESPECTIVE HIGHLY HALOGENATED ORGANIC COMPOUNDS BY FUSION WITH MAGNESIUM

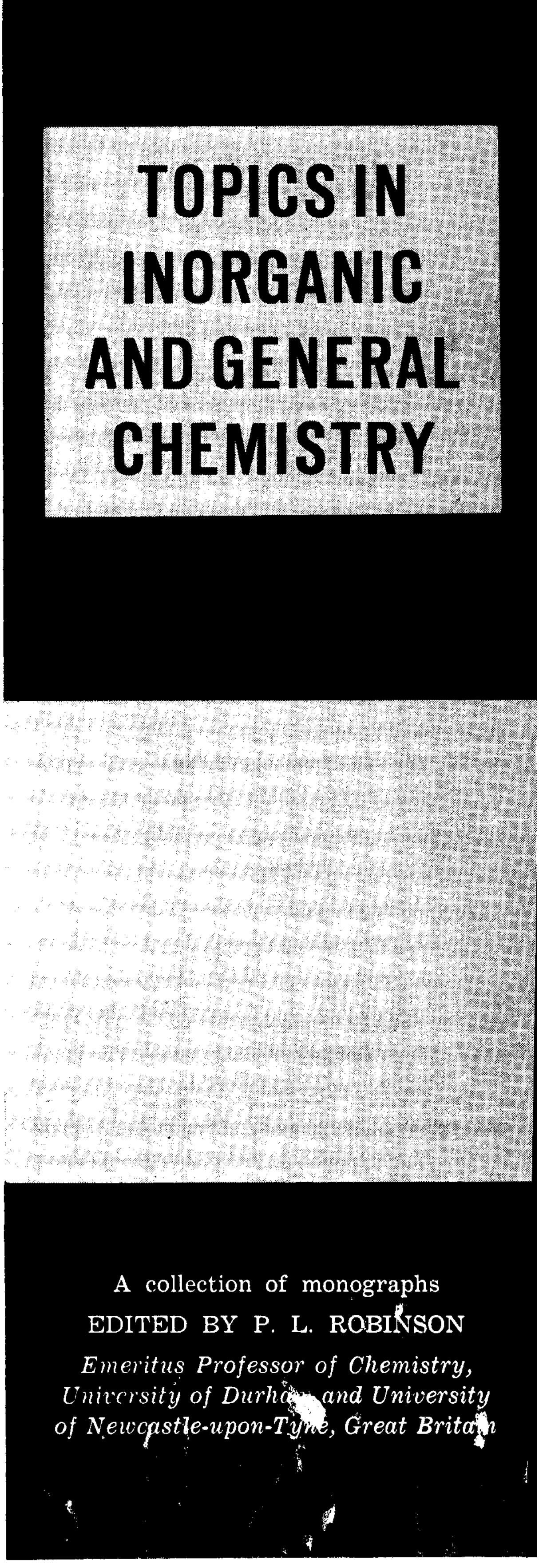
Sample	*% Halogen*		*%*	*%*
	Theoretical	*Found*	*Error*	*Recovery*
Perchloronaphthalene	70.27	70.38	+0.11	100.16
		70.32	+0.05	100.07
Perchlorodiphenyl	71.12	71.21	+0.09	100.13
		71.18	+0.06	100.08
Perchlorophenanthrene	67.85	67.92	+0.07	100.10
		67.89	+0.04	100.06
Chloranil	57.70	57.75	+0.05	100.09
		57.76	+0.06	100.10
Heptachlorotoluene	74.49	74.56	+0.07	100.09
		74.52	+0.03	100.04
Pentachlorotoluene	67.08	67.30	+0.22	100.33
		67.25	+0.17	100.25
Bromanil	75.45	74.92	−0.53	99.30
		74.79	−0.66	99.13
Pentabromotoluene	82.22	81.23	−0.99	98.80
		81.28	−0.94	98.86
Tetrabromo-*o*-xylene	75.81	75.13	−0.68	99.10
		75.37	−0.44	99.42

obtained are listed in Table I. It can be noticed from these figures that in the case of the highly chlorinated compounds the average recoveries are 100.12% with a relative mean error of +0.1%. With bromo-compounds the results fall outside the accepted limit of error, the average recovery being 99.10% with a corresponding error of −0.71%. These slightly low bromine values may be attributed to incomplete fusion and/or incomplete leaching.

Halogen determination by oxygen flask

Highly halogenated organic compounds are classified from the decomposition point of view, using the oxygen-flask method into 3 main classes:

Highly halogenated aromatic compounds. In recent years[8,9] there has been a trend to use water as the sole absorbing medium for halogen. Although this contributes to the simplicity of the procedure for the determination of the partially halogenated compounds, it was found that, in the case of the highly halogenated samples, water is a good absorbent only when the sample weight is less than about 4 mg (equivalent to 2–3.5 mg Cl); above this weight the results were unsatisfactory for the same compounds. Furthermore, water alone did not prove satisfactory for any compound that was partially or highly brominated. The erratic results were attributed to the formation of free halogen which was confirmed qualitatively by absorbing the decomposition products in potassium iodide solution containing few drops of soluble starch where iodine is detected. Therefore, the use of a reducing agent is recommended in such case



MONOGRAPH 1

THE CHEMISTRY OF BERYLLIUM

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Teddington, Great Britain

Beryllium metal and its compounds are the object of lively interest, especially in view of their successful applications in the fields of atomic energy and space technology. Notwithstanding the considerable volume of work published about the metallurgical studies of beryllium metal and its compounds, there has been very little in the way of a recent accounting of the important features of beryllium chemistry as a whole. It is this deficiency which Dr. Everest answers in a critical, concise and essentially complete treatment of the subject.

This volume will be of interest to undergraduate and graduate students specializing in inorganic chemistry as well as scientists and engineers occupied with industrial applications of beryllium and its commercial extraction.

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by C. B. AMPHLETT

Chemistry Division, Atomic Energy
Research Establishment, Harwell,
Great Britain

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Atomic Energy Establishment,
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by N. E. TOPP,

National Chemical Laboratory,
Teddington, Great Britain

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In addition to chemists, this work will prove valuable to metallurgists and solid-state physicists, as well as research students in these fields.

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MONOGRAPH 6

THE CHEMISTRY OF TECHNETIUM AND RHENIUM

by R. D. PEACOCK

Professor of Inorganic Chemistry,
University of Leicester,
Great Britain

Rhenium, the least abundant of the naturally occurring chemical elements, was also the last to be isolated by classical methods. In contrast, technetium was the first of the artificial elements. The chemistry of both has made rapid progress in the last decade, and this advance has been paralleled by the increasing market for rhenium and its derivatives. In this volume a cohesive picture is made of both the earlier work and recent developments. A selective summary of the analytical methods used to estimate the elements is also included.

Teachers in inorganic chemistry, chemists, in particular those working in transition metal chemistry in universities as well as in industry, and metallurgists who require a chemical background in their work, will find this monograph valuable, as will final year students at universities.

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MONOGRAPH 7

THE CHEMISTRY OF SELENIUM, TELLURIUM AND POLONIUM

by K. W. BAGNALL

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Chemistry Division, Atomic Energy
Research Establishment,
Harwell, Great Britain

Prior to the advent of the nuclear reactor, polonium was an unknown entity in the Periodic Table, separable only in microgram amounts. Its chemistry is now well established as a result of the availability of weighable amounts of polonium-210 synthesized by neutron irradiation of natural bismuth. This monograph covers existing knowledge of the chemistry of the group in as complete a fashion as possible. It includes a brief account of the very extensive literature on the organo compounds, a group which has not been reviewed in any detail for over a decade, as well as an account of the chemistry of the halides and complexes. Crystallographic data are included in tabular form.

Dr. Bagnall's work will certainly be interesting to university lecturers in inorganic chemistry and final year students, as well as radiochemists and research workers in the fields of sulphur, selenium and tellurium.

CONTENTS: 1. The Discovery and Uses of the Elements. 2. Separation, Purification and Determination. 3. The Elements, The Hydrides and other Derivatives. 4. Oxides, Oxo-acids, Sulphides and Sulphur-oxo-acids. 5. Halides. 6. Salts formed with Oxo-acids. 7. Carbon Compounds. Subject Index.

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MONOGRAPH 8

INTERACTIONS IN ELECTROLYTE SOLUTIONS

by GEORGE H. NANCOLLAS,

Professor of Chemistry,
State University of New York at
Buffalo, N.Y., USA

The nature of the species present in solutions of electrolytes is a subject of great importance to the chemist. The major part of this volume is concerned with the free energy, enthalpy and entropy changes accompanying ion-pair and complex formation. A comparatively new development has been the determination of reliable calorimetric ΔH values and a feature of the book is the compilation of recent data. The application of new physical methods to the problem of electrolyte solution structure and the rate of formation of complexes are also discussed. Suggestions are included for the efficient use of electronic computers for calculations.

Undergraduate and graduate students in physical chemistry will find this work a valuable reference source, as will analytical chemists, inorganic chemists and electrochemists.

CONTENTS: List of Main Symbols. 1. Introduction. 2. Experimental Methods: Determination of Association Constants. 3. The Association Constant. 4. Relationships Involving the Association Constant. 5. Thermodynamic Properties. 6. Mechanism of Complex Formation and Structure of the Complex. Appendix. Author Index. Subject Index.

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Reduction of the free halogen can be achieved either by using sufficient wrapping material to provide enough hydrogen (the weight ratio of filter paper/sample above 30), or by introducing a suitable amount of reducing agent into the absorption medium. For routine purposes, the use of a reducing agent is obviously preferable to weighing both the sample and the wrapping material for each analysis. Alkaline hydrogen peroxide, aqueous sulphur dioxide, alkaline sodium bisulphite and acidic sodium nitrite were therefore tested. The conditions were adjusted so that the mercurimetric titration could be utilised for the evaluation of the halide ions produced. Both hydrogen peroxide and sodium nitrite can be recommended as reducing agents (Table II). The former is preferred for simplicity and was found to be superior as absorbing medium for all types of halogen compounds.

TABLE II

USE OF ALKALINE HYDROGEN PEROXIDE AND ACIDIC SODIUM NITRITE IN THE MICRODETERMINATION OF HIGHLY CHLORINATED AND BROMINATED ORGANIC COMPOUNDS BY THE OXYGEN-FLASK METHOD

Sample	*% Halogen (theoretical)*	*Alkaline* H_2O_2			*Acidic* $NaNO_2$		
		% Halogen found	*% Error*	*% Recovery*	*% Halogen found*	*% Error*	*% Recovery*
Perchloronaphthalene	70.27	70.25	−0.02	99.97	70.39	+0.12	100.17
		70.32	+0.05	100.07	70.25	−0.02	99.97
Perchlorodiphenyl	71.12	71.20	+0.08	100.11	71.00	−0.12	99.83
		71.00	−0.12	99.83	70.96	−0.16	99.78
Perchlorophenanthrene	67.85	67.70	−0.15	99.78			
		67.52	−0.33	99.51			
Chloranil	57.70	57.80	+0.10	100.17	57.30	−0.40	99.31
		57.50	−0.20	99.65	57.46	−0.24	99.58
Tetrachloro-*o*-xylene	58.17	58.00	−0.17	99.71	58.00	−0.17	99.71
		57.90	+0.27	99.54	57.86	−0.31	99.47
Dichloroaniline	43.77	43.72	−0.05	99.89			
		43.80	+0.03	100.07			
Bromanil	75.47	75.74	+0.27	100.36	75.44	−0.03	99.96
		75.36	−0.11	99.85	75.63	+0.18	100.24
Pentabromotoluene	82.12	82.10	−0.02	99.98	82.30	+0.18	100.22
		81.88	−0.24	99.71	82.26	+0.14	100.17
Tetrabromo-*o*-xylene	75.81	75.70	−0.11	99.85	75.82	−0.01	100.01
		75.60	−0.21	99.72	75.78	−0.03	99.96

It is worth mentioning that the nature of the sample is a very important factor. It was found that some of the highly halogenated compounds *e.g.* α,α-heptachlorotoluene (m.p. 118°, sublimable), and even some of those containing one halogen atom (*e.g.* *p*-chloroaniline (m.p. 70°), *p*-bromoaniline (m.p. 66°), *p*-bromophenol (m.p. 63°)), gave invariably low figures. This was ascribed to the fact that such compounds are either sublimable or low-melting; sublimation or volatilization of undecomposed material may take place as the temperature increases in the flask during combustion. This difficulty was overcome by repeated folding of the filter paper holding the sample in all directions so that several layers surrounded the sample (Table III). This may explain the low results obtained by MÁZOR *et al.*[5], apparently

TABLE III

MICRODETERMINATION OF CHLORINE AND BROMINE IN LOW-MELTING AND SUBLIMABLE HALOGENATED COMPOUNDS (OXYGEN-FLASK METHOD WITH ALKALINE HYDROGEN PEROXIDE AS ABSORBENT)

Sample	*Melting point (°)*	*% Halogen*		*% Error*	*% Recovery*
		Theoretical	*Found*		
α,α-Heptachlorotoluene	118	74.49	74.32	−0.17	99.77
	sub.		74.20	−0.29	99.61
p-Chloroaniline	70	27.79	27.69	−0.10	99.64
			27.80	+0.01	100.04
p-Bromoaniline	66	46.46	46.26	−0.20	99.57
			46.38	−0.08	99.83
p-Bromophenol	63	46.22	46.00	−0.22	99.52
			45.84	−0.38	99.18

using the ordinary wrapping technique, for a group of low-melting and/or sublimable compounds; the authors[5] attributed the error to incomplete combustion and incomplete absorption rather than to the volatility of these compounds.

Highly halogenated aliphatic compounds. Most of the highly chlorinated aliphatic compounds give phosgene[10] together with other chlorinated fragments on pyrolysis or on decomposition at high temperatures in the presence of oxygen or air. However, the obvious attraction of the oxygen flask led us to try it first.

Neither the hydrogen peroxide nor the sodium nitrite procedure was satisfactory, the results being as low as 10% with some compounds (*e.g.* perchloroethane). Increasing the weight ratio of filter paper to sample to about 50 gave little improvement. Attempts to mineralize the halogen, using the oxygen-flask combustion, by mixing the sample with magnesium oxide, barium nitrate and sodium peroxide slightly improved the results. However, the recoveries were still low by about 6%. Mixing the sample with organic substances rich in hydrogen, *e.g.* glucose or benzoic acid, was finally tried. The results obtained following this modification (Table IV) were in good agreement with the theoretical values.

TABLE IV

MICRODETERMINATION OF CHLORINE IN HIGHLY CHLORINATED ALIPHATIC COMPOUNDS (OXYGEN-FLASK METHOD WITH POTASSIUM HYDROXIDE AS ABSORBENT)

	% Halogen		*% Error*	*% Recovery*
	Theoretical	*Found*		
Perchloroethane	89.86	89.88	+0.02	100.02
		89.66	−0.20	99.78
Monochloroacetic acid	37.52	37.55	+0.03	100.08
		37.42	−0.10	99.73
Chloral hydrate	64.30	64.20	−0.10	99.84
		64.00	−0.30	99.53
Trichloroacetic acid	65.09	64.80	−0.29	99.55
		64.82	−0.27	99.59

Highly halogenated liquids. Highly halogenated liquids are characterised by both high vapour pressure and good dissolving power. These two properties render the methods[11] known for halogen determination difficult and unreliable. Glass capillaries are not suitable, since some of the sample is incompletely burnt[12]. Gelatine capsules sometimes leave a dark sticky pearl and, in addition, they soften easily when wetted with such liquids. Capsules made from a strip of sellotape lined with filter paper similar to that suggested by CORNER[12], were found to be resistant to the dissolving properties of such liquids but vaporization by diffusion was still a problem. To decrease the surface area of the sample, it was absorbed in a small pretreated linen thread (3 cm) and placed inside the capsule (shaped in a bag form) containing a small piece of cotton wool. After sealing, weighing and combustion, the halogen determination was carried out as usual.

TABLE V

MICRODETERMINATION OF HALOGEN IN HIGHLY HALOGENATED LIQUID COMPOUNDS BY THE OXYGEN-FLASK METHOD USING ALKALINE HYDROGEN PEROXIDE AS ABSORBENT

Sample	*Boiling point (°)*	*% Halogen*		*% Error*
		Theoretical	*Found*	
Perchloroethylene	121	85.53	85.46	−0.07
			85.72	+0.19
Acetylenetetrachloride	148	84.51	84.26	−0.25
			84.32	−0.19
Trichloroethylene	88	80.97	80.50	−0.47
			80.60	−0.37
Acetylenetetrabromide	152/45 mm	92.47	92.36	−0.11
			92.28	−0.19
Dibromoethylene	113	85.99	85.64	−0.35
			85.68	−0.31

The proposed sellotape bag has the following advantages: (*i*) low and constant blank, (*ii*) impermeability to both liquid and vapour; (*iii*) good combustion characteristics. The results obtained for some highly halogenated liquids (Table V) showed that the method was reliable, the mean error being ±0.24%.

EXPERIMENTAL

Reagents

Unless otherwise specified, all reagents were of analytical-reagent grade.

Magnesium fusion procedure

In a previously steamed, dried, and thin-walled pyrex vial (7.5 × 2 cm) introduce 3–8 mg of the finely powdered sample followed by about 0.1–0.2 g of halogen-free magnesium powder (Carlo-Erba, Milano). Carefully flush the vial with carbon dioxide and flame-seal it; mix the contents thoroughly by shaking and then place the vial in an electrically-controlled furnace at 580–600° for 2 h. Cool the vial, clean it with ethanol and water and then open. Reflux the contents with 20–30 ml of 0.05 *N* nitric acid solution for 30 min, cool and filter into a 50-ml measuring flask, and dilute the contents to the mark with distilled water. Transfer 15 ml of this solution to a conical flask, and add absolute ethanol (80 ml) and 15 drops of diphenylcarbazone solution (alcoholic 0.5%). Titrate with mercury(II) nitrate solution[11] (0.02 *N* for chlorine and 0.01 *N* for bromine). Carry out a blank determination.

Oxygen flask for aromatic compounds

Hydrogen peroxide procedure. Place 9 ml of 10% (v/v) hydrogen peroxide in a 250-ml glass-stoppered flask followed by 1 ml of 0.5 *M* potassium hydroxide solution. Carefully wrap the weighed sample in L-shaped filter paper (3.5 cm × 3 cm), then fold several times in all directions to a small rectangular form, and clamp inside the usual platinum gauze holder. Fill the flask with pure oxygen and insert the stopper with the sample-holder after lighting the fuse as usual. When combustion is complete, shake the flask for 5 min and then let the flask stand for 2–3 min. Remove the stopper, and rinse the walls of the flask and the platinum gauze with 3–4 ml of water. Boil for 3 min to expel the excess of peroxide, cool and add 80 ml of absolute ethanol. Adjust the pH by adding 3 drops of bromophenol blue indicator (alcoholic 0.1% solution) followed by 0.05 *M* nitric acid dropwise till the yellow colour of the indicator is restored. Titrate the halide ion mercurimetrically as above.

Sodium nitrite procedure. Place 9 ml of 0.1 *M* sodium nitrite solution in the flask, which is then filled with oxygen. Prepare the sample in its holder as described above and just before starting the combustion, add 1 ml of 5 *M* nitric acid solution to the flask. After combustion, shake for 5 min, and leave the flask for 2–3 min. Remove the stopper, add 1 ml of 30% hydrogen peroxide, warm gently at 60–70° for 3 min and then cool. Adjust the pH to about 3.5 using bromophenol blue indicator and 2 *M* potassium hydroxide. Carry out the mercurimetric titration as usual.

Oxygen flask for aliphatic compounds.

Place the weighed sample in the L-shaped filter paper, and mix it with 20–30 mg of glucose. Use a 500-ml conical flask, with 2 ml of 0.2 *M* potassium hydroxide solution as absorbent (for chlorinated compounds only), and then insert the stopper holding the sample. After combustion, shake the flask for 7 min, leave it for another 3 min, adjust the pH value as before and titrate the chloride ion produced as usual. Highly brominated aliphatic compounds were not available during this work.

Oxygen flask for liquids.

Weigh a sellotape bag, prepared from a strip (4 cm × 3 cm) lined with a small L-shaped filter paper (2 cm × 1 cm) on the glued side, containing about 20 mg of cotton wool and a linen thread about 3 cm in length. Absorb 3–8 mg of the liquid in the thread by holding one end with a platinum-tipped forceps and the other end in the sample. Introduce the thread in the bag, close tightly and then weigh. Carry out the combustion, absorption and titration as in the *Hydrogen peroxide procedure.*

SUMMARY

The microdetermination of chlorine or bromine in highly halogenated compounds is described. The oxygen flask is used for aromatic, aliphatic and liquid samples with high halogen contents. A microfusion method for some of these compounds is also discussed. As many compounds as possible covering different structures were analysed. Satisfactory results were obtained.

RÉSUMÉ

On décrit un microdosage de chlore ou de brome dans des composés fortement halogénés. On utilise un cylindre d'oxygène pour les échantillons aromatiques, aliphatiques et liquides avec teneur élevée en halogène. On examine également une microméthode par fusion. Les résultats obtenus sont satisfaisants.

ZUSAMMENFASSUNG

Die Mikrobestimmung von Chlor oder Brom in hochhalogenierten organischen Verbindungen wird beschrieben. Aromatische, aliphatische und flüssige Proben werden im Sauerstoff verbrannt. Eine Mikroschmelzmethode für einige dieser Verbindungen wird ebenfalls diskutiert. Es wurden möglichst viele Verbindungen mit verschiedenen Strukturen analysiert. Die Ergebnisse sind befriedigend.

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THE SPECTROPHOTOMETRIC AND TITRIMETRIC DETERMINATION OF GOLD WITH FERROIN AS REAGENT

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(Received March 20th, 1966)

Ferroin is very well known as a redox indicator and as a colorimetric reagent but its applications as a precipitant have been less widely studied. FEIGL AND MIRANDA[1] used the reagent for the detection of cadmium and studied the precipitation of some metal complex anions, including $[AuCl_4]^-$ and $[AuBr_4]^-$. BOBTELSKY AND COHEN[2] studied complexes of gold with 1,10-phenanthroline. HALL AND SMITH[3] determined mercury gravimetrically with ferroin after addition of bromide.

In the course of investigations in this laboratory, it was observed that tetrachloro- and tetrabromoaurate ions formed complexes with ferroin which could be extracted into chloroform and could be used for the spectrophotometric determination of small amounts of gold. It was further found that the reagent could be used for the titrimetric determination of gold, by means of a new technique based on the extraction of the ion-association complex ferroin $[AuBr_4]_2$. In the photometric titration method, 2 moles of the tetrahalogeno-aurate ion react with 1 mole of ferroin, *e.g.*,

$$2\,[AuBr_4]^- + [Fe(1,10\text{-phen})_3]^{2+} \rightarrow [Fe(1,10\text{-phen})_3]\,[AuBr_4]_2$$

EXPERIMENTAL

Apparatus

All spectral measurements were made with Hilger "Uvispek", using 1.00-cm silica cells. An EEL Photometric Titrator was used for all titrations, which were carried out in cells of 40 ml capacity, supplied with the titrator.

Reagents

Standard gold solution. A 0.005 *M* solution of gold was prepared by dissolving the appropriate weight of pure gold (24 carat) in a few ml of aqua regia, evaporating to incipient dryness on a water bath, adding 1 ml of concentrated hydrochloric acid, evaporating almost to dryness and making the volume up with 1 *M* hydrochloric acid. From this solution a 0.00050 *M* solution was freshly prepared by dilution with distilled water.

Standard ferroin solution. A 0.0025 *M* solution was prepared from commercial reagent, 0.025 *M* 1,10-phenanthroline ferrous complex, supplied by Hopkins & Williams, Ltd., by diluting with distilled water. This solution was standardised with

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* Present address: Abu Zaabal Co. for Military and Civil Chemicals, Abu Zaabal, Cairo (U.A.R.).

standard 0.05 *N* cerium(IV) sulphate solution[4]. A 0.00025 *M* solution was prepared by further dilution.

AnalaR-grade potassium bromide was used throughout the work.

The spectrophotometric determination of gold

Procedure. Transfer the gold sample solution to a separating funnel. Add 3 ml of 0.1 *M* potassium bromide solution and 2 ml of 0.0025 *M* ferroin solution and dilute to 20 ml with water. Adjust the pH to 1–3 with 30% sodium acetate solution.

Extract with three 3-ml portions of chloroform and transfer each extract to a dry 10-ml volumetric flask. Make up to the mark with chloroform, and measure the optical density at 510 mμ against a blank treated in the same way.

A calibration curve was prepared using the above procedure. Beer's law was found to be obeyed over the range 20–200 μg per 10 ml. The spectrum of $[Fe(1,10\text{-phen})_3][AuBr_4]_2$ in chloroform is shown in Fig. 1.

