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2. F. FEIGL, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

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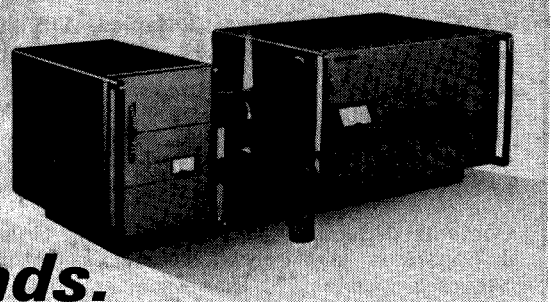

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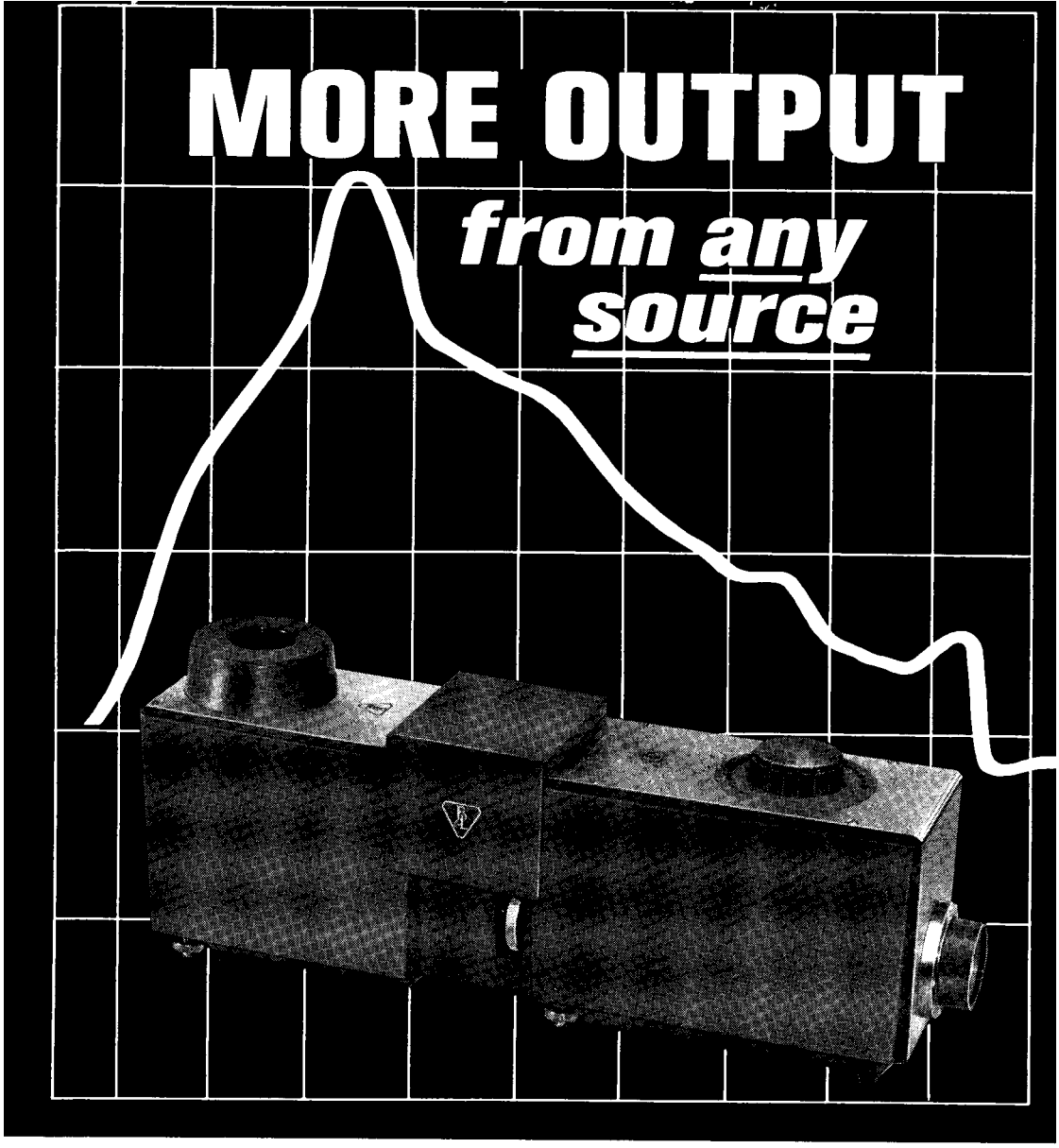

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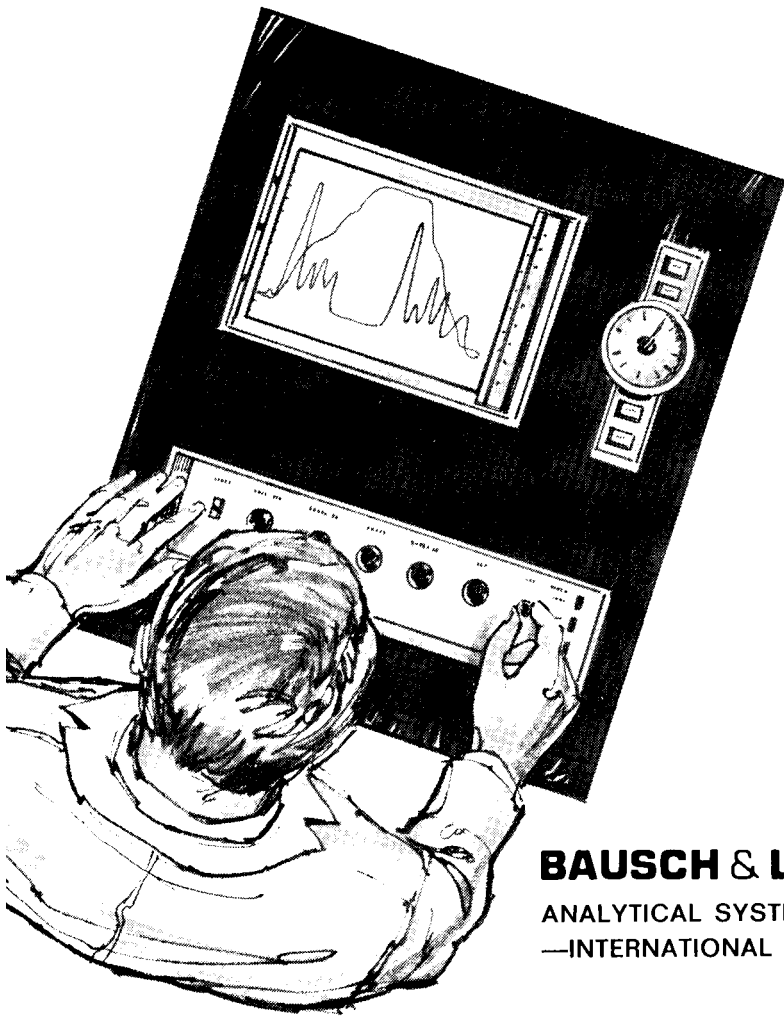

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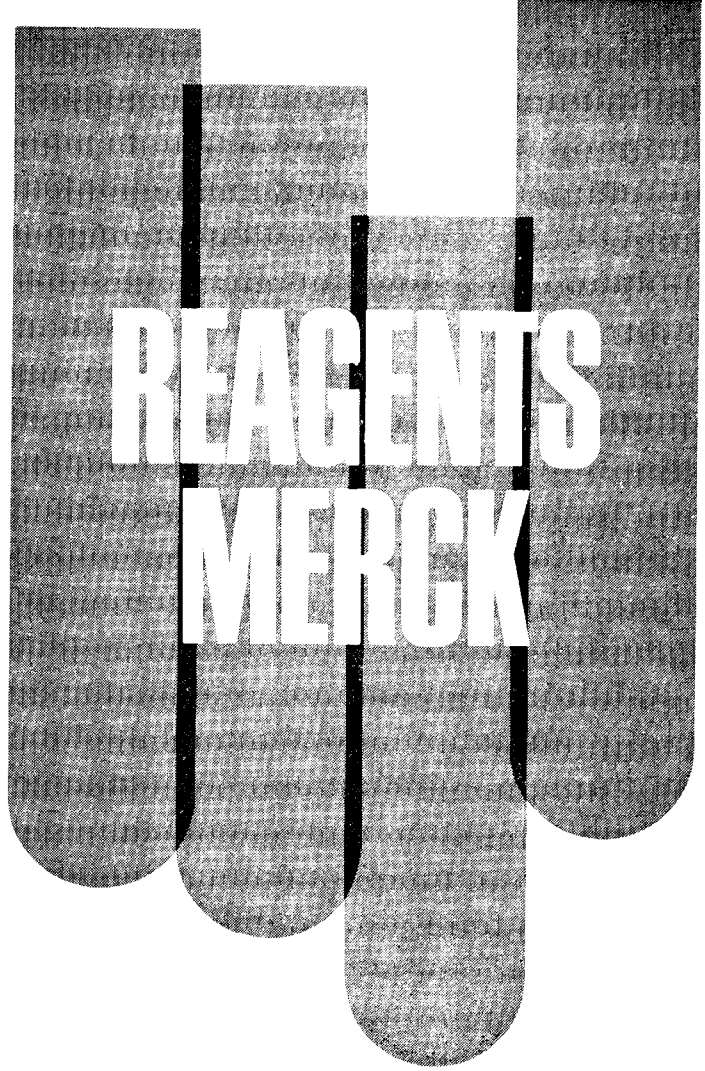

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 43, No. 1, October 1968

NEUTRON ACTIVATION ANALYSIS OF HIGH-PURITY SELENIUM

PART III. DETERMINATION OF PHOSPHORUS, SULFUR AND CHLORINE

Chlorine was determined in selenium by irradiation of 2-g samples for 37 min at a flux of $8 \cdot 10^{10}$ n/cm²/sec. Chlorine was volatilised from hot concentrated nitric acid and precipitated as silver chloride. The isotope ^{38}Cl ($T_{\frac{1}{2}} = 37.3$ min) was counted by γ-spectrometry. Sulfur and phosphorus were determined by irradiating 50-mg samples with and without cadmium shielding for 4 days at a thermal flux of $6 \cdot 10^{12}$ n/cm²/sec and a fast flux of $4 \cdot 10^{11}$ n/cm²/sec. The matrix activities were separated by distillation from sulfuric acid–hydrobromic acid at 200–220°. The isotope ^{32}P ($T_{\frac{1}{2}} = 14.3$ d) was then precipitated, together with phosphate carrier, as ammonium phosphomolybdate, and counted with a G.M. tube. Amounts of 0.4–1 p.p.m. chlorine, 65–520 p.p.b. phosphorus and 1.5–4.6 p.p.m. sulfur were found in high-purity selenium samples.

C. Ballaux, R. Dams and J. Hoste,
Anal. Chim. Acta, 43 (1968) 1–11

DETERMINATION OF CHROMIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY OF CHROMIUM ACETYLACETONATE

DETERMINATION OF CHROMIUM IN SEA WATER

A sensitive atomic absorption method is described for the determination of chromium at sub-microgram levels. Chromium(III) is converted to its acetylacetone complex and extracted into MIBK. The atomic absorption sensitivity is thus enhanced two-fold compared to chromium(III) in aqueous medium. The detection limit of chromium is 0.015 p.p.m. with an acetylene–air flame; the sensitivity obtained with other chromium methods under the same instrumental conditions is compared. The method can be applied to the determination of chromium in sea water; at a level of *ca.* 1.6 μg Cr/l, the precision is $\pm$ 0.06 μg/l.

Yiu-Kee Chau, Soo-San Sim and Yu-Hou Wong,
Anal. Chim. Acta, 43 (1968) 13–18

A NEW APPLICATION OF ATOMIC ABSORPTION SPECTROPHOTOMETRY

DETERMINATION OF PHTHALIC ACID BY SOLVENT EXTRACTION WITH NEOCUPROINE–COPPER(I) CHELATE

A new application of atomic absorption spectrophotometry is reported for the determination of phthalic acid. Phthalic acid is extracted as the ion-pair formed between bis(neocuproine)–copper(I) and the univalent anion of phthalic acid with MIBK; the copper concentration in the extract is then determined by atomic absorption in an air–acetylene flame at the 3247 Å copper line. Optimal conditions are described. The absorbance of the extract showed a linear relationship to the concentration of phthalic acid initially present in the aqueous solution over the range of $4 \cdot 10^{-6}$ to $4 \cdot 10^{-5}$ *M*. The effect of some analogous aromatic carboxylic acids on the phthalate extraction and the composition of the extracted species were also investigated.

T. Kumamaru,
Anal. Chim. Acta, 43 (1968) 19–25

DETERMINATION OF IMPURITIES IN URANIUM COMPOUNDS BY ATOMIC ABSORPTION

A method is described for the determination of 14 elements (Al, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Zn) in uranium and uranium compounds by atomic absorption spectroscopy. A sample is dissolved in 6–8 *N* nitric acid from which the uranium is selectively removed by a single extraction with tributyl phosphate. The aqueous layer is evaporated to dryness and the residue is re-dissolved in 0.2 *N* hydrochloric acid. Any or all of the elements can then be determined in this one solution by atomic absorption spectroscopy. The limits of error in the analyses are less than 10%. Thus, the method gives about the same precision as colorimetric procedures, and it is much more precise than emission spectroscopy.

C. R. WALKER AND O. A. VITA,
Anal. Chim. Acta, 43 (1968) 27–35

ADVANCES IN THE USE OF COMPUTER TECHNIQUES IN FLAME PHOTOMETRY

The range and complexity of the application of computer techniques in flame photometry methods has been extended. Improvements in output formatting are detailed and typical automated analyses are presented. Examples are discussed from both mathematical and analytical points of view. The potential of graphic display consoles is explained in detail.

J. L. MALAKOFF, J. RAMÍREZ-MUÑOZ AND C. P. AIME,
Anal. Chim. Acta, 43 (1968) 37–46

AUTOMATIC CHROMATOGRAPHY OF HYDROXY ACIDS ON ANION-EXCHANGE RESINS

Hydroxy acids are separated on an anion-exchange column and determined automatically by three colorimetric methods: chromic acid oxidation, periodate oxidation and the carbazole reaction. The simultaneous application of three methods facilitates both identification and determination.

B. CARLSSON, T. ISAKSSON AND O. SAMUELSON,
Anal. Chim. Acta, 43 (1968) 47–52

THE SOLUTION CHEMISTRY OF ETHYLMETHYLGLYOXIME

PART I. THE PROTON COMPLEX

The solubility of ethylmethylglyoxime (EMG) was studied as a function of pH. The solubility K_{s1} in 0.1 *M* aqueous solution is 0.0132 ± 0.0006 *M*. The distribution constants K_{D1} of EMG between various organic solvents and 0.1 *M* aqueous solution were found to be −0.47 for chloroform, −0.51 for benzene, −1.10 for carbon tetrachloride and −1.83 for hexane. The acid dissociation constants were determined from potentiometric titrations; the values $pK_{s1} = 10.51$ and $pK_{s2} = 12.02$ were obtained by fitting the experimental data to normalized curves. The UV spectra of $5 \cdot 10^{-5}$ *M* EMG solutions of varying pH were measured between 210 and 290 nm. It is shown that H_2A has an absorption maximum at 226 nm and HA^- and A^{2-} have absorption maxima at nearly the same wavelengths, *i.e.* 258 and 266 nm, respectively. The spectra of HA^- and A^{2-} have approximately the same form. The data are compared with those of dimethylglyoxime (DMG). The distribution constants (org/aq) are 4–5 times higher for EMG. The acid dissociation constants are about the same for EMG and DMG, but EMG is more soluble in water than DMG (13.2 and 5.0 mmoles/l, respectively). The UV spectra of EMG and DMG are very similar.

B. EGNEUS,
Anal. Chim. Acta, 43 (1968) 53–62

POLAROGRAPHIC STUDIES OF URANYL COMPLEXES WITH *TRANS*- AND *CIS*-BUTENEDIOIC ACIDS

The complexation of uranyl ion with fumaric and maleic acids was investigated by polarography and conductometry. The uranyl complexes of the two isomers differ: with fumaric acid, $UO_2(HFum)_2$ and $UO_2Fum_2^{2-}$ were observed whereas with maleic acid, only one chelate, $UO_2Mal_2^{2-}$, was obtained. The dissociation constants obtained from the half-wave potential *vs.* pH plots were $pK_1 = 3.05$ and $pK_2 = 4.55$ for fumaric acid and $pK_1 = 1.90$ and $pK_2 = 5.60$ for maleic acid.

T.-T. Lai and T.-Y. Chen,
Anal. Chim. Acta, 43 (1968) 63–70

NEPHELOMETRIC DETERMINATION OF GOLD WITH DI-2-THIENYLKETOXIME

A nephelometric method for the determination of microgram quantities of gold with di-2-thienylketoxime is described. The yellow gold complex, which has the empirical formula $Au(C_9H_6NOS_2)_2OH$, forms a stable suspension when gelatin is added as protective colloid. Many foreign ions do not interfere in 5-fold amounts. If necessary, a preliminary isopropyl ether extraction of gold can be used.

W. J. Holland and J. Gerard,
Anal. Chim. Acta, 43 (1968) 71–75

POTENTIOMETRIC TITRATIONS WITH ION-EXCHANGING MEMBRANE ELECTRODES

PART III. EXPERIMENTAL RESULTS

Potentiometric titrations with ion-exchanging membrane electrodes for end-point detection are described for simple precipitation and acid–base reactions. When only monovalent ions are present, there is a qualitative agreement between the titration curves obtained and the theoretically calculated curves.

F. P. IJsseling and E. van Dalen,
Anal. Chim. Acta, 43 (1968) 77–87

DISSOCIATION CONSTANTS OF N,N′-BIS(2-CARBOXYETHYL)DITHIOOXAMIDE

The dissociation constants of N,N′-bis(2-carboxyethyl)dithiooxamide have been determined by potentiometric and spectrophotometric methods. They were calculated by a modified Ricci formula and by a weighted least-squares treatment. The thermodynamic constant pK_3^T is 12.32. At ionic strength 1.00, $pK_1 = 3.76$, $pK_2 = 4.74$, $pK_3 = 11.41$ and $pK_4 = 14.19$.

G. L. Van de Cappelle and M. A. Herman,
Anal. Chim. Acta, 43 (1968) 89–94

THE ANALYSIS OF SILVER(II) OXIDE

Five methods for the analysis of silver(II) oxide have been critically examined and modified procedures are proposed. The effects of varying temperature, solution composition, and amount of oxide have been studied for methods based on (*a*) the oxidation of iron(II) sulphate in the presence of sulphuric acid or acetate-buffered media; (*b*) the oxidation of iodide ion in neutral saturated solution or in acetate-buffered solution, and (*c*) the oxidation of water to yield oxygen from strong acid solutions.

C. P. Lloyd,
Anal. Chim. Acta, 43 (1968) 95–107

ATOMIC FLUORESCENCE SPECTROSCOPY OF BERYLLIUM

The atomic fluorescence of beryllium has been observed. A high-intensity beryllium hollow-cathode lamp was used as the source. Oxy–acetylene and nitrous oxide–acetylene flames were studied. A newly designed burner assembly for nitrous oxide–acetylene flames used for atomic fluorescence studies is described. The sensitivity for beryllium at 2349 Å was 10 p.p.m. in the oxy–acetylene flame and 0.5 p.p.m. in the nitrous oxide–acetylene flame. The analytical calibration curves for both flames are presented. No significant interference was found from the cations studied. Some anionic interferences were removed by EDTA. The effects of some organic solvents were investigated.

J. W. Robinson and C. J. Hsu,
Anal. Chim. Acta, 43 (1968) 109–117

DETECTION OF GASEOUS ORGANIC COMPOUNDS BY THEIR INFRA-RED EMISSION STIMULATED BY A LASER BEAM

Excitation by a carbon dioxide laser has been used to obtain the infra-red emission spectra of a number of gaseous aliphatic hydrocarbons. The experimental set-up is described and the spectra obtained are correlated with bond vibrations and are shown to be similar to infra-red absorption spectra. The future requirements of this technique are discussed and its analytical possibilities are indicated.

J. W. Robinson, C. Woodward and H. M. Barnes,
Anal. Chim. Acta, 43 (1968) 119–128

m-CHLOROPERBENZOIC ACID AS A REAGENT FOR THE DETERMINATION OF UNSATURATION IN NATURAL AND CYCLIZED RUBBER

(Short Communication)

E. Gipstein, F. Nichik and J. A. Offenbach,
Anal. Chim. Acta, 43 (1968) 129–131

INDIRECT DETERMINATION OF SODIUM AND POTASSIUM IN MIXTURES BY EXTRACTION OF THEIR DIPICRYLAMINATES INTO NITROBENZENE

(Short Communication)

M. Kyrš, M. Pivoňková and P. Selucký,
Anal. Chim. Acta, 43 (1968) 132–134

THE DETECTION OF TRACES OF BARIUM OR STRONTIUM BY INDUCED PRECIPITATION

(Short Communication)

A. Vaughan and A. Townshend,
Anal. Chim. Acta, 43 (1968) 134–136

THE ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM BY THE MOLYBDOVANADOPHOSPHORIC ACID METHOD

(Short Communication)

R. Jakubiec and D. F. Boltz,
Anal. Chim. Acta, 43 (1968) 137–140

THE MASS SPECTRA OF ORGANIC MOLECULES

by J. H. Beynon, R. A. Saunders and A. E. Williams, Research Department, Imperial Chemical Industries Ltd., Manchester, Great Britain

7 x 10″, ix + 510 pages, 20 tables, 181 illus., 547 lit. refs., 1968, Dfl. 97.50

Contents: 1. The principles and methods of mass spectrometry. 2. Types of ions in the mass spectra of organic compounds. 3. The mass spectra of hydrocarbons. 4. The mass spectra of oxygenated compounds. 5. The mass spectra of nitrogen compounds. 6. The mass spectra of sulphur compounds. 7. The mass spectra of halogenated compounds. 8. The mass spectra of boron compounds. 9. The mass spectra of phosphorus compounds. 10. The mass spectra of silicon compounds. 11. Examples of structure determination from mass spectra. Appendix 1. Peaks commonly encountered in the mass spectra of organic compounds. Appendix 2. The masses and abundances of nuclides commonly encountered in the mass spectra of organic compounds. References. Indexes.

MASS SPECTROMETRIC ANALYSIS OF SOLIDS

edited by A. J. Ahearn, Member of Technical Staff, Bell Telephone Laboratories, Inc., Murray Hill, New Jersey, U.S.A.

5½ x 8½″, viii + 175 pages, 13 tables, 46 illus., 242 lit. refs., 1966, Dfl. 30.00

Contents: 1. Introductory survey. 2. The production of ions from solids. 3. Photographic emulsions as ion detectors in quantitative mass spectrography. 4. Analysis of special samples. 5. Mass spectrographic microprobe analysis. Indexes.

ATOMIC-ABSORPTION SPECTROSCOPY

and Analysis by Atomic-Absorption Flame Photometry

by J. Ramírez-Muñoz, Principal Applications Chemist at Beckman Instruments Inc. and Scientific Research Collaborator of the C.S.I.C., Spain

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NEUTRON ACTIVATION ANALYSIS OF HIGH-PURITY SELENIUM

PART III. DETERMINATION OF PHOSPHORUS, SULFUR AND CHLORINE

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(Received May 6th, 1968)

In previous papers[1,2] the determination of bromine and tellurium were described. Other important impurities are phosphorus, chlorine and especially sulfur. These elements have already been determined in various materials[3,4] and in selenium[5–8]. Chlorine is usually determined by γ-spectrometry of the short-lived ^{38}Cl after separation by volatilisation and precipitation as silver chloride. For large concentrations (>10 p.p.m.) non-destructive activation analysis of chlorine in selenium can be applied[7]. When a double irradiation technique is used, sulfur and phosphorus can be determined through the isotope ^{32}P or sulfur and chlorine through the isotope ^{35}S. A separation of the matrix activities was obviously required: precipitation of selenium in the elementary state and sulfide precipitation of arsenic and germanium were found to be satisfactory.

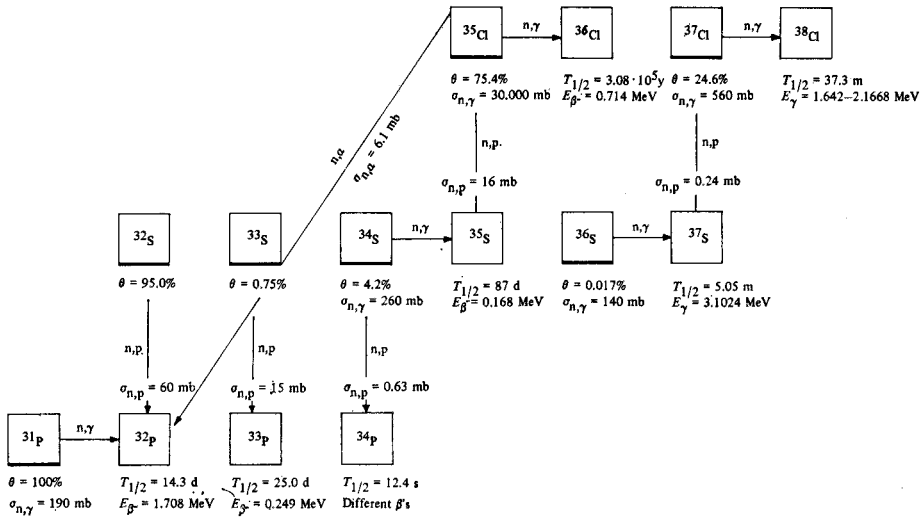
NUCLEAR DATA, IRRADIATION CONDITIONS AND INTERFERENCES

Reactor neutron irradiation of the elements phosphorus, sulfur and chlorine gives rise to the isotopes listed in Table I[9–12]. From this Table the various methods of determination for these elements and the nuclear interferences are apparent. In the present work, chlorine was determined by counting ^{38}Cl while sulfur and phosphorus were determined through the ^{32}P-activities from cadmium-covered and uncovered samples. These activities were corrected for the contribution of the exo-ergic $^{35}Cl(n,\alpha)^{32}P$ reaction and for the $^{31}P(n,\gamma)^{32}P$ and $^{32}S(n,p)^{32}P$ reactions. This method seemed preferable to the counting of the low-energy ^{35}S, especially since this reaction is interfered with by the exo-ergic reaction $^{35}Cl(n,p)^{35}S$. Short irradiations favour the $^{32}S(n,p)^{32}P$ over the $^{34}S(n,\gamma)^{35}S$ reaction, as the half-lives are respectively 14.3 and 87 d. The counting of ^{36}S was not considered, as the natural abundance and the activation cross-section of ^{36}S are too small to be applied in activation analysis.