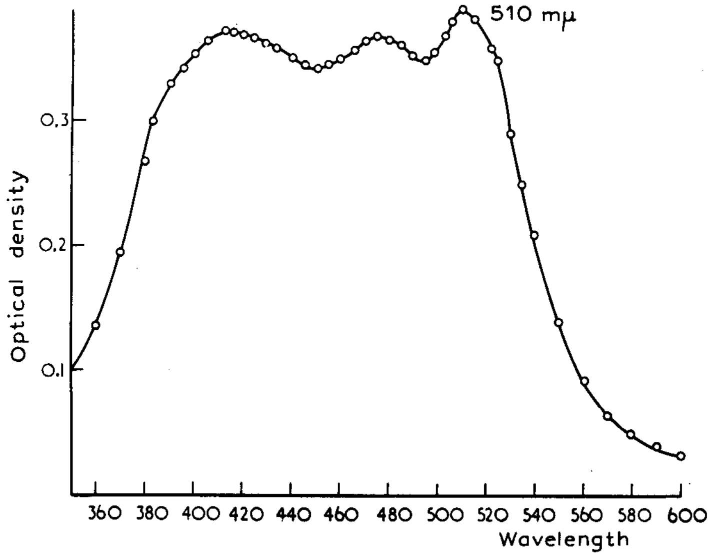


Fig. 1. Spectrum of $[Fe(1,10\text{-phen})_3][AuBr_4]_2$ in chloroform.

Effect of diverse ions. The influence of diverse ions on the spectrophotometric determination of gold is shown in Table I.

From the results it can be seen that Pt^{4+}, Pd^{2+}, Hg^{2+}, Ir^{4+} and Os^{4+} do not interfere up to a ratio of 1:1; Ru^{4+} does not interfere up to a ratio of 1:2; Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+} and Cr^{3+} do not interfere. The results are reproducible with an average error of ±1%.

The photometric titration of gold using a two-phase system

Procedure. Transfer a measured volume (0.5–1.5 ml) of gold solution (0.00050 *M*) to a titration cell. The titration cell must be clean otherwise droplets of water adhere to the walls of the cell in the chloroform layer, resulting in inaccurate measurement of the optical density. Add 1 ml of 0.1 *M* potassium bromide and dilute to 10 ml

TABLE I

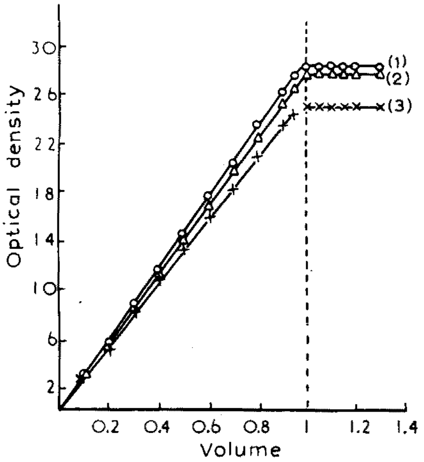
INFLUENCE OF DIVERSE IONS ON THE SPECTROPHOTOMETRIC METHOD

Diverse ion		*Gold (µg)*		*% Error*
(mg)		*Taken*	*Found*	
Co^{2+}	10	50	50.3	+0.60
	20	100	100.8	+0.80
	10	100	101	+1.0
Cu^{2+}	10	50	49.4	−1.2
	20	50	49.6	−0.80
	40	50	50.3	+0.60
Ni^{2+}	10	50	50	0.0
	40	50	50.1	+0.2
Fe^{3+}	10	50	50	0.0
	20	100	100	0.0
	50	100	99.7	−0.30
Zn^{2+}	10	50	50.20	+0.40
	10	50	50.10	+0.20
Mn^{2+}	20	50	50.40	+0.80
	20	50	50.50	+1.0
Cr^{3+}	20	50	49.6	−0.80
	20	50	50.3	+0.60
Rh^{3+}	0.1	50	49.7	−0.60
	0.2	50	49.5	−1.00
Pt^{4+}	0.02	50	50.2	+0.40
	0.05	50	49.6	−0.80
	0.2	50	46.0	−8.0
	0.2	50	45.5	−9.0
Pd^{2+}	0.02	50	50.10	+0.2
	0.05	50	49.70	−0.6
	0.2	50	45.0	−10.0
	0.2	50	44.5	−11.0
Ir^{4+}	0.05	100	100.50	+0.50
	0.1	100	99.30	−0.70
	0.2	100	97.50	−2.5
Ru^{4+}	0.05	50	50.2	+0.4
	0.1	50	49.9	−0.2
	0.2	100	99.2	−0.8
	0.3	100	98	−2
Os^{4+}	0.05	50	49.4	−1.2
	0.10	100	99.6	−0.4
	0.20	100	97.0	−3.0
Hg^{2+}	0.05	100	100.6	+0.6
	0.10	100	99.1	−0.9
	0.20	100	96.2	−3.8

with 0.05 *M* hydrochloric acid. If necessary, adjust the pH to 1–3 by means of a 30% solution of sodium acetate. Finally, add 15 ml of chloroform. Place the cell in the titrator and stir vigorously for 2 min. Stop the stirring, and allow the two phases to separate for 3–4 min, when the chloroform layer will become clear. Read the optical density using a green filter (No. 604) or adjust the galvanometer to zero optical density. Titrate with 0.00025 *M* ferroin solution from a 2-ml microburette, adding the

titrant in 0.1-ml portions at the beginning and in smaller portions near the end-point. Stir vigorously for 2 min after each addition and allow to stand for 3–4 min before reading the optical density. Plot a curve showing the relationship between volume of titrant and optical density (see Fig. 2).

2



3

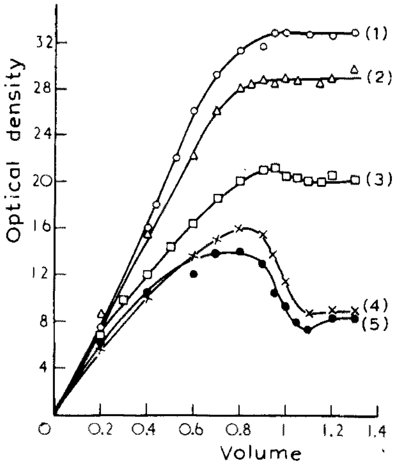


Fig. 2. 1 ml gold solution (0.0005 *M*) + 1 ml KBr (0.1 *M*) diluted with: (1) 10 ml water, pH 2; (2) 10 ml of 0.05 *M* HCl, pH 1; (3) 10 ml water, pH adjusted to 3 with sodium acetate.

Fig. 3. 1 ml gold solution (0.0005 *M*) diluted with: (1) 10 ml of water; (2) 0.1 *M* HCl; (3) 0.2 *M* HCl; (4) 0.5 *M* HCl; (5) 1 *M* HCl.

Standardisation of ferroin. Transfer 10 ml of 0.0025 *M* ferroin solution to a titration cell and dilute with 30 ml of 1 *M* sulphuric acid. Use a blue filter (No. 602). Titrate quickly with standard 0.05 *N* cerium(IV) sulphate solution. The solution becomes slightly turbid and the optical density increases a little during the titration. The end-point is determined by a sharp fall in the optical density to zero, when the solution becomes clear and blue in colour.

The effect of diverse ions. To examine the effect of diverse ions on the titrimetric determination of gold, varying amounts of different ions were added to the gold sample contained in the titration cell. The results of replicate analyses are shown in Table II.

It will be seen from the results that Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Zn^{2+}, Cr^{3+} and Mn^{2+} do not interfere in the determination of gold. However, Ru^{4+} forms a soluble complex which is not extractable into chloroform but consumes the reagent and so interferes. The other platinum metals, Pt^{4+}, Pd^{2+}, Ir^{4+}, Os^{4+}, but not Rh^{3+}, as well as Hg^{2+} and ClO_4^- interfere by forming non-extractable precipitates and consuming the reagent, while iodide and thiocyanate form extractable compounds, but interfere.

The method is particularly suitable for the determination of small quantities of gold (50–250 μg). It is accurate to within ±1%.

Notes

(1) Tetrachloro- and tetrabromo-aurate ions form complexes with ferroin which

TABLE II

INFLUENCE OF DIVERSE IONS ON THE TITRIMETRIC METHOD

Diverse ion (mg)		*Gold (μg)*		*Difference*	*% Error*
		Present	*Found*		
Ni^{2+}	20	80	80.30	+0.30	+0.4
	10	80	80.70	+0.70	+0.9
	30	120	119.40	−0.60	−0.5
	10	120	120.20	+0.20	+0.17
Cu^{2+}	30	100	100.40	+0.40	+0.4
	10	100	100.60	+0.60	+0.6
	40	100	100	0.0	0.0
	20	150	150.40	+0.40	+0.27
	20	150	150.70	+0.70	+0.47
	10	150	149.40	−0.60	−0.40
Co^{2+}	30	100	99.8	−0.20	−0.20
	10	100	99.6	−0.40	−0.40
	10	80	80.3	+0.30	+0.40
Fe^{3+}	10	100	101	+1.00	+1.0
	30	100	100.5	+0.50	+0.5
	50	100	99.6	−0.40	−0.40
Zn^{2+}	10	100	100.6	+0.60	+0.60
	20	100	100	0.0	0.0
Cr^{3+}	20	150	150.6	+0.60	+0.40
	10	100	100.3	+0.30	+0.30
Mn^{2+}	10	100	100.5	+0.50	+0.50
	20	100	99.8	−0.20	−0.20

can be extracted into chloroform, but not into toluene, benzene or carbon tetrachloride.

(2) The tetrachloro-complex is not stable in chloroform, the titration curve is rounded near the end-point and results are not reproducible (Fig. 3). The colour in the chloroform layer fades completely after 3 h, even when excess ferroin is present in the aqueous layer. High concentrations of acid accelerate the decolorisation.

(3) The tetrabromoaurate complex is more stable, the colour persisting for at least 12 h, and the end-point is both sharp and reproducible. Best results were obtained in the pH range 1–3.

(4) The two-phase technique possesses several general advantages. No volume correction is required; the sensitivity can be increased by extracting the product of the reaction into a smaller volume of the organic phase, and intensely coloured titrants can be used, if they are not extracted into this phase.

SUMMARY

A spectrophotometric and a photometric titration method in a two-phase system for the determination of gold with ferroin is reported. Both methods are rapid and reproducible with an accuracy of ±1%. In the spectrophotometric determination Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+} and Cr^{3+} do not interfere with the determination of gold and Pt^{4+}, Pd^{2+}, Hg^{2+}, Ir^{4+} and Os^{4+} can be tolerated up to a ratio of 1:1. The titrations can also be carried out in the presence of a number of diverse ions, *e.g.*

Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Zn^{2+}, Cr^{3+}, Mn^{2+}, without interference; the platinum metals and Hg^{2+} cause interference but, by the use of the spectrophotometric procedure, this can be reduced.

RÉSUMÉ

On décrit une méthode de titrage spectrophotométrique et photométrique, en système à deux phases pour le dosage de l'or au moyen de ferroïne. Les deux procédés sont rapides et reproductibles, avec une exactitude de ±1%. Lors du dosage spectrophotométrique, Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+} et Cr^{3+} ne gênent pas l'analyse de l'or; Pt^{4+}, Pd, Hg^{2+}, Ir^{4+} et Os^{4+} peuvent être tolérés jusqu'à un rapport 1:1. Les titrages peuvent également être effectués en présence d'un certain nombre d'ions, tels que Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Zn^{2+}, Cr^{3+}, Mn^{2+} sans interférence. Les métaux du platine et le mercure(II) gênent, mais en utilisant le procédé spectrophotométrique, on peut diminuer leur interférence.

ZUSAMMENFASSUNG

Es wird über eine spektralphotometrische Methode und eine photometrische Titration zur Bestimmung von Gold mit Ferroin in einem 2-Phasensystem berichtet. Beide Methoden arbeiten schnell und reproduzierbar mit einer Genauigkeit von ±1%. Die spektralphotometrische Bestimmung von Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+} und Cr^{3+} stört bei der Bestimmung von Gold nicht; Pt^{4+}, Pd^{2+}, Hg^{2+}, Ir^{4+} und Os^{4+} können bis zu einem Verhältnis von 1:1 toleriert werden. Die Titrationen können auch in Gegenwart einer Anzahl von Ionen z.B. Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Zn^{2+}, Cr^{3+}, Mn^{2+} ohne Störungen ausgeführt werden. Die Platinmetalle und Hg^{2+} verursachen Störungen, jedoch können diese durch die Verwendung des spektralphotometrischen Verfahrens verringert werden.

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A PHOSPHORIMETRIC INVESTIGATION OF SEVERAL SULFONAMIDE DRUGS: A RAPID DIRECT PROCEDURE FOR THE DETERMINATION OF DRUG LEVELS IN POOLED HUMAN SERUM WITH SPECIFIC APPLICATION TO SULFADIAZINE, SULFAMETHAZINE, SULFAMERAZINE AND SULFACETAMIDE

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Sulfonamides are amides of sulfanilic acid. Sulfanilamide is the parent compound of the derivatives of sulfanilic acid. The sulfonamides were among the early chemotherapeutic agents and are still of considerable importance as bacteriostatic agents. Previous methods of determination have been based on the presence of the primary amine group present in all of the sulfonamides. The widely used method of BRATTON AND MARSHALL[1] for the determination of free sulfonamides includes diazotizing the sulfa drug and coupling it with N-(1-naphthyl)-ethylenediamine dihydrochloride to form the colored azo dye, which is measured spectrophotometrically. On the other hand, the method described in this manuscript involves only the extraction of the drug into a solvent which will form a clear rigid glass at 77°K and phosphorimetric measurement using an instrument which can accurately measure the intensity of emitted radiation when the sample is excited with ultraviolet radiation at the exciting wavelength of the compound of interest.

Since its first suggested use as a means of chemical analysis by KEIRS, BRITT AND WENTWORTH[2], phosphorimetry has been applied successfully in a number of areas and shown to be a powerful method when coupled with proper separation methods. WINEFORDNER AND LATZ first introduced phosphorimetry as a sensitive, selective method of analysis for trace amounts of drugs in blood serum and plasma[3,4]. Since their work, phosphorimetry has been used for trace analysis of drugs and metabolites of pesticide residues in blood and urine[5,6]. In all of these studies the compound of interest was either extracted from the biological fluid with a volatile solvent, the solvent evaporated and the compound redissolved in a second solvent which formed a clear rigid glass at liquid nitrogen temperatures; or the compound was extracted by a component solvent of a solvent mixture which will form a clear rigid glass at liquid nitrogen temperatures. In both cases, the extraction step increases the possibility for contamination and error. Ideally, it would be preferable to use the extracting solvent to form a rigid glass at 77°K. Generally, extracting solvents are poor for phosphorimetric measurements because they often form snows, or crack at liquid nitrogen temperatures. In addition, solvents, which may form a rigid glass at 77°K, may tend to crack or form snows when a small quantity of water is dissolved in them. In a preliminary study of possible phosphorimetric solvents, WINEFORDNER AND ST. JOHN[7] found that absolute ethanol was satisfactory and that its water content was not highly critical. WINEFORDNER AND TIN[5] performed an extensive study of drug analysis using absolute ethanol as the solvent for phosphorimetric measurement. It was later shown by HOLLIFIELD AND WINEFORDNER[8] that ethanol could be used as either an acidic, basic or neutral solvent for phosphorimetric studies.

In this paper, it has been found that absolute alcohol has other qualities which make it a very favorable solvent for phosphorimetry. In addition to the considerable solubility of most drugs in ethanol, the relative ease of preparing it in phosphorimetric grade, its ease of attainability and low cost, it has been found that ethanol will generally freeze to a clear rigid glass at 77°K with a water content as high as 5%. Of course, the frequency of cracking of the ethanol–water solutions increases with an increase in the amount of water present. However, cracking becomes troublesome only above 5% water concentration although ethanolic solutions with a water content as high as 8% will generally freeze to a clear rigid glass.

Moreover, absolute ethanol competes vigorously for any available water, and hence protein in specimens introduced directly into absolute ethanol tend to precipitate. Taking advantage of these solvent characteristics, a simple, rapid direct method involving no separation steps for drug analysis in pooled human serum is presented to demonstrate the usefulness and scope of phosphorimetry.

In this paper, the spectral peaks (uncorrected for instrumental response) of the emission and excitation spectra of a number of sulfonamides in rigid ethanol at 77°K are given. In addition, the phosphorescence decay times and approximate limits of detection are given for the same compounds. The sulfonamides have been studied primarily to illustrate the great sensitivity of phosphorimetry as a method of analysis. The determination of sulfadiazine, sulfamethazine, sulfamerazine and sulfacetamide in pooled human serum by the method used here is to be interpreted as the total drug level in serum (both free and acetylated forms) because acetylation of the primary amine group does not decrease the intensity of phosphorescence emission for a particular compound. These determinations are also without regard to drug absorption by the blood cells; however, with proper modification the drug concentration of whole blood samples should also be possible without any additional difficulty.

EXPERIMENTAL

Apparatus

All phosphorimetric measurements were made with the Aminco-Bowman spectrofluorimeter (No. 4-8202, American Instrument Co., Silver Spring, Md.) equipped with an Aminco-Kiers phosphoroscope attachment (Cat. No. C27-62140), a potted RCA 1P28 photomultiplier tube, and an X-Y recorder (No. 1620-814, manufactured for American Instrument Co. by Electro Instruments, Inc., San Diego, Calif.). The source was a high-pressure xenon arc powered by the solid state high voltage power supply provided with the instrument. Relative phosphorescence intensities were obtained directly from the Aminco photomultiplier–microphotometer supplied with the spectrofluorimeter by multiplying the meter reading (in % T) by the coarse meter multiplier. All studies were performed at constant slit width (slit arrangement no. 4)[9].

Reagents

Ethanol was used as the solvent for all studies. Absolute ethanol was distilled through a 6-ft. vacuum-jacketed and silvered column with a reflux ratio of 15:1. The column was packed with 3/8″ coil helices. Only the center fraction of the distillate was saved and this was checked for acceptable phosphorimetric background.

Standard stock solutions were prepared as described below. The following sulfonamides (Nutritional Biochemicals Corporation, Cleveland, Ohio) were prepared with 50 mg of the compound per 50 ml of phosphorimetrically pure ethanol: azosulfamide, phthalylsulfacetamide, phthalylsulfathiazole, sodium sulfathiazole, succinyl sulfathiazole, sulfabenzamide, sulfacetamide, sulfadiazine, sulfaguanidine, sulfamerazine, sulfamethazine, sulfanilamide, sulfapyridine, and sulfathiazole. Of the above, sulfadiazine required acidic ethanol to achieve the desired concentration of 1 mg/ml solution. Solutions used for determining spectra and analytical curves were prepared by serial dilution (1:10) of the stock solutions with phosphorimetrically pure ethanol to a final concentration of 10^{-8} mg/ml.

Versatol (General Diagnostics Div., Warner-Chilcott Div., Morris Plains, N.J.) was used as the pooled human serum.

Procedure

Recording spectra. Excitation and emission curves were recorded for all compounds according to instructions given in the manufacturer's operating manual[9]. The drug dilution chosen for recording the spectra was the lowest dilution of the compound intense enough to still give sharply defined peaks. Decay times were recorded on the same solutions used for the spectral recordings. The limit of detection was taken as that drug concentration which resulted in a signal twice the root-mean-square fluctuation in the background (blank–ethanolic solution with no drugs) readings (the fluctuation was due partially to noise but mainly due to variability in the background reading during a series of blank measurements).

Calibration of instrument. Prior to measuring relative intensities of phosphorescence, for any of the compounds of interest, a standard solution of 0.2 mg of toluene in 100 ml of ethanol was prepared. This solution was used to calibrate the photomultiplier photometer daily to correct for instrumental variations and to assure the use of the same standard working curves over an extended period of time. The instrument was calibrated using the toluene solution at 77°K by adjusting the fine sensitivity knob to such a position that under constant conditions of slit width, sample tube, sample concentration, excitation and emission wavelengths, and shutter speed, the same relative intensity was obtained each time the instrument was used.

Obtaining working curves. Working curves were obtained for sulfadiazine, sulfamerazine, sulfamethazine and sulfacetamide by plotting relative phosphorescence intensity *vs.* drug concentration in ethanol over a range of 10^{-4} μg/ml up to 100 μg/ml. All measurements were made at the excitation peak wavelength and emission peak wavelength for the compound of interest. In every case, the background phosphorescence due to the ethanol was subtracted from the phosphorescence intensity due to the drug–ethanol solution. For all but the very lowest concentrations of the drugs, the background due to the ethanol was insignificant.

Preparation of the 'unknown' samples for phosphorimetric measurement. Two methods were used to prepare samples of serum with a known concentration of the drug and recoveries from both types of samples were equally good.

In the first method a standard solution of the drug in saline was prepared. One ml of the stock drug in saline solution was added to the serum just before the serum was deproteinized to give effective serum concentrations of 0.1, 1.0 and 10 mg of drug/100 ml of serum. This resulted in a considerable dilution of the serum and consequently required dilution of the serum blank (the blank consisting of serum with no drug present). The diluted blank and "unknown" samples were then deproteinized by adding 1 ml each of blank and serum "unknown" to 9 ml of ethanol. The resulting mixture was shaken for 3 min, poured into acid-washed centrifuge tubes and spun down for 4 min. One ml of the resulting supernate was then added to 9 ml of ethanol, mixed and the phosphorescence intensity of the sample measured. For concentrations of the order of 0.1 mg/100 ml of serum, better recoveries were obtained when 1 ml of the supernate was added to only 1 ml of ethanol giving a dilution of 1:20 instead of the 1:100 dilution for higher concentration.

The second method of sample preparation varied only in that 1 ml of standard drug solution was added directly to 8 ml of ethanol, and the serum was then added directly to this solution to give effective serum concentrations of 0.1 mg/100 ml, 1.0 mg/100 ml and 10.0 mg/100 ml. The resulting mixture was treated as in the first method. Of course, the blank now required no dilution.

Measurement of phosphorescence due to drugs. The phosphorescence intensity was measured for the blank (versatol with no drugs) at dilutions of 1:20 and 1:100. The photometer signal due to the phosphorescence intensity of the "unknown" samples of concentrations greater than 0.1 mg/100 ml of serum was measured at the dilution of 1:100. The photometer signal due to the phosphorescence intensity of the 0.1 mg/100 ml "unknown" was measured at 1:20 dilution in ethanol. The photometer signals due to the phosphorescence intensity of the blank at the corresponding dilutions were subtracted from those of the "unknown" samples yielding corrected values of relative phosphorescence signals due to the presence of the drug alone. The concentrations (in mg/ml) of drug present in the diluted sample were taken from the working curve, and multiplied by the dilution factor of the sample (100 if greater than 0.1 mg/100 ml serum, 20 if 0.1 mg/100 ml serum) to give the actual concentration of drug present in the serum "unknown".

Versatol was used for all for background determinations because the background produced by a number of Versatol samples never varied more than 5%. The origin of the phosphorescence background due to serum has been discussed in detail by WINEFORDNER AND LATZ[3]. The phosphorescence background of serum has been shown to be due to protein or constituents derived from protein. The background can thus be easily corrected for by the above procedure.

RESULTS AND DISCUSSION

In Table I the wavelengths for the phosphorescence excitation and emission peaks (uncorrected for instrumental characteristics) when using the experimental setup and conditions described above are given[4]. No spectra are given here because they would be characteristic of the instrumentation used[4]. Although several methods of correcting spectra for experimental factors are available[10,11], it is felt that corrected

TABLE I

PHOSPHORESCENCE PARAMETERS OF SEVERAL SULFONAMIDES: WAVELENGTHS OF EMISSION AND EXCITATION PEAKS[a,b], DECAY TIMES AND LIMITS OF DETECTION

Sulfonamide	*Excitation λ (mμ)*	*Emission λ (mμ)*	*Decay time (sec)*	*Limit of detection (μg/ml)*
Azosulfamide	290	440	0.9	Very weak[c]
Phthalylsulfacetamide	290	415	0.6	0.001
Phthalylsulfathiazole	305	405	0.9	1.0
Sodium sulfathiazole	270, 315 (m)	410	1.4	1.0
Succinyl sulfathiazole	310	420	1.3	Very weak[c]
Sulfabenzamide	305	405	0.7	0.001
Sulfacetamide	280	410	1.3	0.0001
Sulfadiazine	275	410	0.7	0.001
Sulfaguanidine	305	405	0.7	0.01
Sulfamerazine	280	405	0.7	0.0001
Sulfamethazine	280	410	0.8	0.0001
Sulfanilamide	270 (m), 300	405	1.3	0.001
Sulfapyridine	310	425, 440 (m)	1.4	0.0001
Sulfathiazole	310	420	0.9	1.0
Diacetylsulfanilamide	280	405	1.3	0.001

[a] All wavelengths are uncorrected for instrumental characteristics.
[b] (m) indicates the most intense peak.
[c] Phosphorescence is not analytically useful.

spectral peaks would not yield any more useful data than those listed in the Table. In any analysis, the analyst must select the optimum wavelengths of excitation and emission for his own instrumental setup for the compounds of interest. However, for an experimental setup and conditions similar to those above, the optimum wavelengths should not vary a great deal from those given in Table I. The phosphorescence decay times and limits of detection are also given in Table I.

In Table II, the results for the analysis of sulfacetamide, sulfadiazine, sulfamerizine, and sulfamethazine in serum are given. Each result reported is the average

TABLE II

RECOVERIES OF SULFONAMIDES FROM POOLED HUMAN SERUM[a]

Sulfonamide	*Amount added (mg/100 ml serum)*	*Amount found (mg/100 ml serum)*	*Recovery (%)*
Sulfacetamide	10.0	9.7	97
	1.0	1.03	103
	0.1	0.095	95
Sulfadiazine	10.0	10.0	100
	1.0	1.05	105
	0.1	0.093	93
Sulfamerazine	10.0	9.5	95
	1.0	0.92	92
	0.1	0.095	95
Sulfamethazine	10.0	9.9	99
	1.0	1.04	104
	0.1	0.102	102

[a] Each result is the average of 6 determinations.

of 6 determinations. The relative standard deviation of each result is about 5%. The sulfacetamide and sulfamerizine analyses were performed using working curves prepared on a log–log plot over the range of interest. The analyses of sulfadiazine and sulfamethazine were performed by using a working curve over the range of interest and by comparison with standard samples containing the compound in ethanol. The standard samples were diluted and their phosphorescence intensity measured in the same manner as the "unknown" sample.

The standard samples were always chosen so that their concentration was in the same range as the effective serum concentration of the "unknown" sample. The latter method gave the most accurate results, and the best recoveries.

Dilutions and frequency of cracking at 77°K. It was observed experimentally that dilutions of 1:100 of the protein-free ethanol at concentrations of 10 mg/100 ml serum and 1 mg/100 ml serum gave relative phosphorescence signals well up on the linear portions of the analytical curves, and excellent recoveries were obtained at these concentrations and dilutions. A 1:100 dilution for a concentration of 0.1 mg/100 ml serum, in most of the above cases, resulted in relative intensities of phosphorescence down on the lower limits of the analytical curves, and the recoveries, while good by the working curve method, were only about 75% in most cases. When the standard sample method was used, better recoveries (*ca.* 90%) could be obtained using 1:100 dilutions for the 0.1 mg/100 ml serum. The working curves, however, were found to be quite satisfactory for this lower concentration when the protein-free ethanol sample was diluted 1:20 instead of 1:100. A 1:20 dilution of the 0.1 mg/100 ml serum sample resulted in a relative intensity signal well up on the linear portion of the analytical curve, and so a 1:20 dilution is recommended for concentrations of sulfonamides in the concentration range of 0.1 mg/100 ml serum. No noticeable increase in cracking frequency of the ethanol samples was noted at dilution with water at 1:100. However, at dilutions of 1:20, the frequency of cracking at 77°K increased considerably, but presented no great handicap in the analysis.

Analysis of sulfonamides in serum. It was experimentally shown that at and above 10 mg of sulfonamide/100 ml of serum, the background due to the presence of the serum became insignificant. For the drugs and concentrations studied here, it has been shown that the correction for the serum background in the diluted samples was sufficiently low to allow recoveries of 100 ±10% even when the effective concentration of the drug was as low as 0.1 mg/100 ml of serum. Recoveries below this concentration are poorer because the contribution to the total phosphorescence from the drug alone at the diluted concentration of the sample would be exceedingly small in comparison to the contribution from the serum. From Table I, it can be seen that the diacetyl derivative of sulfanilamide has essentially the same limit of detection and overlapping excitation and emission wavelengths as sulfanilamide. From this comparison and that of the relative phosphorescence signals of the two compounds at different concentrations, it is likely that any measurement of the relative intensity of phosphorescence of a mixture of these compounds would be a measure of the total intensity due to both without regard to individual concentrations. Because in the human body, sulfa drugs become acetylated to varying degrees by the liver, the above observation indicates that any measurement of a particular sulfa drug by this rapid direct method would then be a measure of the total drug level including both its free and its acetylated forms. However, it is necessary, that the above comparison be made for each individual drug. In order to determine total sulfonamide concentration by the method of BRATTON AND MARSHALL as reported by ANNINO[12] the sulfonamides must first be deacetylated by acid hydrolysis which involves heating in a boiling water bath with 4 *M* hydrochloric acid for 1 h. This step is not necessary when phosphorimetry is used as the measurement method. Other advantages which result from the phosphorimetric measurement are the following: no chemical reactions are necessary and hence no added reagents are used to develop a colored compound because phosphorescence is a physical property of the sulfonamide itself; because no reagents are added, there are no side reactions or contaminants to be considered; ethanol is a nearly ideal solvent because it performs the multiple functions of solvent, protein precipitant and freezing medium for the intensity measurement; finally, the phosphorimetric method of measurement is very sensitive and selective, gives low limits of detection for the compounds, wide ranges of linearity for working curves and consequently wide ranges of concentration over which one can measure sulfonamides.

Drug analyses by the rapid, direct method. The above method of analysis used for the determination of the sulfonamides in serum is so simple and so fast (about 10 min for complete determination using the standard sample method) that it has wide possibilities. Some of the sulfonamides have quite low limits of detection. On the other hand, the phosphorescence background of human serum is relatively high. However, the method described still yielded very good accuracy and recoveries even for sulfonamide concentrations as low as 0.1 ml/100 ml serum. This method, then, should be of some use in a number of clinical and pharmacological studies, especially because of the added utility of ethanol as a deproteinating agent. Because the method is so general, it could be useful for measuring other organic systems, where the background in many instances will be much lower than that found in human serum. Such areas of study might include biology, food, plants, and water pollution. It should be noted, however, that this method is not directly applicable if several strongly phosphorescing substances have excitation and emission wavelengths which overlap because then a suitable separation procedure would have to be used before the phosphorimetric measurement unless only a measure of the total phosphorescing species is desired.

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SUMMARY

Phosphorescence excitation and emission spectral peaks, lifetimes, and limits of detection of several sulfonamide drugs of pharmacological importance in rigid (77°K) ethanolic solution are given. A direct method for the determination of trace amounts of 4 of these drugs in serum is presented. The method should be generally applicable to many phosphorescent compounds in biological fluids.

RÉSUMÉ

Les auteurs ont effectué une étude sur la phosphorescence, les spectres d'émission et les limites de détection de plusieurs sulfamidés, d'importance pharmacologique (en solution alcoolique et 77°K). On propose une méthode directe pour le dosage de traces de ces drogues dans le sérum. Cette méthode peut s'appliquer à de nombreux composés phosphorescents dans des liquides biologiques.

ZUSAMMENFASSUNG

Phosphoreszenzanregung und spektrale Emissionspeaks, Lebenszeiten und Nachweisgrenzen mehrerer Sulfonamide von pharmakologischer Bedeutung in fester (77°K) äthanolischer Lösung werden angegeben. Eine direkte Methode für die Bestimmung von Spuren von 4 dieser Arzneimittel (Sulfadiazin, Sulfamethazin, Sulfamerazin und Sulfazetamid) in Serum wird vorgeschlagen. Die Methode sollte für viele phosphoreszierende Verbindungen in biologischen Flüssigkeiten allgemein anwendbar sein.

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DOSAGE DIRECT DE TRACES DE BORE DANS L'ACIER PAR LA METHODE FLUORIMETRIQUE A L'HYDROXY-2-METHOXY-4-CHLORO-4'-BENZOPHENONE (HMCB)

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Le microdosage du bore présente dans le domaine de la métallurgie un intérêt considérable car des traces de cet élément peuvent avoir une influence déterminante sur les propriétés mécaniques et physico-chimiques des métaux, alliages et aciers. Elles constituent, d'autre part une impureté très gênante lorsqu'elles sont contenues dans les matériaux utilisés pour la construction de réacteurs atomiques à cause de la grande section efficace que présente le bore aux neutrons thermiques.

Parmi les méthodes permettant le dosage de traces de cet élément dans les aciers figurent presque exclusivement celles qui font appel à la spectrophotométrie. Elles permettent le dosage de teneurs de l'ordre du p.p.m. Elles utilisent divers réactifs dont principalement la curcumine[1], l'acide carminique[2], la quinalizarine[3-5], la dianthrimide[6,7], l'azométhine H[8] et certains dérivés alcoylés de la thionine[9-11], plus particulièrement le bleu de méthylène[12,13].

La curcumine a été, à cause de sa sensibilité, le réactif le plus employé mais les méthodes qui l'utilisent sont laborieuses et très délicates. En effet, la formation du complexe "bore–curcumine" dépend de nombreux facteurs et les conditions de développement de la coloration sont difficiles à contrôler. Ainsi, les résultats sont peu reproductibles ce qui explique d'ailleurs le nombre élevé de variantes proposées pour cette méthode. La réaction est gênée par divers éléments, de sorte qu'une séparation préalable du bore est toujours nécessaire; celle-ci se limite généralement à la distillation du triméthylborate.

Avec les dérivés de l'anthraquinone—acide carminique, quinalizarine, dianthrimide—les réactions sont moins sensibles qu'avec la curcumine, par contre elles sont plus sélectives et reproductibles. Toutefois les conditions de travail doivent être bien établies et rigoureusement contrôlées. La cause d'erreur la plus importante vient de la concentration du milieu réactionnel en acide sulfurique car les caractéristiques spectrales des solutions colorées et singulièrement leur densité optique en dépendent. La concentration du réactif et le temps de développement de la coloration jouent également un rôle important. Les réactions ne sont généralement gênées que par la précipitation d'ions métalliques. Dans certains cas on y remédie par une simple centrifugation mais on préfère éliminer ces ions par électrolyse sur cathode de mercure, par distillation du triméthylborate ou à l'aide de résines échangeuses d'ions.

Parmi les dérivés anthraquinoniques la dianthrimide est le réactif le plus sensible. Il permet de doser 0.0005–0.02% de bore dans les aciers[6] et semble surclasser actuellement, avec les dérivés de la thionine, les autres réactifs proposés pour ce dosage.

La réaction que fournit l'azométhine H avec l'acide borique a fait l'objet d'une étude systématique; elle permet aussi le dosage du bore dans l'acier[8]. Le développement de la coloration se fait en milieu aqueux ce qui est avantageux. Toutefois la réaction est gênée par certains éléments et sa sensibilité est inférieure à celle qui utilise la dianthrimide et les dérivés de la thionine. L'élimination des éléments gênants s'effectue sur résine échangeuse d'ions.

Parmi les réactifs à base de thionine, le dérivé tétraméthylé (bleu de méthylène) semble être le plus intéressant. Il donne un complexe fortement coloré avec l'ion BF_4^-, extractible dans certains solvents organiques. Il permet de doser 0.0002 à 0.25% de bore[12] et 0.001 à 0.004%[13] de bore dans l'acier. La méthode dont le principe est la mise en solution directe de l'échantillon en milieu fluoré[13] est la plus avantageuse à cause de sa rapidité. Aucun élément entrant dans la composition des aciers étudiés ne gêne la réaction sauf le fer dont le FeF_4^- est extrait. On évite cet effet gênant en ajoutant de l'acide phosphorique à la solution.

La méthode au bleu de méthylène a le grand avantage d'être très sensible et rapide mais elle est assez délicate et fait intervenir pour la mise en solution de l'échantillon et l'extraction du complexe, plusieurs réactifs.

A notre connaissance, parmi toutes les techniques qui ont été proposées pour la détermination de traces de bore dans l'acier, seule la méthode à la dianthrimide permet un dosage direct, sans séparation ou extraction préliminaire du bore[7].

Le but du présent travail est d'appliquer la méthode fluorimétrique à l'hydroxy-2-méthoxy-4-chloro-4'-benzophénone (HMCB)[14,15] au dosage direct de traces de bore dans l'acier. En effet grâce à la sensibilité, à la fidélité et la sélectivité de ce réactif il est possible d'effectuer un dosage du bore précis, rapide, sans séparation et ne faisant intervenir qu'un nombre très limité de réactifs et d'opérations analytiques. Des travaux relatifs à l'application de cette méthode à d'autres types d'acier sont en cours.

PARTIE EXPÉRIMENTALE

Réactifs, matériel et appareillage

(*a*) Hydroxy-2-méthoxy-4-chloro-4'-benzophénone (HMCB); (*b*) acide sulfurique (d = 1.84) p.a. Merck; (*c*) solutions d'acide borique (p.a. Merck) à 2 μg/ml et 0.2 μg/ml dans H_2SO_4 conc., conservées dans des flacons en quartz; (*d*) solution d'hydroxyde de sodium (p.a. Merck) $3 \cdot 10^{-1}$ *M* conservée dans un flacon en polyéthylène; (*e*) eau bidistillée dans un appareil en quartz; (*f*) tubes à essai en quartz transparent, diamètre 14 mm, longueur 130 mm, Société Electrothermique de la Tour-de-Trême; (*g*) tubes à centrifuger, à fond pointu et en verre peu boraté (remarque 1); (*h*) spectrofluorimètre Zeiss (ZFM4C); lampe à mercure; cuves de quartz de 1 cm, étalon fluorescent Zeiss.

Application de la méthode à l'HMCB au dosage direct de traces de bore dans les aciers doux

Nous avons étudié 2 aciers B.C.S. No. 275 et 273 dont la teneur en bore est de

0.001% et 0.0025% respectivement; la composition exacte de ces aciers est donnée au Tableau I.

Une étude comparative des spectres apparents d'excitation et de fluorescence de solutions sulfuriques d'acier en absence et en présence de réactif d'une part et des solutions sulfuriques du complexe "B–HMCB" a montré que, dans les conditions de dosage, aucun élément entrant dans la composition des aciers étudiés ne gêne la réaction fluorescente "B+HMCB". D'autre part, les fluorescences parasites, présentées par les solutions sulfuriques de l'échantillon, sont négligeables. Enfin, les dilutions sont telles qu'aucune précipitation d'ion métallique ne se produit en solution sulfuri-

TABLEAU I

COMPOSITION DES ACIERS B.C.S. No. 275 ET 273 (%)

	No. 275	*No. 273*		*No. 275*	*No. 273*
C	0.16	0.14	Co	0.059	0.021
Si	0.39	0.22	Ti	0.035	0.070
S	0.010	0.019	As	—	—
P	0.020	0.012	Sn	0.040	0.065
Mn	0.50	0.49	Al	0.020	0.060
Ni	0.080	0.030	Zr	0.015	Traces
Cr	0.165	0.075	N	—	—
Mo	0.095	0.045	Pb	0.0050	0.0030
Cu	0.205	0.160	Nb	0.035	0.0003
V	0.050	0.045	Ta	0.003	0.020
W	0.05	0.28	Fe	98.1	98.3
			B	0.001	0.0025

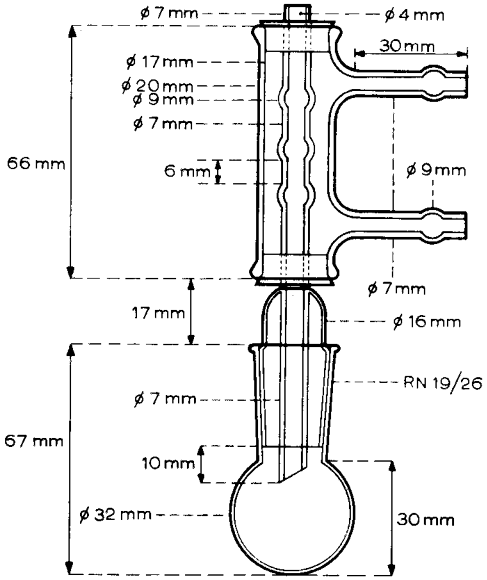

Fig. 1.

que. C'est pourquoi il est possible de développer directement la fluorescence à partir de la solution de l'échantillon, sans séparation préalable.

Mode opératoire

Mise en solution. Des prises de 10 à 20 mg d'acier sont dissoutes dans 1.5 ml d'H_2SO_4 à 25% (v/v) dans un dispositif à reflux à 50–60° (v. Fig. 1). Pour éviter toute perte en bore pendant la mise en solution, on introduit dans le réfrigérant une goutte (0.05 ml) d'une solution de soude $3 \cdot 10^{-1}$ *M* qui est maintenue par capillarité à l'intérieur de l'extrémité inférieure de celui-ci. Cette goutte monte par pression, éclate à son arrivée dans la première boule du réfrigérant et se reforme à l'extrêmité inférieure de ce dernier et ceci pendant toute l'opération de la mise en solution. Celle-ci terminée on refroidit dans un bain glace–eau, on détache avec précaution le réfrigérant, on lave l'intérieur de ce dernier par 2 fois 1 ml d'H_2SO_4 conc., puis l'intérieur du bouchon rôdé par 3 fois 1 ml et l'extérieur par 2 fois 1 ml d'H_2SO_4 conc. On transvase le contenu du ballon dans un tube à centrifugation (remarque 1), lave le ballon par 2 fois 1 ml d'H_2SO_4 conc., transvase de nouveau et on centrifuge. Après centrifugation on introduit la solution dans un ballon jaugé de 20 ml, place dans le tube à centrifuger 1.5 ml d'H_2SO_4 conc., agite avec une fine baguette en quartz pour mettre en suspension les particules insolubles et chauffe à 300° environ. On laisse refroidir, centrifuge et introduit dans le ballon de 20 ml. On traite de nouveau les particules insolubles de la même manière (1.5 ml H_2SO_4 conc. puis à 300°), centrifuge et transvase. On lave bien le tube à centrifugation par des petites portions d'H_2SO_4 conc. en prenant toutefois soin de ne pas remettre en suspension dans le liquide de lavage les particules décantées, et transvase chaque fois dans le ballon de 20 ml. On lave finalement par l'H_2SO_4 conc. le ballon qui a servi pour la mise en solution, transvase et complète au trait de jauge.

Développement de la fluorescence et mesures. Dans des tubes à essai en quartz, numérotés de 1 à 6, on introduit successivement:

Numéro de tube	1	2	3	4	5	6
ml H_2SO_4 conc.	2.8	2.8	2.7	2.6	$2.8-v$	$2.7-v$
v ml de solution sulfurique d'acier préparée	0	0	0	0	v	v
ml solution d'HMCB à 0.0105% dans H_2SO_4 conc.	0.2	0.2	0.2	0.2	0.2	0.2
ml de solution d'acide borique à 50 ng B/ml dans H_2SO_4 conc. (remarque 2)	0	0	0.1	0.2	0	0.1

On homogénéise les solutions, chauffe 35 min dans une étuve à 70°, ferme les tubes par des bouchons en polyéthylène, refroidit, introduit dans une cuve de quartz de 1 cm d'épaisseur et mesure la transmission (*T*) à 490 nm en excitant les solutions par le triplet du mercure (filtre 365 nm). Avant chaque mesure l'appareil doit être calibré au moyen d'un étalon fluorescent stable.

RÉSULTATS

Si $T_1, T_2, \ldots T_6$ = transmissions des solutions 1, 2, . . . 6

$T_B = (T_1 + T_2)/2$ = transmission moyenne du blanc (remarque 3)
$T_A = (T_3 + T_4)/2$ = transmission moyenne de la solution étalon
$t_A = T_A - T_B$ = transmission de 7.5 ng de bore
$t_5 = T_5 - T_B$ = transmission de x ng de bore contenus dans v ml de la solution de l'échantillon
$t_6 = T_6 - T_B$ = transmission de $x+5$ ng
p = poids en g de l'échantillon (prise)

nous avons:

par la méthode (*a*) de l'étalon externe: $\% \, B_{ext} = \dfrac{1.5 \cdot 10^{-5} t_5}{v p t_A}$

par la méthode (*b*) mixte: $\% \, B_{mix} = \dfrac{10^{-5}(1.5 t_6 - t_A)}{v p t_A}$

Enfin si une courbe d'étalonnage a été préalablement établie la teneur en bore peut aussi être directement déterminée sur cette courbe (méthode *c*) (remarque 4).

Dans le Tableau II nous donnons les résultats de nos déterminations.

TABLEAU II

DOSAGE DIRECT DANS LES ACIERS DOUX

v (ml)	*mg d'acier*	*% B · 10³*			*v (ml)*	*mg d'acier*	*% B · 10³*		
		Méthode a	*Méthode b*	*Méthode c*			*Méthode a*	*Méthode b*	*Méthode c*
Acier No. 275: prise (p) = 0.022151 g					*Acier No. 275: prise (p) = 0.01672 g*				
0.6	0.66453	1.29	1.15	1.37	0.6	0.5016	1.13	1.25	1.21
0.8	0.86604	1.28	1.14	1.36	0.8	0.6688	1.05	1.17	1.11
1.0	1.10755	1.33	1.30	1.39	1.0	0.8360	1.07	1.11	1.11
1.2	1.32906	1.29	1.21	1.36	1.2	1.0032	1.13	1.22	1.18
1.4	1.55057	1.26	1.30	1.32	1.4	1.1704	1.20	1.27	1.25
1.6	1.77208	1.22	1.26	1.27	1.6	1.3776	1.16	1.22	1.20
Acier No. 273: prise (p) = 0.01227 g					*Acier No. 273: prise (p) = 0.01137 g*				
0.6	0.36810	2.34	2.41	2.31	0.6	0.34110	2.34	2.26	2.52
0.7	0.42945	2.38	2.43	2.33	0.7	0.39795	2.58	2.24	2.78
0.8	0.49080	2.34	2.18	2.28	0.8	0.45480	2.43	2.17	2.61
0.9	0.55215	2.53	2.38	2.30	0.9	0.51165	2.50	2.22	2.67
1.0	0.61350	2.35	2.28	2.28	1.0	0.56850	2.40	2.14	2.57
1.1	0.67485	2.37	2.33	2.29					

Remarques

(*1*) Les tubes à centrifugation doivent être préalablement traités par un mélange sulfonitrique et par l'acide sulfurique à l'ébullition.

(*2*) Cette solution doit être préparée avant le développement de la fluorescence à partir d'une solution de stock plus concentrée.

(*3*) Un blanc préparé directement ou selon le mode opératoire donne pratiquement la même fluorescence.

(*4*) Les teneurs en bore ont été déterminées sur une courbe d'étalonnage résultant d'une étude de la fidélité de la méthode à l'HMCB et qui nous a auparavant servi pour d'autres dosages[15].

Nous remercions le Fonds National Suisse, Commission pour la Science Atomique, grâce auquel nous avons pu entreprendre ce travail.

SUMMARY

A simple and rapid method for the direct determination of traces of boron in mild steels, using 2-hydroxy-4-methoxy-4'-chlorobenzophenone (HMCB) as the fluorimetric reagent for boron is proposed.

ZUSAMMENFASSUNG

Es wird eine einfache und schnelle fluorimetrische Methode zur Bestimmung von Spuren Bor in Stählen mit 2-Hydroxy-4-methoxy-4'-chlorobenzophenon vorgeschlagen.

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THERMAL ANALYSIS OF SOME METAL BENZOHYDROXAMATES

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Benzohydroxamic acid (BHA, N-benzoylhydroxylamine) was first prepared in 1872 by LOSSEN[1]. It has been used extensively in analytical chemistry as a colorimetric reagent and as a precipitant, the principal applications being in the determination of vanadium[2–4], manganese[5,6], molybdenum[2], iron[7,8], thorium[9], uranium[2,10], titanium[11], copper[12], cobalt[12] and nickel[12].

No reports on thermal analysis of BHA chelates have appeared in the literature. The present paper deals with the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of BHA and its precipitates with some common metals. The precipitates studied were those with aluminum(III), cadmium(II), cobalt(II), copper(II) (2 precipitates), iron(III), lanthanum(III), lead(II), manganese(II), nickel(II), uranium(VI) and zinc(II).

EXPERIMENTAL

Thermal analysis apparatus

The DTA and TGA apparatus has been described elsewhere[13,14].

Thermal analysis procedures

TGA was carried out at a heating rate of 8°/min with samples of varying size, depending on the metal ion in the chelate. The thermobalance was checked by determining the weight of residue in the crucible after a reasonable cooling period.

DTA runs were carried out using 20–30 mg of chelate for runs in oxygen, about 60 mg for runs in nitrogen, mixed with enough 180-mesh silicon carbide to give about 600 mg of material in the sample block. About 600 mg of silicon carbide was used as reference material. The covered block was then heated at 8°/min at a gas flow rate of about 20 ml/min.