When the double irradiation technique is applied with ^{32}P counting, one can expect that the chlorine concentration should not exceed certain limits compared to the sulfur and phosphorus contents. The same consideration is true for the ratios of sulfur to phosphorus. OP DE BEECK AND HOSTE[13] calculated the amounts of sulfur and phosphorus which can be determined simultaneously, as a function of irradiation

TABLE I

NUCLEAR PROPERTIES OF PHOSPHORUS, SULFUR AND CHLORINE



time and thermal-to-fast neutron fluxes:

$$g_S \leqslant \frac{k'}{4}\left(\frac{1}{k'}-\frac{1}{k}\right)^2 \varepsilon N \frac{f^2{}_t}{f_t}\left(\frac{\sigma\cdot\theta}{M}\right)_P^2\left(\frac{M}{\sigma\cdot\theta}\right)_S\left(1-\exp-\frac{0.693 t_{irr}}{T_{\frac{1}{2}}}\right)\frac{t_1 t_2}{t_1+t_2} g_P{}^2 \qquad (1)$$

$$g_P \leqslant \frac{k}{4}\left(\frac{1}{k'}-\frac{1}{k}\right)^2 \varepsilon N \frac{f^2{}_t}{f_t}\left(\frac{\sigma\cdot\theta}{M}\right)_S^2\left(\frac{M}{\sigma\cdot\theta}\right)_P\left(1-\exp-\frac{0.693 t_{irr}}{T_{\frac{1}{2}}}\right)\frac{t_1 t_2}{t_1+t_2} g_S{}^2 \qquad (2)$$

where g_S, g_P = amounts of sulfur and phosphorus
k, k' = cadmium ratios of phosphorus and sulfur
ε = counting efficiency
N = Avogadro's number
f_t, f_f = thermal and fast neutron fluxes
M = atomic mass
t_1, t_2 = counting time of the samples

Equations (1) and (2) include the condition that the count rate of ^{32}P through the $^{31}P(n,\gamma)^{32}P$ reaction is at least two times higher than the standard deviation on the count rate of ^{32}P through the $^{32}S(n,p)^{32}P$ reaction for the irradiation without cadmium and *vice versa* for the irradiation under cadmium.

When the amount of sulfur is much higher than that of phosphorus, an irradiation in the reflector of the reactor can be performed; in the inverse case an irradiation in the core of the reactor becomes necessary.

The activities A_1 and A_2 (counts/min/g sample) in the cadmium-covered and in the uncovered sample are as follows:

$$A_1 = a_1[P] + b_1[S] + c_1[Cl] \qquad (3)$$

$$A_2 = a_2[P] + b_2[S] + c_2[Cl] \qquad (4)$$

where the square brackets represent concentrations in μg/g sample.

a = counts/min ^{32}P per μg P due to the $^{31}P(n,\gamma)^{32}P$ reaction
b = counts/min ^{32}P per μg S due to the $^{32}S(n,p)^{32}P$ reaction
c = counts/min ^{32}P per μg Cl due to the $^{35}Cl(n,\alpha)^{32}P$ reaction.
Values for a, b and c can be determined from phosphorus, sulfur and chlorine standards.

After the determination of the chlorine concentration by an irradiation for 37 min at a flux of $8 \cdot 10^{10}$ n/cm^2/sec (Thetis reactor) and counting ^{38}Cl, the sulfur and phosphorus concentrations can be calculated from eqns. (3) and (4). The specific activities of ^{32}P, due to phosphorus, sulfur and chlorine, irradiated for 4 days at a site of the BR-2 reactor, are listed in Table II. The ratios $k = a_2/a_1$, $k' = b_2/b_1$ and $k'' = c_2/c_1$ are the well-known cadmium ratios, with values of 141, 1.11 and 1.14, respectively. As can be seen from this Table, if the 3 elements are present in equal amounts, the interference of sulfur and chlorine on the phosphorus content will be 2.1 and 0.6%. If these elements are irradiated under cadmium, a positive error in the sulfur content of 37.0% will be caused by phosphorus and a positive error of 26.5% by chlorine.

TABLE II

SPECIFIC ACTIVITIES OF ^{32}P DUE TO PHOSPHORUS, SULFUR AND CHLORINE

	a	b	c
Irradiation without Cd $f_t = 6 \cdot 10^{12}$ n/cm^2/sec	22.784	487	132
Irradiation with Cd $f_t = 4 \cdot 10^{11}$ n/cm^2/sec	162	438	116

Under the stated irradiation conditions, the cadmium ratio of phosphorus is large while those of sulfur and chlorine are rather small. The limits of the sulfur to phosphorus ratios, which can be calculated from eqns. (1) and (2), are therefore relatively large:

$$g_P \geq 3.5 \cdot 10^{-3} \sqrt{g_S} \qquad g_S \geq 1.1 \cdot 10^{-1} \sqrt{g_P}$$

The experimental values:

$$g_P \geq 1.9 \cdot 10^{-3}\ \mu g \qquad g_S \geq 0.59 \cdot 10^{-1}\ \mu g$$

for 1 μg of sulfur or phosphorus respectively are in reasonable agreement with these data, if one considers that g_P and g_S are proportional to the square of the neutron flux.

Furthermore, it appears from Table II that the chlorine content should not exceed 20 times that of sulfur and about 952 times that of phosphorus, if the same statistical conditions are taken into account.

The interferences $^{33}S(n,p)^{33}P$ and $^{30}Si(n,\gamma)^{31}Si \xrightarrow{\beta^-} {}^{31}P(n,\gamma)^{32}P$ on the determination of sulfur and phosphorus and the interferences $^{38}Ar(n,p)^{38}Cl$ ($\sigma = 0.7$ mb[12]), $^{41}K(n,\alpha)^{38}Cl$ ($\sigma = 2.4$ mb[12]) and $^{36}S(n,\gamma)^{37}S \xrightarrow{\beta^-} {}^{37}Cl(n,\gamma)^{38}Cl$ on the determination of chlorine can be neglected as the concentrations of these elements, if present at all, are very low.

DETERMINATION OF CHLORINE

Chemical separation

Non-destructive activation analysis of chlorine in the selenium samples under investigation appeared to be impossible. γ-Spectrometry shows only the photopeaks of ^{83}Se (1.309 and 1.880 MeV) in the energy region of the ^{39}Cl photopeaks (1.642 and 2.1668 MeV). Discrimination against lower-energy radiation and the use of a lead absorber do not substantially improve the situation. Thus, a fast and efficient separation technique for chlorine had to be developed. The volatilisation of chlorine from hot concentrated nitric acid was studied with tracers; 98.6% of the chlorine could be absorbed in ice-cooled silver nitrate solution. The decontamination from the isotopes ^{75}Se, ^{76}As and ^{22}Na was very satisfactory. About 45 min after the end of irradiation, the silver chloride precipitate was ready to be counted.

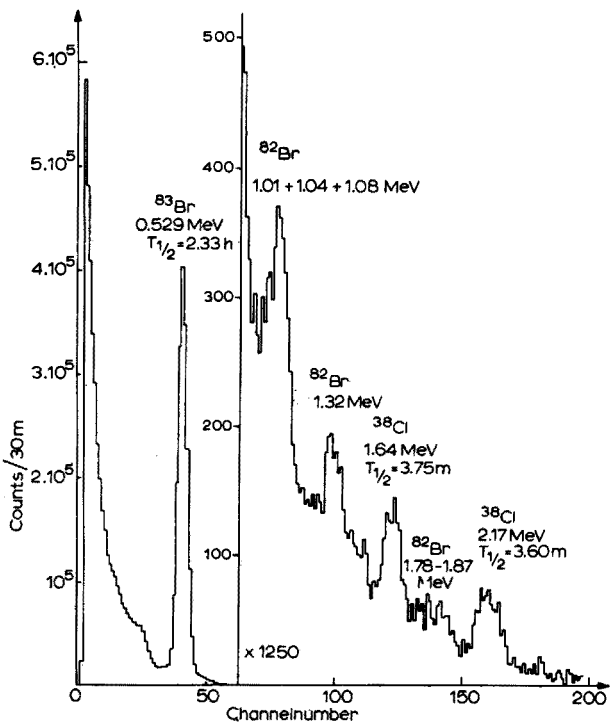
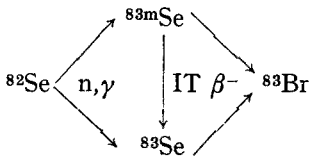


Fig. 1. γ-Spectrum of the ^{38}Cl-fraction separated from irradiated selenium.

Counting

Figure 1 shows the γ-spectrum of a silver chloride precipitate, separated from 2 g of selenium which had been irradiated during 37 min at a neutron flux of $8 \cdot 10^{10}$ n/cm^2/sec. The sample was measured for 30 min with a $3 \times 3''$ NaI(Tl) detector, coupled to a 400-channel pulse-height analyser. Decay curve analysis of the activities measured at 1.64 and 2.17 MeV resulted in half-lives of 37.5 and 36.0 min, values which agree well with the half-life of ^{38}Cl (37.3 min[10]).

The 0.529-MeV peak is due to ^{83}Br formed by the nuclear reaction:



The half-life of 2.33 h corresponds with the value given in the literature (2.39 h[10]). This isotope does not show any photopeaks above 1.4 MeV. The other peaks are due to ^{82}Br: one day after irradiation, when the sample was measured again, a pure ^{82}Br-spectrum was obtained.

The following counting technique was eventually applied: 3 h after the first measurement of 30 min, counting was repeated during 31.8 min *i.e.* 30 min corrected for the decay of ^{82}Br. This spectrum was stripped from the first and a 1.8-min background correction added.

In Fig. 2 the spectrum obtained after these operations is compared with a pure ^{38}Cl spectrum. It is clear that the ^{82}Br interference is no longer present. Moreover, results calculated from measurements of the 1.64-MeV and 2.17-MeV peaks give rise to the same values. Interferences in these energy regions thus seem unlikely.

Procedure

A selenium sample of 2 g was irradiated together with a chlorine standard

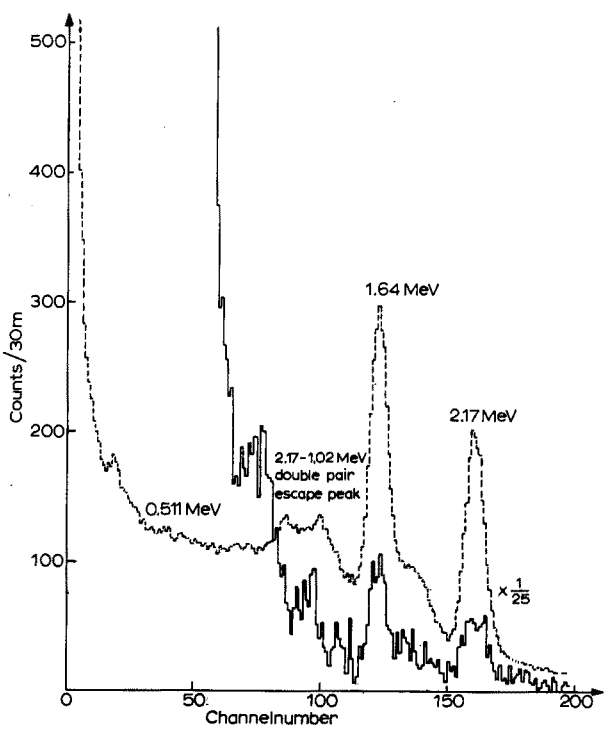


Fig. 2. γ-Spectra of ^{38}Cl. (---) 59.4 μg Cl; (—) chlorine separated from selenium.

(2 mg of ammonium chloride) during 37 min at a flux of $8 \cdot 10^{10}$ n/cm^2/sec. After irradiation, the sample was etched twice with 4 N nitric acid and transferred to an all-glass distillation apparatus. The selenium was dissolved by adding 40 ml of 14 N nitric acid containing 10 mg of chloride carrier. During the dissolution, chlorine was volatilized by means of a moderate stream of carbon dioxide and collected in 20 ml of ice-cooled 0.02 N silver nitrate solution. The distillate was filtered and the precipitate washed 4 times with 0.1 N nitric acid and once with alcohol and ether. The silver chloride precipitate was then counted for 30 min. The standard was dissolved in water and the solution made 2 N in nitric acid, and 10 mg of chloride and 1 ml of 0.4 N silver nitrate were added. After filtration, the precipitate was washed as described above and counted for 3 and 3.2 min at a 3-h interval. Time was not available to dry and weigh the selenium after the etch. The amount of selenium analyzed was determined afterwards from the ratio of the activities of the nitric acid solution and the etching solution.

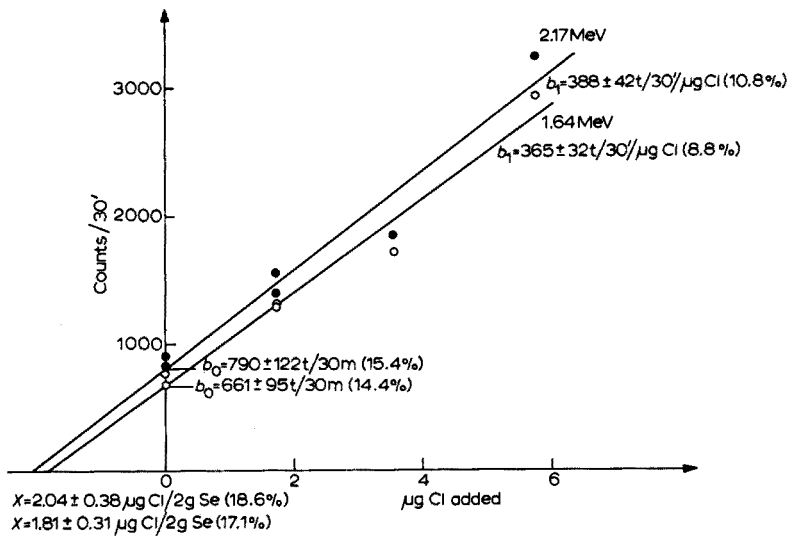


Fig. 3. Addition method of analysis for chlorine.

Results

To investigate possible systematic errors, an addition method of analysis was performed. Powdered selenium was etched with 4 N ultra-pure nitric acid and washed with demineralized water. In clean quartz ampoules, 2-g samples were weighed and spiked with sodium chloride solutions. The quartz ampoules were dried, sealed and their content thoroughly mixed by shaking. The samples were irradiated two by two, together with a 1% cobalt–aluminium wire as flux monitor. Chlorine was separated and counted as described above. From the results (Fig. 3), no systematic error was found in the considered concentration range. Because of the double counting technique and the low count rates, relatively large standard deviations occur. Typical results for three selenium samples are given in Table III.

TABLE III

DETERMINATION OF PHOSPHORUS, SULFUR AND CHLORINE (p.p.m.)

Sample no.	*Method of analysis*	*Phosphorus found*	*Sulfur found*	*Chlorine found*
1	Addition method	$0.51^{9} \pm 0.04^{3}$ (8.3%)	4.60±0.14 (3.0%)	0.97±0.17 (17.5%)
2	Classical method	0.079^{5}	1.36	0.66
		0.091^{2}	1.51	0.68
		0.079^{1}	1.62	
		$0.083^{3} \pm 0.004^{0}$ (4.8%)	1.50±0.08 (5.3%)	0.67±0.01 (1.5%)
3	Classical method	0.068^{3}	2.02	0.40
		0.061^{2}	1.98	0.32
		$0.064^{8} \pm 0.003^{6}$ (5.6%)	2.00±0.02 (1.0%)	0.36±0.04 (11.1%)

SIMULTANEOUS DETERMINATION OF SULFUR AND PHOSPHORUS

Chemical separation

Phosphorus is usually separated as magnesium ammonium phosphate or as ammonium molybdophosphate. Arsenic forms similar compounds whereas considerable amounts of selenium coprecipitate. A prior separation of these elements is therefore necessary. Distillation permits the simultaneous separation of the two elements. From a sulfuric acid–hydrobromic acid solution, more than 99.999% of selenium and arsenic can be distilled at 200–220°, while 98.8% of the phosphorus is recovered in the residue, as was shown by tracer experiments. Phosphate can be precipitated from the residue as ammonium phosphomolybdate; owing to the presence of sulfuric acid, which delays the precipitation, an increased amount of ammonium molybdate and a longer digestion time are necessary. It appeared that only about 98% of the carrier-free ^{32}P, from the $^{32}S(n,p)^{32}P$ reaction, is present as orthophosphate; the other 2% is probably a mixture of pyro-, tri-, tetraphosphate and other long-chained polyphosphates, chemical forms which do not react with ammonium molybdate[14]. Under the experimental conditions used, more than 99% of ^{32}P was recovered in the phosphomolybdate precipitate. The yield of the total operation was at least 95%.

Counting

The radiochemical purity of the phosphomolybdate precipitate, separated from 50 mg of selenium, irradiated without a cadmium filter during 4 days at a flux of $6 \cdot 10^{12}$ n/cm^2/sec, was checked by three different methods.

(*1*) The absorption curve was compared with a pure ^{32}P-standard. As shown in Fig. 4, after subtraction of the contribution of the γ-component, a value of $E_{\beta^-}(\mathrm{Max}) = 1.75$ MeV was obtained by Feather analysis. This value agrees well with the literature value (1.708 MeV[10]).

(*2*) From decay-curve analysis (Fig. 5), a small long-lived contamination was found. After correction for this interference, a value of $T_{\frac{1}{2}} = 14.2$ d was obtained, which agrees well with the value given in the literature (14.3 d[10]).

(3) γ-Spectrometry of the precipitate was applied. Only small photopeaks of ^{75}Se could be detected.

For the determination of sulfur and phosphorus, the precipitates were counted for 10 min with an end-window G.M. tube (thickness 3 mg/cm^2, dead time: 300 μsec). The samples were also measured for 30 min by γ-spectrometry. In the samples not covered with cadmium, some ^{75}Se appeared to be present, whereas this interference was negligible in the cadmium-covered samples. When ^{75}Se was present, a correction (5–10%) was applied by means of a ^{75}Se precipitate which was counted with the two radiation detectors. (^{75}Se does not emit β^--particles.)

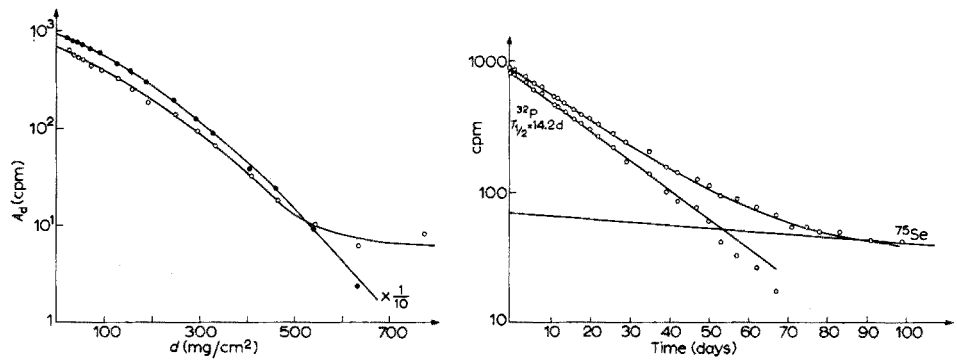


Fig. 4. Absorption curves. • ^{32}P tracer. ○ ^{32}P separated from 50 mg Se irradiated for 4 days at $5 \cdot 10^{12}$ n/cm^2/sec.

Fig. 5. Decay of the ^{32}P-fraction separated from selenium.

Procedure

In a cadmium box (thickness 1 mm, length 2 cm, width 1.9 cm) 6 quartz ampoules were placed containing three 50-mg selenium samples, 10 mg of diammonium hydrogen phosphate, 10 mg of potassium sulfate and 10 mg of potassium chloride. This cadmium box was placed at the bottom of an aluminium capsule. Above this an empty aluminium cylinder was placed (length 1.3 cm, width 1.9 cm) and above this another aluminium cylinder (length 2.0 cm, width 1.9 cm) containing 6 identical samples. The empty aluminium cylinder serves to eliminate most of the influence of the cadmium box at the other end of the irradiation capsule. The capsule was irradiated for 4 days at a thermal flux of $6 \cdot 10^{12}$ n/cm^2/sec and a fast flux of $4 \cdot 10^{11}$ n/cm^2/sec.

One day after the end of irradiation, the selenium was washed with dilute nitric acid and water to remove surface contamination. After drying and weighing, the samples were dissolved in 10 ml of 14 *N* nitric acid containing 2 mg of phosphorus ($(NH_4)_2HPO_4$) and 1 mg of arsenic (As_2O_3). This solution was transferred to a Scherrer distillation apparatus, 20 ml of 35 *N* sulfuric acid were added and a moderate stream of carbon dioxide was bubbled through the solution. For the collection of the matrix activities, three vessels, each containing 60 ml of 2 *N* sodium hydroxide, were used. After heating to 200°, 35 ml of 40% hydrobromic acid were added dropwise from the separatory funnel at 200–220° (time *ca.* 1 h).

After cooling, 100 mg of selenium carrier were added, the solution was heated

to 200° and 20 ml of 40% hydrobromic acid were added in the same way. The addition of carrier and the distillation was repeated twice.

The residue of the distillation was transferred to a beaker and neutralised with 6 *N* ammonium hydroxide. After addition of 15 ml of 14 *N* nitric acid and 30 ml of 34% ammonium nitrate solution, the solution was heated to 80° and 35 ml of 3% ammonium molybdate was added dropwise. After standing overnight, the solution was filtered and the precipitate washed with a solution containing 50 g of ammonium nitrate and 37.5 ml of 14 *N* nitric acid per liter. The precipitate was dried with alcohol and ether, heated for 1 h at 200°, weighed and counted.

The standards were dissolved in dilute (*ca.* 1 *N*) nitric acid to eliminate adsorption of ^{32}P on the glass wall[14]. After dilution, aliquots containing 10 μg of chlorine, 2 μg of sulfur, 0.1 μg of phosphorus or 10 μg of phosphorus for the cadmium-covered sample were taken and 2 mg of phosphorus carrier and 15 ml of 35 *N* sulfuric acid were added. After heating for 1 h at 200°, ammonium phosphomolybdate was precipitated as described above.

Results

To investigate possible systematic errors, an addition method of analysis was used. Powdered selenium was etched with ultra-pure 4 *N* nitric acid and washed with tridistilled water. After drying, 50-mg samples were weighed in quartz ampoules and spiked with diammonium hydrogen phosphate and potassium sulfate solutions. After drying, sealing and mixing, the ampoules were irradiated and the ^{32}P separated. By means of eqns. (3) and (4), the activities due to sulfur and phosphorus were plotted as a function of the amounts of sulfur and phosphorus added. From Figs. 6 and 7 it appears that no systematic errors occur up to 46.1 ng of phosphorus and 1.02 μg of sulfur added.

Finally, in two other selenium samples, the sulfur and phosphorus contents were determined. The results are given in Table III. Table III also shows that the

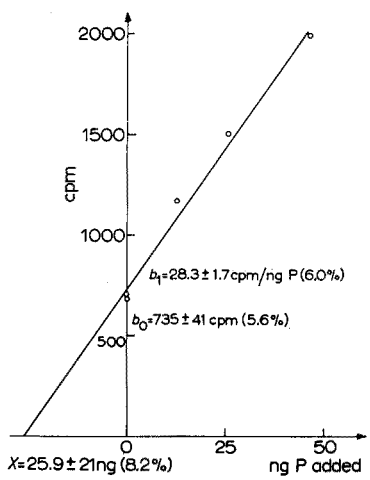


Fig. 6. Addition method of analysis for phosphorus.

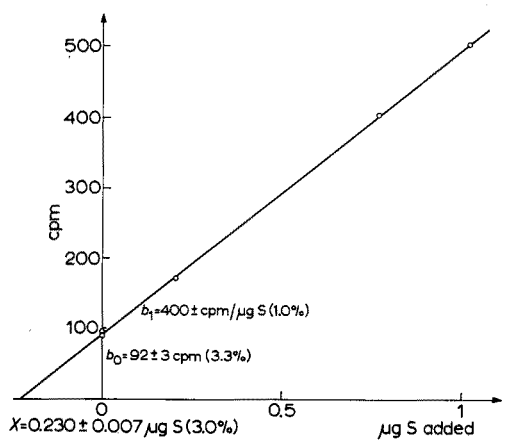


Fig. 7. Addition method of analysis for sulfur.

elements are present in ratios such that the simultaneous determination of sulfur and phosphorus is satisfactory.

The authors thank Mr. TOMBU of the "Metallurgy Hoboken" for providing the selenium samples. The technical assistance of Mrs. J. GORLÉE-ZELS and Mr. E. EVERAERT is gratefully acknowledged.

SUMMARY

Chlorine was determined in selenium by irradiation of 2-g samples for 37 min at a flux of $8 \cdot 10^{10}$ n/cm^2/sec. Chlorine was volatilised from hot concentrated nitric acid and precipitated as silver chloride. The isotope ^{38}Cl ($T_{\frac{1}{2}} = 37.3$ min) was counted by γ-spectrometry. Sulfur and phosphorus were determined by irradiating 50-mg samples with and without cadmium shielding for 4 days at a thermal flux of $6 \cdot 10^{12}$ n/cm^2/sec and a fast flux of $4 \cdot 10^{11}$ n/cm^2/sec. The matrix activities were separated by distillation from sulfuric acid–hydrobromic acid at 200–220°. The isotope ^{32}P ($T_{\frac{1}{2}} = 14.3$ d) was then precipitated, together with phosphate carrier, as ammonium phosphomolybdate, and counted with a G.M. tube. Amounts of 0.4–1 p.p.m. chlorine, 65–520 p.p.b. phosphorus and 1.5–4.6 p.p.m. sulfur were found in high-purity selenium samples.

RÉSUMÉ

On dose le chlore dans le selenium par irradiation d'échantillons de 2 g pendant 37 min à un flux de $8 \cdot 10^{10}$n/cm^2/sec. Le chlore est volatilisé de solutions acide nitrique concentré, chaud et précipité comme chlorure d'argent. L'isotope ^{38}Cl ($T_{\frac{1}{2}} = 37.3$ min) est compté par spectrométrie gamma. Soufre et phosphore sont dosés par irradiation d'échantillons de 50 mg avec et sans couche de cadmium pendant 4 jours à un flux thermique de $6 \cdot 10^{12}$n/cm^2/sec et un flux rapide de $4 \cdot 10^{11}$n/cm^2/sec. Les activités de matrice sont séparées par distillation de milieux acide sulfurique–acide bromhydrique à 200–220°. L'isotope ^{32}P ($T_{\frac{1}{2}} = 14.3$ d) est ensuite précipité avec entraîneur phosphate comme phosphomolybdate d'ammonium et compté avec tube G.M. On a trouvé ainsi 0.4–1 p.p.m. de chlore, 65–520 p.p.b. de phosphore et 1.5–4.6 p.p.m. de soufre dans des échantillons de sélénium très pur.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Chlor, Schwefel und Phosphor mit der Neutronenaktivierungsanalyse in hochreinem Selen beschrieben. Zur Ermittlung des Chlorgehaltes werden 2-g Proben 37 min bei einem Fluss van 8×10^{10}n/cm$^2 \times$ sec bestrahlt und das Chlor aus heisser konzentrierter Salpetersäure verdampft und als Silberchlorid gefällt. ^{38}Cl ($T_{\frac{1}{2}} = 37.3$ min) wird γ-spektrometrisch gezählt. Zur Bestimmung des Schwefels und Phosphors werden 50-mg Proben mit und ohne Cadmium-Folie 4 Tage lang bei einem thermischen Fluss von 6×10^{12}n/cm$^2 \times$ sec und einem schnellen Fluss von 4×10^{11}n/cm$^2 \times$ sec bestrahlt. Die Matrixaktivitäten werden aus einer Mischung von Schwefelsäure und Bromwasserstoffsäure durch Destillation bei 200–220° abgetrennt. Das Isotop ^{32}P ($T_{\frac{1}{2}} = 14.3$ d) wird zusammen mit einem Phosphatträger als Ammonium-

phosphomolybdat gefällt und mit einem Geiger–Müller-Zählrohr gezählt. In den Selenproben wurden 0.4–1 p.p.m. Chlor, 65–520 p.p.b. Phosphor und 1.5–4.6 p.p.m. Schwefel gefunden.