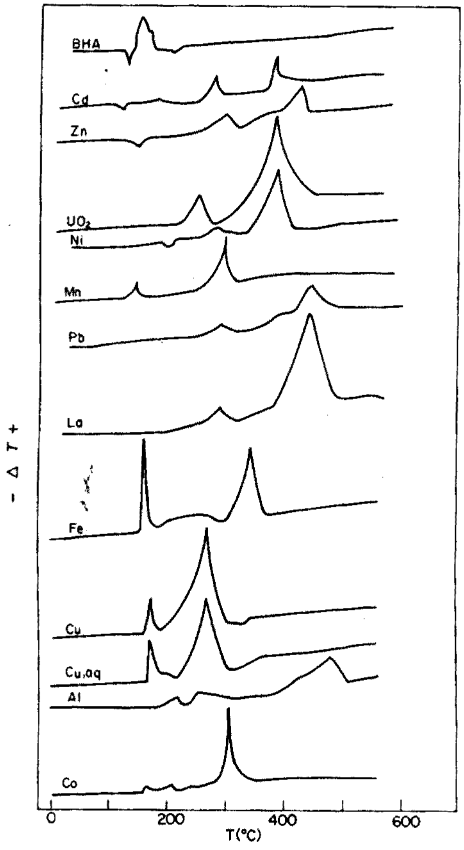
Preparation of chelates

A roughly weighed amount of BHA was dissolved in about 100 ml of water containing 0.5 meq of perchloric acid. Enough metal ion solution was added to the BHA solution to leave an excess of 25–50% BHA. The resulting solution was treated dropwise with 1 *M* sodium hydroxide solution until precipitation occurred. When the metal was non-amphoteric, base addition was continued until a pH of 8–9 was attained. When the metal was amphoteric, the base was added until the precipitate seemed to coagulate. The general reaction involved is:

TABLE I

ANALYSIS OF CHELATES

Chelate	*% C calc.*	*% C found*	*% H calc.*	*% H found*
$Al(BHA)_3 \cdot \frac{3}{2}H_2O$	54.55	54.01	4.58	4.53
$Cd(BHA)_2 \cdot \frac{3}{4}H_2O$	42.23	42.23	3.42	3.48
$Co(BHA)_2 \cdot H_2O$	48.15	48.20	4.04	4.05
$Cu(BHA)_2$	50.20	50.53	3.60	3.74
$Cu(BHA)_2 \cdot \frac{1}{4}H_2O$	49.42	49.62	3.70	3.62
$Fe(BHA)_3 \cdot H_2O$	52.30	52.02	4.18	4.82
$La(BHA)_3 \cdot H_2O$	44.62	44.53	3.57	3.39
$Pb(OH)_2 \cdot 4Pb\ (BHA)_2$	31.16	31.89	2.33	2.54
$Mn(BHA)_2 \cdot \frac{1}{2}H_2O$	50.02	50.07	3.90	3.78
$Ni(BHA)_2 \cdot H_2O$	48.18	48.13	4.04	4.21
$UO_2(BHA)_2$	31.01	31.03	2.23	2.22
$Zn(BHA)_2 \cdot H_2O$	47.28	47.52	3.97	4.12



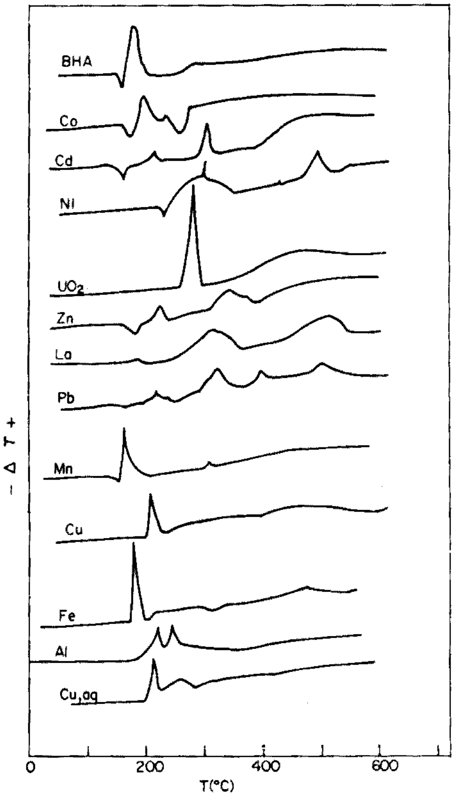
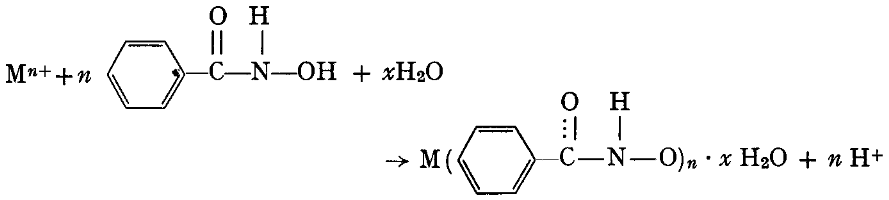


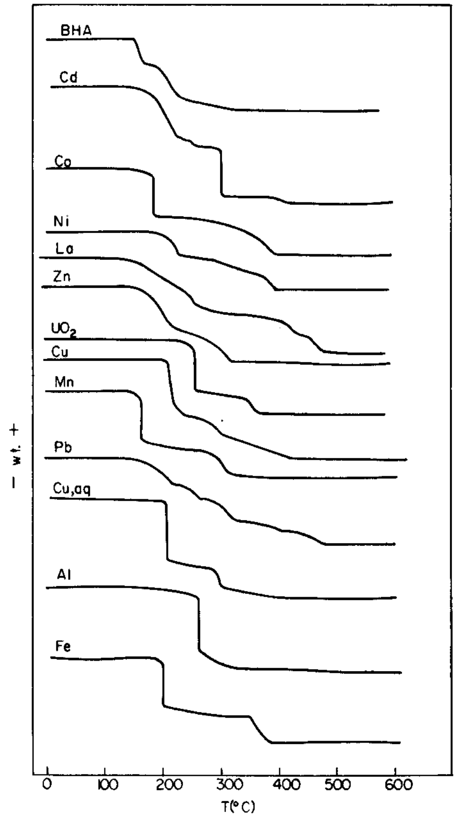
Fig. 1. DTA curves in O_2.
Fig. 2. DTA curves in N_2.



When the metal ion was lead(II), it seemed that hydrolysis could not be prevented with the excess of BHA used in these experiments. When manganese(II) was the metal ion, 10 ml of 1% hydroxylammonium chloride solution was used to prevent the oxidation in basic medium of manganese(II) to manganese(III)[5]. The reducing agent must be added before base addition is begun.

RESULTS AND DISCUSSION

Under the uncontrolled conditions used here, only nickel(II), cobalt(II),



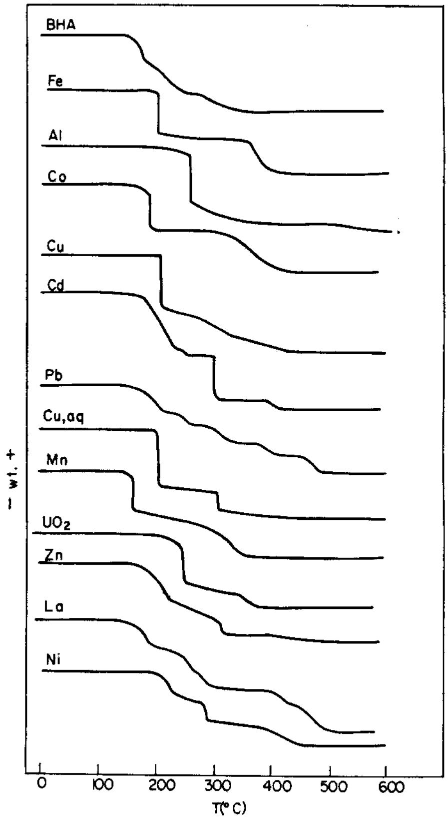


Fig. 3. TGA curves in O_2.
Fig. 4. TGA curves in N_2.

copper(II), cadmium(II) and lanthanum(III) were definitely precipitated quantitatively. The copper(II) began to precipitate as soon as the metal ion solution was added to the acidic BHA solution. This precipitate was found to be different from that obtained by addition of base until a pH of 8–9 was reached. The precipitate formed in the latter case was dark green and analyzed as $Cu(BHA)_2 \cdot \frac{1}{4}H_2O$. The other precipitate was blue-green in color and analyzes as $Cu(BHA)_2$.

No mention is made in the literature of precipitation of aluminum(III), lead(II), lanthanum(III) or manganese(II) with benzohydroxamic acid. The precipitate of each of these metals is, therefore, a new compound. Table I lists the carbon and hydrogen analyses for each of the chelates.

The DTA curves of the chelates and of BHA in oxygen and in nitrogen and the corresponding TGA curves are shown in Figs. 1–4. There seem to be no common features in the set of curves. Some of the chelates decompose exothermically, others

TABLE II

HEATS OF DECOMPOSITION FOR METAL CHELATES

Chelate	*Sample weight (mg)*	*Area*	*Heat evolved or absorbed*		*Heat of decomp. (kcal/mole)*
			(cal)	*(cal/g)*	
$Al(BHA)_3 \cdot \frac{3}{2} H_2O$	52.6	268	−9.59	−182	−84.1
	47.5	250	−8.93	−188	−87.0
$Cd(BHA)_2 \cdot \frac{3}{4} H_2O$	64.5	182	4.30	66.7	26.5
	66.2	184	4.36	65.8	26.2
$Co(BHA)_2 \cdot H_2O$	61.8	139	3.75	60.7	21.2
	64.1	139	3.75	58.5	20.4
$Cu(BHA)_2$	38.6	241	−7.50	−194	−65.2
	40.2	255	−7.92	−197	−66.5
$Cu(BHA)_2 \cdot \frac{1}{4}H_2O$	71.8	256	−8.12	−113	−38.4
	64.6	220	−6.98	−108	−36.8
$Fe(BHA)_3 \cdot H_2O$	37.8	191	−7.32	−194	−93.5
	41.3	204	−7.81	−189	−91.1
$La(BHA)_3 \cdot H_2O$	81.8	25	−0.64	−7.8	−4.4
	97.5	29	−0.74	−7.6	−4.3
$Pb(OH)_2 \cdot 4Pb(BHA)_2$	99.0	1	0.02	0.2	0.4
	94.6	1	0.02	0.2	0.4
$Mn(BHA)_2 \cdot \frac{1}{2}H_2O$	28.7	40	1.27	44.3	14.9
	36.5	53	1.69	46.4	15.6
$Ni(BHA)_2 \cdot H_2O$	60.7	26	0.81	13.3	4.6
	75.2	31	0.97	12.9	4.5
$UO_2(BHA)_2$	52.6	378	−14.8	−281	−152
	49.7	363	−14.2	−286	−155
$Zn(BHA)_2 \cdot H_2O$	62.2	239	6.45	104	37.0
	63.8	258	6.95	109	38.7
BHA (fusion)	67.9	74	1.49	21.9	3.0
	65.1	69	1.38	21.2	2.9
BHA (decomposition)	67.9	1255	−28.7	−423	−58.0
	65.1	1181	−27.0	−415	−56.8

endothermically. No single factor can be used to explain the relative heats of decomposition, although the fact that benzohydroxamic acid itself decomposes exothermically indicates that, in the absence of other complications, the compounds should all decompose exothermically. Table II summarizes the heat of decomposition results, while Table III lists the attempts to correlate the heats of decomposition with other parameters.

TABLE III

PROPERTIES USED IN ATTEMPTS TO CORRELATE THERMAL ANALYSIS DATA

Heat of decomposition
$UO_2(BHA)_2 > Fe(BHA)_3 \cdot H_2O > Al(BHA)_3 \cdot \frac{3}{2}H_2O > Cu(BHA)_2 >$
$Cu(BHA)_2 \cdot \frac{1}{4}H_2O > La(BHA)_3 \cdot H_2O > Pb(OH)_2 \cdot 4Pb(BHA)_2 > Ni(BHA)_2 \cdot H_2O >$
$Mn(BHA)_2 \cdot \frac{1}{2}H_2O > Co(BHA)_2 \cdot H_2O > Cd(BHA)_2 \cdot \frac{3}{4}H_2O > Zn(BHA)_2 \cdot H_2O$

Temperature of DTA decomposition peak
$UO_2(BHA)_2 > Al(BHA)_3 \cdot \frac{3}{2}H_2O > Cu(BHA)_2 \cdot \frac{1}{4}H_2O > Cu(BHA)_2 = Ni(BHA)_2 \cdot H_2O >$
$Fe(BHA)_3 \cdot H_2O > Zn(BHA)_2 \cdot H_2O = Co(BHA)_2 \cdot H_2O > La(BHA)_3 \cdot H_2O >$
$Cd(BHA)_2 \cdot \frac{3}{4}H_2O > Mn(BHA)_2 \cdot \frac{1}{2}H_2O > Pb(OH)_2 \cdot 4Pb(BHA)_2$

Heat of formation of metal oxide
$U_3O_8 > La_2O_3 > Al_2O_3 > Fe_2O_3 > Co_3O_4 > MnO_2 > ZnO > CdO >$
$NiO > PbO > CuO$

Radius of central ion
$Pb^{2+} > La^{3+} > Cd^{2+} > Mn^{2+} > Zn^{2+} > Co^{2+} > Cu^{2+} > Ni^{2+} > Fe^{3+} > Al^{3+}$

Charge-to-radius ratio of central ion
$Al^{3+} > Fe^{3+} > Ni^{2+} > Cu^{2+} > Co^{2+} = La^{3+} > Zn^{2+} > Mn^{2+} > Cd^{2+} > Pb^{2+}$

Molecular weight of chelate
$Pb(OH)_2 \cdot 4Pb(BHA)_2 > La(BHA)_3 \cdot H_2O > UO_2(BHA)_2 > Fe(BHA)_3 \cdot H_2O >$
$Al(BHA)_3 \cdot \frac{3}{2}H_2O > Cd(BHA)_2 \cdot \frac{3}{4}H_2O > Zn(BHA)_2 \cdot H_2O > Co(BHA)_2 \cdot H_2O >$
$Ni(BHA)_2 \cdot H_2O > Cu(BHA)_2 \cdot \frac{1}{4}H_2O > Mn(BHA)_2 \cdot \frac{1}{2}H_2O > Cu(BHA)_2$

Mole percent water
$Al(BHA)_3 \cdot \frac{3}{2} H_2O > Co(BHA)_2 \cdot H_2O = Fe(BHA)_3 \cdot H_2O = La(BHA)_3 \cdot H_2O =$
$Ni(BHA)_2 \cdot H_2O = Zn(BHA)_2 \cdot H_2O > Cd(BHA)_2 \cdot \frac{3}{4} H_2O > Mn(BHA)_2 \cdot \frac{1}{2} H_2O >$
$Cu(BHA)_2 \cdot \frac{1}{4}H_2O > Pb(OH)_2 \cdot 4Pb(BHA)_2 > Cu(BHA)_2 = UO_2(BHA)_2$

The heats of decomposition of the chelates and of BHA and the heat of fusion of BHA were estimated from the areas under the peaks of the DTA runs in nitrogen. The following equation was used for this estimation. Heat per unit area (calories) = $a + b\ (t - 125)$, where a and b are constants which depend on the amplifier range used in the run, and t is temperature (°). The equation is derived by using the known heats of fusion and the measured areas of the fusion peaks of samples of anthracene (apparent m.p. 220°) and of benzoic acid (apparent m.p. 125°), and assuming a linear relationship between temperature and heat change per unit area.

$$\text{at } 2000\ \mu\text{V}, \quad a = 2.71 \cdot 10^{-2}, \quad b = 1.87 \cdot 10^{-4}$$

$$\text{at } 1000\ \mu\text{V}, \quad a = 1.95 \cdot 10^{-2}, \quad b = 1.36 \cdot 10^{-4}$$

Some of the products of the thermal decomposition have been identified as benzonitrile, metal benzoate, metal oxide, aniline, benzamide, carbon dioxide and tars.

In the one instance where a comparison can be made of the heat of decomposition of a BHA chelate and a BPHA (N-benzoyl-N-phenylhydroxylamine, N-phenylbenzohydroxamic acid) chelate, the decomposition of $Cu(BPHA)_2$ is more exothermic than that of $Cu(BHA)_2$.

The copper chelates were found to be soluble at pH 11, and the application of this property to the separation of copper from some other metals is now being studied.

A study of the use of the lanthanum, cadmium, copper, nickel and cobalt chelates as analytical precipitates is planned.

SUMMARY

The preparation and thermal analysis of metal chelates of benzohydroxamic acid (BHA) with Al(III), Cd(II), Co(II), Cu(II) (two compounds), Fe(III), La(III), Pb(II), Mn(II), Ni(II), U(VI) and Zn(II) is discussed. The Al(III), La(III), Pb(II) and Mn(II) chelates are new compounds. DTA and TGA curves of the chelates and of BHA are presented, and the heats of decomposition of the chelates are estimated.

RÉSUMÉ

Les auteurs ont effectué une étude sur la préparation et l'analyse thermique de chélates métalliques de l'acide benzohydroxamique (BHA) avec Al, Cd, Co, Cu, Fe(III), La, Pb, Mn, Ni, U et Zn. Les chélates de Al, La, Pb et Mn sont de nouveaux composés. On donne des courbes de ces chélates ainsi que les chaleurs de décomposition.

ZUSAMMENFASSUNG

Die Herstellung und thermische Analyse der Metallchelate von Benzohydroxamsäure (BHA) mit Al(III), Cd(II), Co(II), Cu(II) (2 Verbindungen), Fe(III), La(III), Pb(II), Mn(II), Ni(II), U(VI) und Zn(II) wird diskutiert. Die Al(III)-, La(III)-, Pb(II)- und Mn(II)-Chelate sind neue Verbindungen. DTA- und TGA-Kurven der Chelate und des BHA werden angegeben und die Zersetzungswärmen der Chelate abgeschätzt.

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THIOTHENOYLTRIFLUOROACETONE: A NEW CHELON

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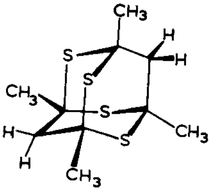
Thioderivatives of the β-diketones have been reported several times in the literature, but no analytical significance has yet been associated with these interesting compounds. While all the dithio-β-diketones reported in the literature to this time are dimeric (*e.g.* dithioacetylacetone, I), and do not chelate, 5 monomeric, monothio-β-diketones have been synthesised and do show tendencies towards chelation with several metals. Recently, Chaston *et al.*[1,2] reported the synthesis of monomeric, monothio-derivatives of acetylacetone, benzoylacetone, dibenzoylmethane, thenoyltrifluoroacetone, and dipivaloylmethane. The nickel chelates of these thioketones were also prepared.



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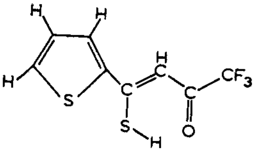

II

The series of chelates of thiothenoyltrifluoroacetone (1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one, II) has been extended to include copper(II), zinc(II), cobalt(II), lead(II), cadmium(II), and palladium(II). Our independent results regarding the chelon and the nickel chelate agree substantially with that obtained by Chaston[2]. The analytical significance of this kind of chelate lies in the volatility and the intense coloration of the metal products. The chelates studied and reported upon in this paper were sublimable and highly colored when compared to their diketone analogues, fairly stable in air, soluble in organic non-polar solvents such as benzene, carbon tetrachloride, and petroleum ether, and soluble in polar solvents such as dimethylformamide, dioxane, and ethanol, but to a lesser degree. Although the quantitative analytical significance of this chelon and its chelates has not yet been fully investigated, the chelon may be of some value at least as a qualitative colorimetric reagent. To illustrate, zinc forms a greenish yellow chelate; lead, an orange product; cadmium, a yellow complex.

All the known thio-derivatives of β-diketones, and where applicable their reported chelates, are summarized in Table I.

TABLE I

THIO-DERIVATIVES OF THE β-DIKETONES AND THEIR CHELATES

Compound	*M.p. (°)*	*Reference*
Dimeric dithioacetylacetone[a]	162.5	3,4
Dimeric thioacetylacetone	131, 138[b]	4,5
Dimeric dithio-3-methylacetylacetone	227	3,6
Dimeric dithioproponylacetone	136	6
Dimeric dithiodiproponylmethane	164–165	6
Dimeric dithiobutyrylacetone	113	4
Dimeric dithiodibutyrylmethane	136	4
Dimeric dithioheptoylacetone	71	4
Dimeric dithiodiheptoylmethane	92	4
Dimeric dithiopivaloylacetone	164	4
Thioacetylacetone (2-mercapto-2-penten-4-one)[b]	... b.p. 50–55/10 mm	2,7
Thiodibenzoylmethane (3-mercapto-1,3-diphenylprop-2-en-1-one)	78	1,2,8
Thiobenzoylacetone (3-mercapto-1-phenylbut-2-en-1-one)	28	1,2
Thiothenoyltrifluoroacetone (1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one)	74	2
Thiodipivaloylmethane (2,2,6,6-tetramethyl-5-mercaptohept-4-en-3-one)	... b.p. 50–60/0.8 mm	2
Chelates:		
$Ni(I)_2$	167	2
$Ni(II)_2$	184	2,8
$Cu(II)_2$	162	8
$Zn(II)_2$	175	8
$Pb(II)_2$	...	8
$Pd(II)_2$	236	8
$Co(II)_3$	229	8
$Ni(III)_2$	225	2
$Ni(IV)_2$	237	2
$Ni(V)_2$	222	2

[a] The dimeric compounds have been assigned an adamantanoid structure as shown for dimeric dithioacetylacetone in Fig. 1.

[b] Dimeric monothioacetylacetone exists in 3 isomers by virtue of the adamantanoid configuration. Two of the isomers are enantiomers (m.p. 131) and the other is meso (m.p. 138).

EXPERIMENTAL

Synthesis of 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one

The above compound shall for the sake of brevity be assigned the symbol STTA indicating that it is a monosulfur-substituted derivative of thenoyltrifluoroacetone commonly known as TTA.

TTA (0.05 mole, 11 g) was dissolved in 200 ml of absolute ethanol and cooled to 0°. The solution was then saturated with dry hydrogen chloride gas, and hydrogen sulfide passed through the reaction mixture at 0° for 4 h. The reaction flask was shaken constantly during the entire time of addition of both gases, with the temperature held at 0°. The resulting dark red-orange solution was poured over 1 lb. of crushed ice, and as the ice melted, the product precipitated from the mixture as a red solid. This solid was collected by filtration, sucked dry, washed with 2 l of water, filtered and dried in the air. Purification was effected by sublimation at 3 mm pressure and a temperature of 45° in the sublimator and 0° in the cold-finger. Care must be taken not to raise the temperature over 60°. The product melts, then decomposes, at temperatures below 75°. Brick red needles of the product were obtained which melted at 62–64°. (Yield 60%. Calcd. for $C_8H_5S_2OF_3$: C, 40.34; H, 2.10; found: C, 40.36; H, 2.44.)

Synthesis of the chelates

A solution of STTA was prepared by dissolving 4.6 g of STTA (0.02 mole) in sufficient absolute ethanol to produce 100 ml of a 0.2 *M* solution. Ten ml of this solution was added to 10 ml of aqueous 0.2 *M* metal acetate (cadmium and palladium acetates were not available so 0.5 g of sodium acetate was added to nitrate solutions of these ions). The metals chosen were Ni(II), Cu(II), Pb(II), Zn(II), Co(II), Cd(II), and Pd(II). The respective chelates precipitated from the reaction mixture immediately. After standing for 30 min, the precipitates were filtered, washed with 100 ml of water, 5 ml of cold (0°) ethanol and sucked dry. The crude chelates were dried in a desiccator over $CaCl_2$ for 48 h. They were purified by crystallization from minimum boiling ethanol. (Calcd. for recrystallized $NiC_{16}H_8S_4O_2F_6$: C, 36.04; H, 1.51; found: C, 35.94; H, 2.13.)

Ultraviolet, visible and infrared spectra

The ultraviolet and visible spectra of the chelon, STTA, and the chelates were recorded with a Beckman DB spectrophotometer. The solvent was absolute ethanol. The spectra of STTA and its nickel chelate are shown in Fig. 1. The absorption maxima and molar extinction coefficients are listed in Table II for the chelon and for the chelates.

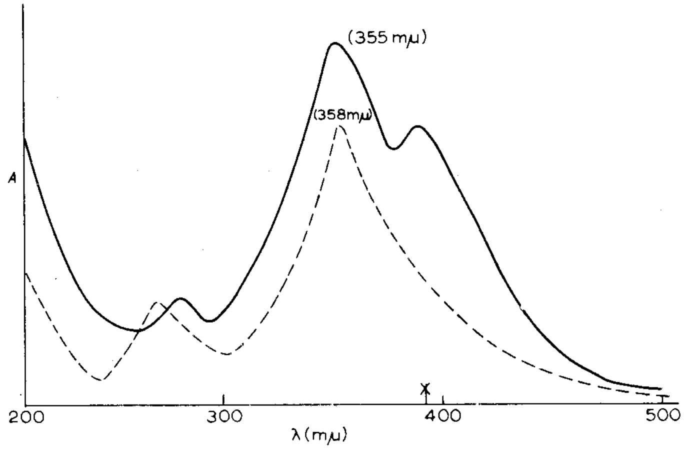

Fig. 1. Ultraviolet–visible spectra of STTA and Ni(STTA)$_2$. ——— STTA; — — — Ni(STTA)$_2$.

The infrared spectra were made with a Beckman IR-5 on nujol mulls of the appropriate compound. Generally, sharp bands were observed. The principal absorption frequencies and their assignments are listed in Table III.

Nuclear magnetic resonance spectra

Carbon tetrachloride solutions of both TTA and STTA were subjected to NMR measurements with a Varian HA-60 spectrometer. The data are summarized in

TABLE II

ULTRAVIOLET AND VISIBLE SPECTRA OF STTA AND CHELATES

Compound	*Color of solid*	*Absorption maxima (mμ)*	*Molar extinction coefficients* *($m^{-1}\ cm^{-1}$)*
Thiothenoyltrifluoroacetone (STTA)	Red	355	$8.45 \cdot 10^3$
$Ni(STTA)_2$	Brown-red	358	$7.75 \cdot 10^3$
$Cu(STTA)_2$	Olive-brown	338	$5.60 \cdot 10^3$
$Zn(STTA)_2$	Yellow-green	374	$4.22 \cdot 10^3$
$Co(STTA)_2$	Brown-black	362	$7.52 \cdot 10^3$
$Pb(STTA)_2$	Orange	345	$3.70 \cdot 10^3$
$Cd(STTA)_2$	Yellow	364	$4.35 \cdot 10^3$
$Pd(STTA)_2$	Brown-red	369	$6.95 \cdot 10^3$

TABLE III

INFRARED SPECTRA OF STTA AND THE CHELATES

Compound	$\nu(C\underline{\cdots}C)$	$\nu(C\underline{\cdots}O)$	$\nu(C\underline{\cdots}S)$	$\nu(C\underline{\cdots}S) + \delta(C\text{–}H)$
STTA	1552 (1570)[a]	1620 (1612)[a]	1258 (1260)[a]	819 (817)[a]
$Ni(STTA)_2$	1539 (1535)[a]	1511 (1502)[a]	1248 (1240)[a]	806 (800)[a]
$Cu(STTA)_2$	1562	1527	1250	810
$Zn(STTA)_2$	1600	1514	1250	810
$Co(STTA)_2$	1550	1495	1242	803
$Pb(STTA)_2$	1540	1505	1250	812
$Cd(STTA)_2$	1585	1513	1251	816
$Pd(STTA)_2$	1539	1505	1241	804

[a] These data are those reported by CHASTON. The frequencies were assigned by him for these absorption bands and are included here for purposes of comparison. Assignments for the other chelates are based on CHASTON's work.

TABLE IV

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF STTA AND TTA

Thenoyltrifluoroacetone	singlet	triplet	triplet	singlet
τ	-4.79	2.11	2.71	3.53
Thiothenoyltrifluoroacetone	singlet	doublet	triplet	singlet
τ	-4.00	2.35	2.88	3.05

Table IV. Idealized spectra are illustrated in Fig. 2 along with the tau assignments. The sample solutions were 10% by weight.

Thermal analyses

The thermal decomposition properties of STTA and its chelates were investigated by both differential and thermogravimetric techniques. The DuPont-900 Thermalanalyzer was employed. Sample thermograms for STTA and its nickel chelate are shown in Fig. 3. Analyses were performed on air-dried samples before recrystallization. The decomposition data for the chelates were rechecked after their purification by recrystallization. The nickel chelate showed a loss of water on

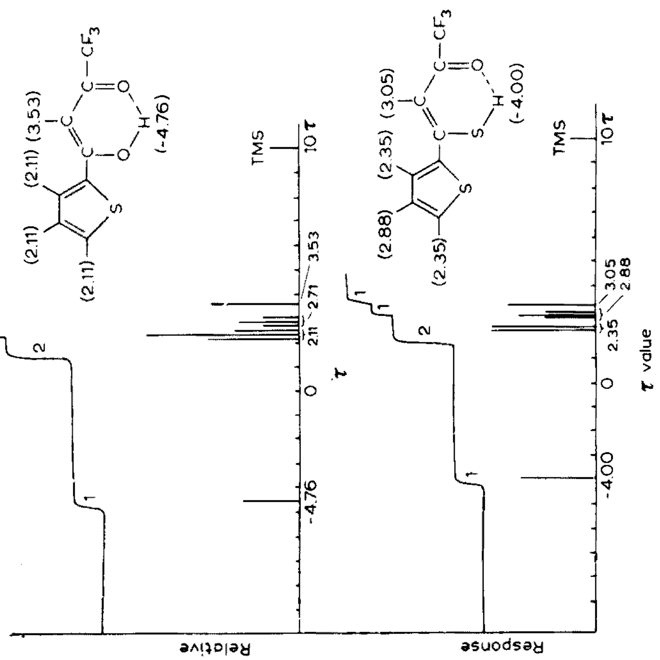

Fig. 2. Nuclear magnetic resonance spectra.

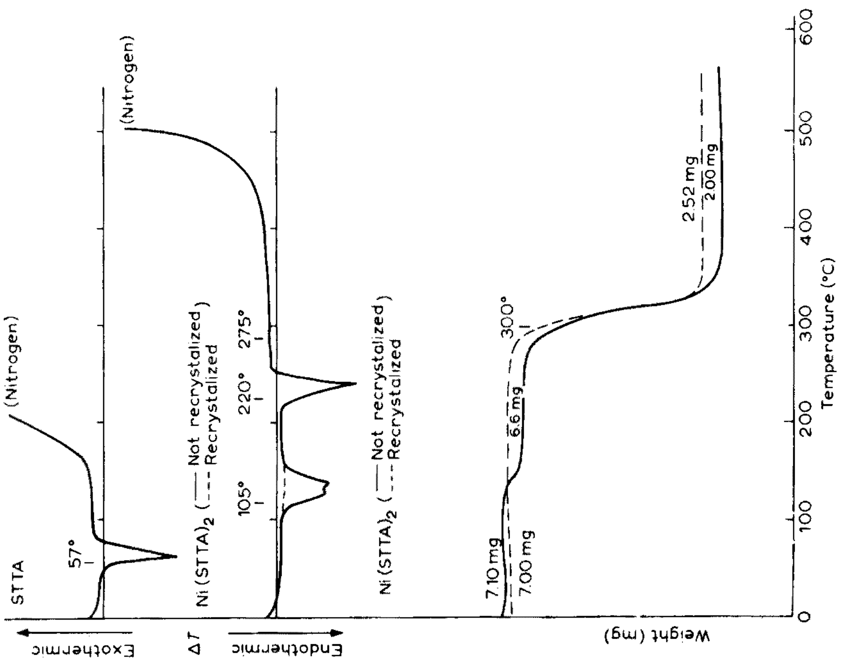

Fig. 3. DTA and TGA thermograms for STTA and its nickel chelate.

TABLE V

THERMAL ANALYSIS DATA

Sample	DTA data		TGA data		
	Observed exothermic changes (°)	Observed endothermic changes (°)	Sample wt. (mg)	Wt. loss (mg)	Observed decomposition temperature (°)
STTA	140	57	...	...	...
$Ni(STTA)_2$	275	220[a]	7.00	4.48	300
$Ni(STTA)_2 \cdot 2H_2O$	275	105, 220[a]	7.10	5.20	125, 300
$Cu(STTA)_2$	375	227[a]	12.60	10.69	275
$Pb(STTA)_2$	250	165 broad	7.50	3.87	175
$Zn(STTA)_2$	185, 300	170[a]	8.15	6.15	150, 650
$Co(STTA)_2$	210	...	7.75	6.05	180, 500
$Cd(STTA)_2$	207	...	2.50	1.78	170, 500
$Pd(STTA)_2$	430	...	4.65	3.50	450
$Pd(STTA)_2 \cdot 2H_2O$	430	100	4.50	3.55	100, 455

[a] These endotherms correspond to fusions. Melting points as determined by a Fisher–Johns Apparatus were for $Ni(STTA)_2$ 235–237; for $Cu(STTA)_2$ 230–231; and for $Zn(STTA)_2$, 177–178.5.

TABLE VI

FRACTIONAL SUBLIMATION DATA

Compound	Maximum temperature in the sublimator (°)	Temperature range of the crystalline zone (°)	Percentage recovery
STTA	45	3° (condenser temp.)	60
$Ni(STTA)_2$	185	148–95	70
$Cu(STTA)_2$	195	150–127	60
$Pb(STTA)_2$	150	120–110	5
$Zn(STTA)_2$	150	119–111	15
$Co(STTA)_2$	146	109–100	10
$Cd(STTA)_2$	165	131–121	30
$Pd(STTA)_2$	169	139–113	28

purification, as did palladium. The remainder of the chelates were unchanged with respect to their thermograms. The data are summarized in Table V.

Fractional sublimation experiments

The chelon, STTA, and each of its chelates were sublimed in a fractional sublimator[9]. The entraining gas was air at 1.3 mm pressure. Table VI summarizes the data for all the chelates as well as STTA.

DISCUSSION

The method of synthesis employed in this preparation of STTA is a modification of that first reported by Mirta[10] for the preparation of thioacetoacetic ester. The concentration of hydrogen chloride in the solvent is of utmost importance to the course of the reaction; if the alcohol is not completely saturated with hydrogen chloride, the reaction does not proceed at any appreciable rate. The temperature of the reaction mixture increases quite rapidly with the brisk addition of hydrogen chloride. Ice water–sodium chloride cooling baths were used to keep the temperature at 0°. CHASTON *et al.* apparently bypassed this problem by cooling their mixture with dry ice and acetone and then allowing the reaction flask and contents to warm up to room temperature after the 2 gases were introduced. This allowed them to shorten their reaction time to a considerable degree. The reaction mechanism is probably quite complex and there is evidence that the concentration of hydrogen chloride in the reaction mixture is critical. The reaction probably proceeds through the keto-form of the diketone. The order of preference for the site of attack appears to be:

$$CH_3 > C_6H_5 > OC_2H_5 > C_4H_3S > CF_3$$

From the resonance and inductive effects of these groups in positions adjacent to a carbonyl group, it is apparent that the attack by hydrogen sulfide is not nucleophilic, for if this were the case then the site adjacent to the CF_3-group would be preferred. Both NMR measurements and mass spectra calculations show that the sulfur is attached to the carbon adjacent to the thienyl group rather than that next to CF_3. Thus the attack could be from an electrophilic species, possibly the H_3S^+ ion, which would also be likely in the highly acidic media. The concentration of the diketone is important to the proper course of the reaction. Solutions must be dilute in order to prevent the dimerization of the thioketone. CHASTON suggests about 2.5% by weight. Our preparation utilized a solution of about 0.025 *M*.

Attempts to chelate dimeric mono- and dimeric dithioacetylacetone were made with several metals. All these efforts ended in failure. The thioketone must be in the monomeric form in order that chelation can be effected. Even after 24 h of refluxing with the appropriate metal, dimeric monothioacetylacetone was recovered unreacted. In addition, the dimerization of thioketones is not a reversible reaction. After 24-h refluxing in 6 *N* hydrochloric acid and ethanol, the dimer is recovered unchanged.

KLOSE *et al.*[11] showed through NMR measurements that the monomeric monothiodibenzoylmethane compound is essentially 100% in the thioenol form. STTA is also essentially all thioenol in character. This is an apparent conclusion from the NMR spectra in Fig. 2. Only one band is found in the enol–thioenol region, and when compared to the spectrum of the starting material it is obviously due to the S-H proton. The spectra of TTA and STTA are shown in Fig. 2 and a comparison to dibenzoylmethane and thiodibenzoylmethane is provided in Table VII. For both sets of compounds, the thioenol proton shows a shift to a higher τ value. This is consistent with the lesser electronegativity of sulfur as compared to oxygen. The

TABLE VII

CHELATE RING, ENOL AND THIOENOL PROTON NMR RESONANCE (τ)

Compound	*Chelate ring-H*	*Enol/ thioenol-H*
Thiodibenzoylmethane	2.52	−5.64
Thiothenoyltrifluoroacetone (STTA)	3.05	−4.00
Dibenzoylmethane	3.19	−7.20
Thenoyltrifluoroacetone (TTA)	3.53	−4.76

proton is better shielded in the thioenol case. The shift of the chelate ring proton in STTA is consistent with that found for thiodibenzoylmethane. Both are shifted to a lower τ value. The apparent triplet for TTA thiophene protons may be an overlapping doublet (2.11 τ). The spectrum of STTA shows a doublet for the analogous protons. The upscale shift for these and the analogous triplet is due to the adjacent sulfur in the thioenol. This demands less of an electron drain from the ring than the enol requires in the case of TTA. In summary, then, the NMR spectrum for STTA is completely consistent with the structure that CHASTON *et al.*[2] proposed on the basis of mass-spectral analysis. It is also consistent with the effects noted by KLOSE[11] for thiodibenzoylmethane.

Examination of the DTA and TGA data for the chelon and its various chelates leads to the conclusion that the compounds have low levels of thermal stability. STTA melts, but decomposes before a boiling point can be reached even under an atmosphere of nitrogen. Of the chelates in this series, only the copper, nickel and zinc chelates are sufficiently stable to fuse before decomposition (227°, 220°, and 170° respectively, as interpreted from the DTA curves). The chelates of nickel and palladium apparently retain 2 molecules of water per formula weight as they are formed but lose it on recrystallization. Endotherms at 105° and 100° for the unrecrystallized nickel and palladium chelates give evidence of this water. Examination of recrystallized sample thermograms does not show the presence of this water in the coordination sphere of these ions. None of the other chelates give any evidence of hydrate formation; thus, they must form as solvent-free chelates. The DTA traces for all these compounds indicate that the thermal decomposition is quite complicated. This is also evidenced by the number of pyrolysis products found in the fractional sublimator tube, and from the lack of uniformity in the thermogravimetric data collected for the chelates. The DTA thermograms do show that the decompositions are exothermic, at least in their total characteristics.

Thermogravimetry does not shed much light on the nature of the decompositions. With the exception of nickel and palladium, which show weight losses at 125° and 100° respectively corresponding to the loss of 2 molecules of water of hydration per formula weight of chelate, weight losses all begin at temperatures about 300°. The chelates of copper, nickel, lead and palladium decompose with a single weight-loss step. Zinc, cobalt and cadmium show 2 well defined weight-loss zones. The greatest problem in interpreting the weight-loss data is that the weights of the residues do not conform to a consistent product. The products at the cut-off temperatures of the thermogravimetric analyses are probably mixtures. If one assumes an empirical formula that seems best to account for the weight of the residue in each case, the weight loss corresponds to 2 moles of the ligand for each formula weight of the chelate in all cases with an average relative error of only 6.57%. The products are inorganic in all cases. These data with a sample calculation are summarized in Table VIII.

Attempts at sublimation of the chelates in a fractional sublimator were successful, even though there was some decomposition in all cases studied. The amount of recovery of chelate varied from a high of 70% for the nickel chelate to a low of 5% for the lead chelate. The chelates of both nickel and Pd were recovered free of water. The chelates all formed in zones of well defined crystals, usually better than those obtained from recrystallization processes. Residue remained in the sub-

TABLE VIII

TGA CALCULATIONS

Chelate	*Ni(STTA)*$_2$	*Cu(STTA)*$_2$	*Pb(STTA)*$_2$	*Zn(STTA)*$_2$	*Co(STTA)*$_2$	*Cd(STTA)*$_2$	*Pd(STTA)*$_2$
Weight of chelate (mg)	7.00	12.60	7.50	8.15	7.75	2.50	4.65
Weight of residue (mg)	1.52	1.91	3.63	2.00	1.70	0.72	1.15
Weight loss found	4.48	10.69	3.87	6.15	6.05	1.78	3.50
Best empirical formula of the residue	$NiSO_4$	CuO	$PbSO_4$	$ZnSO_2$	$CoSO_4$	$CdSO_4$	PdO
Weight loss calculated for chelon (MX_2), and corrected for residue	74.9	85.0	61.5	78.4	81.5	69.1	76.4
% Weight loss found	64.1	84.9	51.6	75.5	78.2	71.1	75.3
Relative error	14.6	0.01	16.1	3.71	4.05	16.2	1.44

Average relative error is 6.57%

limation boats in all determinations. These residues consisted of unidentified organic as well as inorganic matter. Separation of mixtures by sublimation was not attempted, but the temperature zones of the recrystallized sublimates indicate that the use of STTA chelates for this kind of separation would be possible if the decomposition could be controlled. Since air was used as the entrainer gas in the sublimations, the recovery of the chelates may be improved by the use of nitrogen as the entrainer. This has not yet been explored. A summary of the amounts of chelate recovered is given in Table VI. All recovery determinations are based on the weight of the sublimed chelate as scraped from the sublimator tube. Because of the difficulty in removal, these results should be interpreted only in a qualitative manner.

The principal infrared absorption wavelengths are summarized in Table III. The spectra obtained for all the chelates were very similar to that illustrated for the nickel complex. Our data and assignments for STTA and $Ni(STTA)_2$ confirm the data presented by CHASTON. The other chelates which were investigated also show absorptions in the same region as nickel.

The reagent has been found to chelate with a series of representative divalent cations but its overall selectivity has not been established. It is certain though that the divalent ions chelate more readily than do the trivalent ions. For example, iron(III), aluminum(III), and chromium(III) give no indication of chelation.

One of the most interesting analytical aspects of this investigation has been the intense color of a number of the chelates. The chelates of zinc(II), cadmium(II), and Hg(II) were yellow to yellow-green. Lead(II) produced an orange product. Thus, thiothenoyltrifluoroacetone may prove to be a good colorimetric reagent for these cations.

Unfortunately, it has not been possible to reproduce the chelation of mercury(II). An insufficient quantity of chelate was obtained originally for a complete characterization but the product melted at 173° and gave DTA and TGA traces and an infrared spectrum similar to those of the other chelates.

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SUMMARY

The thioderivative of 2-thenoyltrifluoroacetone, 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (STTA) was prepared. NMR and infrared spectra confirmed the previously suggested structure[2]. The sulfur is attached to the carbon adjacent to the thienyl group and exists almost entirely in the thio-enolic form. The chelates of STTA with Ni(II), Cu(II), Pb(II), Zn(II), Co(II), Cd(II), Pd(II) and Hg(II) were prepared in a neutral to slightly basic medium, and characterized by analysis, NMR, infrared, visible and ultraviolet spectra, DTA, TGA and fractional sublimation. The chelates are relatively stable, insoluble in water, soluble in non-polar and some polar organic solvents, sublimable, and intensely colored compared to their normal diketone analogs. The selectivity of the reagent has not been completely established but divalent ions chelate more readily than trivalent ions; Fe(III), Al(III), Cr(III) apparently do not chelate. The new chelon may be useful as a color-developing reagent for the colorimetric analysis of such ions as Zn(II), Cd(II), Hg(II) and Pb(II). The molar extinction coefficients are given for the chelon and the chelates investigated.

RÉSUMÉ

On a préparé les thiodérivés de la 2-thénoyltrifluoroacétone et de la 1,1,1-trifluoro-4-(2-thiényl)-4-mercaptobut-3-en-2-one (STTA). Le soufre est lié au carbone adjacent au groupe thiényl et existe presque entièrement sous forme thio-énolique, en milieu neutre ou légèrement basique. Les chélates de STTA avec Ni, Cu, Pb, Zn, Co, Cd, Pd et Hg ont été préparés; leurs spectres et leurs propriétés ont été examinés. Ce nouveau réactif (STTA) peut être utilisé pour le dosage colorimétrique de Zn, Cd, Hg et Pb. Les coefficients d'extinction molaire sont donnés.

ZUSAMMENFASSUNG

Das Thioderivat des 2-Thenoyltrifluoroaceton, 1,1,1-Trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-on (STTA) wurde hergestellt. KMR- und Infrarotspektren bestätigten die vorgeschlagene Struktur. Der Schwefel wird an den Kohlenstoff gebunden, der an der Thienylgruppe angrenzt und existiert meist völlig in der thioenolischen Form. Die Chelate von STTA mit Ni(II), Cu(II), Pb(II), Zn(II), Co(II), Cd(II), Pd(II) und Hg(II) wurden in einem neutralen bis leicht basischen Medium hergestellt und durch folgende Verfahren charakterisiert: KMR, Infrarot, sichtbare und ultraviolette Spektren, DTA, TGA und fraktionelle Sublimation. Die Chelate sind relativ stabil, unlöslich in Wasser, löslich in unpolaren und einigen polaren organischen Lösungsmitteln, sublimierbar und intensiv gefärbt im Vergleich zu ihren normalen diketonischen Analoga. Eine Selektivität des Reagenzes konnte nicht vollständig bestätigt werden, jedoch bilden die 2-wertigen Ionen leichter als die 3-wertigen Chelate. Fe(III), Al(III), Cr(III) bilden scheinbar keine Chelate. Der neue Chelatbildner ist als farbentwickelndes Reagenz für die kolorimetrische Analyse solcher Ionen wie Zn(II), Cd(II), Hg(II) und Pb(II) geeignet. Einige molaren Extinktionskoeffizienten werden angegeben.

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A MODIFIED AND A NEW STRAIGHT-LINE METHOD FOR DETERMINING THE COMPOSITION OF WEAK COMPLEXES OF THE FORM A_mB_n

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A new method for determining the composition and stability constant of weak complexes of the form AB_n was described in 1960 by ASMUS[1]. KLAUSEN AND LANGMYHR[2] extended the method and demonstrated that it could also be used for ascertaining the value of n (and, under certain conditions, the value of m) in polynuclear complexes of the form A_mB_n $(m > 1)$. The latter authors showed that the method, as suggested by ASMUS, is not capable of distinguishing between mono- and polynuclear species.

The present paper describes two methods for determining the composition of weak complexes of the form A_mB_n: the first method is a modification of the straight-line method of ASMUS, and the second is a new method based on the principles of the straight-line method.

THEORY

Assuming the equilibrium:

$$mA + n\,B \rightleftharpoons A_mB_n \ (m,\ n \geqq 1) \tag{1}$$

then, according to the law of mass action:

$$K = \frac{[A]^m[B]^n}{[A_mB_n]} \tag{2}$$

At equilibrium the concentrations of the reactants are:

$$[A] = a - m[A_mB_n] \tag{3}$$

$$[B] = b - n[A_mB_n] \tag{4}$$

where a and b are the initial concentrations of A and B, respectively.

According to the Beer–Lambert law:

$$[A_mB_n] = \frac{E}{\varepsilon d} \tag{5}$$

where E = extinction, ε = the molar extinction coefficient, and d = the light path in cm.

By combining eqns. (2), (3) and (5):

$$\left(a - m\frac{E}{\varepsilon d}\right)^m [\mathrm{B}]^n = K\frac{E}{\varepsilon d} \tag{6}$$

For $m = 1$, eqn. (6) becomes identical with that developed by ASMUS[1] and used by him as the basis for the plotting of sets of curves.

By maintaining a constant concentration of the reactant A and increasing the concentration of the reactant B, the concentration of the complex approaches an upper limit:

$$\lim_{b \to \infty} [\mathrm{A}_m\mathrm{B}_n] = \frac{a}{m} \tag{7}$$

with a corresponding upper extinction limit of E_0. The combination of eqns. (5) and (7) gives:

$$\varepsilon d = \frac{mE_0}{a} \tag{8}$$

which with eqn. (5), gives:

$$[\mathrm{A}_m\mathrm{B}_n] = \frac{aE}{mE_0} \tag{9}$$

By combining the expressions (2), (3), (4) and (9):

$$K = \frac{\left(a - \frac{E}{E_0}a\right)^m \left(b - \frac{nE}{mE_0}a\right)^n}{\frac{aE}{mE_0}} \tag{10}$$

which may be rewritten as

$$\frac{1}{[\mathrm{B}]^n} = \frac{1}{\left(b - \frac{nE}{mE_0}a\right)^n} = \frac{1}{K}ma^{m-1}\left(1 - \frac{E}{E_0}\right)^m \frac{E_0}{E} \tag{11}$$

By taking the mth root of eqn. (11):

$$\frac{1}{[\mathrm{B}]^{n/m}} = \frac{1}{\left(b - \frac{nE}{mE_0}a\right)^{n/m}} = \left(\frac{1}{K}ma^{m-1}\right)^{1/m}\left(1 - \frac{E}{E_0}\right)\left(\frac{E_0}{E}\right)^{1/m} \tag{12}$$

From the expressions (11) and (12), two graphical methods for determining the composition of weak complexes of the form $\mathrm{A}_m\mathrm{B}_n$ can be developed.