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DETERMINATION OF CHROMIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY OF CHROMIUM ACETYLACETONATE

DETERMINATION OF CHROMIUM IN SEA WATER

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(Received April 22nd, 1968)

Chromium has been identified as an active and essential trace element in animals and in plants[1,2]. Its biological significance has necessitated the development of sensitive methods of determination, and several atomic absorption methods have been described. DELAUGHTER[3] reported a method of chromium determination in brine at the sub-p.p.m. level by complexation with dephenylthiocarbazone followed by extraction into methyl isobutyl ketone. The absorption sensitivity of the complex was rather low (*ca.* 0.025 absorbance for 1 p.p.m. Cr); a 200-g sample was employed and the chromium content was concentrated in 10 ml of final spray solution. Another sensitive method was later reported by FELDMAN AND PURDY[4] by direct extraction of chromium(VI) into methyl isobutyl ketone, with a sensitivity of 0.006 p.p.m.

MCKAVENEY AND FREISER[5] have shown that the chromium(III)–acetylacetone complex can be formed in presence of excess of acetylacetone at pH 6 under reflux conditions and that the complex can be quantitatively extracted into 1:1 acetylacetone–chloroform. Based on this reaction, a sensitive atomic absorption method is described for sub-microgram amounts of chromium. The complexation of chromium by acetylacetone at microgram level, optimum instrument parameters and enhancement of sensitivity of complexation and extraction have been studied and the application of this method to the determination of chromium in sea water is described.

EXPERIMENTAL

Reagents and equipment

Chromium standard solution. Spec-pure chromium powder was dissolved in warm concentrated hydrochloric acid and excess of acid was evaporated off on a water bath. The solution was diluted with *N* hydrochloric acid to give a stock solution containing 10 μg Cr/ml. Working standards were prepared freshly by dilution with water.

Hydrochloric acid was purified by distillation and saturated by hydrogen chloride generated from distillation of concentrated hydrochloric acid.

Acetylacetone and methyl isobutyl ketone (MIBK) were distilled.

A Techtron A.A.4 Atomic absorption spectrophotometer equipped with standard burner A-41 of 10 cm flame path, and a fuel-rich acetylene–air flame was used in the investigation. The source was a hollow-cathode chromium lamp (Atomic Absorption Lamps Pty., Australia).

Procedure

A 10-ml aliquot of solution containing a suitable amount of chromium(III) and buffered to pH 6-7 was refluxed for 30 min with 3 ml of acetylacetone in a 25-ml round-bottom flask fitted with a finger condenser and a small magnetic stirring bar. When the solution had cooled, a drop of *N* hydrochloric acid was added to acidify and the complex was extracted into 8 ml of MIBK by shaking for 1 min in a separatory funnel. The organic extract was adjusted to 10 ml in a volumetric flask. The yield of chromium acetylacetonate was determined by the atomic absorption technique (see below).

RESULTS AND DISCUSSION

Formation of chromium acetylacetonate at the microgram level

The effect of varying the amounts of acetylacetone on the yield of the chromium acetylacetonate complex was studied. From the relative absorbance obtained by the atomic-absorption measurements, it was concluded that 2–4 ml of acetylacetone was optimal for the complexation of 3 μg of chromium(III) in 10 ml of aqueous solution. Amounts less than 2 ml or more than 4 ml resulted in low yields of the complex. It is probable that less than 2 ml of acetylacetone provides an insufficient excess of reagent, whereas more than 4 ml increases the viscosity effect, and thus lowers the feed-rate in the final spray solution because the excess of acetylacetone is extracted into MIBK.

Theoretically, an increase in the hydroxyl ion concentration should favour the formation of acetylacetonates, but no increase in yield was observed when the reaction was carried out at pH 9 by addition of pyridine. The yield was found to be optimal at pH 6–8, and was slightly low at pH 5. Reflux times of 20–60 min had no effect on the yields; a time of 30 min was chosen for convenience.

Optimum instrument parameters for atomic absorption

The optimum instrument parameters were modified slightly from those given by ALLAN[6] for chromium in aqueous solution. The most sensitive resonance line, 3579 Å, of chromium was used. Variations in the cathode-lamp current from 8 to 10 mA and in the slit-width from 76 to 125 μ caused very little change in the sensitivity of the method. For the acetylene–air mixture used, a fuel-rich flame was found to give optimal sensitivity in the usual way. However, when the combustible organic solvent was used as spraying medium, the fuel gas had to be reduced to minimise the noise. Suitable flame mixtures were obtained by adjusting the air to 23 psi and gradually increasing the acetylene flow with pure solvent spraying in, until the luminous feather was about 2 inches long and gave the maximum absorption signal compared to the solvent blank. Under the optimal instrumental conditions, the sensitivity for chromium was 0.015 p.p.m. for 1% absorption.

The optimum instrumental conditions are summarised below:

Spectral line	3579 Å	Gas mixture	Acetylene setting at 3.5 flow meter reading
Cathode-lamp current	8–10 mA		Air 23 psi
Slit-width	100 μ	Flame path	10 cm
		Scale expansion	5×

A comparison of the absorption sensitivity under the same conditions of scale expansion and flame path, was made with chromium in aqueous solution and also with the very sensitive chromium method proposed by FELDMAN AND PURDY[4], the chromium(VI) extract in MIBK being prepared as recommended by these authors. Other instrumental parameters such as optimal flame mixture and flame profile were determined empirically for each spraying solution. The absorption sensitivities expressed as concentration of chromium to give 1% absorption above the blank, are compared in Table I. It was found that with acetylene–air flames, the Cr(III)–acetylacetonate in MIBK was more sensitive than the Cr(VI)–MIBK, and in comparison with chromium in aqueous solution, the present complexation and extraction enhanced the sensitivity by a factor of two times.

TABLE I

ABSORPTION SENSITIVITY OF CHROMIUM (1% ABSORPTION ABOVE BLANK)

Solvent	*Chromium concn. (p.p.m.)*
Chromium(III)–water	0.030
Chromium(VI)–MIBK	0.024
Chromium(III)–acetylacetonate in MIBK	0.015

The high sensitivity (0.006 p.p.m. Cr for 1% absorption) given by FELDMAN AND PURDY for chromium(VI) extracted into MIBK was achieved by passing the light beam 5 times through the burner system, with a 10× scale expansion[4].

Calibration curve

Aliquots of standard solution containing increasing amounts of chromium from 1 to 10 μg were diluted to 10 ml and complexed with acetylacetone as previously described. The linearity of the calibration curve (Fig. 1) obtained indicates that the acetylacetonation yield is constant over the range studied. Other calibration curves for chromium in aqueous solution and for chromium(VI) in MIBK were also shown for comparison.

Interferences

The interference of diverse ions was studied by mixing 100 μg of each of the following cations with 3 μg of chromium in 10 ml of solution and carrying through the whole procedure: iron(III), molybdenum(VI), vanadium(V), titanium(IV), aluminium(III), calcium and sodium. No interference in absorption signal was observed. Iron(III) in amounts greater than 150 μg was found to interfere. Since all the above-mentioned and many other cations readily form complexes with acetylacetone

under ordinary conditions, they can be separated quantitatively at pH 2 from the aqueous phase by extraction with 1:1 acetylacetone–chloroform[7]. When this solvent extraction is incorporated before the acetylacetonation of chromium, up to 1000 μg of each of the above cations can be readily removed by a single extraction.

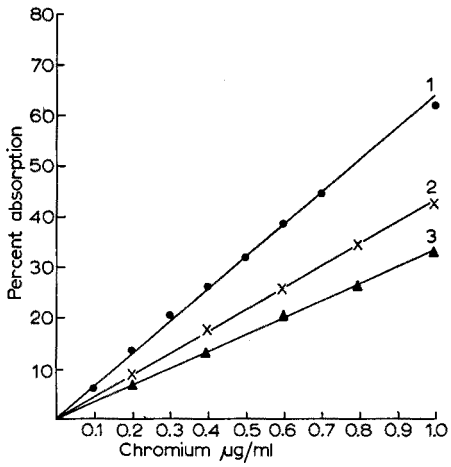

Fig. 1. Calibration curves for chromium. (1) Cr(III)–acetylacetonate in MIBK; (2) Cr(VI) in MIBK; (3) Cr(III) in aqueous solution.

DETERMINATION OF CHROMIUM IN SEA WATER

Concentration of chromium

Chromium in trace amounts can be concentrated by coprecipitation with hydrous oxides of iron(III) or aluminium, or by cocrystallization with dibromooxine[8], or by extraction with ammonium pyrrolidine dithiocarbamate[9]. Since the water samples are generally large, direct extraction is not convenient. The final solution of dibromooxine was found to give serious interference and flame noise. Concentration by chelating resin followed by elution with acid[10] and several chelating agents was also tested, but the recovery of 5 μg of chromium(III) from Chelex 100 on elution with 6 *N* hydrochloric acid was only *ca.* 55–60%, probably because of hydrolysis[10]. Coprecipation with iron(III)[8] was therefore employed.

Recommended procedure

Acidify the sample (5 l)to pH 2 immediately after collection and filter through a 0.5-μ membrane filter. Add with stirring a portion of iron(III) chloride solution containing 15 mg of iron. Adjust the pH to 8–9 with dilute ammonia and allow the precipitate to settle overnight. Siphon the supernate through an acid-washed glass-fiber filter and separate the bulk of the precipitate by centrifugation. Wash the precipitates on the filter and in the centrifuge tube with 15–20 ml of 0.5% ammonium nitrate. Dissolve the precipitate in the minimum amount of 2 *N* hydrochloric acid (5 ml), evaporate the solution almost to dryness and then dilute to *ca.* 10 ml with water. Adjust the pH of this solution to 1–2 and extract the iron with successive 10-ml portions of 1:1 acetylacetone–chloroform until the red iron complex is removed.

Adjust the pH of the aqueous phase to 6–7 with dilute ammonia and continue with the acetylacetonation of chromium as described above.

Calibrate the method by refluxing 3 μg of chromium(III) in 10 ml of solution with acetylacetone, and carry through the complete extraction procedure. Prepare the blank by refluxing a 10-ml aliquot of distilled water with 3 ml of acetylacetone and proceeding as for the sample. The final extract of the chromium acetylacetonate in MIBK is sprayed into the flame for absorption measurement as described above.

Results

The recoveries of chromium by this method were checked by introducing known amounts of chromium(III) into chromium-free sea water (2 l). The results (Table II) indicate that the recoveries are satisfactory over the range of chromium occurring naturally in sea water.

TABLE II

RECOVERIES OF CHROMIUM(III) FROM SPIKED SEA WATER

Cr(III) added (μg)	*Cr recovered (μg)*	*Cr(III) added (μg)*	*Cr recovered (μg)*
1	0.95	8	7.70
2	2.04	10	9.60
5	4.85		

The reproducibility of the procedure was evaluated by analyses of five 5-l surface samples taken from the South China Sea approximately 100 miles off Hong Kong. The chromium content was found to be 1.59 ± 0.06 μg/l.

SUMMARY

A sensitive atomic absorption method is described for the determination of chromium at sub-microgram levels. Chromium(III) is converted to its acetylacetone complex and extracted into MIBK. The atomic absorption sensitivity is thus enhanced two-fold compared to chromium(III) in aqueous medium. The detection limit of chromium is 0.015 p.p.m. with an acetylene–air flame; the sensitivity obtained with other chromium methods under the same instrumental conditions is compared. The method can be applied to the determination of chromium in sea water; at a level of *ca.* 1.6 μg Cr/l, the precision is ± 0.06 μg/l.

RÉSUMÉ

On décrit une méthode sensible pour le dosage du chrome (à l'échelle submicro) par absorption atomique. Le chrome(III) est complexé par l'acétylacétone et extrait dans MIBK. La sensibilité de l'absorption atomique est ainsi augmentée, deux fois par rapport au chrome en solution aqueuse. La limite de détection du chrome est de 0.015 p.p.m. avec une flamme acétylène–air. On compare la sensibilité avec celles obtenues dans des conditions instrumentales similaires. Ce procédé peut être

appliqué au dosage du chrome dans l'eau de mer; pour une teneur en chrome d'environ 1.6 μg Cr/l, la précision est de $\pm$0.06 μg/l.

ZUSAMMENFASSUNG

Eine empfindliche Methode zur Bestimmung von Chrom im Submikrogramm-Bereich mit Hilfe der Flammenabsorptionsspektralanalyse wird beschrieben. Das Chrom(III) wird dabei in den Acetylacetonat-Komplex überführt und mit Methylisobutylketon extrahiert. Die Absorptionsempfindlichkeit wird dadurch doppelt so gross wie bei Verwendung eines wässrigen Mediums. Mit einer Acetylen–Luft-Flamme wird eine Nachweisgrenze von 0.015 p.p.m. Chrom erreicht. Die Methode kann zur Bestimmung von Chrom in Seewasser angewendet werden. Bei einem Gehalt von ca. 1.6 μg Cr/l beträgt die Reproduzierbarkeit $\pm$0.06 μg/l.

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A NEW APPLICATION OF ATOMIC ABSORPTION SPECTROPHOTOMETRY

DETERMINATION OF PHTHALIC ACID BY SOLVENT EXTRACTION WITH NEOCUPROINE–COPPER(I) CHELATE*

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(Received April 15th, 1968)

In recent years atomic absorption spectrophotometry has become an increasingly important tool in analyses for trace amounts of metals, but it has been impossible to determine organic compounds directly. Indirect methods appear necessary for the application of the technique to non-metals; such methods can be based on the stoichiometric formation of ion-pairs with a cationic metal ion chelate which can then be isolated and determined by atomic absorption, the result being related quantitatively to the associated organic compound.

Neocuproine (2,9-dimethyl-1,10-phenanthroline) dissolved in methyl isobutyl ketone (MIBK) has been shown to be a selective extractant for phthalic acid in aqueous solutions containing a moderate amount of copper(I); it is possible to determine the organic acid by spraying the extracted MIBK solution into the flame of an atomic absorption spectrophotometer with a copper hollow-cathode lamp as a light source. A brief preliminary study has been reported[1]. In the present paper, a detailed quantitative study is described, to establish this new application of atomic absorption spectrophotometry. The method for phthalic acid is shown to be rapid and accurate; it is also freer from isomeric interferences and more sensitive than other known methods for phthalic acid, such as gravimetry[2], titrimetry[3,4], polarography[5,6] and UV spectrophotometry[7].

Indirect methods for the determination of nitrate[8], pentachlorophenol[9] and iodide[10], based on the same principle, have recently been reported in short communications.

EXPERIMENTAL

Apparatus

The atomic absorption measurements were made with a Hitachi Model 139-0420 atomic absorption spectrophotometer equipped with a copper hollow-cathode lamp. An air–acetylene flame was used with a 9-cm slot burner which was water-cooled throughout the work. The pH measurements were made with a Hitachi-

* The spectrophotometric determination of anions by solvent extraction with metal chelate cations. Part XXXVI. Part XXXV of this series: K. KOTSUJI *et al.*, *Anal. Chim. Acta*, 42 (1968) 225.

Horiba Model H-5 pH meter. The shaking was carried out with an Iwaki Model KM shaker with a time switch.

Reagents

All the chemicals used were of analytical-reagent grade.

Standard phthalic acid solution. A stock solution of $1.00 \cdot 10^{-2}$ *M* phthalic acid was prepared by dissolving 1.6613 g of phthalic acid, which had been recrystallized from water–ethanol and dried at 110°, to a volume of 1 l with water. This was accurately standardized against sodium hydroxide solution. The standard phthalic acid solution for the experiment was prepared by diluting an aliquot of this stock solution to give a concentration of $1.00 \cdot 10^{-4}$ *M* with water.

Neocuproine solution. A $2.0 \cdot 10^{-3}$ *M* solution of neocuproine was prepared by dissolving 0.4165 g of neocuproine (Wako Pure Chemical Industries) to a volume of 1 l with distilled MIBK.

Copper sulfate solution. A $1.0 \cdot 10^{-2}$ *M* solution was prepared from copper(II) sulfate pentahydrate which had been recrystallized from water.

Buffer solution. The pH 8 phosphate buffer was prepared by mixing $2.5 \cdot 10^{-1}$ *M* potassium dihydrogen phosphate solution and $2.5 \cdot 10^{-1}$*M* disodium hydrogen phosphate solution.

Procedure

Pipet 1 ml of copper(II) sulfate solution, 2 ml of aqueous 5% hydroxylamine sulfate solution, 5 ml of 0.25 *M* phosphate buffer solution and 5 ml of standard phthalic acid solution ($1.00 \cdot 10^{-4}$ *M*) in that order into a 100-ml separating funnel. Dilute the mixture to 25 ml with water and shake the solution for 2 min with 10 ml of neocuproine–MIBK solution. After 20 min, separate the organic phase and dry it with 1 g of anhydrous sodium sulfate. Measure the absorbance due to copper in the MIBK extract with the atomic absorption spectrophotometer against a reagent blank as a reference and express as concentration of phthalic acid initially present in the aqueous phase based on stock phthalic acid solutions as standards. The instrument operating parameters are as follows:

Air flow rate	7.0 l/min
Acetylene flow rate	1.0 l/min
Lamp current	20 mA
Wavelength	3247 Å
Slit-width	0.10 mm
Burner height	adjusted for maximum absorption

RESULTS AND DISCUSSION

Atomic absorption of copper

The air–fuel ratio had a significant effect on the copper absorption. The effects of variation of air–acetylene mixtures are shown in Fig. 1. For convenience gas flow rates were adjusted so that the burner consumes 7.0 l/min of air and 1.0 l/min of acetylene. With this flame condition, the highest sensitivity was obtained when the hollow-cathode lamp was so positioned that the radiation from it passed through the base of the flame just above the tip of the burner.

The effect of lamp current was studied. The absorbance was constant when the lamp current was kept in the range 15–25 mA.

Experiments were also made at various slit-widths. A constant absorbance was obtained irrespective of the slit-width over the range 0.03–0.50 mm.

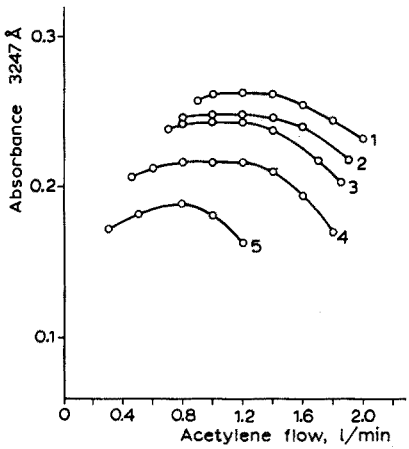

Fig. 1. Effect of variation of air–acetylene mixture on net absorbance for $2.00 \cdot 10^{-5}$ *M* phthalic acid. Air flow (l/min): (1) 8.0, (2) 7.5, (3) 7.0, (4) 6.0, (5) 4.5.

Extraction of phthalic acid with neocuproine–copper(I) chelate

Various commercially available organic solvents were tested for the extraction. Most solvents such as isoamyl alcohol, *n*-hexyl alcohol, chloroform, nitrobenzene or dichloroethane extracted the neocuproine–copper(I) chelate without phthalic acid and relatively non-polar solvents such as carbon tetrachloride, cyclohexane, benzene or chlorobenzene did not extract the chelate with or without phthalic acid. Of all the solvents tried, MIBK containing neocuproine proved to be the most selective extractant for phthalic acid. Moreover, MIBK was a suitable solvent for atomic absorption spectrophotometry because it provides a stable flame during the combustion and a higher sensitivity of measurement. An interesting investigation of solvents in atomic absorption spectrophotometry has been reported by ALLAN[11], who pointed out that a useful gain in sensitivity could be obtained in the determination of copper, when the element complexed with ammonium pyrrolidine dithiocarbamate was extracted into MIBK before spraying.

The extraction efficiency was estimated by extracting with successive 10-ml portions of MIBK containing neocuproine. It was found that 79% of phthalic acid was extracted in a single pass over the range of phthalic acid concentrations studied. In the present work, a single extraction was performed for practical convenience with high reproducibility.

Shaking times for the extraction were varied from 0.5 to 10 min and it was observed that the absorbance of the organic phase reached a maximum after shaking for about 1 min. Hence a time of 2 min was chosen for the extraction.

The effect of pH on the extraction was studied by extracting the phthalic acid from a series of aqueous solutions buffered at various pH values. The pH of the aqueous phase after the extraction was lower than that before the extraction, presumably

because of a partial reaction between MIBK and hydroxylamine. Thus the pH was measured after the extraction. As shown in Fig. 2, the absorbance of the extract against the reagent blank was constant when the pH of the aqueous phase after the extraction lay within the range 2.8–5.5. Estimations of the fraction of the species present, from the acid dissociation constants of phthalic acid (pK_1 3.0, pK_2 5.3), indicated that the univalent anion of phthalic acid predominated in this pH range; it is probable that this univalent anion participates in the extraction. In the method developed here, a pH 8 phosphate buffer solution was conveniently used in order to keep the pH of the aqueous phase after the extraction nearly at 5.

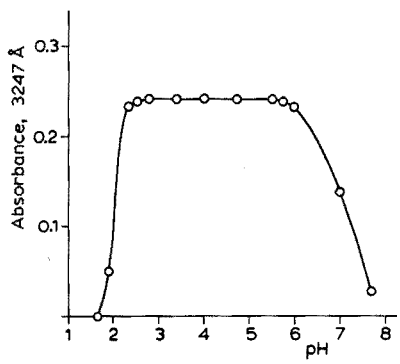

Fig. 2. Effect of pH on net absorbance for $2.00 \cdot 10^{-5}$ *M* phthalic acid. pH measured after extraction.

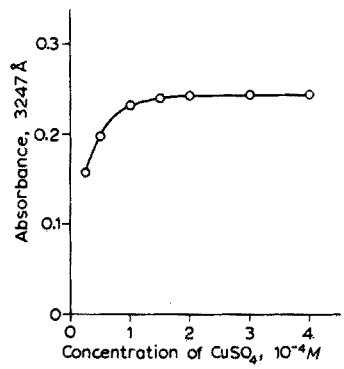

Fig. 3. Effect of concentration of copper(II) sulfate on net absorbance for $2.00 \cdot 10^{-5}$ *M* phthalic acid.

The effect of the concentration of copper(II) sulfate on the extraction was also investigated. The results are shown in Fig. 3. The degree of extraction was constant if the copper concentration was more than $2 \cdot 10^{-4}$ *M* initially present in the aqueous phase when the concentration of phthalic acid was kept at $2.00 \cdot 10^{-5}$ *M*. An excess of at least 10-fold (molar) of the copper sulfate to phthalic acid was necessary for quantitative recoveries. The copper concentration was usually kept at $4.0 \cdot 10^{-4}$ *M*, which was equivalent to half the molar quantity of neocuproine present.

For the quantitative formation of the neocuproine–copper chelate, copper(II) must be reduced to copper(I); in the present work, hydroxylamine sulfate was used as a reductant. It was sufficient that the concentration of hydroxylamine sulfate in aqueous phase was kept at about 0.4%.

Calibration curve

The standard procedure was settled on the basis of the above results. The calibration curve was obtained according to the procedure using varying amounts (1–10 ml) of standard phthalic acid solution ($1.00 \cdot 10^{-4}$ *M*). The calibration curve was linear for the tested concentration range of $4 \cdot 10^{-6}$ to $4 \cdot 10^{-5}$ *M* of phthalic acid initially present in the aqueous phase, and passed through the origin. The absorbance due to copper in the organic phase corresponding to these concentrations of phthalic acid in the original aqueous phase was in the range of 0.049 to 0.486.

Precision

The reproducibility of the proposed method was estimated from the results of 10 sample solutions, each $4.00 \cdot 10^{-5}$ *M* in phthalic acid. The relative standard deviation was calculated to be 1.0%.

Interferences

The effect on the extraction of the neocuproine–copper(I) phthalate into MIBK by isophthalic acid, terephthalic acid and benzoic acid was studied. The results are given in Table I. For the extraction of $2.00 \cdot 10^{-5}$ *M* phthalic acid, equimolar amounts of isophthalic and terephthalic acid did not interfere with the determination. When the same amount of benzoic acid, and 10-fold amounts of both isophthalic acid and terephthalic acid were present, positive errors of about 10% were obtained for phthalic acid.

TABLE I

DETERMINATION OF PHTHALIC ACID IN THE PRESENCE OF DIVERSE SUBSTANCES

(Phthalic acid taken: $2.00 \cdot 10^{-5}$ *M*)

Addition	*Concentration* $\cdot 2 \cdot 10^{-5}$ *(M)*	*Recovery of phthalic acid (%)*
Isophthalic acid	1	100
Isophthalic acid	10	111
Terephthalic acid	1	100
Terephthalic acid	10	110
Benzoic acid	0.1	100
Benzoic acid	1	107
Benzoic acid	10	169

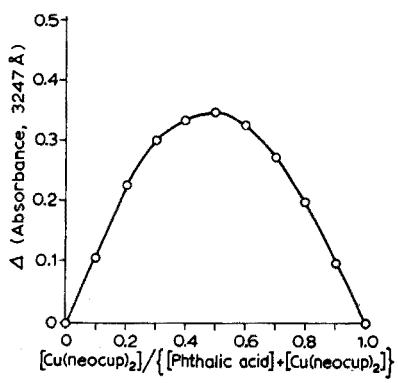

Fig. 4. Continuous variation plots for neocuproine–copper(I) phthalate at pH 4. Total concentration of copper(II) sulfate and phthalic acid $2.5 \cdot 10^{-4}$ *M*, concentration of neocuproine in MIBK $2.0 \cdot 10^{-3}$ *M*.

Composition of extracted species

It has been reported[12] that the molar ratio of copper(I) to neocuproine is 1:2 and that the neocuproine–copper(I) chelate is a univalent cation. Accordingly, continuous variation plots by atomic absorption spectrophotometric method were

successfully made in order to confirm the composition of the bis(neocuproine)–copper-(I) phthalate. The total concentration of copper sulfate and phthalic acid was kept constant at $2.5 \cdot 10^{-4} M$, and then the extraction was done as in the standard procedure with a series of aqueous solutions containing a varying mole ratio of copper to phthalic acid. The resulting curve (Fig. 4), in which the reagent blank was subtracted, shows that a 1:1 associated ion-pair is formed in the MIBK phase between the bis(neocuproine)–copper(I) cation and the univalent anion of phthalic acid. Thus the chemical formula of the extracted species can be represented as $[Cu(neocuproine)_2^+]$. $[C_6H_4(COOH)\ (COO)^-]$.

The author wishes to express his thanks to Professor Y. YAMAMOTO for his kind guidance and encouragement throughout this work and also wishes to thank Miss N. OKAMOTO and Mr. E. TAO for their assistance with the experimental work.

SUMMARY

A new application of atomic absorption spectrophotometry is reported for the determination of phthalic acid. Phthalic acid is extracted as the ion-pair formed between bis(neocuproine)–copper(I) and the univalent anion of phthalic acid with MIBK; the copper concentration in the extract is then determined by atomic absorption in an air–acetylene flame at the 3247 Å copper line. Optimal conditions are described. The absorbance of the extract showed a linear relationship to the concentration of phthalic acid initially present in the aqueous solution over the range of $4 \cdot 10^{-6}$ to $4 \cdot 10^{-5} M$. The effect of some analogous aromatic carboxylic acids on the phthalate extraction and the composition of the extracted species were also investigated.