METHOD I

Method I is based upon eqn. (11) and the plotting of curves for different sets of m and n in a diagram expressing $1/[\mathrm{B}]^n$ as a function of $1/E$.

The applicability of the method will be demonstrated by the plotting of theoretical curves. Presupposing the presence of a series of complexes with the actual composition $\mathrm{A}_{m_0}\mathrm{B}_{n_0}$, the curves in Fig. 1 with the subscripts I show curves for different values of m_0. For the separate values of m_0, the curve is not influenced by the value of n_0; for example, the curve for $m_0 = 2$ will be the same for the series of complexes

A_2B, A_2B_2, A_2B_3, etc. The scale unit on the abscissa is $1/E_0$; on the ordinate the unit is $p = (1/K)ma^{m-1}$. From the latter expression it follows that p is a function of m; however, this dependability does not change the form of the curves.

Figure 1 shows that a straight line is obtained for $m_0 = 1$, while higher values of m_0 give lines which are distinctly curved for lower values of $1/E$. In the further discussion of method I, a difference will be made between the parts of the curves

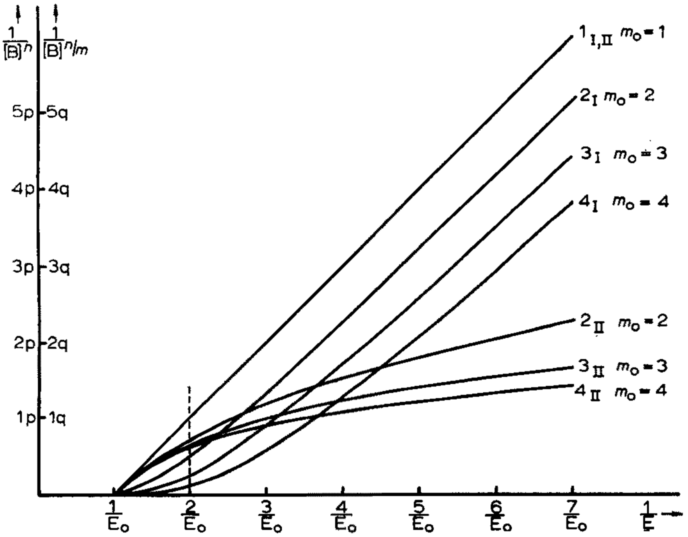

Fig. 1. Theoretical curves obtained by method I (eqn. (11)) and method II (eqn. (12)) for different correct values of $m = m_0$ and $n = n_0$. The subscripts refer to the methods. Scale units on the ordinate axis: for method I $p = (1/K)\ ma^{m-1}$; for method II $q = ((1/K)\ ma^{m-1})^{1/m}$.

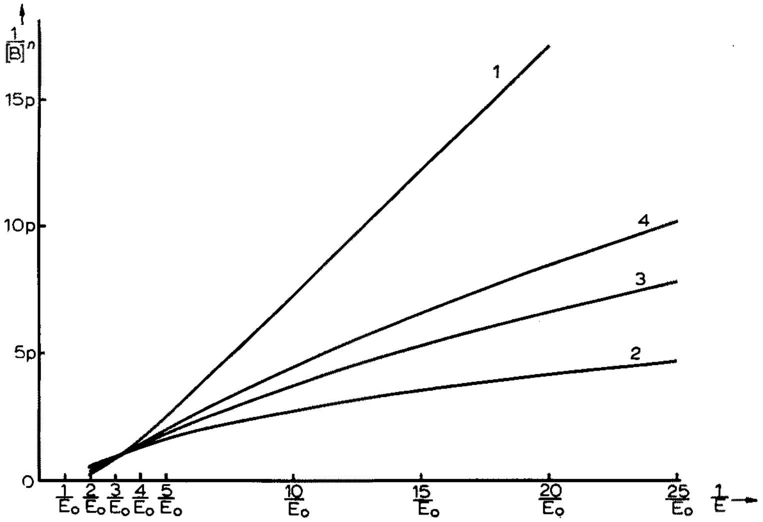

Fig. 2. Theoretical curves obtained by method I, case a for the right value of $m = m_0 = 3$ and different right and wrong values of n. $p = (1/K)\ ma^{m-1}$. Curve 1: $n = n_0$; Curve 2: $n = 1$, $n_0 = 2$; Curve 3: $n = 2$, $n_0 = 3$; Curve 4: $n = 3$, $n_0 = 4$.

corresponding to values on the abscissa above and below $2/E_0$. This limiting value is marked in Fig. 1 with a vertical dotted line.

In case a, *i.e.* for the part of the curves corresponding to values above $2/E_0$, the conditions correspond to those existing in a solution in which the reactant varied (B) is present in deficit. Case b, for values on the abscissa in the range $1/E_0$ to $2/E_0$, corresponds to experimental conditions under which the reactant varied (B) is present in excess.

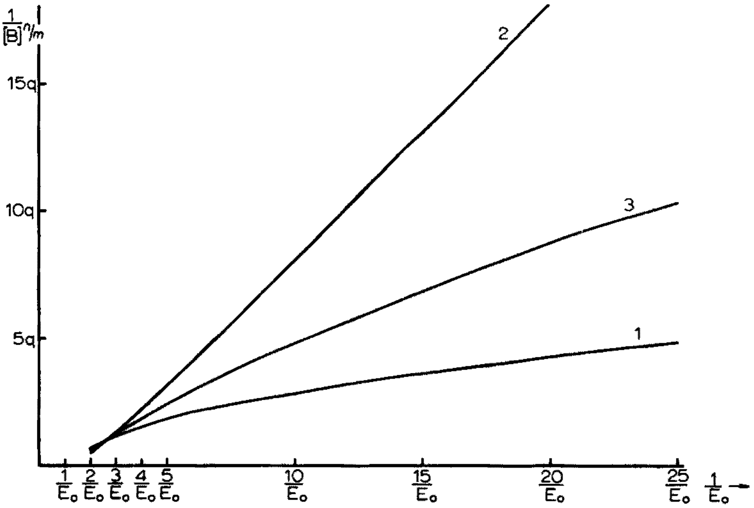

Fig. 3. Theoretical curves obtained by method II, case a for the right value of $m = m_0 = 2$ and different right and wrong values of n. $q = ((1/K)\, ma^{m-1})^{1/m}$. Curve 1: $n = n_0$; Curve 2: $n = 2$, $n_0 = 1$; Curve 3: $n = 3$, $n_0 = 2$.

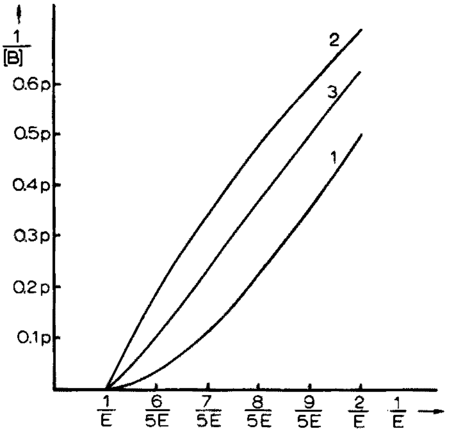

Fig. 4. Theoretical curves obtained by method I, case b for the right value of $m = m_0 = 2$ and different right and wrong values of n. $p = (1/K)\, ma^{m-1}$. Curve 1: $n = n_0$; Curve 2: $n = 1$, $n_0 = 2$; Curve 3: $n = 2$, $n_0 = 3$.

Figures 2 and 4 show (for cases a and b, respectively) theoretical curves for a selection of values of m and n plotted in a diagram with the same scale units as in Fig. 1. The calculations were again based on eqn. (11); the values of m were the correct values $m = m_0$, while the values chosen for n were the correct values $n = n_0$, as well as values $n < n_0$. Figure 2 shows that a nearly straight line is obtained for the correct value of $n = n_0$, lines for wrong values of n being curved. This demonstrated that method I was applicable to case a.

In Fig. 4 all lines are curved, one of the lines for a wrong value of n being straighter than that for the right value. Consequently, method I is not applicable to case b.

METHOD II

Method II is a new method based on eqn. (12) for the plotting of curves for sets of m and n in a diagram expressing $1/[B]^{n/m}$ as a function of $1/E$. A straight line is obtained for the true quotient of n/m.

As for method I, the applicability will be elucidated by the plotting of theoretical curves. Presupposing a selection of complexes with the actual composition $A_{m_0}B_{n_0}$, the curves in Fig. 1 with the subscripts II show the curves obtained for different values of m_0. As apparent from eqn. (12), the form of the curves is not influenced by the value of n_0.

Figure 1 shows that method II gives a straight line only for $m_0 = 1$; all other lines contain distinctly curved parts, although other parts are nearly straight.

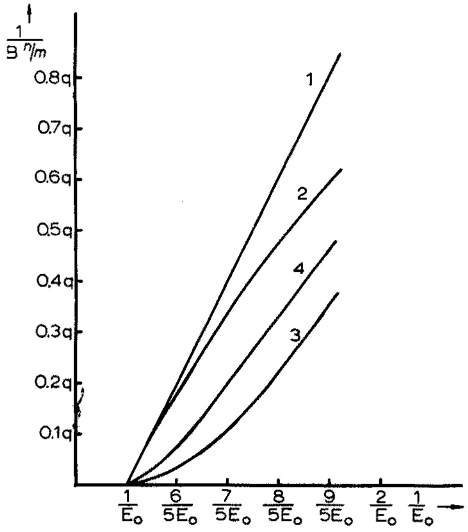

Fig. 5. Theoretical curves obtained by method II, case b for two right values of m and different right and wrong values of n. $q = ((1/K)\ ma^{m-1})^{1/m}$. Curve 1: $m = m_0 = 1, n = n_0$; Curve 2: $m = m_0 = 2, n = n_0$; Curve 3: $m = m_0 = 2, n = 2, n_0 = 1$; Curve 4: $m = m_0 = 2, n = 3, n_0 = 2$.

As for method I, a difference will be made for the parts of the curves corresponding to values on the abscissa above and below $2/E_0$. Case a (values above $2/E_0$) corresponds approximately to conditions under which the reactant varied (B) is present in deficit, and case b (values in the range $1/E_0$ to $2/E_0$)corresponds to conditions under which the reactant varied (B) is present in excess.

In Figs. 3 and 5, theoretical curves for different values of m and n are plotted on the basis of eqn. (12), the scale unit on the abscissa being the same as in Fig. 1, while the unit on the ordinate is

$$q = \left(\frac{1}{K} ma^{m-1}\right)^{1/m}$$

In the calculations the correct values of m were chosen, $m = m_0$, while the values chosen for n included both the correct value, $n = n_0$, as well as values $n > n_0$. From Fig. 3 it can be seen that the wrong values of n give lines which are straighter than that for the true value of n. Method II is therefore not applicable to case a.

From Fig. 5, however, it appears that the straightest lines are obtained for the true values of $n = n_0$. Consequently, method II is applicable to case b.

CONCLUSIONS

The range of applicability of the two methods is apparent from the following Table.

Method	*Case a* *Reactant B in deficit* $1/E > 2/E_0$	*Case b* *Reactant B in excess* $1/E_0 < 1/E < 2/E_0$
I	Applicable	Not applicable
II	Not applicable	Applicable

The applicability tabulated above refers only to systems in which $m > 1$. For $m = 1$ both methods give straight lines for $n = n_0$.

Method I is in principle the method of ASMUS. There are, however, important differences. Before the plotting of curves, ASMUS[1] makes the approximation $[B] \approx b$ which, even in the presence of weak complexes, is disputable; this approximation was also made by KLAUSEN AND LANGMYHR[2].

The curves above relating to method I are strictly theoretical and are not based on any approximations. In order to apply method I to actual systems, it is necessary to know the value of E_0. The value of E_0 is preferably established graphically from a diagram resulting from the use of method II, the curves in this diagram cutting the abscissa at $1/E_0$. Thus, method I offers definite advantages, as compared with the original method of ASMUS.

Method II is a new method based on the principle of varying the concentration of the reactant maintained in excess. The practical application of this method is based upon the approximation $E = E_0$. By maintaining relatively large excesses of the reactant varied, *i.e.* by selecting values of $1/E$ near $1/E_0$, this approximation is practically fulfilled.

For the application of the different straight-line methods, the following survey may be of interest.

The original method of ASMUS. For the complex AB_n the value of n is determined by varying the concentration of the reactant B, the concentration of reactant A being maintained constant and in excess.

The modification by KLAUSEN AND LANGMYHR. For the complex A_mB_n, the value of n is determined as in the original method of ASMUS. The value of m is found by varying the concentration of A, the concentration of B in this case being kept constant and in excess. A disadvantage of this modification is that in many systems different complexes predominate as an excess of A is changed into an excess of B, *i.e.* the values of m and n may not belong to the same complex.

The present method II. For the complex A_mB_n, the value of m/n is determined by varying the excess of the reactant A, the concentration of B being maintained constant. By preparing and measuring a second series of solutions, in which the concentration of A is kept constant and in excess, while the concentration of B is varied, the value of n is determined.

Both series contain an excess of the reactant A and consequently the values of the coefficients m and n can be assumed to belong to the same complex.

Calculation of the stability constant

The stability constant may be calculated using method II and eqn. (10) which gives:

$$K' = \frac{\dfrac{Ea}{E_0 m}}{\left(b - \dfrac{nE}{mE_0}a\right)^n \left(a - \dfrac{E}{E_0}a\right)^m}$$

By introducing the experimental data and the values for m and n, the constant can be calculated.

EXPERIMENTAL

Method II (with the approximation $E = E_0$) was tested on the system boric acid–quinalizarin[3] which react in concentrated sulfuric acid to form a complex with the composition 1:1. The experimental data relating to the present measurements are given in Table I and the resulting curves in Fig. 6.

TABLE I

EXPERIMENTAL DATA RELATING TO THE SYSTEM BORIC ACID–QUINALIZARIN

(Solvent: 93% sulfuric acid. Standard solutions (prepared in sulfuric acid): boric acid $8.00 \cdot 10^{-4}$ M; quinalizarin $1.60 \cdot 10^{-4}$ M. All sample solutions contained 2.00 ml of quinalizarin standard solution. The blank solution contained 2.00 ml of quinalizarin standard solution and 8.00 ml of sulfuric acid)

Solution no.	*Volume (in ml) added of boric acid standard solution – v_b*	*Extinctions (610 nm)*	*Stability constant*[a] $K' \cdot 10^{-5}$ M^{-1}
1	0.80	0.238	0.76
2	1.00	0.259	0.84
3	1.50	0.283	0.88
4	2.00	0.291	0.86
5	2.50	0.296	0.83
6	3.00	0.301	0.91
7	4.00	0.305	0.90

[a] Arithmetic mean value of the stability constant $K' = 0.85 \cdot 10^{-5}$ M^{-1}.

Figure 6 gives values of $\frac{1}{(b - n/m \cdot a)^{n/m}}$ ($b = \frac{v_b}{10}\, 8.00 \cdot 10^{-4}$; values of v_b are given in Table I; $a = \frac{2}{10}\, 1.60 \cdot 10^{-4}$) as a function of $1/E$ for different sets of m and n. As before, the unit on the ordinate axis is $q = \left(\frac{1}{K}\, m a^{m-1}\right)^{1/m}$. In accordance with previous results, Fig. 6 exhibits a straight line for $n/m = 1$.

Method II was further utilized by LANGMYHR AND MYHRSTAD[4] to elucidate the system selenium(IV)–1,1′-dianthrimide (Di); the method in this case demonstrated, in accordance with the results of other methods, the presence of a Se_2Di complex.

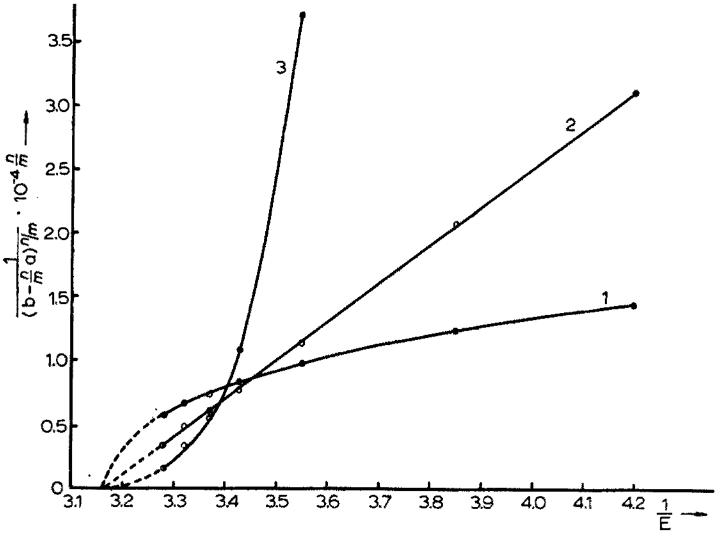

Fig. 6. Experimental curves obtained by method II for the system boric acid–quinalizarin. For experimental details, see the text and Table I. Curve 1: $n/m = \frac{1}{2}$; Curve 2: $n/m = 1$; Curve 3: $n/m = 2$. Curve 2 cuts the abscissa at $1/E = 3.16$, *i.e.* $E_0 = 0.317$.

SUMMARY

A modified ASMUS method and a new method are described for determining the composition and stability of weak complexes of the form A_mB_n. The modified method is applicable to polynuclear complexes and is not based on the approximation necessary originally. The second method is based on variation of the concentration of the reactant being maintained in excess. The method gives a straight line for the correct quotient of n/m and the stability constant can easily be calculated from data extracted from the diagram. The main advantage is that, in combination with the original straight-line method, this method permits the determination of both coefficients (m and n) in the presence of an excess of one of the reactants.

RÉSUMÉ

Une méthode modifiée d'ASMUS et une nouvelle méthode sont décrites pour déterminer la composition et la stabilité de complexes faibles de forme A_mB_n. La méthode modifiée est applicable à des complexes polynucléaires. Le second procédé est basé sur la variation de concentration du "réactant", maintenu en excès. On obtient une droite pour le quotient n/m; la constante de stabilité peut être facilement calculée à partir des valeurs tirées du diagramme. Le principal avantage est qu'en la combinant avec la méthode originale de la droite, cette méthode permet de déterminer les deux coefficients (m et n) en présence d'un excès de l'un des "réactants".

ZUSAMMENFASSUNG

Zur Bestimmung der Zusammensetzung und Stabilität von schwachen Komplexen der Form A_mB_n wurde eine modifizierte ASMUS-Methode und eine neue Methode beschrieben. Die modifizierte Methode ist auf polynukleare Komplexe anwendbar und beruht nicht auf einer Näherung wie bei der Originalmethode. Bei der zweiten Methode wird die Konzentration der im Überschuss anwesenden Reaktionspartner variiert. Die Methode ergibt eine Gerade für den Quotienten n/m. Mit Daten aus dem Diagramm kann die Stabilitätskonstante leicht berechnet werden. Der Hauptvorteil liegt in der Kombination mit der Originalmethode, die die Bestimmung beider Koeffizienten (m und n) in Gegenwart eines Überschusses der Reaktionspartner gestattet.

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CHROMATOGRAPHISCHE TRENNUNG VON METALLIONEN DURCH ELUTION MIT AMMONIUMSULFAT

BESTIMMUNG VON MAGNESIUM, CALCIUM UND STRONTIUM IN SALZREICHEN WÄSSERN

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Metallionen bilden grösstenteils lösliche Sulfatkomplexe. Komplexe von Ionen mit gleicher Ladung weisen meist nur geringe Unterschiede in der Stabilität auf[1]. Daher ist die chromatographische Trennung von Ionen mit gleicher Ladung durch Elution mit Ammoniumsulfat nur zu erreichen, wenn sowohl die Komplexbildung als auch die Austauschkonstanten unterschiedlich sind.

Die Austauschkonstanten ($K_H{}^M$) der Erdalkalien und des Bleis besitzen bedeutend höhere Werte als die übrigen zweiwertigen Metalle, z.B. $K_H{}^{Mg} = 2.60$, $K_H{}^{Ca} = 4.12$*. Die Stabilitätskonstanten (K) der Sulfatkomplexe derselben Metalle haben naheliegende Werte: $\lg K_{MgSO_4} = 2.2$, $\lg K_{CaSO_4} = 2.3$[1]. Es ist naheliegend, dass sich Magnesium und Calcium infolge der unterschiedlichen Austauschkonstanten mit Ammoniumsulfat glatt trennen lassen.

Die Austauschkonstante für Strontium ist 5.14, für Barium 9.10. K des Strontiumsulfatkomplexes ist zwar unbekannt, doch deutet die teilweise Löslichkeit des Strontiumsulfats in Ammoniumsulfatlösung die Bildung eines löslichen Komplexes an. Dieses Verhalten zeigt, dass die Strontium- und Barium-Trennung mit demselben Eluent möglich ist. Die Calcium- und Strontium-Trennung durch Elution aus Sulfokationit mit Ammoniumsulfat ist bereits gelungen[3]. Erwartungsgemäss müssten Metallionen mit naheliegenden Austausch- und Stabilitätskonstanten gleichzeitig eluiert werden. In dieser Hinsicht ist die Untersuchung von Mangan(II) zweckmässig, das die Reihe zweiwertiger Ionen mit naheliegenden Konstanten abschliesst:

Metallionen	Mg	Zn	Co	Cu	Cd	Ni	Mn	Ca
$K_H{}^M$	2.60	2.73	2.96	3.05	3.07	3.10	3.23	4.12
K	2.2	2.3	2.3	2.4	2.4	2.4	2.4	2.3

Auf Grund der Aussagen über die Elution der Manganionen mit Ammoniumsulfat wird es möglich sein das Verhalten dieser Ionen bei der Magnesium- und Calcium-Trennung vorauszusagen.

Metallionen mit grösserer Ladung werden am Kationit stärker adsorbiert und bilden auch beständigere Sulfatkomplexe. Aus diesem Grunde würde ihr Verhalten

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* Die hier angeführten Werte der Austauschkonstanten sind der Monographie von Ringbom[2] entnommen und beziehen sich auf Dowex 50-X8.

bei der Elution mit löslichem Sulfat vermutlich kaum wesentlich von dem der zweiwertigen Ionen abweichen. Experimentell lässt sich das an den Eisen(II, III) überprüfen.

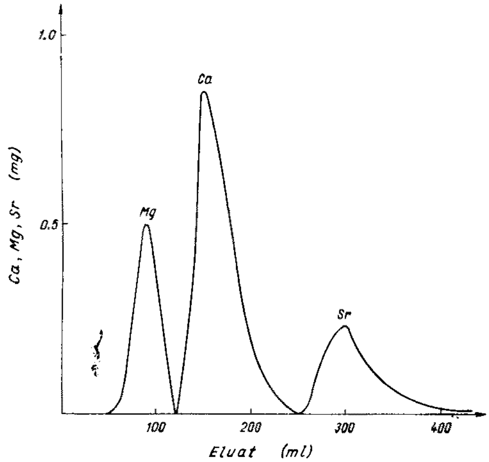
EXPERIMENTELLER TEIL

Bei den Versuchen wurde eine 7/200-mm Kolonne aus etwa 5 g Dowex 50-X10 von Korngrösse 100–150 mesh verwendet. Das Eluat wurde in Portionen zu 10 ml aufgenommen, der Metallionengehalt in den einzelnen Fraktionen nach geeigneten Methoden bestimmt.

Die Menge der Metallionen wechselt von 0.01 bis 0.1 mM mit Ausnahme von Strontium, dessen Konzentration zwischen 0.005 und 0.01 mM schwankt. Bei der Elution von grösseren Mengen setzt sich in der Kolonne ein Niederschlag von Strontiumsulfat ab, der sich allmählich auflöst. Die Elutionskurven aber weisen keine gute Reproduzierbarkeit auf.

Trennung von Magnesium und Calcium

Die Elutionskurven von Magnesium und Calcium trennen sich voneinander wenn die Konzentration des Ammoniumsulfats im Eluent 0.26 M (3.4 %) beträgt. Ist die Menge der beiden Ionenarten etwa 0.1 mM, dann reicht eine Kolonnenhöhe von 200 mm aus (Fig. 1). Bei grösseren Mengen von Calcium wird der Beginn seiner Elutionskurve nach links verschoben; um sie von der Magnesium-Kurve zu trennen, ist eine höhere Kolonne erforderlich. Die Trennung von 0.04 mM Magnesium von 0.4 mM Calcium gelingt beispielsweise bei 270 mm Kolonnenhöhe mit Ammoniumsulfatlösung niedriger Konzentration—0.21 M (Fig. 2).



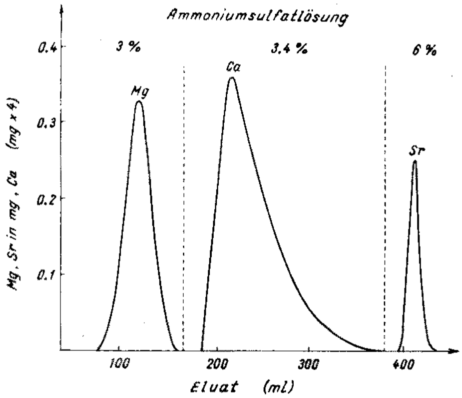


Fig. 1. Elutionskurven für Mg, Ca und Sr mit 3.4%iger Ammoniumsulfatlösung bei Ansatzmengen (in mM): 0.1 für Mg und Ca, 0.01 für Sr.