RÉSUMÉ

On propose une nouvelle application de spectrophotométrie par absorption atomique pour le dosage de l'acide phtalique. L'acide phtalique est dosé par extraction dans un solvant en présence du chélate néocuproïne–cuivre(I). La concentration du cuivre ainsi extrait est déterminée par absorption atomique, dans une flamme air–acétylène, à 3247 Å. L'absorption mesurée donne une relation linéaire avec la concentration de l'acide phtalique initialement présent dans la solution aqueuse pour des concentrations allant de 4×10^{-6} à $4 \times 10^{-5} M$. On examine également l'influence de quelques acides carboxyliques aromatiques sur l'extraction du phtalate ainsi que la composition des particules extraites.

ZUSAMMENFASSUNG

Über eine neue Anwendung der Flammenabsorptionsanalyse zur Bestimmung von Phthalsäure wird berichtet. Phthalsäure wird dabei als Ionenpaar, das aus Bis-(neocuproin)Kupfer(I) und dem einwertigen Anion der Phthalsäure gebildet, mit Methylisobutylketon extrahiert. Die Kupferkonzentration im Extrakt kann dann unter Verwendung einer Luft–Acetylen-Flamme bei 3247 Å der Kupferlinie bestimmt werden. Die dafür erforderlichen optimalen Bedingungen werden angegeben. Die

Absorption des Extrakts zeigt eine lineare Beziehung zur Konzentration der anfänglichen Phthalsäure in der wässrigen Lösung in einem Bereich von 4×10^{-6} bis $4 \times 10^{-5} M$. Der Einfluss einiger analoger aromatischer Carboxylsäuren auf die Phthalsäure-Extraktion und die Zusammensetzung der extrahierten Spezies wurde ebenfalls untersucht.

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DETERMINATION OF IMPURITIES IN URANIUM COMPOUNDS BY ATOMIC ABSORPTION*

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Accurate and rapid determinations of many elements, in the parts per million range and lower, are required to assess conformance to specifications for uranium used throughout the nuclear fuel cycle. Until recently, most analyses for impurities in uranium have been performed by emission spectroscopy or colorimetry, both of which have inherent disadvantages. Emission spectroscopy by carrier distillation has poor precision, and colorimetric methods are time-consuming and subject to many interferences. In view of the disadvantages of the existing methods and the occasional need for lower limits of detection, the relatively new atomic absorption technique was investigated.

By means of atomic absorption, HUMPHREY[1] has measured magnesium in uranium directly by the addition method; GRAFF AND MULLIN[2], using a high solids-premix burner, have analyzed uranium metal and compounds for several impurities by direct aspiration of either 2% or 10% uranium solutions. In contrast, JURSIK[3] has analyzed uranium for a few elements at the relatively high concentration levels of 50–1000 p.p.m. after separating uranium by solvent extraction.

While the direct analysis of uranium solutions is sometimes satisfactory, direct aspiration of uranium has several disadvantages: (*1*) uranium at more than 1 mg/ml absorbs radiation at the wavelengths used for the analysis of most elements, so the uranium concentration must be known and controlled; (*2*) as the uranium concentration increases, the density and viscosity of the sample solution increase and cause the aspiration rates to decrease, (*3*) uranium suppresses the absorption of several elements; and (*4*) direct aspiration of uranium solutions, particularly those highly enriched in uranium-235, presents radioactive contamination problems.

To eliminate these disadvantages, uranium should be separated from the impurities. The use of tributyl phosphate (TBP) to extract uranium from many ions is well established. WRIGHT[4], who has made a critical literature survey of TBP as a uranium extractant, reports that it provides an efficient separation of uranium from most elements, and its stability in strong nitric acid is excellent. Initial experiments in this work with the TBP extraction system gave satisfactory separations of uranium from the 14 elements investigated. Refined experiments were then designed to study several parameters of the separation and subsequent analysis by atomic absorption.

* Presented in part at Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 5–10, 1967.

DISCUSSION

The elements investigated include aluminum, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, sodium, potassium, nickel, and zinc. They are among those of concern to uranium processors since all contribute to non-volatile fluoride residues in the production or volatilization of the uranium hexafluoride used in the gaseous diffusion process for separating uranium isotopes. Analyses, based on standard recommended procedures for each element, were performed on a Perkin-Elmer Model 303, Atomic Absorption Spectrometer.

Effect of uranium

The problems associated with the direct analysis of uranium solutions by atomic absorption were emphasized by the following series of analyses. Several standards which contained purified uranium and known amounts of impurities were prepared. The uranium concentrations tested were 0, 10, 20, and 30 mg U/ml, and four solutions were prepared at each uranium concentration level. One of the 4 solutions at each level was used as a blank and known amounts of 7 elements (cadmium, cobalt, copper, iron, manganese, nickel, and zinc) were added to each of the other 3. Thus, for each uranium concentration, each impurity existed at 3 concentration levels. These standards were aspirated directly into a high solids-premix burner and analyzed according to standard procedures.

Uranium at concentrations up to 30 mg/ml did not seriously affect the determination of cadmium (0.4–0.6 μg/ml), copper (0.5–1.0 μg/ml), and zinc (1.6–2.4 μg/ml). In the worst instance, cadmium results were 15% low at the 0.4 μg/ml level in a 30 mg/ml uranium solution. The bias was determined by analyzing the same amount of cadmium in a uranium-free solution. Thus, it is possible to analyze some elements at selected concentration levels directly in uranium solutions if the aspiration of radioactive solution does not present a serious contamination problem.

On the other hand, Figure 1 shows the effect of uranium on the atomic absorption analysis of cobalt, iron, manganese, and nickel. Uranium severely suppresses the atomic absorbance of iron and manganese, while cobalt and nickel are affected to a lesser extent. An additional problem in the analysis of cobalt and nickel in uranium solutions, however, was the difficulty in obtaining reproducible readings because of electronic noise level. Thus, a preliminary uranium separation is required for reliable analyses.

Extraction efficiency of tributyl phosphate (TBP)

To evaluate the efficiency of tributyl phosphate (TBP) as a uranium extractant, uranium was extracted with 100 ml of purified TBP from each of 12 samples containing 8.0 g U in 100 ml of 6 *N* nitric acid. The TBP layer was washed twice with 6 *N* nitric acid, and the combined aqueous solutions were washed with 50 ml of carbon tetrachloride. Each aqueous layer was evaporated to dryness, redissolved in 0.2 *N* hydrochloric acid, and analyzed for uranium by the basic-peroxide method[5]. The analyses showed that 98.5–99.3% of the uranium was removed by a single extraction.

To improve the separation efficiency of uranium further, a backwash of the uranium-depleted aqueous phase with 50 ml of 20% TBP in carbon tetrachloride

was included. Analyses of raffinates from samples treated in this manner showed that 99.9% of the total uranium had been extracted.

During the extraction of relatively large quantities of uranium, the density of the TBP phase increases. For example, when 20 g of uranium is extracted into 200 ml of TBP, the organic phase becomes more dense than the aqueous phase, and

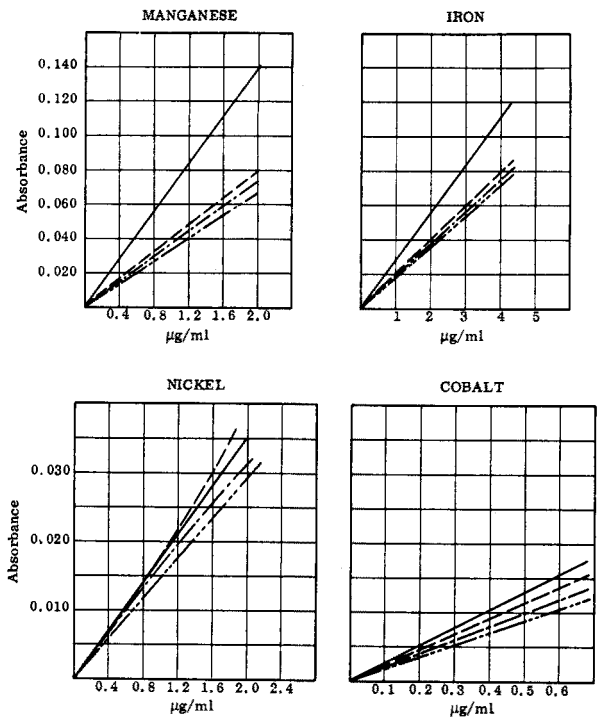

Fig. 1. Effect of U on the direct determination. (—) standard; (— —) 10 mg, (—·—) 20 mg, (—··—) 30 mg U/ml.

the two phases show poor separation. This problem was eliminated by adding 50 ml of hexane *after* the extraction; the addition of hexane, which combines with the TBP phase, decreases the density of the organic layer. Hexane must be added after the extraction of uranium since its presence at the outset decreases the extraction coefficient of TBP significantly.

Effect of anions

The two anions of primary concern were fluoride and phosphate. For large concentrations, both ions reportedly interfere with atomic absorption analysis of most elements; however, in the analysis of 14 elements in uranium-free standards containing up to 3 mg/ml of phosphate and 1 mg/ml of fluoride, no interference was detected. Large quantities of fluoride, however, can interfere in the extraction procedure by complexing uranium, but this problem is avoided by fuming sample solutions with nitric acid before the extraction step.

Another consideration was the possible hydrolysis of TBP in 6 *N* nitric acid to form orthophosphate during the extraction of uranium. Colorimetric analysis of raffinates from several extractions showed that only 0.2–0.3 mg of orthophosphate was produced by each 100 ml of TBP, indicating the excellent stability of TBP in nitric acid.

Limits of detection and sensitivity

Standards containing impurities at two concentration levels were prepared to determine the sensitivity and utility of the method. The low impurity concentration range was 0.12–0.60 μg/g U, and the high impurity concentration range was 5.0–52.5 μg/g U; 20 g of uranium was used for each standard at the low concentration level, and the atomic absorption analyses were performed on 10 ml of solution. For the high concentration level of impurities, 8 g of uranium was taken, and the atomic absorption analyses were performed on 100 ml of solution. The results of these analyses are listed in Table I. The sensitivities reported for elements other than aluminum, calcium, and magnesium, which were analyzed with a nitrous oxide burner, are not necessarily the maximum attainable since only one set of operating conditions was used for flame temperature and burner position.

TABLE I

DETERMINATION OF IMPURITIES IN URANYL NITRATE STANDARDS BY ATOMIC ABSORPTION

Element	*Low impurity concentration level (p.p.m.)*		*High impurity concentration level (p.p.m.)*		*Calculated sensitivity*[a] *(μg/g U/1% absorption)*
	Added	*Found*	*Added*	*Found*	
Al	—	—	34.5	32.7	0.63
Ca	0.48	0.51	25.5	23.9	0.04
Cd	0.12	0.11	7.50	7.50	0.02
Co	0.12	0.12	7.50	7.50	0.09
Cr	0.52	0.50	52.5	53.1	0.38
Cu	0.16	0.12	13.5	13.5	0.04
Fe	0.60	0.63	40.5	40.4	0.08
Mg	0.48	0.46	25.5	26.0	0.005
Mn	0.12	0.09	16.5	16.5	0.02
Ni	0.24	0.17	20.7	19.4	0.19
Pb	—	—	5.0	5.0	0.31
Zn	0.52	0.50	30.0	29.9	0.01

[a] Based on data from the low concentration level.

These results clearly show that by using a large sample size, impurities can be determined accurately even in the concentration range of 0.1–0.6 μg/g U. The detection limits, which are about one-fifth of the sensitivities, range from 0.001 μg/g U for Mg to 0.1 μg/g U for Al.

EXPERIMENTAL

Reagents

Pure uranous–uranic oxide (U_3O_8). Hydrolyze redistilled uranium hexafluoride

in deionized water to form uranyl fluoride. Evaporate the solution to dryness in a platinum dish and pyrohydrolyze the residue at 900° for 6–8 h with occasional stirring to form U_3O_8.

n-*Tributylphosphate (TBP).* Wash 500 ml of purified tributylphosphate with at least four 500-ml portions of deionized water to remove sodium and orthophosphate.

Lanthanum chloride—50 mg/ml. Transfer, to a 1-l separatory funnel, 200 ml of saturated lanthanum nitrate solution, 400 ml of 2.0 *N* aluminum nitrate and 300 ml of purified TBP. Shake vigorously for 2 min to extract lanthanum. Discard the aqueous layer and wash the TBP phase twice with 100 ml of deionized water. Discard these washings. Transfer the TBP phase to a 1-l beaker. Add 500 ml of calcium-free acetone or ethanol and 50 ml of water. Distill ammonium hydroxide into this solution until precipitation of lanthanum hydroxide is complete. Filter and wash the precipitate with deionized water. Ignite at 800° to form lanthanum oxide. Dissolve 58.64 g of lanthanum oxide in purified hydrochloric acid and dilute to 1 l with deionized water.

Purified nitric acid. Distill approximately 1700 ml of concentrated nitric acid into a 2-l plastic bottle containing 400 ml of deionized water. A quartz still is preferable for the distillation, but if one is not available, Pyrex glassware is satisfactory. Determine the specific gravity of the distilled nitric acid and calculate the normality. Prepare a 6.0 *N* solution by appropriate dilution of the purified acid with deionized water.

Purified hydrochloric acid. Distill and determine normality as for nitric acid. Prepare a 0.2 *N* solution by appropriate dilution of the purified acid with deionized water.

Standard stock solution—100 μg/ml of each element. Prepare a stock solution containing all elements to be determined by dissolving 0.100 g±0.1 mg of pure metals in purified nitric or hydrochloric acid. Convert the nitrate solutions to chloride when feasible by digestion with hydrochloric acid. Add lead as a nitrate. Dilute to 1 l with 0.2 *N* hydrochloric acid. After a preliminary analysis has been made on an unknown sample to determine the approximate concentration of impurities, aliquots of the stock solution are diluted to give concentrations that bracket the sample.

Carbon tetrachloride. Wash 1 l of carbon tetrachloride (reagent grade) with 100 ml of 0.1 *N* nitric acid and then 100 ml of deionized water.

Hexane. Wash 1 l of hexane (reagent grade) with 100 ml of 0.1 *N* nitric acid and then with 100 ml of deionized water.

Sample preparation

Uranous–uranic oxide (U_3O_8), uranium trioxide (UO_3), and uranium dioxide. Weigh to the nearest mg sufficient sample to give 8–20 g of uranium in a platinum dish or Teflon beaker. Dissolve the sample in purified concentrated nitric acid with 1 ml of acid per g of oxide. Evaporate the solution to near dryness and dilute the residue to 100 ml with 6 *N* nitric acid.

Uranium hexafluoride (UF_6), uranyl fluoride (UO_2F_2), and uranium tetrafluoride (UF_4). Hydrolyze uranium hexafluoride in deionized water to form uranyl fluoride. Pyrohydrolyze uranyl fluoride or uranium tetrafluoride samples, that are

not to be analyzed for volatile fluorides, at 900° to form U_3O_8, and treat the oxide as described above*.

Dissolve samples to be analyzed for volatile fluorides in nitric acid; digest with nitric acid to remove fluorides. The addition of hydrogen peroxide will increase the dissolution rate of uranium tetrafluoride. After the sample is dissolved, dilute to 100 ml with appropriate quantities of purified nitric acid and water to give a 6 *N* nitric acid solution.

Note. Blanks containing all reagents *must* be run through the entire procedure.

Separation and determination

Transfer the sample solution containing up to 10 g of uranium to a 250-ml separatory funnel using 6 *N* nitric acid to rinse the beakers. Use a 500-ml separatory funnel for samples containing 10–20 g of uranium. (Plastic separatory funnels are preferred.) Add 50 ml of purified TBP to the separatory funnel for each 4 g of uranium. Shake the separatory funnel vigorously for 2 min to extract the uranium and let the phases separate completely (this requires about 15 min).

Note. When samples containing 15–20 g of uranium are extracted, the density of the TBP phase is greater than the aqueous phase; therefore, 50 ml of purified hexane is added to decrease the density of the TBP phase. The hexane is added after the extraction since a mixture of TBP–hexane lowers the extraction efficiency.

Transfer the aqueous phase to a second separatory funnel. Wash the TBP phase with two 30-ml portions of 6 *N* nitric acid, adding these washings to the second separatory funnel. Wash the aqueous phase with 50 ml of 20% TBP in carbon tetrachloride. After separation, drain off the organic phase, and wash the aqueous phase twice with 25 ml of carbon tetrachloride. Transfer the aqueous phase to a Teflon beaker or platinum dish and evaporate the solution to dryness.

Dissolve the residue in 0.2 *N* hydrochloric acid and dilute to a desired volume according to the following table:

Impurity (μg/g U)	*Wt. of uranium (g)*	*Volume (ml)*
0.1–0.5	20	10
0.5–1	20	25
1–5	10	25
5–50	10	50–100
>50	5	100

Analyze for the desired elements by the standard atomic absorption techniques, comparing the sample measurements to those of known standards in the same concentration ranges.

Note. Samples to be analyzed for calcium or magnesium require the addition of lanthanum or strontium to eliminate suppression. Pipet an aliquot of the sample into a volumetric flask and add sufficient lanthanum or strontium chloride to give

* When uranium fluorides containing chromium are pyrohydrolyzed, a nitric acid insoluble compound, postulated as $UO_2 \cdot UO_3 \cdot Cr_2O_3$, is formed. Consequently, samples to be analyzed for chromium must be fumed with perchloric acid *after* dissolution with nitric acid to dissolve this uranium–chromium compound. A few drops of hydrogen peroxide are added to reduce Cr(VI) to Cr(III) before extraction of the uranium.

10 mg/ml. Dilute to volume with 0.2 *N* hydrochloric acid and analyze by comparison to known standards also containing lanthanum or strontium.

RESULTS

Analysis of prepared standards. Precision and accuracy

To test the reliability of the TBP extraction procedure and subsequent analyses by atomic absorption, standards containing 8.0 g U and 14 impurities were prepared in 6 *N* nitric acid. Two analyses were made at each of 3 impurity concentration levels.

The uranium was extracted as described above, and the raffinates were analyzed by atomic absorption spectrometry. The results of the analyses are shown

TABLE II

CONCENTRATION OF IMPURITIES IN PREPARED STANDARDS

Element	*μg/g U added*	*μg/g U found*		*Element*	*μg/g U added*	*μg/g U found*	
Al	15.0	15.0	15.0	Fe	15.0	15.1	16.4
	25.0	22.9	23.3		30.0	30.2	31.7
	40.0	38.0	35.9		50.0	50.8	49.9
Ca	3.0	2.95	2.91	Mg	3.0	2.95	3.21
	6.0	6.00	6.02		6.0	5.98	6.19
	9.0	8.87	9.01		9.0	9.14	9.00
Cd	3.0	3.0	3.0	Mn	3.0	3.0	3.0
	5.0	5.0	5.0		10.0	10.0	10.0
	10.0	10.0	10.0		15.0	15.0	14.9
Co	3.0	3.0	3.0	Ni	10.0	9.85	10.0
	5.0	5.0	5.0		15.0	14.1	14.8
	10.0	10.0	10.0		25.0	24.65	23.0
Cr	15.0	15.0	15.9	Pb	5.0	4.92	—
	35.0	35.5	35.0		10.0	10.13	—
	60.0	60.0	60.6		15.0	14.79	—
Cu	5.0	5.0	5.10	Zn	15.0	15.0	14.9
	10.0	10.13	10.0		25.0	25.0	25.0
	15.0	15.0	14.8		35.0	35.0	34.9

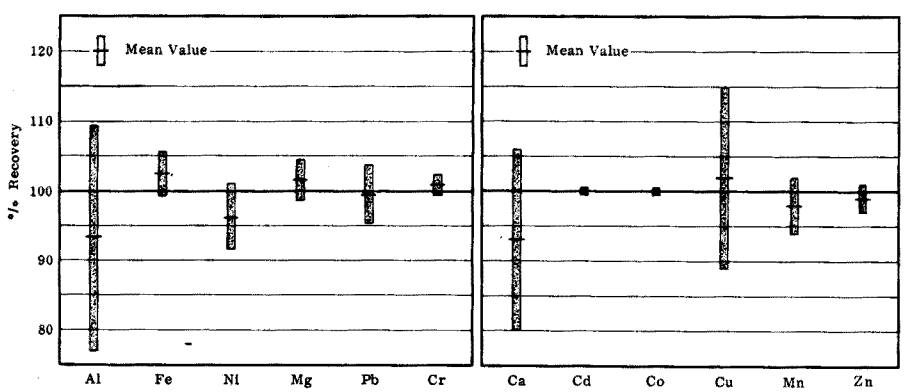

Fig. 2. Accuracy and precision of analysis of prepared standards.

in Table II. The pooled data, presented graphically in Fig. 2, were evaluated statistically and showed no significant biases.

Comparison of methods

To compare atomic absorption with other methods of analysis for impurities in uranium, samples of unknown composition were analyzed for impurities by emission spectroscopy, colorimetry, and atomic absorption. Two different solutions were analyzed, and an average value for each element was established for 16 spectrographic analyses by carrier distillation, 16 colorimetric analyses (by available methods), and 8 analyses by atomic absorption. A limit of error (L.E.) in μg/g U/analysis, for each analytical technique, was established for the determination of each element. The results are presented graphically in Fig. 3. In general, there are no significant biases between atomic absorption and colorimetric results, and the atomic absorption results gave slightly better precision. Carrier distillation spectrographic results tended, in nearly all cases, to be low, and as expected, gave much poorer precision than either of the other methods. For potassium and zinc, atomic absorption had the additional advantage that it was sensitive enough to detect both elements at well below the spectrographic limit.

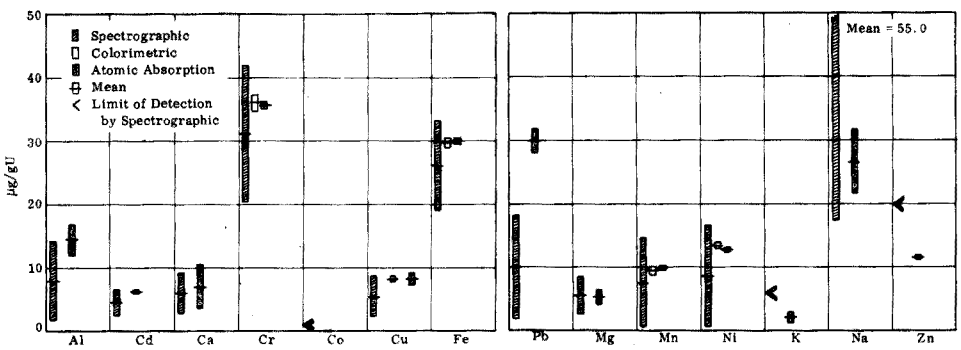

Fig. 3. Comparison of analyses of unknowns by different methods.

An important consideration is the time required for each of the three different methods. An analysis of five elements in a single sample by colorimetric techniques requires about 10 man-hours, while the atomic absorption analysis of 14 elements requires only six. Although a carrier distillation spectrographic analysis requires only 3 h and as many as 22 elements can be determined, it is less precise and less accurate than atomic absorption. Thus, the advantages of the atomic absorption method over the spectrographic are accuracy, precision, and the range of concentrations that can be handled by concentration or dilution of the sample.

SUMMARY

A method is described for the determination of 14 elements (Al, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Zn) in uranium and uranium compounds by atomic absorption spectroscopy. A sample is dissolved in 6–8 *N* nitric acid, from which the uranium is selectively removed by a single extraction with tributyl phos-

phate. The aqueous layer is evaporated to dryness and the residue is re-dissolved in 0.2 *N* hydrochloric acid. Any or all of the elements can then be determined in the solution by atomic absorption spectroscopy. The limits of error in the analyses are less than 10%. Thus, the method gives about the same precision as colorimetric procedures, and it is much more precise than emission spectroscopy.

RÉSUMÉ

On décrit un dosage de 14 éléments (Al, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Zn) dans l'uranium et ses composés au moyen de la spectroscopie par absorption atomique. L'échantillon à analyser est dissous dans l'acide nitrique 6–8 *N*, l'uranium est ensuite éliminé sélectivement par simple extraction à l'aide de tributylphosphate. La couche aqueuse est évaporée à sec, le résidu est redissous dans l'acide chlorhydrique 0.2 *N*. Les limites d'erreur de ces analyses sont inférieures à 10%. Cette méthode donne approximativement la même précision que les procédés colorimétriques, elle est beaucoup plus précise que la spectroscopie d'émission.

ZUSAMMENFASSUNG

Mit der Flammenabsorptionsspektralanalyse werden im Uran und in Uranverbindungen folgende 14 Elemente bestimmt: Al, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Na und Zn. Die Probe wird in 6- bis 8-*N* Salpetersäure gelöst und das Uran selektiv mit Tributylphosphat abgetrennt. Die wässrige Schicht wird zur Trockne eingedampft, der Rückstand in 0.2 *N* Salzsäure gelöst. In dieser Lösung können dann alle Elemente flammenabsorptionsspektroskopisch bestimmt werden. Der Analysenfehler ist kleiner als 10% und besitzt damit dieselbe Genauigkeit wie kolorimetrische Verfahren. Das Verfahren ist sehr viel genauer als die Emissionsspektroskopie.

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ADVANCES IN THE USE OF COMPUTER TECHNIQUES IN FLAME PHOTOMETRY*

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The rapid development of new instrumental techniques in analytical applications of atomic-absorption flame photometry, besides the use of emission flame photometry in research and routine analysis, leads continuously to new areas in which new or modified computer techniques can be used for the reduction of data and for easier and more accurate obtaining of results.

Since the application of computer techniques in flame photometry problems was discussed previously[1], new techniques have been developed. These are summarized in the present paper and some examples are given as a complement to the techniques previously described. Most of the techniques described, that require plotting of the final results, refer to two-dimensional plots of the dependent variable as a function of an independent variable fixed at the operator's choice, with all other variables existing in the chemical system held constant during the experiment.

Two of the cases described, calibration curves and flame profiles, can be considered together since they are based on the use of three variables, with one held constant in each case. For calibration curves, the variation of absorbance as a function of analyte concentration with the elevation of the burner held constant is measured, whereas for flame profiles variation of absorbance as a function of burner elevation with the analyte concentration held constant is measured.

A set of experimental values obtained by measuring the signals of several standards of analyte concentration at consecutively increasing burner elevations provides the operator with three variables. Hence, it is possible to represent calibration curves, flame profiles and three-dimensional plots[2].

EXPERIMENTAL

Instrumentation

For computing and plotting techniques. (*a*) IBM System 360, Model 40, 256K memory. In previous work[1], an IBM 1410, 40K memory was used but was later replaced with the present system. (*b*) CalComp Digital Plotter, Model 565. (*c*) IBM 2250, Model 1 cathode-ray tube on-line display scope with alphameric keyboard, light pen and function keys.

For flame photometry techniques. (*a*) Beckman DU® flame spectrophotometer with A.C. power supply, SERA, and 10-in Bristol recorder. (*b*) Beckman DU®-2

*Presented at the 18th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1967.

spectrophotometer equipped with A.C. power supply, SERA, Beckman 5-in recorder and Model 1300 atomic-absorption accessory, Beckman laminar flow burner (air–acetylene flame), and Beckman turbulent flow burner (air–hydrogen flame). (*c*) Beckman Model 979 atomic-absorption spectrophotometer, equipped with a 10-in Beckman potentiometer recorder and used with a Beckman laminar flow burner (air–acetylene flame and nitrous oxide–acetylene flame), and a Techtron laminar flow burner (air–acetylene flame).

Operating conditions for determinations by atomic-absorption flame photometry for different analytes were as published in *Flame Notes**.

Solutions

Sample solutions. These were prepared with distilled water, background solution (diluted acid solutions, solutions containing releasers), or organic solvents.

Standard solutions. Solutions were prepared by diluting stock solutions with distilled water, background solution or organic solvents.

Blanks were prepared according to the type of solvent used for samples and standards.

ANALYTICAL SYSTEMS STUDIED

Linearity and percentual sensitivity tests—Calibration tests

Linearity and percentual sensitivity tests, including the items mentioned below, were performed by means of the programs already described[1]:

(1) Transformation of per cent absorption readings into absorbance.
(2) Calculation of slope of the calibration curve.
(3) Calculation of the percentual concentration limit.
(4) Calculation of the percentual sensitivity.
(5) Determination of the linear portion of the calibration curve.
(6) Plotting of data points and calibration curve when necessary.

It is frequently helpful to use log–log representation of the calibration curves for the expression: $A = mC$ where A = absorbance, m = slope of the linear portion of the calibration curve, and C = analyte concentration in the test solution. Thus:

$$\log A = \log C + \log m$$

which is the equation of a straight line with a slope equal to one and with an intercept at $\log m$, where $\log m$ is directly related to the value of the percentual concentration limit (PCL)[3].

This representation allows for an easy graphical solution for PCL since:

$$\log \mathrm{PCL} = \log 0.0044 - \log m.$$

Manual calibration of PCL in this manner is slow and subject to errors caused in fitting the proper straight line, and by calibration of the intercept to the straight line and the absorbance value of 0.0044. Slight errors in the slope caused by improper choice of the best-fit straight line, and by curvature in the higher portions of the curve, cause significant errors in the calibration of PCL.

An addition was made to the existing program to perform the transformation

*Obtainable from Beckman Instruments, Inc., Fullerton, Calif. 92634, U.S.A.

to the log–log coordinates of the experimental data. A least-squares, linear fit is then performed on the transformed data and PCL is calculated on the basis of this fit as described above. Errors in PCL due to the curvature of the log–log transformation of the data are minimized by allowing error limits in the linear fit to be specified. Points at the higher levels of concentration are deleted until these error limits are met. It is also possible to delete any bad points in the fit.

Figures 1 and 2 show the tabular output from this program. This output is the same as that presented previously[1] except for the addition of another set of values for RPCL and RPS. The first set corresponds to the values calculated on the basis of the slope of the linear portion of the data in rectangular coordinates. The second set of values was obtained by the method described above.

Because of the number of points involved in this test and the nature of the system, very poor linearity was found when a 10% error criterion was used for the

MG 2852 NOAF-LAAS 0.05 15 MA LEAN 0.0 INCHES
SINGLE COLD

ELEMENT	WAVE LENGTH	BURNER INSTRU.	OPER-ATION	CONDI-TION	SLOPE	RPCL	RPS
MG	2852	LAAS O	.05	.0	0.02342	0.18618E 00 0.17180E 00	0.53711E 01 0.58209E 01

CONCENTRATION	PERCENT ABSORPTION				ABSORBANCE
	AB1	AB2	AB3	AB4	
0.0	0.0	0.0	0.0	0.0	0.0
1.0000	5.0000	0.0	0.0	0.0	0.0223
1.50000	9.0000	0.0	0.0	0.0	0.0410
2.0000	12.0000	0.0	0.0	0.0	0.0555
3.0000	14.5000	0.0	0.0	0.0	0.0680
5.0000	23.1000	0.0	0.0	0.0	0.1141
10.0000	43.0000	0.0	0.0	0.0	0.2441
20.0000	67.7000	0.0	0.0	0.0	0.4908
50.0000	93.2000	0.0	0.0	0.0	1.1675

THIS SAMPLE IS LINEAR BETWEEN CONCENTRATION LIMITS OF 0.0 AND 50.000

Fig. 1. Linearity and percentual sensitivity tests — calibration tests.

MG 2852 NOAF-LAAS 0.05 15 MA LEAN 0.0 INCHES
TRIPLE COLD

ELEMENT	WAVE LENGTH	BURNER INSTRU.	OPER-ATION	CONDI-TION	SLOPE	RPCL	RPS
MG	2852	LAAS O	.05	.0	0.04787	0.91071E 01 0.83043E 01	0.10980E 02 0.12042E 02

CONCENTRATION	PERCENT ABSORPTION				ABSORBANCE
	AB1	AB2	AB3	AB4	
0.0	0.0	0.0	0.0	0.0	0.0
0.5000	5.5000	0.0	0.0	0.0	0.0246
1.0000	10.3000	0.0	0.0	0.0	0.0472
1.5000	17.7000	0.0	0.0	0.0	0.0846
2.0000	22.8000	0.0	0.0	0.0	0.1124
3.0000	26.9000	0.0	0.0	0.0	0.1361
5.0000	41.2000	0.0	0.0	0.0	0.2306
10.0000	68.5000	0.0	0.0	0.0	0.5017
20.0000	88.9000	0.0	0.0	0.0	0.9547

THIS SAMPLE IS LINEAR BETWEEN CONCENTRATION LIMITS OF 0.0 AND 20.0000

Fig. 2. Linearity and percentual sensitivity tests — calibration tests.

linear fit. Upon inspection, it was decided that the system could be considered linear for the purpose of calibration curves. The run shown has had the error tolerance removed so that the calculations are based on a linear system.

This particular example was chosen from the available samples because of the deviation of the points from the best-fit straight line. This type of data makes manual calculations and tracing of the best straight line difficult and inaccurate. With the procedure described, it can be processed as easily as a normal set of data with more accuracy than the manual methods.

Figures 3 and 4 are the rectangular coordinate plots from this run. Figure 5 shows the composite plot of the log–log transformation of the data. This gives a graphic display of the change in RPCL due to the changes in the system. In this case, the only change to the system was in lengthening the path of the beam.

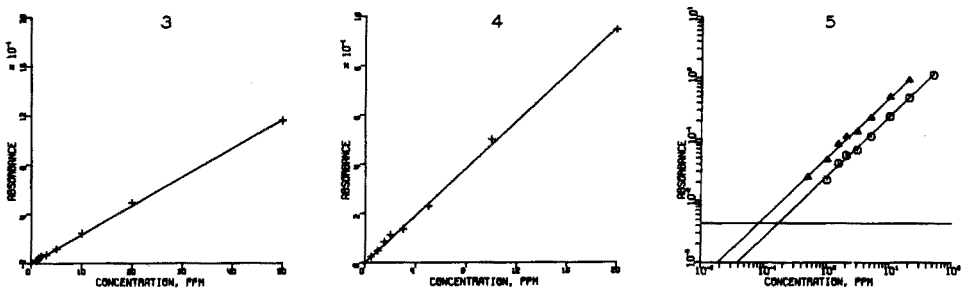

Fig. 3. Linearity and percentual sensitivity tests. Calibration tests. Conditions as for Fig. 1.

Fig. 4. Linearity and percentual sensitivity tests. Calibration tests. Conditions as for Fig. 2.

Fig. 5. Linearity and percentual sensitivity tests. Calibration tests. Conditions as for Figs. 1 and 2; ⊙ single cold, ▲ triple cold.

Addition method (multi-addition technique)

Mono-addition techniques have already been described[4]. For more reliable results, it is advisable to use a multi-addition technique. This technique can be applied for emission and atomic-absorption flame photometry problems, as long as the response of the chemical-instrumental system (sample solution plus instrument) is linear. If the response is linear up to a limit and then shows curvature, it is still possible to delete one or more of the experimental points at the high concentration levels.

This process is relatively easy by manual plotting but the transformation of readings into absorbances, plotting of absorbances *vs.* concentration, tracing the best-fit straight line to all the points, and reading the unknown concentration, is time-consuming for routine analysis.

The simple equations used in mono-addition techniques are as follows:
For emission: $C_S = \{\Delta E_S/(\Delta E_T - \Delta E_S)\}\, C_A$
For atomic absorption: $C_S = \{A_S/(A_T - A_S)\}C_A$
where ΔE_T, ΔE_S = net emissions (total and sample), A_T, A_S = absorbances (total and sample), C_S = sample concentration, and C_A = added concentration. These equations become much more complicated when they involve the multiple readings and multiple added concentrations necessary to calculate the parameters for the straight line fit and final sample concentration calculation.

Programs have been developed to perform the transformation into net emissions or absorbances, to calculate the least square, best-fit straight line to the data points, and calculate the unknown concentration on the basis of the straight line. The data are then readily available for a proper evaluation of the system.

PLATINUM TLFB-AAS 979 MULTI-ADDITION METHOD

SYSTEM	C1A	C2A	C3A	C4A	CS	A1T	A2T	A3T	A4T	AS	CS FOUND	
SERIES A	10.0000	20.0000	0.0	0.0	0.0	0.0306	0.0434	0.0	0.0	0.0205	17.4783	17.4783
SERIES B	10.0000	20.0000	0.0	0.0	0.0	0.0325	0.0448	0.0	0.0	0.0246	23.5598	23.5598
SERIES C	10.0000	20.0000	0.0	0.0	0.0	0.0311	0.0414	0.0	0.0	0.0232	24.9608	24.9608
SERIES D	10.0000	20.0000	0.0	0.0	0.0	0.0367	0.0462	0.0	0.0	0.0232	20.6931	20.6931
TWO ADDITIONS	10.0000	20.0000	0.0	0.0	0.0	0.0323	0.0440	0.0	0.0	0.0227	21.0537	21.0537
THREE ADDITIONS	10.0000	20.0000	50.0000	0.0	0.0	0.0323	0.0440	0.0697	0.0	0.0227	24.9399	24.9399

Fig. 6. Addition method (multi-addition technique).

Figure 6 shows a typical tabular output of the multi-addition program. The first line is a descriptive title of the run; the second line is composed of the standard column headings supplied by the program. The column labeled "SYSTEM" is an alphameric description supplied by the programmer. The columns labeled "CnA" and "AnT" are the concentrations added and absorbances given by the readings taken at those levels, respectively. "C_S" is the expected concentration of the sample, "A_S" is the absorbance based on the signal of the sample, and "C_S FOUND" is the calculated concentration of the sample. The last column is the difference between the expected and calculated concentration of the sample. Any zero value in the output indicates no value was given for that parameter.

In the example shown, Series A, B, C, and D correspond to four sets of readings on the same solutions. The two-addition system uses the average of the four series. The three-addition system is made up of the average of all available readings for the solution, including a higher point at which the calibration curve is not longer

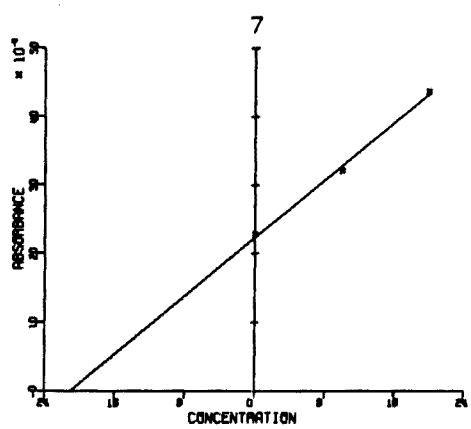

Fig. 7. Addition method (multi-addition technique). Conditions as in Fig. 6; two additions.

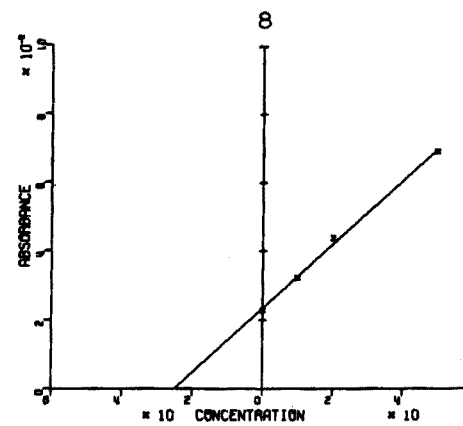

Fig. 8. Addition method (multi-addition technique). Conditions as in Fig. 6; three additions.

SINGLE STANDARD TESTS – LINEAR SYSTEMS

SYSTEM	STANDARDS C	A	ERROR	C	A	ERROR	CS ADDED	ABSOR-BANCE	CS FOUND	DIFFERENCE
CE 2862 NOAF .2	0.0	0.0	0.0	1000.000	0.046	−0.000	500.000	0.0223	481.7527	−18.2473
CR 3579 NOAF .2	0.0	0.0	0.000	5.000	0.509	−0.000	2.000	0.1858	1.8260	− 0.1740
CR 3579 NOAF .2	0.0	0.0	0.000	10.000	0.959	−0.000	2.000	0.1858	1.9377	− 0.0623
CR 3579 NOAF .2	0.0	0.0	0.0	2.000	0.186	−0.000	1.000	0.0862	0.9280	− 0.0720

TWO STANDARD TESTS – LINEAR SYSTEMS

SYSTEM	STANDARDS C	A	ERROR	C	A	ERROR	CS ADDED	ABSOR-BANCE	CS FOUND	DIFFERENCE
CR 3579 NOAF .2	0.500	0.040	−0.000	2.000	0.186	−0.000	1.000	c.0862	0.9719	−0.0281

INTERPOLATION TESTS – LINEAR SYSTEMS

SYSTEM	STANDARDS C	A	ERROR	C	A	ERROR	CS ADDED	ABSOR-BANCE	CS FOUND	DIFFERENCE
BA 5536 NOAF .2	10.000	0.070	0.000	50.000	0.481	−0.000	20.000	0.1707	19.8207	−0.1793
BA 5536 NOAF .2	10.000	0.070	− 1.224	20.000	0.171	0.666	20.000	0.1707	19.8898	−0.1102
	50.000	0.481	− 0.059							
CR 3579 NOAF .3	0.500	0.040	13.183	1.000	0.086	9.601	2.000	0.1858	1.9384	−0.0616
	5.000	0.509	− 4.922	10.000	0.959	1.192				

Fig. 9. Interpolation method in linear systems.

SYSTEM	STANDARDS C	A	ERROR	C	A	ERROR	CS ADDED	ABSOR-BANCE	CS FOUND	DIFFERENCE
GE 2651 NOAF .3	5.000	0.053	−1.066	10.000	0.094	0.900	50.000	0.3665	46.5781	− 3.4219
	20.000	0.180	0.001	100.000	0.561	−0.000				
GE 2651 NOAF .3	5.000	0.053	5.872	10.000	0.094	−3.720	20.000	0.1805	21.4307	1.4307
	50.000	0.367	−0.000	100.000	0.561	−0.000				
FE 2483 NOAF .2	2.000	0.111	0.000	10.000	0.419	0.0	5.000	0.2343	5.1986	0.1986
NB 3349 NOAF .2	50.000	0.029	6.391	100.000	0.056	−3.780	200.000	0.1107	228.0593	28.0593
	500.000	0.232	0.100							
NB 3349 NOAF .2	50.000	0.029	0.002	200.000	0.111	−0.268	100.000	0.0555	95.9646	− 4.0354
	500.000	0.232	0.001							

Fig. 10. Interpolation method in non-linear systems.

linear. This is reflected in an erroneously high value of C_S FOUND. Figures 7 and 8 show the plotted output corresponding to the systems labeled "Two Additions" and "Three Additions".

Interpolation method in linear systems

Three main cases are presented in emission and atomic-absorption flame photometry.

(1) Calibration method. Several standards are measured, the readings are converted to suitable values for plotting *vs.* analyte concentration, and a calibration curve is traced.

(2) Two-standard method. Two standards of composition close to that of the unknown are read, the readings are converted and a linear segment of the working curve is traced.

(3) Single-standard method. Once the instrument has been zeroed with a blank solution, only one standard is measured, whose concentration is generally higher than that of the sample, and a straight line is traced between the zero point and the standard point.

All of these cases can be solved by graphical or calculation techniques, since they all involve the use of a straight-line calibration curve. Manual plotting plus manual graphical interpolation are sources of errors. Even manual calculation can introduce numerical operator errors. All the methods are time-consuming.

A single program has been developed to handle these three cases. Data points presented determine the method to be used. This program accepts from one to three readings of per cent absorption at from 2 to 10 levels of concentration. For the single-standard method, the zero–zero point or blank is inserted along with the standard reading in the point. For the two-standard and calibration methods, only the readings of the standards in the experimental point are input. A least-square, linear fit is used for the interpolation calculation of the unknown concentration. Figure 9 shows three runs on this program. The first run shows single-standard tests, the second a two-standard test, and the third a combination of two-, three- and four-standard tests.

Interpolation method in non-linear systems

Some calibration curves in atomic absorption show a linear portion at the lower concentration levels with some curvature at the higher levels. Others show curvature starting at the very low concentration levels. The appearance of curvature makes any manual numerical calculation difficult and limits the operator to graphical techniques with the inconveniences already mentioned. Many times a calibration or working curve may be constructed using a linear fit over the lower portion of the data and the single or multiple quadratic segments over the curved portion of the data. This gives the opportunity of applying automatic calculations. In the programs developed, error limits are specified by the operator and a calibration curve is constructed using line segments within these error limits. Interpolation is then performed on this calibration curve.

Figure 10 shows a tabular output for tests run on non-linear systems. The first column, labeled "SYSTEM" is a 15-character label for the set of data. Under "STANDARDS", the columns "C", "A", and "ERROR" are the concentration and absorbance of the standards and the per cent error in the calibration curve. "C_S ADDED"

is the concentration of the sample, if known, and "ABSORBANCE" is the absorbance of the sample. "C_S FOUND" and "DIFFERENCE" are the calculated concentration of the sample and the absolute difference between the added and calculated concentrations of the sample.

Figures 11 and 12 are the plotted output corresponding to the first two systems in the run. The readings of the standards are designated by the symbol X, and the interpolated point by +. The plots show the similarity expected between the two sets of data since they were identical systems with the only variations being the levels of concentrations used. These calibration curves seem to be representative of the system and could be used for future work.

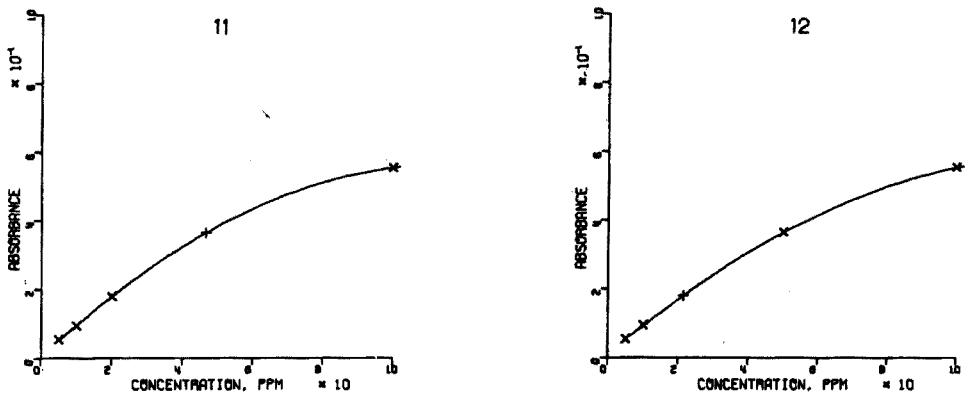

Fig. 11. Interpolation method in non-linear systems. Corresponding to GE 2651 NOAF.3 of Fig. 10.

Fig. 12. Interpolation method in non-linear systems. Corresponding to GE 2651 NOAF.3 of Fig. 10.

GRAPHIC FLAME PHOTOMETRY WITH MAN/MACHINE INTERACTION

In dealing with results calculated from experimental data, there occur certain errors which can not be compensated for without operator intervention. One example of this is linearity. A bad point at a low level of concentration in what should be a linear sample may cause incorrect results. In the past, it has been necessary for the operator to decide which point is bad, delete that point or loosen the tolerance limits and re-submit the run, which is time-consuming. To eliminate delay and to take advantage of the operator's knowledge of his system and possible errors, graphic flame photometry has been developed with an IBM 2250 Model I CRT Display Scope. This system allows reduction of data, compensation for any errors in the data, and final plotted and tabular output of only those sets which the operator specifies. This system is now in use in linearity and percentual sensitivity tests, flame profiles and three-dimensional representation for calibration curves and flame profiles.

The flame photometry data are cataloged on disk and assigned a catalog number. Preliminary conversion from per cent absorption to absorbance is completed and a tabular listing is returned. The input can than be scanned for obvious input errors. The program is called in from the scope, and the required data set and the required phase of the program are then specified. In the linearity and percentual sensitivity portion of the program, a working curve is built using linear and quadratic segments; the points to be deleted, and the range of the segments used can be speci-

fied. When a satisfactory working curve is obtained, the percentual sensitivity, RPCL and slope of the linear portion can be calculated and the curve stored to be retrieved later for the three-dimensional representation.

The flame-profile portion of the program similarly allows representative curves to be built from the input points and then stored for the three-dimensional plot. During the building of the curves, the actual data points and the calculated points are displayed in tabular form so that the accuracy of the working curves can be checked.

At any point in the program, the plotted and tabular output previously received from the batch processing programs can be recorded. Figure 13 shows a typical output of the scope program.

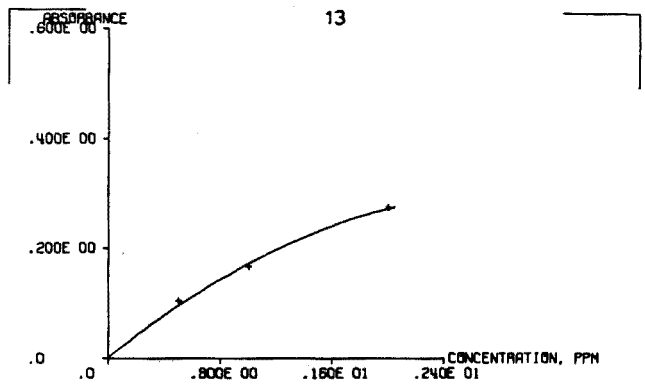

Fig. 13. Graphic flame photometry with man/machine interaction.

CONCLUSION

All the examples presented use atomic-absorption methods. Most of the programs described can be extended to emission methods. The system developed provides a fast and efficient method of data reduction along with the flexibility of the manual method. The use of on-line computer graphics takes advantage of the speed and accuracy of the computer for data reduction, and the knowledge of the operator for decision-making.

SUMMARY

The range and complexity of the application of computer techniques in flame photometry methods has been extended. Improvements in output formatting are detailed and typical automated analyses are presented. Examples are discussed from both mathematical and analytical points of view. The potential of graphic display consoles is explained in detail.

RÉSUMÉ

Le domaine et la complexité d'application des techniques "computer" en photométrie de flamme ont été étendus. On présente diverses analyses automatiques typiques. Des exemples sont discutés des points de vue mathématique et analytique.

ZUSAMMENFASSUNG

Das Ausmass und die Komplexität der Anwendung von Computer-Techniken bei flammenphotometrischen Methoden werden im einzelnen erklärt. Verbesserungen in der Ausgabe werden beschrieben und typische automatische Analysen angegeben. Beispiele werden sowohl vom mathematischen als auch von analytischen Gesichtspunkten aus diskutiert. Die Möglichkeit einer graphischen Darstellung wird im einzelnen besprochen.

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AUTOMATIC CHROMATOGRAPHY OF HYDROXY ACIDS ON ANION-EXCHANGE RESINS

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A method for the chromatographic separation of hydroxy acids on anion-exchange resins combined with automatic colorimetric analysis of the eluate was described in a previous paper[1]. Two analytical channels were used in this monitor. In one of these, part of the eluate was analyzed by chromic acid oxidation which gives a response with all the eluted hydroxy acids. In the second channel, another part of the eluate was analyzed by a carbazole method which gives a strong response with uronic acids and some keto acids, but no response with aldonic acids and a weak reaction with aldobionic and lactic acids.

Later work has shown that the monitor is extremely useful in the analysis of mixtures containing several uronic and aldonic acids. With complicated mixtures containing other types of hydroxy acids also, it is desirable to use a monitor in which the periodate oxidation of the eluted compounds can be studied simultaneously. A three-channel monitor which fulfills this requirement is described in this paper.

EXPERIMENTAL

The principle of the method is illustrated in Fig. 1. By means of a peristaltic pump the eluate was divided into four streams. One of these streams was passed to a fraction collector or, when no additional identification was required, to the waste.

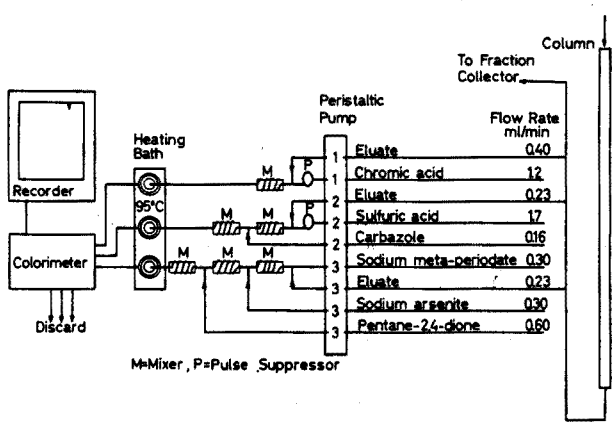

Fig. 1. Principle of the analysis system. (1) Chromic acid channel; (2) carbazole channel; (3) periodate channel.

The other streams were used for automatic analysis, two by the chromic acid and carbazole methods described by JOHNSON AND SAMUELSON[1] and the third by periodate oxidation with subsequent determination of the formaldehyde formed after cleavage of the hydroxy acids. The method is a modification of that devised by SAMUELSON AND STRÖMBERG for the automatic determination of alditols[2]. The modifications were made so that the same heating bath and three-channel photometer could be employed for the three analytical methods. The equipment was of the same type as used earlier[1], with the exception that the recorder (Philips PR 3500) was modified so as to permit individual changes of the range expansion in all three channels.

The eluate stream which passed to the periodate channel was mixed in a T-fitting with 0.015 *M* sodium metaperiodate buffered at pH 7.0. The mixing was completed and the periodate oxidation carried out in a horizontal reaction coil kept at 25°. The residence time was 2 min. To destroy the unreacted periodate, 0.2 *M* sodium arsenite solution, neutralized with hydrochloric acid to pH 7, was introduced in the liquor stream. This reaction was carried out in a second coil of the same type (residence time 1.5 min) kept at the same temperature. The determination of formaldehyde was made with 0.02 *M* pentane-2,4-dione in 2 *M* ammonium acetate solution, 0.05 *M* with respect to acetic acid. This reagent was introduced before the solution passed into a horizontal coil (residence time 40 sec) where mixing was completed. The reaction mixture was then passed into a vertical reaction coil submerged in the same heating bath as used for the chromic acid and carbazole channels (95°). The residence time was 5.5 min.

The horizontal coils (10 mm in diameter) and connections were made of Teflon tubing (i.d. 1.2 mm). To prevent gas bubbles in the analysis system, the reagent solutions were boiled continuously before they were introduced into the monitor. The color developed in the periodate channel was measured at 410 nm in a flow cell of air-bypass type. The recorder was run with a scale expansion of 2. The chromatographic equipment was the same as described earlier[1] and the volume distribution coefficients of the eluted compounds were calculated as usual[3]. The separated acids were the same as those used in previous work in this laboratory[1,4] with the exception of allonic, iduronic and reductinic acids which were kindly supplied by Dr. O. THEANDER, Stockholm and L-*ribo*-5-hexulosonic (5-ketotalonic), D-*lyxo*-5-hexulosonic (5-ketomannonic), alluronic and altruronic acids, the preparation of which will be described in a forthcoming paper.

RESULTS AND DISCUSSION

Typical chromatograms obtained by elution with 0.5 *M* acetic acid and with 0.08 *M* sodium acetate are reproduced in Figs. 2 and 3. A period of about 7 h was required to complete these runs. As usual all solutes were recorded in the chromic acid channel (full line) whereas among the acids studied in these runs, only uronic and 5-hexulosonic acids gave a strong response in the carbazole channel (broken line). A medium response in this channel was recorded with the aldobionic acids and a weak response with other acids also.