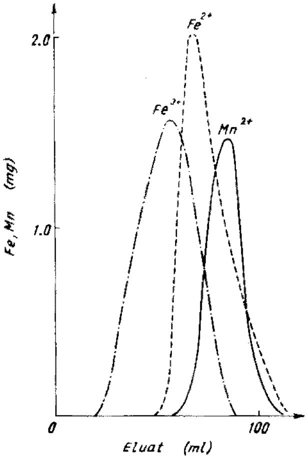
Fig. 2. Elutionskurven für Mg, Ca und Sr mit Ammoniumsulfatlösung von Konzentrationen 3, 3.4 und 6% und Ansatzmengen (in mM) 0.04 für Mg, 0.4 für Ca und 0.01 für Sr.

Trennung von Strontium und Barium

Strontium lässt sich gleichfalls mit 0.26 *M* Ammoniumsulfatlösung eluieren (Fig. 1). Ist die Lösung konzentrierter (0.46 *M*, 6%), dann kann Strontium mit einem kleineren Volumen eluiert werden (Fig. 2). Hierbei wird Barium am Kationit zurückgehalten. Die quantitative Adsorption des Bariums am Kationit unter den Elutionsbedingungen für Calcium und Strontium wurde in zweifacher Weise festgestellt: (*a*) Beide Eluate wurden auf Bariumgehalt untersucht—es war spektroskopisch kein Barium nachweisbar. (*b*) Das aus dem Kationit mit 4 *N* HCl eluierte Barium wurde gravimetrisch bestimmt—die gefundene Menge stimmte mit der in die Kolonne gebrachte sehr gut ein. Bei der Trennung von Strontium und Barium ist deren Konzentrationsverhältnis belanglos, wenn die Strontiummenge die angegebenen Grenzen nicht überschreitet.

Verhalten von Mangan(II)- und Eisen(II und III)-Ionen

Die Elutionskurven der Mangan- und Ferroionen mit 0.26 *M* Ammoniumsulfatlösung fallen mit der des Magnesiums mit derselben Lösung fast zusammen, während die der Ferriionen etwas nach links verschoben ist (Fig. 3). Es erwies sich, dass kleine Mengen an Ferriionen nach der Elution der Hauptmasse an der Kolonne haften bleiben, offenbar in Form von Ferrihydroxyd. Sie gehen allmählich in das Eluat über, wenn die Kolonne mit Ammoniumsulfatlösung ausgewaschen wird. Völliges Fortschwemmen aus dem Kationit wird mit Salz- oder Salpetersäure erreicht. Ein ähnliches Verhalten zeigen auch die Ferroionen.



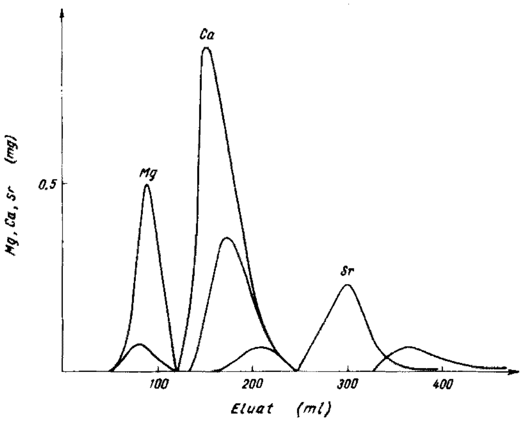


Fig. 3. Elutionskurven für Fe(II und III)- und Mn(II)-ionen mit 3.4%iger Ammoniumsulfatlösung; Ausgangsmengen (in m*M*) etwa 0.1.

Fig. 4. Elutionskurven für Mg, Ca und Sr mit 3.4%iger Ammoniumsulfatlösung bei Ansatzmengen (in m*M*): 0.01 und 0.1 für Mg; 0.01, 0.05 und 0.1 für Ca; 0.005 und 0.01 für Sr.

Aus den experimentellen Angaben wurden die Verteilungskoeffizienten (K_d) der untersuchten Elemente berechnet (Tabelle I).

Um die Abhängigheit des K_d von der Menge der Metallionen zu untersuchen, wurden die Elutionskurven für verschiedene Ansatzmengen (in mM) aufgenommen (Fig. 4).

Dieses Verhalten muss man in Auge behalten, denn die Trennung könnte sich dann als nicht quantitativ erweisen, wenn die Konzentration der Metallionen in der Ausgangslösung höher ist als die, bei der die Untersuchungen durchgeführt werden.

Bestimmung von Mg, Ca und Sr in salzreichen Wässern

Die chromatographische Trennung der Erdalkalien durch Elution mit Ammoniumsulfatlösung wurde für die Bestimmung von dem Mg-, Ca- und Sr-Gehalt in salzreichen Wässern angewendet.

TABELLE I

VERTEILUNGSKOEFFIZIENTEN DER METALLIONEN

Metallione	K_a
Fe(III)	12.2
Fe(II)	14.7
Mg	17.4
Mn(II)	17.4
Ca	29.5

In Wässerproben, die zur Analyse gelangen, schwankt der Gesamtgehalt an Mineralien zwischen 1 und 123 g/l, mit NaCl als Hauptbestandteil. Da das Eisen teilweise am Kationit haften zu bleiben pflegt, muss es zweckmässig vorher nebst Aluminium mit der Sulfosalicylsäure als Komplex gebunden werden.

Die Kationitkolonne, in einem Glasrohr von 90 cm Höhe und 7 mm Durchmesser angelegt, ist 27 cm hoch. Die Durchlaufgeschwindigkeit beträgt 1 ml/min und wird durch die Flüssigkeitshöhe über der Kolonne geregelt. Die Kolonne wird mit 200 ml 2 N HNO_3 und dann mit Wasser bis zur neutralen Reaktion des Filtrats ausgewaschen. Das Rohr wird nach Auffüllung mit Wasser bis zur völligen Suspendierung des Kationits umgeschüttelt. Nach Abfluss des Wassers leitet man durch die Kolonne 50 ml einer mit Ammoniumhydroxyd alkalisierten 0.21 M Ammoniumsulfatlösung (pH = 8.5–9.0) und spült dann mit 20 ml Wasser nach.

Da bei den angegebenen Ausmassen der Kolonne eine quantitative Trennung erzielt werden kann, darf die Calciummenge in dem zu analysierenden Wasservolumen 15 mg nicht überschreiten (die Ca- und Mg-Konzentration wird vorher annäherungsweise komplexometrisch bestimmt). Liegt die Mineralisierung höher als 30–40 g/l, so ist die Probe entsprechend zu verdünnen.

Analysengang. Das zu analysierende Wasservolumen wird mit 0.1 g Sulfosalicylsäure versetzt und mit Ammoniumhydroxyd bis pH 8.5–9.0 alkalisiert. Dann lässt man die Lösung die Kolonne passieren. Der Becher und die Kolonne werden ein paarmal mit insgesamt 15 ml einer 0.5%iger Sulfosalicylsäurelösung mit pH 8.5–9.0 ausgewaschen. Das Magnesium wird mit 170 ml 3%iger Ammoniumsulfatlösung eluiert, wobei die ersten 25 ml des Eluats, die ja Eisen, doch kein Magnesium enthalten, verforfen werden. Fünf ml des nächstfolgenden Eluat werden mit Eryochromschwarz T geprüft. Calcium eluiert man mit 240 ml 3.4%iger Ammoniumsulfatlösung. Fünf ml des nächsten Eluat prüft man auf Ca-gehalt. Strontium wird mit 30 ml 6 M HCl eluiert.

Um in den Reagenzien den Gehalt an den zu bestimmenden Komponenten zu ermitteln, werden durch die Kolonne die Eluenten in derselben Reihenfolge und in gleichen Volumina geleitet, worauf die Bestimmung von Ca, Mg und Sr nach den einschlägigen Methoden erfolgt.

Magnesiumbestimmung. Der aliquote Teil von 25 bzw. 50 ml wird in einem Pyrexbecher auf ein geringes Volumen eingedampft, mit 4 ml Königswasser versetzt, mit einem Uhrglas halbverdeckt und auf dem Sandbad bis zur Vertreibung des Ammoniumsulfats und Verdunstung der Schwefelsäure erwärmt. Den Trockenrückstand löst man in 15 ml Wasser, gibt 0.5 ml ammoniakalische Puffer sowie Eryochromschwarz T hinzu und titriert mit Hilfe einer Mikrobürette mit 0.002 *M* EDTA-Lösung.

Calciumbestimmung. Ein aliquoter Teil des Eluats von 25 bzw. 50 ml wird auf 200 ml verdünnt, mit 4 ml 6 *N* KOH und etwas Thymolphthaleinfluorexon versetzt und mit derselben EDTA-Lösung titriert.

Strontiumbestimmung. Die spektrophotometrische Methode mit *o*-Kresolphthaleinkomplexon[4] kann mit Erfolg eingesetzt werden, wenn der Sr-Gehalt in dem zu analysierenden Wasservolumen höher ist als 0.1 mg, da die Extinktion der Blindprobe, beim Arbeiten mit bidestilliertem Wasser und Reagenzien p.a., 0.04 mg Sr entspricht (die Färbung geht auf Verunreinigungen, namentlich mit Ca und Fe, zurück). Bei geringeren Mengen ist es zweckmässig, entweder mit reineren Reagenzien und in Polyätilen- bzw. Teflongefässen zu arbeiten oder eine spezifische Methode anzuwenden. Hier wurde folgende spektralanalytische Methode benutzt: der aliquote Teil von 5 ml des salzsäuren Eluats wird durch Verdunstung auf ein geringes Volumen eingeengt, mit 0.5 ml HNO_3 versetzt, und bis zur Vertreibung der Ammoniumsalze erhitzt. Als innere Standardlösung setzt man 1 ml Thoriumnitratlösung (1 mg Th je 1 ml) hinzu und dampft dann zur Trockne ein. Der Trockenrückstand wird mittels einer Mikrobürette mit 2 ml 0.1 *N* HCl versetzt. Mit Hilfe einer mit einer Mikrometerschraube versehenen Mikropipette wird 0.1 ml dieser Lösung entnommen und auf leichtkonkave Fläche einer Kupferelektrode von 6 mm Durchmesser aufgetragen, die dann durch IR-Bestrahlung bis zur Verdunstung der Lösung erwärmt wird. Von jeder Probe werden drei Elektroden bereitgestellt.

Zur Bereitung der Eichelektroden bringt man je 5 ml des salzsäuren Eluats der Blindprobe in vier Becher und vertreibt die Ammoniumsalze. Nach Zusatz der inneren Standardlösung und je 0.2 bzw. 0.4 bzw. 0.8 ml der Eichlösung (0.025 mg Sr/ml) wird zur Trockne erhitzt, dann der Rückstand in 2 ml 0.1 *N* HCl gelöst. Aus jeder Lösung (die eine Lösung stellt die Blindprobe dar) werden 3 Elektroden bereitet.

Spektrographie Vorschrift:

Quarz Spektrograf mit mittlerer Dispersion.

Anregungsquelle: ein Funkengenerator, $c = 0.01$ μF, $L = 0.15$ mH.

Gegenelektrode: Kupferelektrode vom Durchmesser 6 mm mit abgerundetem Ende; Elektrodenabstand 2 mm, Spalt 15 μ, Belichtung 1 min.

Platten ORWO, Typ Blauhart.

Strontiumlinie: 4077.71 Å; Thoriumlinie: 4019.14 Å.

Analysenergebnisse für 4 Wasserproben sind in der Tabelle II zusammengestellt.

TABELLE II

ANALYSENERGEBNISSE

Metallion (g/l)	*Wasserproben*				*Standardabweichung (g/l)*	*Variationskoeffizient (%)*
	1	*2*	*3*	*4*		
Mg	0.247	0.177	0.588	0.021		
	0.242	0.174	0.578	0.020		
		0.184		0.022		
		0.185			0.0047	1.9
Ca	1.81	1.20	6.08	0.34		
	1.88	1.24	6.03	0.34		
	1.82	1.29				
		1.28			0.033	1.4
Sr		0.018		0.005		
		0.020		0.006		
		0.019		0.004		
		0.017		0.005		

AUSWERTUNG DER ERGEBNISSE

Ammoniumsulfat erwies sich als ein geeignetes Reagens für die chromatographische Trennung der Metalle Mg, Ca, Sr und Ba voneinander. Besonders unentbehrlich ist es bei der Trennung geringer Strontiummengen von Barium. Unter den für die Trennung der Erdalkaliionen geeigneten Bedingungen, gelingt zugleich die Trennung der zwei- und der dreiwertigen Ionen mehrerer Metalle. Im Vergleich zu den Methoden, die für die chromatographische Trennung der Erdalkalien Lösungen von EDTA[5], DCTA[6], Milchsäure[7] und Zitronensäure[8] verwenden, hat die Methode mit Ammoniumsulfat den Vorteil, dass das Elutionsmittel die direkte Bestimmung der Metallionen im Eluat often nicht behindert. Wo Ammoniumsulfat störend wirkt, kann es verhältnismässig leicht entfernt werden.

Die Nachteile der Methode gehen auf die Verunreinigungen zurück, die dem Ammoniumsulfat eigen sind. Daher muss der Wert der Blindprobe stets sorgfältig ermittelt werden.

ZUSAMMENFASSUNG

Es wurde die Möglichkeit zur chromatographische Trennung von Mg, Ca, Sr, Ba, Fe(II und III) und Mn(II) durch Elution mit Ammoniumsulfatlösung untersucht und die optimalen Bedingungen für die Trennung von Erdalkalien voneinander ermittelt. Die Methode wurde für die Trennung der Ionen von Mg, Ca und Sr in salzreichen Wässern angewendet. Die Bestimmung von Mg und Ca erfolgte auf mikrokomplexometrischem, die Sr Bestimmung auf spektralanalytischem Wege. Die Variationskoeffizienten betragen 1.9% bei Mg und 1.4% bei Ca.

SUMMARY

The chromatographic separation of Mg, Ca, Sr, Ba, Fe(II, III) and Mn(II) by elution with ammonium sulphate solution from Dowex 50-X10 was studied. The optimum conditions for the separation of the alkaline earths from each other were established. The method was applied for the separation of Mg, Ca and Sr in salt waters; Mg and Ca were determined by EDTA titration and Sr spectrographically, the coefficient of variation being 1.9% for Mg and 1.4% for Ca.

RÉSUMÉ

Les auteurs proposent une méthode de séparation chromatographique de Mg, Ca, Sr, Ba, Fe(II et III) et Mn avec élution au moyen d'une solution de sulfate d'ammonium. Ce procédé a été appliqué à la séparation Mg, Ca, Sr dans des eaux salées. Mg et Ca sont dosés par titrage à l'EDTA et Sr par spectrographie. Les coefficients de variation sont 1.9% pour Mg et 1.4 % pour Ca.

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SHORT COMMUNICATIONS

Internal electrolysis for the separation of ions. Part II. Determination of antimony and lead in presence of other ions. Separation and determination of Ag, Bi, Cu, Pb, Cd and Sb

In a previous paper[1] the separation and determination of copper, cadmium, silver and bismuth by means of internal electrolysis with a zinc anode through suitable pH control and addition of complexing agents, were described. In further work on this very simple technique, it was shown that the method can be used for the determination of lead and antimony in presence of other ions, and for the separation and determination of copper, cadmium, silver, bismuth, antimony and lead from each other by control of the experimental conditions.

Apparatus and solutions

A Cambridge pH indicator and the apparatus assembly consisting of a platinum gauze cathode and a zinc plate anode were the same as used earlier[1]. A copper plate, in place of zinc, as anode was used only when silver was to be separated from bismuth.

The chemicals used were of highest purity.

Antimony solution. This was prepared by dissolving antimony trichloride in water containing sufficient hydrochloric acid to prevent hydrolysis, and was standardized iodimetrically[2].

Lead solution. This was prepared from lead nitrate in water with the addition of a little nitric acid, and was standardized by titration with EDTA[3].

Standard solutions of copper, cadmium, bismuth and silver and of other cations and anions as well as 10% solutions of complexing agents such as sodium potassium tartrate, EDTA (disodium salt) and potassium cyanide were the same as reported previously[1].

General procedure

The metal ion to be deposited mixed with the other ions, each 5–10 times the quantity of the depositable ion, was taken in a tall beaker. When an interfering ion was studied, an amount of this ion 50–100 times greater than that of the ion to be deposited was taken.

For the separation and determination of lead, tartrate and cyanide, each at least 10 times the total weight of the ions present, were added to the solution and then after dilution to 250–300 ml or to any required volume to keep the ions and complexing agents in solution, the pH was adjusted to 9.0–10.0.

For the determination of antimony in presence of other ions an amount of EDTA, 10 times the weight of the ions to be complexed, was added before the solution was diluted as stated above and adjusted to pH 8.5–9.5.

The Pt–Zn electrode assembly with previously weighed platinum gauze cathode was then placed in either of the solutions. After the time necessary for deposition, the apparatus assembly was removed and washed with water over the solution. The cathode was then disconnected from the anode, washed again with alcohol, dried at 80°–90° and weighed as described previously[1].

Before further use, the platinum cathode was cleaned with acid to remove any previous deposit, washed with water and alcohol, heated to redness over a non-luminous flame, cooled in a desiccator and weighed.

Determination and separation of lead

At pH 9–10 in the presence of tartrate and cyanide, lead was completely deposited as the metal on the platinum cathode and thus determined after separation from Fe, Al, Cr, Ti, Th, Zr, Be, Zn, Mn, Ni, Co, W, V, La, In, Tl(I), Ta and alkali and alkaline earth metals. Results are shown in Table I.

For the determination of *copper and lead*, the solution containing both ions was treated with a 10-fold weight of EDTA, diluted to 250 ml and adjusted to pH 9.0. Copper was first deposited completely in 24 h, washed, dried and weighed as described in the *General procedure*; then lead was deposited from the residual solution at pH 2.5, washed, dried, etc. Results are given in Table II.

TABLE I

DETERMINATION AND SEPARATION OF LEAD FROM OTHER IONS

(Deposition time 6.0 h)

pH	*Pb*	
	taken (mg)	*found (mg)*
9.0	2.64	2.64
9.5	2.64	2.63
9.0	1.32	1.32
10.0	3.96	3.95
9.0	3.96	3.93
10.0	1.32	1.33

TABLE II

DETERMINATION OF COPPER AND LEAD

Cu		*Pb*	
taken (mg)	*found (mg)*	*taken (mg)*	*found (mg)*
2.14	2.11	2.64	2.64
1.07	1.05	3.96	3.95
3.21	3.20	1.32	1.31

TABLE III

SIMULTANEOUS DETERMINATION OF SILVER, BISMUTH AND LEAD

Ag		*Bi*		*Pb*	
taken (mg)	*found (mg)*	*taken (mg)*	*found (mg)*	*taken (mg)*	*found (mg)*
2.0	1.98	1.93	1.92	2.64	2.62
3.0	2.99	0.96	0.94	1.32	1.32
1.0	1.0	2.89	2.87	3.96	3.95

TABLE IV

DETERMINATION AND SEPARATION OF ANTIMONY FROM OTHER IONS

(Deposition time 1.5 h)

pH	*Sb*	
	taken (mg)	*found (mg)*
8.5	2.50	2.48
8.5	1.25	1.25
9.0	3.75	3.73
9.0	2.50	2.50
9.0	3.75	3.72

When lead and cadmium are present in a mixture, the metals can be deposited successively in the presence of EDTA by simple pH adjustment[1].

For the determination of *lead, silver and bismuth*, EDTA and potassium cyanide (each 10 times the weight of the total ions) were added to the solution which was then diluted to 250 ml and adjusted to pH 9.0. Both silver and bismuth were completely deposited within 12 h, washed, dried and weighed. These metals were then separately deposited in about 6 h each, silver with a copper anode and bismuth with the zinc anode[1]. The main residual solution was then evaporated to 250 ml and an excess of formaldehyde was added. Lead was then deposited at pH 2.5, washed, etc., in the usual way. Results are shown in Table III.

Determination and separation of antimony

With EDTA as the complexing agent and at pH 8.5–9.5, antimony was quantitatively deposited as the metal and thus separated from Be, Zn, Mn, Co, Ni, Sn(IV), Al, La, Cr, Ga, In, Tl(I), Zr, Th, Te(IV), Nb, Ta, V, W, U(VI), Cd, Pb, As(V), Ti and alkali and alkaline earth metals. Typical results are shown in Table IV.

Iron(III) in amounts about 10 times that of antimony prevented the deposition of the latter in the presence of EDTA and cyanide in the pH range 2.5–10, but had no effect at pH 0.5–1.0; more than 1000 mg of iron(III) could be tolerated in the deposition of 1.25–2.50 mg Sb in the latter range with deposition times of 3 h. This effect of iron(III) was fully utilized in the separation of antimony from bismuth or silver and from lead or cadmium.

For the determination of *antimony, bismuth and silver*, iron(III) (at least 10 times the weight of antimony present) was added followed by EDTA and potassium cyanide (each 10 times the total weight of the metal ions). The solution was then diluted to 250 ml and the pH adjusted to 8.5–9.0. Both silver and bismuth were then deposited and finally determined as described previously[1]. An excess of formaldehyde was then added to the residual solution and the pH adjusted to 1.0; antimony was then deposited completely in 3 h. Results are given in Table V.

TABLE V

DETERMINATION OF ANTIMONY, BISMUTH AND SILVER

Ag		*Bi*		*Sb*	
taken (mg)	*found (mg)*	*taken (mg)*	*found (mg)*	*taken (mg)*	*found (mg)*
1.0	1.0	2.89	2.86	1.25	1.25
2.0	1.99	1.93	1.93	2.5	2.48
3.0	2.97	0.96	0.94	3.75	3.72

For *separation from copper*, EDTA and an excess of cyanide were added before deposition of antimony at pH 8.5–9.5; copper was then deposited after cyanide had been masked with formaldehyde. However, if the solution also contained iron(III), simple pH control in presence of EDTA allowed successive deposition of copper and antimony. Ten-fold weights of iron(III) and EDTA were added as indicated for the Sb–Bi–Ag separation and then copper was deposited at pH 9.0 and antimony at pH 1.0. Results are shown in Table VI.

For the determination of *antimony, lead and cadmium*, iron(III) and EDTA were added as in the Cu–Sb method. Lead was then deposited at pH 2.5, cadmium at pH 4.0 and finally antimony at pH 1.0, the volume of solution being maintained at 250 ml. Cadmium deposited completely in 12 h. Results are shown in Table VII.

Determination of Ag, Bi, Cu, Cd, Pb and Sb

In this case, iron(III), EDTA and cyanide were added as in the Ag–Bi–Sb

TABLE VI

DETERMINATION OF COPPER AND ANTIMONY

Cu		*Sb*	
taken (mg)	*found (mg)*	*taken (mg)*	*found (mg)*
2.14	2.12	2.5	2.46
3.21	3.19	1.25	1.24
1.07	1.06	3.75	3.72

TABLE VII

SEPARATION OF LEAD, CADMIUM AND ANTIMONY

Pb		*Cd*		*Sb*	
taken (mg)	*found (mg)*	*taken (mg)*	*found (mg)*	*taken (mg)*	*found (mg)*
1.32	1.32	2.66	2.64	2.5	2.47
2.64	2.63	1.33	1.33	3.75	3.73
3.96	3.93	3.99	3.96	1.25	1.25

TABLE VIII

SEPARATION OF Ag, Bi, Cu, Pb, Cd AND Sb

Taken (mg)						*Total deposit (mg)*	*Found (mg)*					
Ag	*Bi*	*Cu*	*Pb*	*Cd*	*Sb*	*Ag+Bi*	*Ag*	*Bi*	*Cu*	*Pb*	*Cd*	*Sb*
2.0	1.93	2.14	2.64	2.66	2.50	3.90	1.97	1.92	2.14	2.63	2.65	2.47
1.0	1.93	1.07	1.32	1.33	2.50	2.95	1.00	1.93	1.07	1.30	1.32	2.50
2.0	0.96	3.21	3.96	1.33	3.75	2.97	1.98	0.96	3.19	3.94	1.33	3.74

method; the volume was then adjusted to 250–300 ml and the pH to 9.0. Silver and bismuth were then deposited over a period of 12 h. After being washed, this deposit was dissolved in dilute nitric acid and silver and bismuth were separately deposited[1]. The residual solution containing Cu, Cd, Pb and Sb was concentrated and an excess of formaldehyde added. Copper was then deposited at pH 9.0, and lead, cadmium and antimony were deposited at pH values of 2.5, 4.0 and 1.0 respectively. For all these depositions, the volume of the solution was maintained at 250–300 ml and each time the same Pt–Zn assembly was used, the cathode being freshly cleaned and weighed between determinations. Thus by the simple control of pH, Cu, Cd, Pb and Sb were determined one by one in the same solution. Typical results are shown in Table VIII.