In the run in acetic acid (Fig. 2) all the acids were well separated, and the advantage of using the 3-channel analyzer instead of only chromic acid oxidation is that additional information of value for the identification of the compounds is

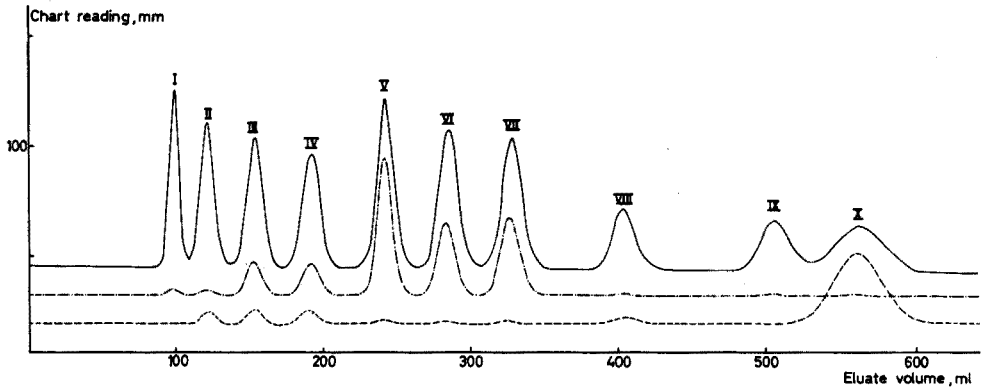

Fig. 2. Separation of levulinic (I), melibionic (II), cellobionic (III), maltobionic (IV), D-ribonic (V), D-*glycero*-D-*gulo*-heptonic (VI), D-gluconic (VII), lactic (VIII), L-rhamnoic (IX) and D-galacturonic acid (X). Chromic acid method —; carbazole method ----; periodate method ·····. Eluant: 0.5 *M* acetic acid; flow rate: 7.7 ml min^{-1} cm^{-2}; resin bed: 6 × 760 mm, Dowex 1-X8, 24–27 μ.

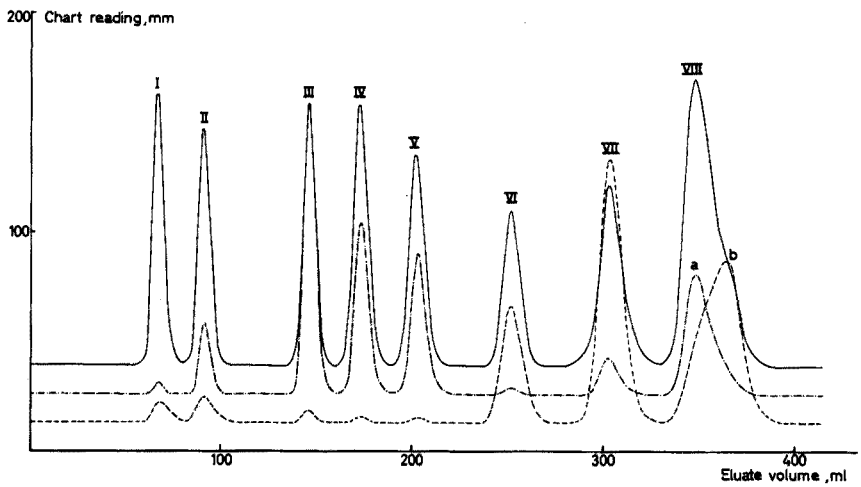

Fig. 3. Separation of melibionic (I), cellobionic (II), α-D-glucoisosaccharinic (III), D-gluconic (IV), D-allonic (V), L-guluronic (VI), D-*lyxo*-5-hexulosonic (VII), D-*xylo*-hexulosonic (VIII a) and L-*ribo*-5-hexulosonic acid (VIII b). Chromic acid method —; carbazole method ----; periodate method ·····. Eluant: 0.08 *M* sodium acetate, pH 5.9; flow rate: 5.2 ml min^{-1} cm^{-2}; resin bed: 6 × 710 mm, Dowex 1-X8, 17–20 μ.

gained, both from the carbazole reaction and from the periodate oxidation. In the chromatogram recorded in Fig. 3 the first 7 bands are well separated from each other whereas the last band contained two seriously overlapping acids. As shown in separate runs, the first of these gave only a slight reaction with carbazole but a strong response with periodate, whereas the opposite holds true for the second acid. It is seen that despite the serious overlapping a quantitative analysis of the complex mixture can be obtained by evaluation of the elution curves recorded in the carbazole and periodate channels. In the analyses of complex mixtures obtained in hydrolyzates from wood pulps, the advantages of the new system have proved to be of great value.

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TABLE I

DISTRIBUTION COEFFICIENTS AND PERIODATE RESPONSE INDICES OF HYDROXY ACIDS

Acid	*Distribution coefficient, D_v*			*Periodate response index*	
	0.5 M HAc	*1 M HAc*	*0.08 M NaAc*	*0.5 M HAc*	*0.08 M NaAc*
6-O-α-D-Galactopyranosyl-D-gluconic	4.5		2.6	0.03	0.04
4-O-β-D-Glucopyranosyl-D-gluconic	5.8		3.7	0.20	0.31
4-O-α-D-Glucopyranosyl-D-gluconic	7.3		3.7	0.23	
D-*glycero*-D-*gulo*-Heptonic	10.8		6.6	0.44	
D-Allonic	9.4		8.6		0.64
D-Gluconic	12.5		7.2	0.55	0.63
D-Idonic	12.5		6.8		
6-Deoxy-L-mannonic	19.3		10.9	0.02	
D-Ribonic	9.2		9.2	0.70	0.74
D-Xylonic	15.7		8.2	0.70	0.75
2-Deoxy-D-*erythro*-pentonic	2.7		8.4	0.74	
α-D-Glucoisosaccharinic	6.0		6.0		1.04
D-*xylo*-Hexulosonic		60.9	14.8		0.47
D-*lyxo*-5-Hexulosonic		14.5	12.8		0.20
L-*ribo*-5-Hexulosonic		27.1	15.4		0.22
D-Alluronic		16.0	11.3		0.04
D-Altruronic		17.9	11.8		0.03
D-Galacturonic		10.5	8.4	0.01	
D-Guluronic		11.6	10.7		0.03
D-Iduronic		18.2	13.8		
2,4-Dihydroxybutyric	14.6		11.7	~0	
3,4-Dihydroxybutyric	3.4		9.3	0.87	
Lactic	15.1		13.8	0.01	0.01
Reductinic	11.4		43.7	0.02	
Kojic	1.2		2.5	0.03	

The distribution coefficients of the acids studied in the present work are listed in Table I together with their response indices, defined as the area of the curve recorded in the periodate channel divided by that recorded in the chromic acid channel. This index is very useful for identification purposes and is a valuable complement to the carbazole response index discussed earlier[1].

In the elution with 0.5 *M* acetic acid, the periodate oxidation took place at pH 3.0, whereas the elution with 0.08 *M* sodium acetate gave a pH of 6.5 in the oxidation mixture. This explains the fact that the response indices are dependent upon the applied eluant (*cf.* ref. 5).

Periodate is known to react rapidly at room temperature with hydroxy acids having a glycol configuration. The reaction stops when a carbon atom is reached which does not contain an unsubstituted hydroxyl or carbonyl group. Aldonic acids are readily oxidized whereas 2-hydroxy acids such as glycolic acid react only slowly[6]. Formaldehyde is formed only when primary alcohol groups are present. Hence, it would be expected that within the investigated group of acids those which contain a CH_2OH group will give a strong response with pentane-2,4-dione provided that the neighbouring group is either a hydroxyl or a keto group.

This is confirmed by the reproduced chromatograms and by the results listed in Table I. It is seen that aldonic acids give a strong response in the periodate channel, but 6-deoxymannonic acid is not recorded. Likewise, 3,4-dihydroxybutyric acid gives a strongly positive reaction whereas 2,4-dihydroxybutyric acid does not react. Glucoisosaccharinic acid which contains two primary hydroxyl groups gives the highest response index.

Among the acids containing aldehyde or keto groups, the hexulosonic acids give curves comparable to those of the aldonic acids. 5-Hexulosonic acids give about one-third as strong a response as do aldonic acids. The hexuronic acids are not recorded or give a very slight response in this channel. This is in agreement with the results obtained by SPRINSON AND CHARGAFF[7]. Likewise, it is possible to distinguish between various types of linkages in aldobionic acids[8]. This is demonstrated by the fact that, as expected, 4-O-β-D-glucopyranosyl-D-gluconic acid (cellobionic) and 4-O-α-D-glucopyranosyl-D-gluconic acid (maltobionic) give a much more intense color than does 6-O-α-D-galactopyranosyl-D-gluconic acid (melibionic).

Some acids which do not contain a primary hydroxyl group with a neighbouring hydroxyl or keto group give a weak but reproducible response in the periodate channel. This is explained by the fact that neither the periodate oxidation nor the reaction with pentane-2,4-dione is quite specific[9]. Glyoxylic acid, which is one of the reaction products formed in most of the periodate oxidations studied, gave a response which was about 1% of that recorded with formaldehyde of the same concentration.

The areas of the curves recorded in the periodate channel are well suited for quantitative determinations of the acids with high response indices in this channel. In repeated runs carried out immediately after one another without a change of pump tubings, the maximum deviation from the mean was $\pm 3\%$. When the pump tubings are changed the monitor has to be recalibrated if high accuracy is required. In the analysis of mixtures which are not too complicated, the recalibration can be omitted if a suitable internal standard is incorporated in the mixture to be analyzed. The temperature during the periodate oxidation and treatment with arsenite is not

critical. For example, with gluconic acid an increase in temperature of 10° gave an increase in response of about 1%.

The financial support of the Swedish Council for Applied Research is gratefully acknowledged.

SUMMARY

Hydroxy acids are separated on an anion-exchange column and determined automatically by three colorimetric methods: chromic acid oxidation, periodate oxidation and the carbazole reaction. The simultaneous application of three methods facilitates both identification and determination.

RÉSUMÉ

On propose une séparation d'hydroxyacides sur colonne échangeuse d'anions avec dosage automatique à l'aide de trois méthodes colorimétriques: oxydation à l'acide chromique, oxydation au périodate et réaction au carbazole. L'application simultanée de ces trois méthodes facilite soit l'identification, soit le dosage.

ZUSAMMENFASSUNG

Hydroxy-Säuren werden an Anionenaustauscher-Kolonnen getrennt und automatisch durch die 3 folgenden kolorimetrischen Methoden bestimmt: Chromsäureoxydation, Perjodatoxydation und die Carbazol-Reaktion. Die gleichzeitige Anwendung dieser 3 Methoden erleichtert sowohl die Identifizierung als auch die Bestimmung.

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THE SOLUTION CHEMISTRY OF ETHYLMETHYLGLYOXIME

PART I. THE PROTON COMPLEX

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In the investigation of the chemical reactions between metal ions and dialkyldioximes, information concerning the influence of the alkyl groups on certain properties of the dioximes and their metal salts, *e.g.* solubility, distribution between organic solvents and aqueous solution, acid dissociation constants and complex formation constants, is of considerable importance analytically. Of the lower dialkyldioximes, *i.e.* dimethylglyoxime (DMG), ethylmethylglyoxime (EMG) and diethylglyoxime (DEG), only DMG has been studied extensively[1,2] and only some of the properties mentioned above have been determined for EMG and DEG[3,4].

The aim of the present investigation was to determine solubility constants, distribution constants between organic and aqueous solutions and acid dissociation constants for EMG. A study of its complexes with copper and nickel will follow.

The UV spectra between 210–290 nm were also measured and resolved into their components. This was carried out in order to compare the results with the theoretical calculations on DMG spectra published by Roos[5].

EXPERIMENTAL

Chemicals

The ethylmethylglyoxime was prepared by the method of Belcher *et al.*[6] and was recrystallized 3 times from water–alcohol mixtures. The chloroform (Merck, p.a.) was washed 3 times with distilled water to remove alcohol and to saturate the solvent with water. The sodium perchlorate was prepared by a technique used at KTH, Stockholm[7]. All other chemicals were of analytical grade. The organic solvents were saturated with water before use. The ionic strength of the aqueous phase was kept constant at 0.1 *M*.

Instruments

Spectrophotometric determinations of EMG were performed with a Beckman DB or DU spectrophotometer.

The UV spectra of EMG at different pH were measured on a Perkin-Elmer Hitachi 139 spectrophotometer with a photomultiplier amplifier, quartz 1-cm cells being used in all cases. The pH measurements were performed with a Beckman Research pH meter, a Beckman glass electrode 41260 type E-2 and a Beckman frit junction calomel electrode 39071. In the solubility experiments the pH meter was

standardized against 0.01 *M* perchloric acid–0.09 *M* sodium perchlorate (pH = 2.000). For pH measurements in connection with the spectral recordings, the pH meter was standardized against a buffer solution of 0.0200 *M* ammonium perchlorate, 0.01965 *M* ammonia, 0.07 *M* sodium perchlorate (pH = 9.240). The potentiometric titrations of EMG to determine K_{a1} and K_{a2} were followed with a Radiometer pHM 4 equipped with a Radiometer glass electrode G 202B and a Radiometer calomel electrode K 401. All experiments were carried out in a thermostatted room at 25°.

Solubility experiments

Solutions containing $NaClO_4$, NaOH, NH_3, NH_4ClO_4 (ionic strength = 0.1 *M*) were saturated with EMG by filtering the solutions through a column containing the dioxime. Each solution was filtered 3 times to ensure saturation. A known volume of the filtrate was diluted with 0.09 *M* sodium perchlorate–0.01 *M* perchloric acid to transform the dioxime completely to the undissociated acid form. The concentration of the EMG was then determined spectrophotometrically by measuring the UV absorbance of EMG at 250 nm. The hydrogen ion concentration of each filtrate was also measured.

Distribution experiments

Equal volumes (15 ml) of 0.005 *M* EMG in 0.1 *M* sodium perchlorate and an organic solvent were mixed in 50-ml centrifuge tubes and shaken overnight for about 20 h. To a known volume (3–10 ml) of the aqueous phase, excess nickel acetate and 1 ml of sodium phosphate buffer solution (0.0616 *M* $H_2PO_4^-$ + 0.0461 *M* HPO_4^{2-}) of pH 6.65 were added. The aqueous phase was adjusted with 0.1 *M* sodium perchlorate to a volume of 10 or 15 ml. The nickel complex with EMG was extracted with an equal volume (10 or 15 ml) of fresh organic solvent and the absorbance of the "new" organic phase was measured at 366 nm. The original organic phase was analysed by adding nickel acetate in excess and 1 ml of buffer solution (pH 6.65) to a known volume (3–10 ml) of the phase and adjusting the volume of the organic phase to 10 or 15 ml with fresh organic solvent saturated with water. The aqueous phase was adjusted to the same volume as the organic phase with 0.1 *M* sodium perchlorate. A corresponding calibration curve for $Ni(HA)_2$ was constructed for each organic solvent.

Potentiometric titrations

The dissociation constants of EMG were determined by potentiometric titrations of 50 ml of 0.005 *M* EMG in 0.1 *M* sodium perchlorate with carbonate-free 0.1 *M* sodium hydroxide. The titration vessel was covered with "parafilm" (Marathon, Division of American Can Company), and nitrogen was passed over the solution. The e.m.f. was read after each addition of sodium hydroxide. The glass electrode was standardized before each titration by titrating 50 ml of 0.1 *M* sodium perchlorate with 0.1 *M* sodium hydroxide. The following equation was used:

$$e = e_0 - RTF^{-1}\ln 10 \log [OH^-] + k[OH^-]$$

The constants e_0 and k were obtained by plotting $e + RTF^{-1}\ln 10 \log [OH^-]$ against $[OH^-]$ where e is the value of the e.m.f. obtained after each addition of sodium hydroxide. $[OH^-]$ and $\log[OH^-]$ were calculated from v ml NaOH added, according

to $[OH^-]=vt/(50+v)$. In the titration of EMG the values of $\log[OH^-]$ were calculated from the e.m.f. readings, assuming that e_0 and k remain unchanged after the calibration. The pH ($-\log h$) was calculated from the ionic product of water at 25° and 0.1 M ionic strength, *i.e.* $h[OH^-]=10^{-13.81}$.

UV absorption spectra

The UV absorbances for solutions of EMG in the pH range 9–13 were measured between 210 and 290 nm. The solutions were prepared so as to contain $5\cdot10^{-5}$ M EMG and the pH was adjusted with buffer solutions containing NH_4^+, NH_3, OH^-. The ionic strength was kept constant at 0.1 M with sodium perchlorate. The reference solution was prepared in the same way but without EMG. The solutions were allowed to equilibrate for 10 min before the absorbance and the pH values were measured.

Symbols

H_2A = the acid form of EMG
a = $[A^{2-}]$
h = $[H^+]$
K_{a1} = $h[HA^-]/[H_2A]$
K_{a2} = $ha/[HA^-]$
K_{s1} = $[H_2A]$ (solution saturated with H_2A)
S = total solubility of EMG
C_A = total concentration of EMG
K_{D1} = $[H_2A]_{org}/[H_2A]$
Z = the ratio between the concentration of protons released and the concentration of dioxime (eqn. (4))
v = ml NaOH added during a titration
v_0 = initial volume in the titration vessel
t = titre of NaOH
C_{OH} = total concentration of NaOH added
e = e.m.f. reading during a titration
e_0, k constants
E = observed absorbance
E_2, E_1, E_0 = molar absorptivities of H_2A, HA^- and A^{2-}, respectively.

TREATMENT OF DATA AND RESULTS

Solubility experiments

The total solubility of EMG is given by

$$S=[H_2A]+[HA^-]+[A^{2-}] \quad (1a)$$

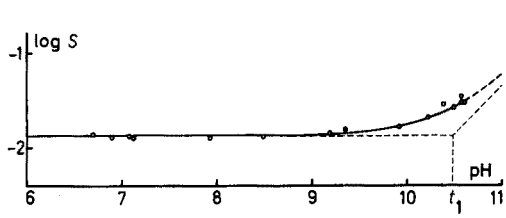
or

$$S=K_{s1}+K_{s1}K_{a1}/h+K_{s1}K_{a1}K_{a2}/h^2 \quad (1b)$$

The third term will contribute discernibly to the solubility only at pH greater than 10.6, since $pK_{a1}=10.51$ and $pK_{a2}=12.02$ (see determination of acid dissociation constants below).

The experimental data were plotted as $\log S$ against $-\log h$ (Fig. 1). The data give $\log K_{s1}=-1.88\pm0.02$ or $K_{s1}=(1.32\pm0.06)\ 10^{-2}$ M. If the second acid dissocia-

tion constant is neglected in eqn. (1b), the normalized curve[8,9] $Y = \log(1+u)$; $X = \log u$, fits the data in Fig. 1. The intersection of the asymptotes, t_1 in Fig. 1 gives $pK_{a1} = 10.48$. This value agrees well with the value $pK_{a1} = 10.51$ obtained from the potentiometric titrations. When the solubilities of EMG (0.0132 M) and DMG (0.005 M)[10] are compared, it is observed that K_{s1} for EMG is higher than for DMG in spite of the lower molecular weight of DMG. This probably reflects stronger forces in the solid state, *i.e.* the larger ethyl group interferes with the lattice structure[11-13].



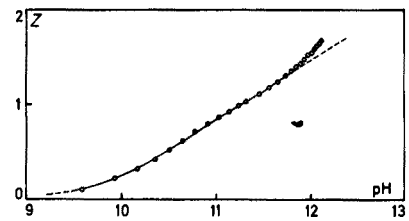


Fig. 1. Solubility of EMG as a function of pH. The dashed curve was calculated neglecting the second dissociation constant. The asymptotes with slope 0 and 1 intersect at t_1, defined by $\log S = \log K_{s1}$ and $-\log h = pK_{a1}$.

Fig. 2. Graphical determination of the acid dissociation constants of EMG. The full-drawn curve is the normalized curve $Y = (pu + 2u^2)/(1 + pu + u^2)$; $X = \log u$, with $p = 5.70$. The circles are experimental values from one representative titration.

TABLE I

THE DISTRIBUTION AND SOLUBILITY CONSTANTS OF EMG AND DMG FOR SOME ORGANIC SOLVENTS ($\Delta \log K_{D1} = \log K_{D1EMG} - \log K_{D1DMG}$)

Solvent	*EMG*		*DMG*		$\Delta log\ K_{D1}$
	K_{D1}	$log\ K_{D1}$	$log\ K_{s1}$	$log\ K_{D1}$ *(calc.)*	
Benzene	0.308	−0.511	−3.49	−1.19	0.68
Hexane	0.0147	−1.833	—	—	—
CCl_4	0.0801	−1.096	−4.22	−1.92	0.82
$CHCl_3$	0.339	−0.469	−3.40	−1.10	0.63

Distribution experiments

The results of the distribution experiments are presented in Table I. The values of $\log K_{D1}$ for DMG in Table I were calculated from the ratio of the values of the solubility in organic solvents and water. The introduction of an alkyl group, CH_2, into a molecule will increase the distribution constant by a factor of about 4 (0.6 log units)[14,15]. From the values of $\Delta \log K_{D1}$ it is observed that this is approximately true for EMG and DMG.

The distribution constants are, as would be expected, less for non-polar than for polar solvents and benzene. Approximate values of $\log K_{D1}$ for solvents which can form hydrogen bonds with EMG, for instance isoamyl alcohol, hexone, isopropyl ether, can be calculated from values for DMG[2] by using the following equation:

$$\log K_{D1} = \log K_{s1(DMG,org)} - \log K_{s1(DMG,aq)} + 0.6.$$

The results obtained for some solvents are shown in Table II.

TABLE II

CALCULATED VALUES OF LOG K_{D1} FOR EMG FOR SOME ORGANIC SOLVENTS

Solvent	*DMG*		*EMG*
	log K_{s1}	*log* K_{D1} *(calc.)*	*log* K_{D1} *(calc.)*
BuOH	−1.25	1.05	1.65
i-BuOH	−1.42	0.88	1.48
i-AmOH	−1.35	0.95	1.55
Et_2O	−1.00	1.30	1.90

Acid dissociation constants

Since EMG is a very weak dibasic acid and the acid dissociation products overlap (see Fig. 3), a curve-fitting method[8,9] was used to evaluate the constants from the experimental data. The following equations are valid:

$$C_{OH} = vt/(v_0+v) = [HA^-] + 2[A^{2-}] + [OH^-] \quad (2)$$

$$C_A = [H_2A] + [HA^-] + [A^{2-}] \quad (3)$$

C_{OH} and C_A are calculated for each v. $[OH^-]$ is obtained from the e.m.f. as described above. The number of OH^- per EMG which react with H_2A is given by

$$Z = \frac{[HA^-] + 2[A^{2-}]}{[H_2A] + [HA^-] + [A^{2-}]} \quad (4)$$

Z is determined experimentally from

$$Z = (C_{OH} - [OH^-])/C_A \quad (5)$$

$[H_2A]$, $[HA^-]$ and $[A^{2-}]$ can be eliminated by using the definitions of K_{a1} and K_{a2}

$$Z = \frac{h/K_{a2} + 2}{h^2/K_{a1}K_{a2} + h/K_{a2} + 1} \quad (6)$$

If we introduce the normalized variable

$$u^2 = K_{a1}K_{a2}/h^2 \text{ or } h = u^{-1}K_{a1}^{\frac{1}{2}}K_{a2}^{\frac{1}{2}}$$

$$Z = \frac{u^{-1}K_{a1}^{\frac{1}{2}}K_{a2}^{-\frac{1}{2}} + 2}{u^{-2} + u^{-1}K_{a1}^{\frac{1}{2}}K_{a2}^{-\frac{1}{2}} + 1} \quad (7)$$

This represents a family of curves with the parameter $p^2 = K_{a1}/K_{a2}$. Introducing p in eqn. (7) we obtain

$$Z = \frac{pu + 2u^2}{1 + pu + u^2} \quad (8)$$

To find the unknown constants K_{a1} and K_{a2}, the experimental data $(C_{OH} - [OH^-])/C_A$ were plotted against $-\log h$ (Fig. 2) and fitted to a family of standardized curves, $Y = (pu + 2u^2)/(1 + pu + u^2)$; $X = \log u$ with p between 5 and 6.

For $Z = 1$, eqn. (6) gives $K_{a1}^{-1}K_{a2}^{-1}h^2 = 1$. From the value of $\log h$ at $Z = 1$ and the value of the parameter p of the best fit, pK_{a1} and pK_{a2} are calculated to be $pK_{a1} = 10.51 \pm 0.02$ and $pK_{a2} = 12.02 \pm 0.02$ (Table III). The first dissociation constant

has previously only been determined in aqueous–dioxan solutions with an ionic strength of 0.1 M, and an extrapolated value[3] from these experiments is $pK_{a1} = 10.41$. Table IV gives some of the values for DMG reported in the literature. In Fig. 2 it is also observed that the titration curve differs from the normalized curve at high pH. This may be due to the instability of the glass electrode. Furthermore, in this region Z according to eqn. (5), has to be calculated from rather large quantities of both C_{OH} and $[OH^-]$.

TABLE III

DETERMINATION OF pK_{a1} AND pK_{a2} FOR EMG

	pK_{a1}	pK_{a2}	p
	10.53	11.99	5.50
	10.51	12.01	5.63
	10.49	12.03	5.89
	10.53	12.03	5.63
Mean values	10.51	12.02	5.69

TABLE IV

DISSOCIATION CONSTANTS OF DMG

pK_{a1}	pK_{a2}	p	*Ref.*
10.45	—	—	16
10.48	—	—	3
10.55	12.00	5.31	18
10.60	11.85	4.22	17

Tables III and IV show that K_{a1} and K_{a2} are practically the same for EMG and DMG.

In Fig. 3 the distribution of $[H_2A]$, $[HA^-]$ and $[A^{2-}]$ is shown as a function of pH ($-\log h$).

UV spectra of EMG

From Fig. 4 (plot of absorption against wavelength) it is obvious that EMG has at least two different absorption maxima. The first appears at 226 nm and is due to undissociated H_2A. The second maximum appears at 260–266 nm and is caused by the HA^- and A^{2-} species. In alkaline solutions with pH > 11 the isosbestic point is slightly shifted towards longer wavelengths. This is due to a small difference in the absorption of the species HA^- and A^{2-}. In order to interpret the absorption difference between HA^- and A^{2-}, the spectra in Fig. 4 were resolved into their components $E_2[H_2A]$, $E_1[HA^-]$ and $E_0[A^{2-}]$. The following equations were used to determine the molar absorptivities of H_2A, HA^-, A^{2-} at different wavelengths:

$$E = E_2[H_2A] + E_1[HA^-] + E_0[A^{2-}] \quad (9)$$

$$C_A = [H_2A] + [HA^-] + [A^{2-}] \quad (10)$$

Dividing E by C_a and introducing K_{a1} and K_{a2}, we obtain:

$$(E/C_a)(hK_{a1}^{-1}K_{a2}^{-1} + K_{a2}^{-1} + h^{-1}) = hE_2K_{a1}^{-1}K_{a2}^{-1} + E_1K_{a2}^{-1} + h^{-1}E_0 \quad (11)$$

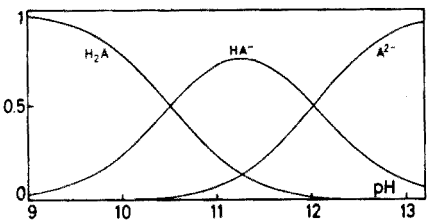
$(E/C_a)(hK_{a1}^{-1}K_{a2}^{-1}+K_{a2}^{-1}+h^{-1})$ is called A and is calculated for each wavelength and pH, using the values of K_{a1} and K_{a2} determined potentiometrically. Eqn. (11) will have two asymptotes,

$$\log A = \log E_2 - \log K_{a1}K_{a2} + \log h \quad \text{when } h \to \infty$$

and

$$\log A = \log E_0 - \log h \quad \text{when } h \to 0.$$

The experimental data for each wavelength are plotted as log A against $-\log h$ (Fig. 5a, b).



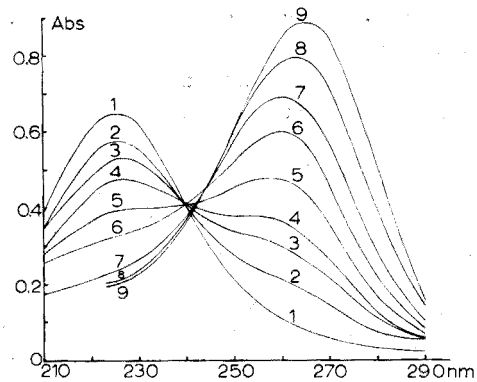
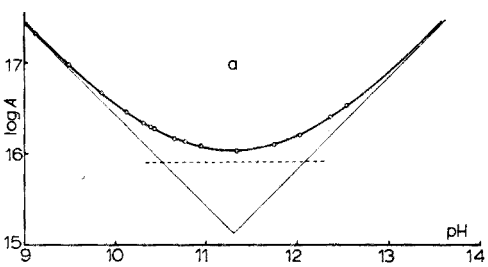


Fig. 3. Distribution diagram for EMG as a function of pH.

Fig. 4. Absorption spectra of EMG at different pH. Total concentration of EMG is $5 \cdot 10^{-5}$ M.

Solution nr.	*pH*
1	9.122
2	9.846
3	10.126
4	10.390
5	10.652
6	10.954
7	11.378
8	12.025
9	12.554



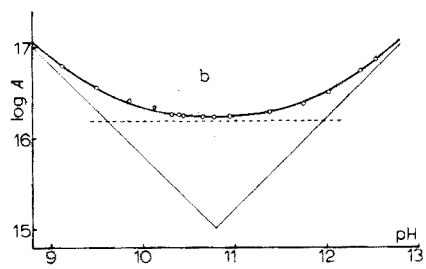


Fig. 5. Determination of the molar absorptivities of the EMG species. The experimental data, log A, are plotted as a function of pH. The full-drawn curve is the normalized curve $Y = \log (u + p + u^{-1})$; $X = \log u$, and the straight lines are the asymptotes to the curve. The dashed line is the line $Y = \log p$. Total concentration of EMG is $5 \cdot 10^{-5}$ M. (5a) 240 nm, $p = 6$ and (5b) 258 nm, $p = 15$.

As can be seen from eqn. (11) the data should fit the normalized curve[8,9] $Y=\log(u+p+u^{-1})$; $X=\log u$.

From the positions of the asymptotes $Y=X$ and $Y=-X$ and the line $Y=\log p$ for the best fit between the data and the normalized curve, E_2, E_1 and E_0 are calculated using the following equations:

$$\log A=\log E_0-\log h \text{ (corresponding to } Y=X)$$

$$\log A=\log E_2-\log K_{a1}K_{a2}+\log h \text{ (corresponding to } Y=-X)$$

$$\log A=\log E_1K_{a2}^{-1} \text{ (corresponding to } Y=\log p).$$

The resolved spectra of EMG are presented in Fig. 6 as molar absorptivities against wavelength. Figure 6 shows that the absorption maximum at 260 nm is shifted to a somewhat higher wavelength when the pH is increased. This is attributed to the removal of the second proton.

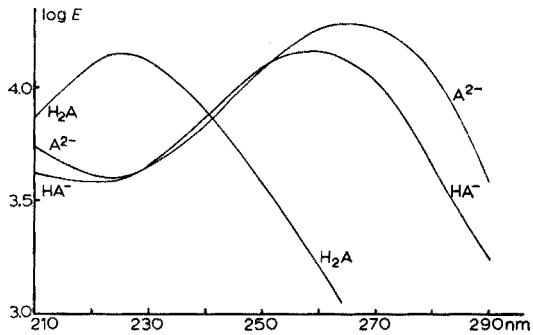


Fig. 6. The molar absorptivity spectra of H_2A, HA^- and A^{2-}, determined from a $5\cdot10^{-5}$ M solution of EMG. The data are given in Table V.

TABLE V

MOLAR ABSORPTIVITIES OF H_2A, HA^- AND A^{2-} OBTAINED FROM EQN. (11) (SEE TEXT)

nm	*log* E_2	*log* E_1	*log* E_0	*p*
210	3.87	3.62	3.74	4
223	4.14	3.58	3.59	3
230	4.11	3.65	3.65	3.5
240	3.90	3.87	3.83	6
250	3.58	4.09	4.08	10.5
258	3.28	4.16	4.23	15
264	3.05	4.14	4.28	18
270	(2.87)	4.04	4.26	17
280	(2.74)	3.66	4.07	11
290		3.24	3.58	

No absorption maxima between 210 and 220 nm, corresponding to one observation for DMG[19], could be detected, but the spectra in Fig. 4 are otherwise similar to those obtained earlier for DMG[19-21]. The molar absorptivity of HA^- has a maximum at 258 nm and that of A^{2-} has a maximum at 266 nm. As the spectra for HA^- and A^{2-} are similar, the determination of pK_{a1} and pK_{a2} from spectrophotometric data would be rather difficult.

The experimental data are also in good agreement with the theoretical calculations on the *cis*-form of DMG performed by Roos[5]. These calculations refer to isolated molecules or ions. The difference between the ethyl and methyl substitutions should be negligible, but the solvent effect may be important, especially at high pH.

The author wishes to thank the head of the department, Professor David Dyrssen, for his valuable advice, Mrs. Susan Jagner, fil.lic., M.A., for revising the English text, and Mrs. Helle Persson, ing., for drawing the figures.

SUMMARY

The solubility of ethylmethylglyoxime (EMG) was studied as a function of pH. The solubility K_{S1} in 0.1 *M* aqueous solution is 0.0132 ± 0.0006 *M*. The distribution constants K_{D1} of EMG between various organic solvents and 0.1 *M* aqueous solution were found to be -0.47 for chloroform, -0.51 for benzene, -1.10 for carbon tetrachloride and -1.83 for hexane. The acid dissociation constants were determined from potentiometric titrations; the values $pK_{a1} = 10.51$ and $pK_{a2} = 12.02$ were obtaining by fitting the experimental data to normalized curves. The UV spectra of $5 \cdot 10^{-5}$ *M* EMG solutions of varying pH were measured between 210 and 290 nm. It is shown that H_2A has an absorption maximum at 226 nm and HA^- and A^{2-} have absorption maxima at nearly the same wavelengths, *i.e.* 258 and 266 nm, respectively. The spectra of HA^- and A^{2-} have approximately the same form. The data are compared with those of dimethylglyoxime (DMG). The distribution constants (org/aq) are 4–5 times higher for EMG. The acid dissociation constants are about the same for EMG and DMG, but EMG is more soluble in water than DMG (13.2 and 5.0 mmoles/l, respectively). The UV spectra of EMG and DMG are very similar.

RÉSUMÉ

On a effectué une étude sur la solubilité de l'éthylméthylglyoxime (EMG) en fonction du pH. La solubilité K_{S1} dans une solution aqueuse 0.1 *M* est de 0.0132 ± 0.0006 *M*. Les constantes de partage K_{D1} de EMG entre divers solvants organiques et une solution aqueuse 0.1 *M* sont: -0.47 pour le chloroforme, -0.51 pour le benzène, -1.10 pour le tétrachlorure de carbone et -1.83 pur l'hexane. Les constantes de dissociation acides sont déterminées par titrage potentiométrique. Ils ont les valeurs: $pK_{a1} = 10.51$ et $pK_{a2} = 12.02$. Les spectres UV de solutions $5 \cdot 10^{-5}$ *M* EMG à divers pH sont mesurés entre 210 et 290 nm: H_2A présente un maximum d'absorption à 226 nm, HA^- et A^{2-} à 258 et 266 nm respectivement. Les spectres HA^- et A^{2-} ont approximativement la même forme. Comparée à la diméthylglyoxime (DMG), les constantes de partage (org/aq) sont 4–5 fois plus fortes pour EMG. Les constantes de dissociation acide sont approximativement les mêmes pour EMG et DMG. Cependant EMG est plus soluble dans l'eau que DMG (respectivement 13.2 et 5.0 mmoles/litre). Les spectres de EMG et DMG sont très similaires.

ZUSAMMENFASSUNG

Die Löslichkeit von Äthylmethylglyoxim (ÄMG) wurde in Abhängigkeit vom

pH-Wert untersucht. Die Löslichkeit K_{S1} in 0.1 *M* wässriger Lösung beträgt 0.0132 ± 0.0006 *M*. Die Verteilungskonstante K_{D1} von ÄMG zwischen verschiedenen organischen Lösungsmitteln und 0.1 *M* wässriger Lösung betragen −0.47 für Chloroform, −0.51 für Benzol, −1.10 für Tetrachlorkohlenstoff und −1.83 für Hexan. Die Säuredissoziationskonstanten wurden durch potentiometrische Titrationen bestimmt. Ihre Werte betragen: $pK_{a1} = 10.51$ und $pK_{a2} = 12.02$. Die UV-Spektren von $5 \cdot 10^{-5} M$ ÄMG-Lösungen wurden in Abhängigkeit vom pH-Wert zwischen 210 und 290 nm gemessen. Es konnte gezeigt werden, dass H_2A ein Absorptionsmaximum bei 226 nm, HA^- bei 258 nm und A^{2-} bei 266 nm besitzt. Die Spektren der beiden letzteren Spezies haben näherungsweise dieselbe Form. Die Daten werden mit denen von Dimethylglyoxim (DMG) verglichen. Die Verteilungskonstanten sind 4- bis 5-mal grösser als die des DMG. Die Säuredissoziationskonstanten sind für ÄMG und DMG etwa gleich, jedoch besitzt ÄMG eine grössere Löslichkeit in Wasser als DMG (13.2 bzw. 5.0 mmol/l). Die UV-Spektren von ÄMG und DMG sind sehr ähnlich.

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POLAROGRAPHIC STUDIES OF URANYL COMPLEXES WITH *TRANS*- AND *CIS*-BUTENEDIOIC ACIDS

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(Received April 15th, 1968)

The equilibria involved in the interaction of uranyl ion with carboxylic acids including maleic acid have been studied potentiometrically[1]. The effects of the structural differences of fumaric and maleic acids on the stabilities of complexes formed with copper(II), copper(I), silver and zinc have been investigated[2]. ANDREWS AND KEEFER[3] have investigated the copper(I) chloride complexes of maleic and fumaric acids; with fumaric acid a 1:1 complex of the type $H_2Fum \cdot CuCl$ was formed whereas with maleic acid, $H_2Mal \cdot CuCl$ and $HMal \cdot CuCl^-$ complexes were found. The complexes of chromium with maleate and fumarate have been studied conductometrically[4].

In the present work, the uranyl fumarate and uranyl maleate systems were studied polarographically in order to examine differences in the behaviour of the uranyl complexes with the two geometric isomers of butenedioic acid.

EXPERIMENTAL

Apparatus

The polarograms were obtained with a Sargent Model XII Polarograph. The applied potentials were measured with a Leeds and Northrup Student Potentiometer. A modified H-cell with external saturated calomel reference electrode was maintained at $30 \pm 0.1°$ during the measurements. Hydrogen gas, scrubbed by passing through an alkaline solution of sodium pyrogallate, was used to remove oxygen from solutions. The dropping mercury electrode used had a flow rate of 2.147 mg/sec and a drop time of 3.75 sec in a solution containing 1 m*M* uranyl perchlorate, 0.16 *M* maleic acid, 0.10 *M* sodium perchlorate and 0.002% Triton X-100, at an applied potential of −0.300 V *vs.* S.C.E. and at a mercury height of 71.7 cm.

The pH values of the solutions were adjusted with perchloric acid or sodium hydroxide and determined by a Toa Denpa HM-5A glass electrode pH meter. A Toa Electronics Model CM-IDB Electrolytic Conductivity Meter with a cell having a cell constant of 2.0 was used for the conductometric titration.

Chemicals

The preparation and analysis of the uranyl perchlorate solution used were the same as described previously[5].

A 1.00 *M* stock solution of disodium fumarate was prepared by dissolving

16.004 g of the salt (Wako Pure Chemical Industries Co., special grade) in sodium hydroxide solution and diluting the solution to 100 ml with distilled water.

A 1.00 *M* stock solution of maleic acid was prepared by dissolving 9.802 g of maleic anhydride (extra pure reagent) in 100 ml of distilled water.

Triton X-100 (0.002% solution) was used as maximum suppressor. Sodium perchlorate was used as supporting electrolyte.

RESULTS AND DISCUSSION

Nature of the reduction

The polarographic characteristics of the uranyl fumarate complex were studied systematically over the pH range 2.03–5.70, with ligand concentrations varying from 0.04 to 0.64 *M*. It is obvious from Table I that, owing to the weak buffer action, the lower the ligand concentration, the lower the pH value at which the irreversibility

TABLE I

POLAROGRAPHIC CHARACTERISTICS AND REVERSIBILITY OF THE URANYL FUMARATE COMPLEX

$C_{H_2Fum}(M)$	pH	$-E_{\frac{1}{4}}$ (*V vs. S.C.E.*)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$	*Slope of log plot*	i_d (*μA*)
0.04	2.27	0.187	0.064	0.062	3.4
	2.50	0.194	0.063	0.063	3.6
	2.70	0.204	0.064	0.061	3.5
	3.00	0.225	0.066	0.064	3.4
	3.50[a]	0.228	0.070[a]	0.072[a]	3.2
0.08	2.03	0.188	0.063	0.060	3.6
	2.50	0.208	0.064	0.062	3.4
	3.00	0.240	0.065	0.063	3.4
	3.24	0.250	0.066	0.064	3.2
	3.75[a]	0.274	0.081[a]	0.079[a]	3.0
0.16	2.50	0.232	0.060	0.058	3.5
	3.50	0.288	0.060	0.061	3.3
	4.49	0.333	0.065	0.062	2.7
	4.90	0.340	0.066	0.063	2.6
	5.10[a]	0.345	0.072[a]	0.069[a]	2.7
0.32	3.24	0.299	0.057	0.060	3.3
	4.00	0.345	0.060	0.060	3.0
	4.80	0.374	0.066	0.063	2.7
	5.00	0.380	0.064	0.061	2.6
	5.30[a]	0.385	0.080[a]	0.077[a]	2.7
0.48	3.24	0.323	0.059	0.060	3.2
	3.96	0.366	0.060	0.061	3.1
	4.25	0.374	0.066	0.064	2.9
	4.80	0.390	0.064	0.061	2.7
	5.25[a]	0.402	0.072[a]	0.070[a]	2.6
0.64	3.78	0.345	0.056	0.058	3.2
	4.30	0.378	0.060	0.060	2.8
	4.98	0.395	0.065	0.064	2.7
	5.28	0.400	0.064	0.064	2.6
	5.70[a]	0.414	0.066[a]	0.065[a]	2.6

[a] Irreversible waves.

TABLE II

POLAROGRAPHIC CHARACTERISTICS AND REVERSIBILITY OF THE URANYL MALEATE COMPLEX

$C_{H_2Mal}(M)$	pH	$-E_{\frac{1}{4}}$ (V vs. S.C.E.)	$E_{\frac{1}{4}}-E_{\frac{1}{2}}$	Slope of log plot	i_d (μA)
0.10	1.50	0.185	0.062	0.060	3.2
	1.90	0.190	0.060	0.061	3.0
	2.50	0.225	0.066	0.062	3.0
	3.62	0.291	0.064	0.060	3.0
	4.40	0.343	0.061	0.061	3.0
	5.40	0.402	0.066	0.064	2.9
	6.50	0.425	0.064	0.060	2.9
0.16	1.01	0.184	0.060	0.061	3.3
	1.76	0.193	0.060	0.062	3.2
	2.00	0.208	0.058	0.059	3.3
	3.10	0.275	0.060	0.061	3.3
	4.22	0.340	0.059	0.060	2.9
	5.90	0.426	0.060	0.060	3.2
	6.44	0.428	0.063	0.062	3.0
0.20	1.00	0.184	0.061	0.061	3.5
	1.80	0.202	0.063	0.060	3.1
	2.47	0.245	0.063	0.064	3.0
	3.50	0.310	0.062	0.060	3.2
	4.72	0.384	0.063	0.063	3.0
	5.83	0.433	0.060	0.058	3.1
	6.70	0.430	0.063	0.062	2.9
0.32	1.10	0.187	0.062	0.060	3.2
	1.80	0.210	0.061	0.061	3.1
	1.98	0.227	0.061	0.062	3.2
	2.94	0.286	0.060	0.059	3.2
	4.26	0.373	0.057	0.058	3.2
	5.58	0.430	0.059	0.061	2.8
	6.05	0.435	0.060	0.061	2.9
	6.50	0.433	0.062	0.060	2.9

TABLE III

EVIDENCE FOR REVERSIBLE AND DIFFUSION-CONTROLLED REDUCTION

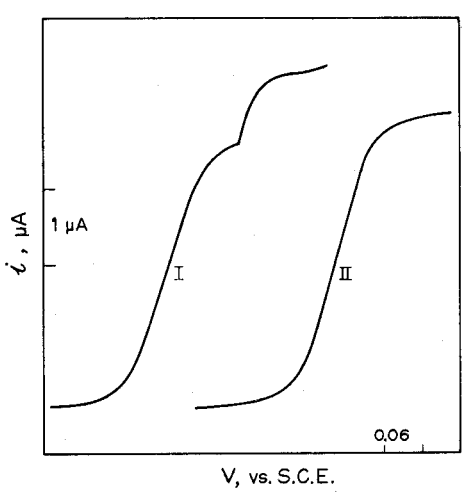
	Uranyl fumarate	*Uranyl maleate*
Temp. coeff. of $E_{\frac{1}{4}}$ (mV/°)(20–40°)	0.608	0.188
Temp. coeff. of i_d (%/°)	1.60	0.32
$i_d/h^{\frac{1}{2}}$ (h = 51.5–78.3 cm)	0.420±0.007	0.407±0.005

appeared. However, as the ligand concentration increased, the lower limit of pH value had to be raised simultaneously to avoid precipitation of fumaric acid.

The polarographic characteristics of the uranyl maleate system were studied over the pH range 1.00–6.70 and the ligand concentration range 0.10–0.32 M (Table II). In the pH range 1.5–2.5, as shown in Fig. 1, two waves were observed. The second wave was ill-defined; it decreased with increase in pH, disappearing at pH 2.5. The second wave in this pH range is attributed to the reduction of the undissociated maleic acid with a pK_1 1.92[6].

The slopes of the traditional plot of $E_{d.e.}$ *vs.* log $i/(i_d-i)$ and the values of $E_{\frac{1}{4}}-E_{\frac{3}{4}}$ are 0.056–0.066 (Tables I and II), which indicates that the electrode reactions are one-electron reversible processes.

The temperature coefficients of the half-wave potential and diffusion current and the values of $i_d/h^{\frac{1}{2}}$ for both the isomeric systems are summarized in Table III; these data also indicate that the reductions are one-electron reversible and diffusion-controlled processes.



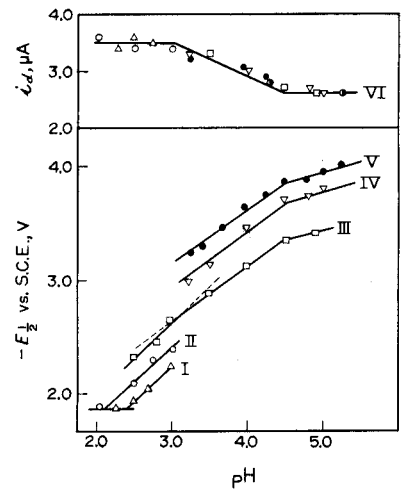


Fig. 1. Polarograms of the uranyl maleate complex. 1 m*M* $UO_2(ClO_4)_2$, 0.32 *M* H_2Mal and 0.002% Triton X-100. (I) pH 1.98; (II) pH 2.94.

Fig. 2. Effect of pH on the half-wave potential and diffusion current of the uranyl fumarate complex. 1.0 m*M* $UO_2(ClO_4)_2$, 0.15 *M* $NaClO_4$, 0.002% Triton X-100 and various concentrations of fumaric acid: △ 0.04 *M*; ○ 0.08 *M*; □ 0.16 *M*; ▽ 0.32 *M*; ● 0.48 *M*; ◑ 0.64 *M*.

Effect of pH on half-wave potential and diffusion current

Figure 2 shows the half-wave potential of the uranyl fumarate complex as a function of pH. For a 0.04 *M* ligand concentration below pH 2.40, the half-wave potential remains constant at −0.186 V *vs.* S.C.E., which is identical with the first half-wave potential of the simple uranyl ion, showing that no chelate is formed.

The half-wave potential *vs.* pH plots break at pH 3.05 and 4.55. Below pH 3.05, the slope of the straight line is −0.060, indicating that the reduction takes place with the consumption of one hydrogen ion. In the pH range 3.05–4.55, the slope of the line is −0.050, which indicates that one hydrogen ion or hydroxyl ion is involved in the electrode reaction. Above pH 4.55, the half-wave potentials become essentially independent of pH, which shows that no hydrogen ion or hydroxyl ion is involved.

The diffusion currents of the uranyl fumarate complex are practically independent of the ligand concentration (Table I). The diffusion currents remain constant, 3.5 μA, below pH 3.0 (Curve VI, Fig. 2), which indicates the existence of a complex species of constant composition, and then decrease linearly as the pH increases to 4.55, which indicates the deprotonation of the ligand species and transformation to

another complex species. Above pH 4.55, the deprotonation of ligand species is complete and the diffusion current reaches a constant value of 2.6 μA.

The effect of pH on the half-wave potential of uranyl maleate is shown in Fig. 3. Below pH 1.50 with ligand concentrations below 0.32 M, there is no chelation, the half-wave potentials being constant at -0.185 V *vs.* S.C.E. Between pH 1.50 and 1.90 for maleic acid concentrations above 0.10 M, the half-wave potentials decrease with increase in pH; the slope is -0.115, which indicates participation of two hydrogen ions. In the pH range 1.90–5.60, the half-wave potentials still decrease linearly; the slope of -0.06 V here indicates a one-electron reaction. Above pH 5.60, the half-wave potential is independent of pH.

The diffusion currents of uranyl maleate are independent of ligand concentration and pH value, which shows that only one species exists in the pH range tested (Table II).

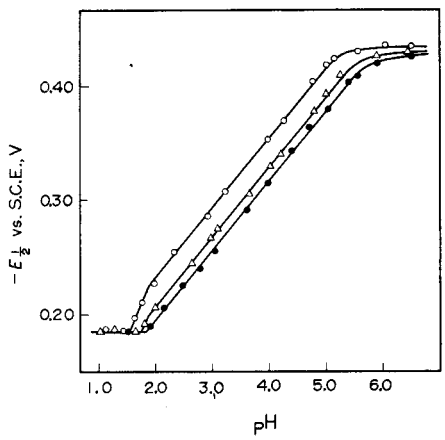


Fig. 3. Effect of pH on the half-wave potential of the uranyl maleate complex. 1.0 mM $UO_2(ClO_4)_2$, 0.15 M $NaClO_4$, 0.002% Triton X-100 and various concentrations of maleic acid: • 0.10 M; △ 0.16 M; ○ 0.32 M.

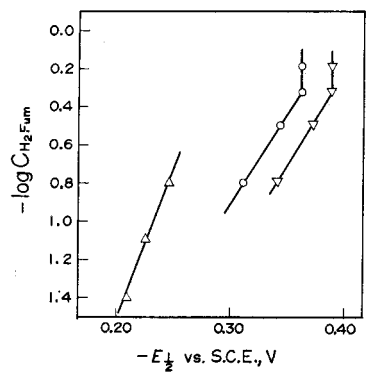


Fig. 4. Effect of ligand concentration on the half-wave potential of the uranyl fumarate complex at various pH values: △ pH 2.75; ○ pH 4.00; ▽ pH 4.75.

Effect of ligand concentration on half-wave potential

The dependence of the half-wave potential of the uranyl fumarate complex on ligand concentration is shown in Fig. 4. The data show that the ligand number p of the uranium(VI) fumarate complex is the same as the ligand number q of the uranium(V) fumarate complex at any pH provided that the ligand concentration exceeds 0.48 M. For ligand concentrations below 0.48 M and pH values lower than 3.05, the value of $\Delta E_{\frac{1}{2}}/\Delta\log C_{H_2Fum}$ is -0.060, showing that $p-q=1$. Above pH 3.05 the value of $\Delta E_{\frac{1}{2}}/\Delta\log C_{H_2Fum}$ is -0.110, which shows that $p-q=2$ in these pH ranges.

The variation of the half-wave potential of the uranyl maleate complex with ligand concentration is shown in Fig. 5. Below pH 5.60, the value of $\Delta E_{\frac{1}{2}}/\Delta\log C_{H_2Mal}$ is -0.060, *i.e.* $p-q=1$, except for maleic acid concentrations below 0.13 M (at pH 1.80) where the half-wave potential is constant. Above pH 5.60, the value of $\Delta E_{\frac{1}{2}}/\Delta\log C_{H_2Mal}$ approaches zero, *i.e.* $p=q$.

Metal–ligand ratio of complexes

Conductometric titrations of uranyl perchlorate with sodium fumarate or maleic acid indicated that the metal–ligand ratio was 1:2 for the uranyl complexes of both the *trans* and *cis* butenedioic acids when the ligand was present in excess.

Dissociation constants of butenedioic acids

It was shown previously[7,8] that the plots of $(E_{\frac{1}{2}})_c$ *vs.* pH should break at the pK_1 and pK_2 values of diprotic acid ligands. The pK_1 and pK_2 values of fumaric acid were found to be respectively 3.05 and 4.55 from the break points in Fig. 2.

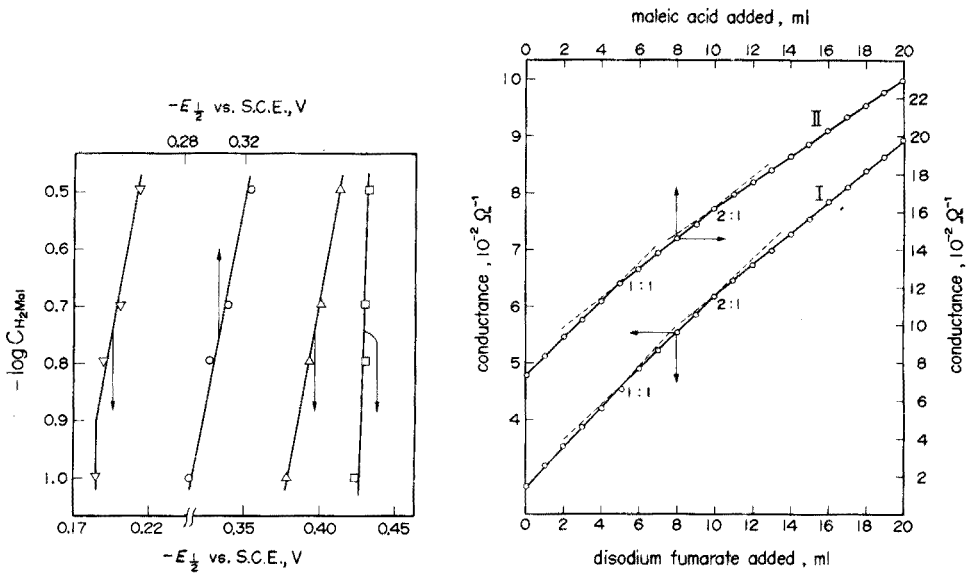


Fig. 5. Effect of ligand concentration on the half-wave potential of uranyl maleate complex at various pH values: ▽ pH 1.80; ○ pH 3.50; △ pH 5.00; □ pH 6.50.