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Automatic spectrographic determination of gases in metals etc.

The use of a high temperature hollow-cathode discharge for the determination of oxygen in steel has been reported[1]. This method has now been extended to include the determination of other gaseous elements in a variety of materials, notably nitrogen and oxygen in steel and uranium carbide, oxygen in tungsten and copper, and hydrogen in zirconium and zircaloys.

The simultaneous measurement of oxygen and nitrogen necessitated the incorporation of a second channel in the spectrometer but for the determination of hydrogen, since it is an independent analysis, only resetting of the monochromator is required. Experiments showed that the most sensitive atomic nitrogen lines at 4110.0 Å and 4099.9 Å were unsuitable because of spectral interference by vanadium and attention was turned to possible molecular bands; of these the N_2 1st positive band head at 3914.4 Å was finally chosen, because of its sensitivity, freedom from interference and convenience from design considerations. The installation of a second channel for nitrogen was further complicated by the fact that the most intense emission was recorded when viewing directly into the cathode cavity, whereas the oxygen spectrum has to be viewed across the axis of the cathode to minimise the high background associated with the interior of the hot cavity. To meet these requirements and to obviate a cumbersome mirror system or the use of two monochromators, a standard ½M Spex monochromator designed on a Czerny-Turner mounting was modified so that it is, in effect, a double monochromator as shown diagrammatically in Fig. 1; this arrangement is the subject of a patent application. One exit slit is aligned to measure the intensity of the O_2 7772/5 Å multiplet and the adjacent background radiation, in the first-order spectrum, and the second exit slit is aligned to measure the N_2 1st positive band head at 3914.4 Å in the second-order spectrum. Adequate sensitivity is

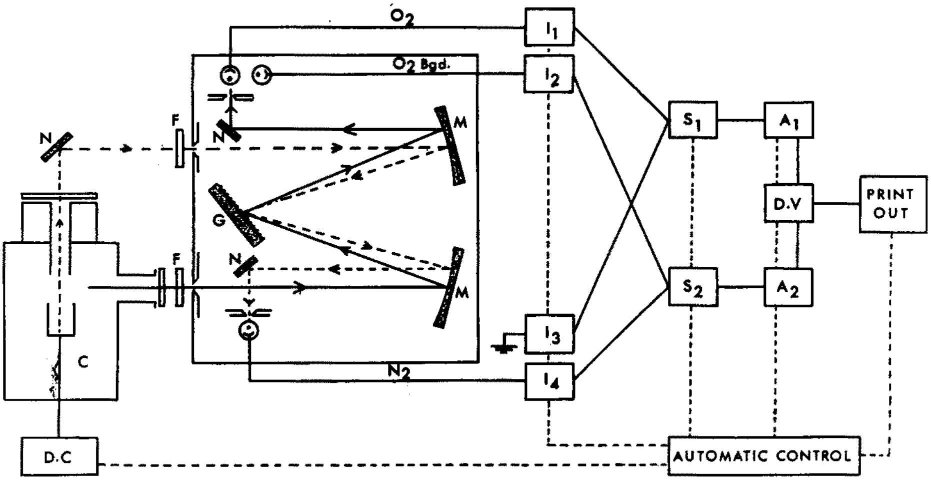

Fig. 1. Schematic layout of the apparatus. C, cathode chamber; F, filters; M, concave mirrors; N, plane mirrors; G, plane grating; I, integrators; S, selectors; A, amplifiers; D.V., digital voltmeter; D.C., high-voltage D.C. source unit.

recorded for nitrogen (and incidentally for hydrogen) without monitoring the adjacent background. Suitable filters are mounted at the entrance slits to act as order sorters. With the exit slits accurately aligned relative to one another, minor drifts in the alignment of the monochromator are adjusted by rotating the grating in the usual way.

To accommodate the longer emission time of nitrogen the integration period is extended to 2.5 min and during the next 30 sec, while the source is switched off, the readings are printed out and the integrators reset. At appropriate intervals, samples are fed into the cathode during the reset period. Uranium carbide and tungsten are analysed under similar conditions except that they are dropped into the cathode encapsulated in nickel sheet which appears to form a homogeneous melt with the samples in the hot cathode, a correction being made for the small oxygen and nitrogen contents of the nickel. In the determination of oxygen in copper the samples are dropped into a cathode containing a bath of 0.5 g of nickel. The source controls are maintained at a fixed setting which corresponds to a current of 0.9 A with a clean cathode containing only the nickel bath. The current decreases as the proportion of copper in the bath increases but this does not appear to affect the evaluation of the oxygen contents.

For the determination of hydrogen in zirconium the monochromator is realigned so that the "oxygen channel" measures the intensity of the hydrogen line at 6562.8 Å. The discharge is run at 0.8 A and care must be taken to ensure that this value is not exceeded, otherwise the samples are liable to melt and give anomalous results. An integration time of 90 sec is adequate to allow complete evolution of hydrogen from samples weighing up to 100 mg.

As previously reported, standard steel samples or synthetic standards can be used to calibrate the apparatus for the determination of oxygen. This calibration has been found to apply equally well for the determination of oxygen in uranium carbide, tungsten and copper. No satisfactory synthetic standard has been found for the determination of nitrogen and standard samples of steel and uranium carbide are used to calibrate for the determination of nitrogen in steel and uranium carbide respectively. Different factors were obtained for these 2 matrix materials.

TABLE I

DETERMINATION OF NITROGEN IN STEEL

Sample	*NBS standard samples*				*BISRA V.F. standard*		*B.C.S. No. 149 pure iron*	*Low N_2 steel*
	8i	*101E*	*343*	*125a*	*BN*[a]	*CR*		
Certificate of analysis % N_2	0.018	0.039	0.074	0.002	0.016	0.0060	0.012	0.0059[c]
Hollow cathode % N_2[b]	0.0175	0.034	0.072	0.0055	(0.016)	0.0055	0.012	0.0063
No. of determinations	14	12	15	15	14	6	2	10
Standard deviation	—	—	—	0.0035	—	—	—	0.00095
Coefficient of variation	15%	20%	25%	—	7%	—	—	—

[a] Used as standard, observations extended over a period of 4 weeks.
[b] Sample weights of 4–6 mg used for the N.B.S. standards and 20–50 mg for the others.
[c] Vacuum fusion figure.

The results of analyses by this technique carried out on independently analysed samples are summarised in the Tables I to IV.

In general, there is reasonable agreement between the results obtained by the hollow-cathode technique and other methods. The apparent reproducibility is in many cases more a measure of the sample heterogeneity than the performance of the method; with the more homogeneous samples (*e.g.* the coppers), the coefficient of variation is an acceptable figure.

Estimates of the limit of detection for the respective analyses are listed in

TABLE II

DETERMINATION OF OXYGEN AND NITROGEN IN URANIUM CARBIDE

Sample	*A*	*B*	*C*	*D*
Oxygen (%)				
By vac. fusion	0.09	0.20	0.07	0.026
By hallow cathode[a]	0.12	0.20	0.06	0.024
No. of determinations	12	12	6	5
Coefficient of variation (%)	20	25	—	—
Nitrogen (%)				
By chemical method	0.051	0.037	0.037	0.022
By hollow cathode[b]	(0.051)	0.048	0.035	0.018
No. of determinations	12	9	6	6
Coefficient of variation (%)	20	23	—	—

[a] Sample weights of 8–10 mg used for Samples A, B and C and 15–25 mg for D.
[b] Sample A used for calibration.

TABLE III

DETERMINATION OF OXYGEN IN TUNGSTEN AND COPPER

Sample	*Copper*		*Tungsten*		
	1	*2*	*1*	*2*	*3*
p.p.m. O_2 (vac. fusion)	290	150	5.5	35	22
p.p.m. O_2 (hollow cathode)[a]	295	160	7.3	25	20
No. of determinations	7	4	11	5	5
Standard deviation (p.p.m.)	32	—	11.5	6.6	
Coefficient of variation (%)	11	—	—	—	—

[a] Sample weights of 30–50 mg used.

TABLE IV

DETERMINATION OF HYDROGEN IN ZIRCONIUM AND ZIRCALOYS

Sample	*Zr metal*[a]	*Zircaloy*	
		A	*B*
p.p.m. H_2	46	140	150
p.p.m. H_2 (hollow cathode)[b]	(46)	133	143
No. of determinations	11	5	4
Coefficient of variation (%)	5.0	4.6	

[a] Used for calibration.
[b] Sample weights of 20–50 mg used.

Table V. These are based on the variations in the blank readings and are quoted at the 3 σ level of significance. The improvement in the limit of detection for oxygen in steel over that previously reported has resulted from the use of the new high-dispersion monochromator. The higher limits in the analysis of uranium carbide and tungsten are inevitable because of the increased variation due to oxygen and nitrogen in the nickel "cans"; in the case of nitrogen the variation is also due to the less favourable calibration factor.

TABLE V

LIMIT OF DETECTION

Material analysed	*Limit of detection (in μg)*		
	O_2	N_2	H_2
Steel	0.35	0.55	—
Uranium carbide	1.5	2.5	—
Tungsten	0.65	—	—
Copper	0.75	—	—
Zirconium	—	—	0.05

Grateful acknowledgement is made to: The British Iron & Steel Research Association (BISRA) for supplying the Standard Steel Samples, The British Non-Ferrous Metals Research Association for the copper samples, J. A. CALDWELL of Murex Ltd. for a tungsten sample, and Mr. H. I. SHALGOSKY who arranged for the alternative methods of analysis.

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Gas chromatographic analysis of a mixture of hydrogen and oxygen with a modified sampling device*

Gas analysis of hydrogen has been extensively studied by various methods[1]. HILL AND GRIFFITH[2] designed an instrument for direct determination of hydrogen in oxygen, but there is no convenient method of analysing directly and simultaneously both hydrogen and oxygen in a gaseous mixture in very small amounts.

Gas chromatography may be used to analyse a gaseous mixture of hydrogen and oxygen in amounts of *ca.* 10^{-8} mole. The advantages of gas chromatography over gas analysis are that it is convenient and time-saving, that hydrogen and oxygen can be determined simultaneously and directly, and that the presence of other gases, *e.g.* impurities or leakage, can be detected automatically.

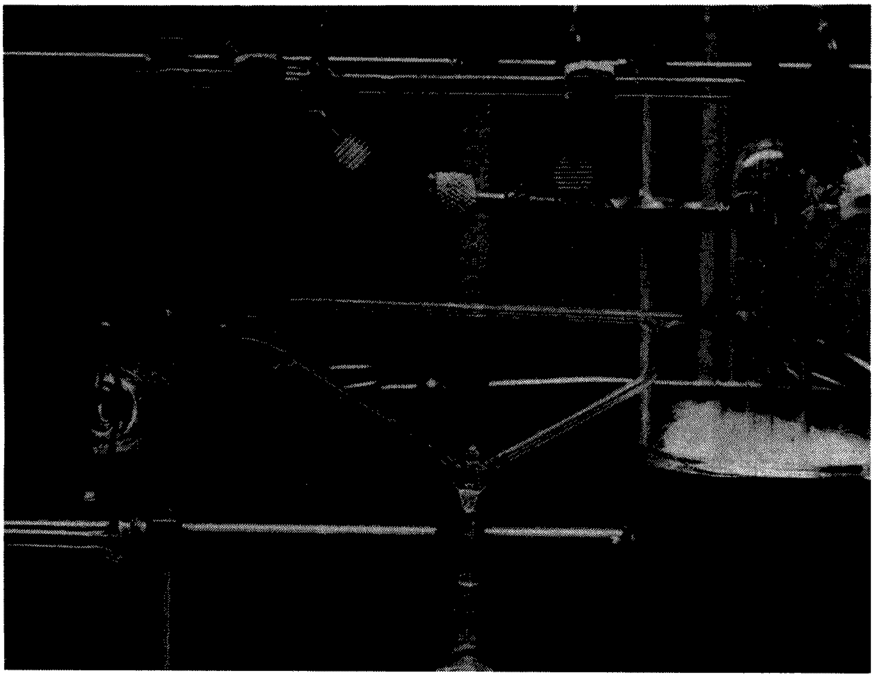

Fig. 1. Sampling device for gas chromatography.

Experimental

An Aerograph gas chromatograph (Wilkens A-90, conductivity detector) equipped with a Honeywell preamplifier (2HLA-7) and an electronic recorder was used with the following modifications.

An attempt was made to use the entire sample without loss. The original sampling device, which caused loss of sample and led to poor resolution because of dead volume, was by-passed by a specially designed triangular sampling device (Fig. 1). The gaseous sample was collected by a Toepler pump, which transports and concentrates the gases without loss, and was stored in the left branch of the device. The carrier gas continuously passed into the column through the horizontal limb of the device. By suitable manipulation of the 3-way pressure stopcocks, the gas sample was completely pushed into the column by carrier gas flowing through the right and left arms of the device. It was also found that a smaller diameter in the storage section than that in the pipe-line favored better resolution. The design is recommended where no loss of sample can be tolerated.

Argon, instead of helium, was chosen in order to have strong signal for hy-

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* This work represents part of a research project supported by the U.S. Atomic Energy Commission, and submitted in partial fulfilment of requirements for the Ph.D. degree at the University of Minnesota, Minneapolis, Minnesota, U.S.A. The work was completed at National Taiwan University.

drogen and fair good signal for oxygen. Since the Aerograph instrument was originally designed for helium, and helium has a much larger conductivity than argon, an additional resistance had to be added to balance the pen of the recorder in the range of operation. A 10-ft. molecular sieve 5A column was selected for best separation.

Results

A chromatogram for a mixture of hydrogen and oxygen with an amount of the order of 10^{-7} mole is shown in Fig. 2. The initial instability in the base line is due to a shift in the flow path of the carrier gas on manipulating the stopcocks.

Seventeen runs with oxygen–hydrogen molar ratios ranging from 0.4 to 3.1 were carried out to confirm the independent responses of hydrogen and oxygen as well as the reproducibility. The results agreed with the calculated values for known mixtures within the experimental error[3]. Any leak in the vacuum system could be detected from an increased peak height for oxygen and the appearance of a peak for nitrogen.

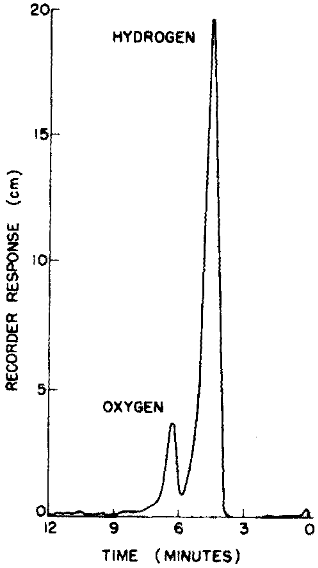

Fig. 2. Typical chromatogram. Detector temperature, 110°; column temperature, 35°; filament current, 110 mA; outlet pressure, 35 psi; flow rate, 61.2 ml/sec.

The helpful advice of Prof. HERBERT S. ISBIN in this work is very greatly appreciated.

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(Received March 23rd, 1966)

BOOK REVIEWS

R. THEISEN, *Quantitative Electron Microprobe Analysis*, Springer Verlag, Berlin, 1965, iv + 170 pp., price DM 24.—.

THEISEN reviews briefly a number of factors to be considered in obtaining quantitative information from the electron probe microanalyser. He then considers in greater detail the non-linearity between emerging X-ray intensity and concentration arising from the atomic number dependence of X-ray absorption, electron absorption and electron backscatter, and gives in outline the development of his own method for correcting a simple linear relation to take account of these effects. Unfortunately, the argument is so obscured by the omission of important steps and symbols, inadequate definition of variables and confused notation that the reader is left in no position to assess its validity. The detailed review of correction procedures by other authors, promised on an early page, is never forthcoming, although some of these are given brief, but not always accurate, mention. The reviewer has found misleading errors in the appended list of references and incorrect numbering of references in the text.

The latter and major part of the book is devoted to compilations of data and computed tables to facilitate the calculation of concentration using the formula finally developed by THEISEN and incorrectly quoted on page 17. It is claimed that greater success has been obtained with this formula, when tested on more than a hundred results from different laboratories, than with previous, unspecified, methods. The reviewer has tested the formula on 23 results, from 3 different laboratories and found a mean relative error of 13.5% after correction, compared with 1.4% using another method and 11.9% for the uncorrected data. In the course of carrying out these calculations, inaccuracies were detected in the table of wavelengths and the excitation potentials quoted for the L and M lines were found to be incorrect; the table of effective Lenard coefficients contains at least one error. The compilation of X-ray absorption coefficients is of doubtful value since the reference made to the recent measurements on which it is based is too vague to permit their accuracy to be compared with that of previous measurements. The advantage of having tables of computed data is to a large extent offset by the effort and time involved in performing quite complicated interpolations between the values presented. The calculation certainly takes longer than the few minutes indicated.

The reviewer would hesitate to commend this book to either of the two groups of microanalysts the author has in mind, the average user whose interest is in a quick and reliable method for processing his data or the more critical reader who is looking for a clearly presented review of the physical basis of correction procedures.

P. M. MARTIN (Harwell)

Treatise on Analytical Chemistry. Part II. Analytical Chemistry of Inorganic and Organic Compounds, Vol. 11 (section B: Organic Analysis), Edited by I. M. KOLTHOFF AND P. J. ELVING, Interscience Publishers – J. Wiley and Sons, Inc., New York, 1965, xxii + 573 pp., price 150 s.

Ce volume contient les chapitres suivants: nomenclature des liaisons organiques (43 p.), stabilité des liaisons organiques (10 p.), cinétique des réactions organiques (53 p.), détermination de constantes physiques (20 p.), analyses biologiques (env. 50 p.). La seconde partie traite de la détermination des éléments dans les substances organiques en 4 chapitres dont un est consacré à la description des ultramicro-méthodes pour le détermination des C–H, du N, des halogènes, du P et des différents groupements fonctionnels (env. 70 p.). Dans les chapitres suivants sont exposées les méthodes pour la détermination des C–H (env. 100 p.), azote (d'après DUMAS et KJELDAHL, env. 80 p.). En conclusion du volume, les méthodes de détermination du phosphore dans les substances organiques sont décrites (env. 50 p.).

Le chapitre des ultramicro-méthodes nous donne une vue d'ensemble de tous les procédés connus et requis pour tous les éléments des substances organiques.

Lors de la description des méthodes pour la détermination de C–H, on trouve des indications étendues quant à l'appareillage, aux réactifs, à la technique de combustion, ainsi qu'à l'élimination des éléments gênants. En ce qui concerne les méthodes pour la détermination de l'azote, les diverses modifications du procédé de DUMAS sont exposées et les différentes parties de l'appareillage modifié sont dûment expliquées. Dans la méthode KJELDAHL, en plus de la description du procédé, on a évoqué les liaisons azotées pour lesquelles cette méthode est défectueuse.

Le dernier chapitre traite la détermination du phosphore dans les composés organiques. Après énumération des divers procédés de minéralisation, des méthodes gravimétriques, volumétriques et physiques pour la détermination de l'acide phosphorique sont décrites. Des procédés pour l'élimination des éléments gênants sont donnés. Par contre la titration avec du cérium(III), qui, en combinaison avec la combustion dans un flacon rempli d'oxygène, représente une méthode simple et sûre, n'a pas été retenue par les auteurs.

Après un premier examen de ce volume, on garde une impression mitigée, de la confusion tout d'abord provenant du fait qu'il est difficile de savoir sur quelles bases ont été établies l'ordonnance des diverses matières. Une abondance de renseignements, de références ensuite, qui si elle alourdit le texte, sera néanmoins précieuse aux spécialistes de ces questions.

D. MONNIER (Genève)

Treatise on Analytical Chemistry. Part II. Analytical Chemistry of Inorganic and Organic Compounds, Vol. 12 (section B: Organic Analysis (continued)), Edited by I. M. KOLTHOFF AND P. J. ELVING, Interscience Publishers – J. Wiley and Sons, Inc., New York, 1965, 383 pp., price 113 s.

Ce volume traite du dosage des éléments suivants dans les composés organiques: oxygène (57 p.), soufre (60 p.), fluor (52 p.), bore (72 p.), silicium (54 p.), métaux (78 p.).

Parmi les méthodes examinées pour la détermination de l'oxygène, la méthode gravimétrique est décrite de façon approfondie; l'exposé est complété par des dessins très détaillés de l'appareillage. Il est regrettable par contre que la méthode iodométrique d'UNTERZAUCHER, qui présente beaucoup d'avantages et qui est certainement plus utilisée que la méthode gravimétrique, ne soit traitée que superficiellement.

Dans le chapitre concernant le soufre, les procédés connus de la destruction de la substance organique par réduction ou oxydation et de la détermination du sulfure ou du sulfate ainsi formé, par des méthodes gravimétriques, volumétriques ou physiques sont décrits. Des méthodes permettant la détermination simultanée du soufre et d'autres éléments, comme les halogènes, phosphore, etc. sont aussi évoquées.

Dans la description des méthodes de dosage du fluor, différents procédés de minéralisation sont indiqués. Les éléments gênants sont cités ainsi que les méthodes permettant leur élimination. La détermination du fluor après la minéralisation par des méthodes gravimétriques, volumétriques et physiques est énumérée et en partie décrite d'une manière étendue. En fin de chapitre, les méthodes éprouvées sont soulignées. Lors de la description de la séparation de HF par distillation, le très simple appareillage de ROTH (voir HOUBEN–WEYL, vol. II, p. 136) ainsi que l'emploi de vapeur d'eau surchauffée n'ont pas été retenus par l'auteur.

Le chapitre traitant du bore comprend tout d'abord les méthodes de minéralisation puis les différentes possibilités de détermination de l'acide borique. Comme procédés recommandables, la combustion dans le flacon rempli d'oxygène et la méthode de CARIUS, suivi par une titration de l'acide borique, sont proposés. Pour la détermination du silicium dans les substances organiques, différents procédés de minéralisation sont décrits comme dans les chapitres précédents, ainsi que des méthodes de détermination du SiO_2. Au chapitre "autres éléments" les méthodes de minéralisation des substances organiques qui contiennent des métaux sont données mais on ne trouve aucune indication sur la détermination de ces éléments eux-mêmes.

La bibliographie est bien faite et on y trouve un grand nombre de références mais on peut se demander si chaque publication doit être citée lorsqu'elle ne donne que des modifications peu importantes d'un procédé déjà connu.

On peut considérer comme positif et intéressant le chapitre concernant les méthodes recommandables qui sont décrites très exactement. C'est sur ce point qu'il aurait fallu insister alors que de nombreuses répétitions auraient pu être évitées. Par exemple la méthode de flacon rempli d'oxygène est traitée dans le chapitre du soufre à la page 80 et une seconde fois dans le même chapitre à la page 104. De plus on la trouve plus ou moins décrite dans l'exposé sur le fluor (p. 148) et le bore (p. 192) bien que cette technique soit identique pour tous ces éléments.

D. MONNIER (Genève)

Anal. Chim. Acta, 36 (1966) 411

P. DELAHAY, *Double Layer and Electrode Kinetics*, Interscience Publishers – J. Wiley and Sons, Inc., New York, 1965, xi + 321 pp., price 110 s.

This book is concerned with the essential ideas underlying the present understanding of the electrical double layer and electrode kinetics. The interrelationship between these two fields has not always been sufficiently stressed in the past. It is evident, however, that a satisfactory interpretation of the results of electrode kinetic measurements can only be made if the role of the electrical double layer is taken into account. A monograph which emphasises and illustrates this point is therefore welcome.

After a brief historical introduction, the book is divided into two parts of approximately equal length. Part I deals with the electrical double layer and is complete in itself. Part II deals with electrode kinetics, relying on much of the material developed in Part I. This is the essential feature of the book, namely the treatment of electrode kinetics in relation to the properties of the electrical double layer. Mass transfer, methodology and instrumentation, which are dealt with extensively elsewhere, are only briefly mentioned. Such specialized topics as electrocrystallization, anodic films and semiconductor electrodes have been omitted.

The material is presented in a clear and concise manner. The ideas are developed in mathematical form and illustrated by a large number of results on specific systems drawn from a wide range of sources. These are generally systems in aqueous solution but systems involving non-aqueous solutions and molten salts are also briefly mentioned. An extensive list of references is given at the end of each chapter.

The book will provide an excellent background for the reader interested in electrode reactions, and will prove stimulating to those who have more experience in this field.

D. R. WHITEHOUSE (Birmingham)

VOL. 36 NO. 3 ANALYTICA CHIMICA ACTA NOVEMBER 1966

CONTENTS

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152E