Fig. 6. Conductometric titration. (I) 20 m*M* $UO_2(ClO_4)_2$ 5 ml + H_2O 145 ml + 20 m*M* Na_2Fum *x* ml; (II) 60 m*M* $UO_2(ClO_4)_2$ 5 ml + H_2O 145 ml + 60 m*M* H_2Mal *x* ml.

These values are in good agreement with the literature values[6], $pK_1 = 3.02$ and $pK_2 = 4.38$[6]. Similarly, from Fig. 3, the pK_1 and pK_2 values of maleic acid were found to be respectively 1.90 and 5.60 (literature values[6]: 1.92 and 6.22).

Complex species and electrode reactions

The complex species and electrode reactions of the uranyl fumarate complexes for 3 pH ranges are described below.

$pH < pK_1$ (3.05). The predominant ligand species must be protonated and the half-wave potential of the uranyl fumarate complex must obey the equation[8],

$$(E_{\frac{1}{2}})_c = \text{constant} - 0.060(p-q)\log C_{H_2Fum} - 0.060(p-q)\text{pH} \qquad (1)$$

Since $\Delta(E_{\frac{1}{2}})_c/\Delta\text{pH} = -0.060$, then $p-q=1$ which is in accordance with the value obtained from $\Delta(E_{\frac{1}{2}})_c/\Delta\log C_{H_2Fum} = -0.060$. Thus, the complex species and electrode reaction can be represented as

$$UO_2(HFum)_2 + H^+ + e \rightleftharpoons UO_2(HFum) + H_2Fum$$

$pK_1 < pH < pK_2$ *(4.55)*. The predominant ligand species must be deprotonated. The $p-q$ values obtained from $\Delta(E_{\frac{1}{2}})_c/\Delta pH = -0.06$ and $\Delta(E_{\frac{1}{2}})_c/\Delta \log C_{H_2Fum} = -0.110$ are not identical (for the former $p-q=1$ and for the latter $p-q \simeq 2$). This discrepancy can be ascribed to a two-step electrode reaction:

$$UO_2Fum_2^{2-} + H^+ + e \rightleftharpoons UO_2Fum^- + HFum^-$$

$$UO_2Fum^- \rightleftharpoons UO_2^+ + Fum^{2-}$$

$pH > pK_2$ *(4.55)*. Above pH 4.55, the deprotonation of the ligand species is complete and the chelate formed is $UO_2Fum_2^{2-}$, the half-wave potential of which obeys the following equation[8]:

$$(E_{\frac{1}{2}})_c = \text{constant} - 0.060(p-q)\log C_{H_2Fum} \quad (2)$$

This equation indicates that the half-wave potential of the chelate is a function of the concentration of the chelating agent and independent of the pH value. This agrees with the data in Fig. 2. If $\Delta(E_{\frac{1}{2}})_c/\Delta \log C_{H_2Fum} = -0.110$ is introduced into eqn. (2), then $p-q \simeq 2$. Consequently, the electrode reaction can be expressed as

$$UO_2Fum_2^{2-} + e \rightleftharpoons UO_2^+ + 2\ Fum^{2-}$$

From Figs. 3 and 5 and Table II, it is evident that only one chelate species, $UO_2Mal_2^{2-}$, exists in the following 3 pH ranges for the uranyl maleate system and the half-wave potential of the complex can be derived as[7],

$$pH < pK_1\ (1.90).\ (E_{\frac{1}{2}})_c = \text{constant} - 0.060(p-q)\log C_{H_2Mal} - 0.120(p-q)pH \quad (3)$$

$$pK_1 < pH < pK_2\ (5.60).\ (E_{\frac{1}{2}})_c = \text{constant} - 0.060(p-q)\log C_{H_2Mal} - 0.060(p-q)pH \quad (4)$$

$$pH > pK_2\ (5.60).\ (E_{\frac{1}{2}})_c = \text{constant} - 0.060(p-q)\log C_{H_2Mal} \quad (5)$$

When $p-q=1$ (Fig. 5) is introduced into eqns. (3), (4) and (5), then $\Delta(E_{\frac{1}{2}})_c/\Delta pH = -0.120$, -0.060 and 0, respectively. These results are in accordance with the data of Fig. 3.

Thus, the electrode reactions of the uranyl maleate complex in these pH ranges can be written, respectively, as:

$$UO_2Mal_2^{2-} + 2H^+ + e \rightleftharpoons UO_2Mal^- + H_2Mal$$

$$UO_2Mal_2^{2-} + H^+ + e \rightleftharpoons UO_2Mal^- + HMal^-$$

$$UO_2Mal_2^{2-} + e \rightleftharpoons UO_2Mal_2^{3-}$$

The authors thank the National Council of Science for financial support of this work.

SUMMARY

The complexation of uranyl ion with fumaric and maleic acids was investigated by polarography and conductometry. The uranyl complexes of the two isomers differ: with fumaric acid, $UO_2(HFum)_2$ and $UO_2Fum_2^{2-}$ were observed whereas with maleic acid, only one chelate, $UO_2Mal_2^{2-}$, was obtained. The dissociation constants obtained from the half-wave potential *vs.* pH plots were $pK_1 = 3.05$ and $pK_2 = 4.55$ for fumaric acid and $pK_1 = 1.90$ and $pK_2 = 5.60$ for maleic acid.

RÉSUMÉ

La complexation de l'uranyle avec acides fumarique et maléïque est examinée par polarographie et conductométrie. Les complexes uranyle des deux isomères sont différents: on décèle $UO_2(HFum)_2$ et $UO_2Fum_2^{2-}$, tandis que pour l'acide maléïque on n'observe qu'un chélate $UO_2Mal_2^{2-}$. Les constantes de dissociation obtenues à partir des potentiels de demi-vague (*vs.* pH) sont: pour l'acide fumarique $pK_1 = 3.05$ et $pK_2 = 4.55$, pour l'acide maléïque $pK_1 = 1.90$ et $pK_2 = 5.60$.

ZUSAMMENFASSUNG

Die Komplexbildung des Uranyl-Ions mit Fumar- und Malein-Säuren wurden polarographisch und konduktometrisch untersucht. Es wurden folgende Spezies gefunden: $UO_2(HFum)_2$, $UO_2Fum_2^{2-}$ und $UO_2Mal_2^{2-}$. Aus dem Halbstufenpotential in Abhängigkeit vom pH-Wert ergaben sich folgende Dissoziationskonstanten: Für die Fumarsäure $pK_1 = 3.05$ und $pK_2 = 4.55$; für die Malein-Säure $pK_1 = 1.90$ und $pK_2 = 5.60$.

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NEPHELOMETRIC DETERMINATION OF GOLD WITH DI-2-THIENYLKETOXIME

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The work described in this paper constitutes part of an investigation into the use of thienylketoximes as analytical reagents. Previously, the reactions of di-2-thienylketoxime and the structure of the complexes formed with palladium(II) were reported[1] and nephelometric[2] and gravimetric[3] procedures for palladium(II) based on the formation of chloropalladium(II) complexes with di-2-thienylketoxime were described. The reagent was also used for the gravimetric determination of gold(III)[4]. The purpose of the present work was to determine microgram amounts of gold nephelometrically. The literature contains little information about thiophene derivatives in complex formation with the transition metals. 2-Thienyltransaldoxime serves as an analytical reagent for palladium(II)[5], and thenoyltrifluoroacetone has been used for the separation of zirconium and hafnium[6]. The stability constants of the metal complexes of 2-thiophene-carboxylic acid[7] have been measured.

Thionalide has been used to determine gold nephelometrically[8]. Colorimetric methods for gold involve absorptivity measurements on colloidal gold solutions, on the colored oxidized product of the organic precipitant, or on an organic extract of the colloidal suspension. Oximes in general form stable complexes with transition metals and are widely used for their detection and estimation.

EXPERIMENTAL

Instrumentation and reagents

A Model 7 Coleman Photo-Nephelometer was used for the nephelometric measurements. A Model 23-A direct reading pH meter was employed for pH determinations.

Generator solution. Coleman certified nephelos standards were employed to standardize the nephelometer.

Di-2-thienylketoxime. The reagent was synthesized and purified as described previously[1]. A 0.2% solution in Fisher certified-reagent dioxane was prepared and allowed to stand for 3 days before use.

Standard gold solutions. Fisher ACS reagent, $HAuCl_4 \cdot 3H_2O$ was used. A stock solution containing 1 mg of gold per ml was prepared by dissolving the gold chloride in water. This solution was standardized gravimetrically by BEAMISH's hydroquinone method[9]. The gold(III) standard solutions were prepared by appropriate dilution.

Solutions of diverse ions. Reagent-grade chlorides, nitrates, sulfates or per-

chlorates were employed in the preparation of solutions of diverse cations. Sodium, potassium or ammonium salts were used for diverse anions.

Recommended nephelometric procedure

Gold(III) stock solution was diluted to give a solution containing 6 μg of gold per ml and the pH was adjusted to 3.6–4.2 with 0.01 *N* potassium hydroxide or hydrochloric acid. Transfer aliquots containing 50–200 μg of gold to 50-ml volumetric flasks and dilute each sample to 35 ml with distilled water. Swirl and add 1 ml of 0.2% reagent. Swirl again and allow to stand in the dark for 6 h. Add 8 ml of aqueous 1% gelatin solution as stabilizer, dilute to the mark, and invert the flasks slowly 50 times by wrist over a 4-min interval. Fill the cuvette with sample and record the transmission after 1 min. The galvanometer sensitivity was set using the Coleman certified nephelos standards so that each scale division equalled 4 Coleman nephelos units. The largest sample concentration for the calibration curve was set to read 100% transmittance by the blank control. Plotting the scale readings against gold(III) concentration gave a straight line over the range 1.0–4.0 p.p.m.

RESULTS

Composition of the gold complex

The suspension was coagulated by allowing it to stand overnight. The precipitate obtained was filtered and analyzed. Elemental analysis showed the compound to be a 2:1 complex containing one hydroxide group. (Calculated for $Au(C_9H_6NOS_2)_2OH$: 34.29%C, 2.08%H, 31.23%Au; found 34.12%C, 2.08%H, 31.14%Au.)

Effect of variables

Constant scale readings were obtained for gold solutions between pH 3.6 and 4.2. Solutions outside these pH limits gave very little turbidity.

The procedure outlined above was followed with a number of solutions of the same gold(III) content, the time allowed between the additions of the reagent and gelatin being varied. Constant readings were obtained after 6 h of standing.

The most satisfactory results were obtained with 1 ml of the 0.2% reagent solution.

The total amount of reagent added to solutions of the same gold(III) content was maintained constant while the amount of dioxane was varied. Constant readings were obtained with 0.8–1.2 ml of dioxane in 50 ml; higher concentrations tend to decrease the turbidity.

Constant readings were obtained in the temperature range 20 to 25°.

Accuracy and precision

Known gold(III) solutions were prepared and the concentrations determined. The results are given in Table I. The relative standard deviation for a gold(III) concentration of 2.4 p.p.m. based on 11 determinations was $\pm 4\%$.

Effect of diverse ions

Suspensions were prepared for solutions containing the same concentration of gold(III) to which had been added various amounts of other cations or anions.

The results are given in Table II. The ion concentrations except for sodium, potassium and perchlorate represent the upper allowable limits.

Bismuth(III), iron(III), ruthenium(III), palladium(II), rhodium(III), silver(I), bromide and iodide interfere. Some of these interferences can be eliminated as described below.

TABLE I

DETERMINATION OF KNOWN SAMPLES OF GOLD CONCENTRATION

Gold present (p.p.m.)	*Gold found (p.p.m.)*	*Deviation (p.p.m.)*	*Gold present (p.p.m.)*	*Gold found (p.p.m.)*	*Deviation (p.p.m.)*
4.2	4.4	+0.2	2.4	2.4	0.0
3.6	3.7	+0.1	1.8	1.8	0.0
3.0	2.9	−0.1	1.2	1.2	0.0

TABLE II

EFFECT OF DIVERSE IONS ON THE NEPHELOMETRIC DETERMINATION OF GOLD

(Gold concentration 2.5 p.p.m.)

Ion	*Ion concn. (p.p.m.)*	*Au found (p.p.m.)*	*Ion*	*Ion concn. (p.p.m.)*	*Au found (p.p.m.)*
$Na^+(NaClO_4)$	100	2.5	$Te^{4+}(TeCl_4)$	3	2.4
$K^+(KClO_4)$	100	2.5	$NH_4^+((NH_4)_2SO_4)$	22	2.5
$Be^{2+}(Be(NO_3)_2)$	5	2.5	$Cd^{2+}(CdSO_4)$	10	2.5
$Mg^{2+}(Mg(ClO_4)_2)$	4	2.5	$VO_3^-(NH_4VO_3)$	15	2.4
$Ca^{2+}(CaSO_4)$	10	2.5	$Cr_2O_7^{2-}(K_2Cr_2O_7)$	30	2.4
$Ba^{2+}(Ba(NO_3)_2)$	20	2.5	$PtCl_6^{2-}(H_2PtCl_6)$	8	2.5
$Cr^{3+}(CrK(SO_4)_2)$	10	2.6	$SO_4^{2-}(Na_2SO_4)$	70	2.5
$Mn^{2+}(MnSO_4)$	10	2.4	$NO_3^-(KNO_3)$	60	2.5
$Re^{7+}(Re_2O_7)$	15	2.5	$HPO_4^{2-}(Na_2HPO_4)$	8	2.5
$Os^{8+}(OsO_4)$	20	2.6	EDTA(Na-salt)	15	2.4
$Co^{2+}(Co(NO_3)_2)$	5	2.5	$CO_3^{2-}(Na_2CO_3)$	10	2.4
$Ni^{2+}(Ni(NO_3)_2)$	5	2.5	$F^-(NaF)$	3	2.5
$Cu^{2+}(CuSO_4)$	3	2.6	$Cl^-(NaCl)$	10	2.4
$Tl^+(Tl_2SO_4)$	15	2.5	Na citrate	15	2.4
$Zn^{2+}(Zn(NO_3)_2)$	5	2.5	$ClO_4^-(KClO_4)$	430	2.6
$Hg^{2+}(HgCl_2)$	12	2.5	$OAC^-(NaOAC)$	10	2.4
$Pb^{2+}(Pb(NO_3)_2)$	3	2.5	$Ir^{3+}(K_3Ir(NO_3)_6)$	3	2.4

Separation of iron(III). Dilute the solution containing 600 μg of gold(III) and 1 mg of iron(III) (as nitrate) to 10 ml and add 3.5 mg of phosphate as sodium phosphate. Filter the yellowish iron phosphate precipitate, evaporate the filtrate and dilute to 100 ml. Use a 20-ml aliquot for the recommended procedure described above. The phosphate remaining in solution is below 8 p.p.m.

Separation of bismuth(III). Dilute the solution containing 600 μg of gold(III) and 4.6 mg of bismuth nitrate in 0.1 *M* hydrochloric acid to 50 ml. Filter the white precipitate of bismuth oxychloride, evaporate the filtrate and dilute to 100 ml. Use a 20-ml aliquot for the recommended procedure.

Separation of bromide and iodide. Dilute the solution containing 600 μg of gold(III) and 3 mg of bromide as potassium bromide to 20 ml and bubble chlorine gas through the heated sample. Evaporate to dryness and dilute to 100 ml; use a

20-ml aliquot. In the same way interference from iodide up to 18 p.p.m. was eliminated.

Separation of ruthenium(III). Pass chlorine gas through the solution, evaporate to dryness, dilute to 100 ml and use a 20-ml aliquot.

The results of these separations are given in Table III.

TABLE III

RESULTS OF ELIMINATION OF INTERFERENCES

(Gold concentration 2.4 p.p.m.)

Ion	*Limit of ion concn. (p.p.m.)*
$Bi^{3+}(Bi(NO_3)_3 \cdot 5H_2O)$	8
$Fe^{3+}(Fe(NO_3)_3 \cdot 9H_2O)$	4
$Ru^{3+}(RuCl_3 \cdot H_2O)$	5
Br^-(KBr)	12
I^-(KI)	18

If the diverse ion concentration in the sample is higher than the limits stated in Table II, then an isopropyl ether extraction of the gold from 6 *N* hydrochloric acid can be carried out[10]. The amount of diverse ion extracted with the gold chloride must be kept below the limit stated in Table II. Gold(III) was extracted from large amounts of platinum(IV), nickel(II) and palladium(II) as follows: a sample containing 600 μg of gold(III) and a 100-fold amount of one of the above metal chlorides was separated by an isopropyl ether extraction. The gold ether layer was evaporated to dryness, heated with aqua regia, and evaporated twice with 5-ml portions of concentrated hydrochloric acid. The samples were diluted to 100 ml and 20-ml aliquots were used for the determination. This procedure could also be used for rhodium(III) and silver(I). The theoretical gold concentration was 2.4 p.p.m. For the sample containing a 100-fold amount of platinum(IV), the gold recovered was 2.5 p.p.m.; for the 100-fold amount of palladium(II), the gold recovered was 2.4 p.p.m., and for the 100-fold amount of nickel, the gold recovered was 2.2 p.p.m. The values given are an average of at least 3 runs. Based on the separation of gold from these 3 metal ions the error was $\pm 10\%$.

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SUMMARY

A nephelometric method for the determination of microgram quantities of gold with di-2-thienylketoxime is described. The yellow gold complex, which has the empirical formula $Au(C_9H_6NOS_2)_2OH$, forms a stable suspension when gelatin is added as protective colloid. Many foreign ions do not interfere in 5-fold amounts. If necessary, a preliminary isopropyl ether extraction of gold can be used.

RÉSUMÉ

On décrit une méthode néphélométrique pour le dosage de microquantités d'or

à l'aide de di-2-thionylcétoxime. Le complexe d'or jaune $Au(C_9H_6NOS)_2$ OH forme une suspension stable, en utilisant la gélatine comme colloïde protecteur. De nombreux ions étrangers ne gènent pas (teneur 5 fois celle de l'or). Il est possible, si nécessaire, d'effectuer une extraction préliminaire de l'or dans l'éther isopropylique.

ZUSAMMENFASSUNG

Es wird eine Nephelometrische Methode zur Bestimmung von Mikrogrammen Gold mit Di-2-thienylketoxim beschrieben. Der gelbe Goldkomplex mit der empirischen Formel $Au(C_9H_6NOS_2)_2OH$ bildet eine stabile Suspension, wenn Gelatine als Schutzkolloid zugegeben wird. Zahlreiche Fremdionen stören nicht bis zu einem 5-fachen Überschuss. Falls erforderlich, kann eine vorhergehende Extraktion des Goldes mit Isopropyläther durchgeführt werden.

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POTENTIOMETRIC TITRATIONS WITH ION-EXCHANGING MEMBRANE ELECTRODES

PART III. EXPERIMENTAL RESULTS

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(Received March 21st, 1968)

In two recent papers[1], the theoretical aspects of the use of ion-exchanging membrane electrodes for determining end-points in potentiometric titrations were discussed. For cation- as well as for anion-exchanging membranes the theoretical titration curves were calculated for simple precipitation reactions with only univalent ions present in the reference solution (M^+X^-), the solution to be titrated (N^+Y^-) and the reagent (A^+B^-). For strong acid and strong base ion-exchanging membrane electrodes, the titration curves were calculated for the following titration reactions:

$$N^+Y^- + A^+B^- \rightarrow NB\downarrow + A^+Y^-$$

$$N^+Y^- + A^+B^- \rightarrow AY\downarrow + N^+B^-$$

However, it is to be expected that the same titration curves will hold for acidimetric titrations of strong acids with strong bases or *vice versa* when the conditions mentioned above are fulfilled.

The most important conclusion to be derived from the calculations was the strong influence of the ratio of the diffusion coefficients of the counter-ions participating in the titration reaction on the shape of the titration curves.

In this paper, it is shown that the calculated titration curves can be obtained in practice when the necessary precautions are taken.The experimental curves obtained for simple precipitation and acidimetric titrations are discussed.

EXPERIMENTAL

Apparatus

As the membrane potential to be measured develops fairly slowly, an automatic titration apparatus was built along the following lines:

(*1*) addition of a small amount of the reagent solution during a time t_1;

(*2*) a waiting period (t_2) during which the membrane potential could reach its equilibrium value;

(*3*) measurement and registration of the membrane potential during a time t_3, whereupon a further small amount of the reagent solution was added and the same cycle ($t_1+t_2+t_3$) was repeated. In this way, the titration was continued till about twice the amount of reagent needed for the precipitation or the neutralization was added.

The automatic titration apparatus is shown in Fig. 1. A Metrohm Multidosimat E 415 motor-driven piston burette was used; the potentiometric recorder was a Philips PR 2210/00 model. The programming apparatus, consisting of

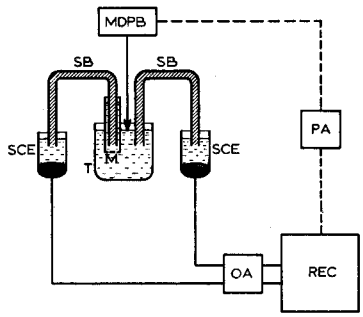

Fig. 1. Block diagram of titration apparatus. M = membrane, T = titration vessel, SB = salt bridges, SCE = saturated calomel electrodes, MDPB = motor-driven piston burette, REC = recorder, OA = operational amplifier system, PA = programming apparatus.

a relay system, activated by a multivibrator, was electrically connected with the motor-driven piston burette and with the motor of the chart-drive mechanism of the recorder. The piston burette was capable of delivering fixed amounts of reagent to the solution to be titrated. The magnitude of these deliveries was dependent on the time during which the motor of the piston burette was switched on (2 sec) by a relay controlled by the programming apparatus. The potentiometric recorder measured the potential difference between the two reference electrodes continually. After a waiting period, following the addition of the reagent, the chart drive was switched on by the programming apparatus for a fixed period (30 sec) and the potential difference between the reference electrodes was registered. After the registration a further amount of reagent was added and the whole cycle was repeated. Because of the relatively high impedance of the membrane cell, it was necessary to use an operational amplifier system to match the impedance of the cell with the optimal input impedance of the recorder. With the programming apparatus it was possible to add amounts of reagent of 0.1 or 0.2 ml at a time; after each delivery a waiting period of 0.25, 0.5, 1, 2 or 5 min could be chosen.

The titration cell consisted of a thermostatted glass vessel with a volume of about 50 ml (Fig. 2). The rotating membrane electrode consisted of a synchronous motor coupled with interchangeable nylon gears to a vertical hollow shaft, that was used for supporting the membrane holder. Rotation speeds of 600, 900 and 1200 rev./min could be obtained. The rotation was necessary in order to obtain the conditions that were postulated in the theoretical calculations, *i.e.*, control of the flux of the diffusing species through the membrane by internal membrane conditions and not by the solutions adhering to the membrane. The membrane holder in which the membrane was clamped can also be seen in Fig. 2. When necessary, two rubber sealing rings were inserted on either side of the membrane in order to prevent leakage of solution. Both the reference solution and the solution to be titrated were connected to reference electrodes (saturated calomel) by agar bridges containing a solution of

1 *M* potassium nitrate for argentimetric titrations; for acidimetric titrations the bridges were saturated with potassium chloride. The potential differences between the reference electrodes were actually measured, but by assuming that the membrane potential was the only variable potential in the cell circuit, the variation of the membrane potential during a titration could be derived from the titration curves.

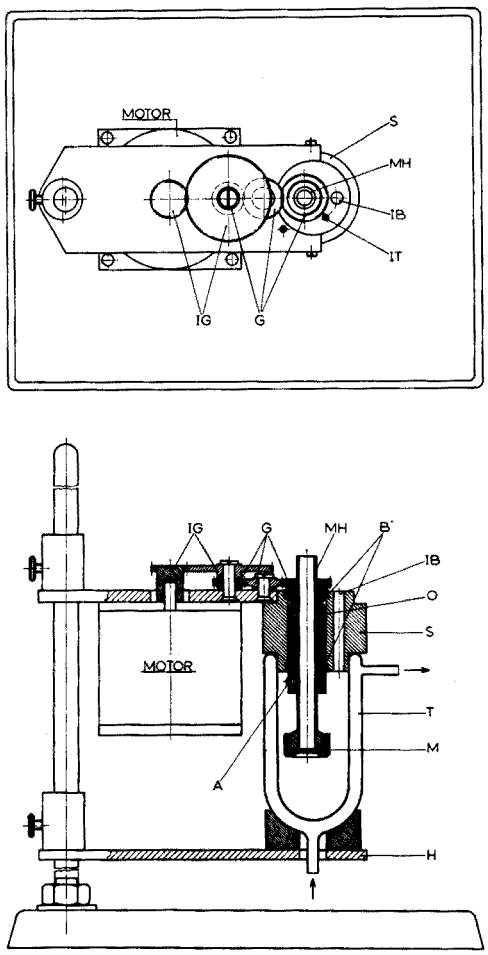

Fig. 2. Design of the thermostatted titration vessel and the membrane holder. IG = interchangeable cog-wheels (Delrin), G = cog-wheels (Delrin), S = interchangeable support for rotating membrane electrode (Perspex), IB = inlet for salt bridge, IT = inlet for titrant, MH = membrane holder (Perspex), H = holder for titration vessel with adjustable height, B = bearings, O = O-ring, A = screw adjustment, M = membrane, T = double-walled glass titration vessel with inlet and outlet for circulating thermostatted water (25°).

Some titrations were done in which only the outer solution was stirred and fairly satisfactory results were obtained. The use of an automatic titrator is, of course, not obligatory, but is convenient when many titrations of the same type must be done, and appears also to give more accurate results.

TABLE I

PROPERTIES OF THE MEMBRANES USED IN THE INVESTIGATIONS[a]

Trade name	*Manufacturer*	*Matrix*	*Ionic group*	*Capacity meq/g dry membrane*
Permaplex C 20	Permutit Co. Ltd., England	Polystyrene-divinylbenzene	$-SO_3^-$	3
Permaplex A 20	Permutit Co. Ltd., England	Polystyrene-divinylbenzene	$-NR^+$	2
Nepton AR 111 A	Ionics Inc., U.S.A.	Polystyrene-divinylbenzene	$-NR^+$	2.0
Asahi CK 1	Asahi Chem. Co., Japan	Polystyrene-divinylbenzene	$-SO_3^-$	2.8
Asahi CA 1	Asahi Chem. Co., Japan	Polystyrene-divinylbenzene	$-NR^+$	2.0
Asahi CA 2	Asahi Chem. Co., Japan	Polystyrene-divinylbenzene	$-NR^+$	2.5
X	Prepared in own laboratory	Polyethylene	$-SO_3^-$	0.05–0.65[b]

[a]All figures are approximate, since the properties of the membranes can differ considerably from batch to batch.
[b]The capacity of the X membranes can be made to vary considerably, depending on the conditions during the sulphonation.

Membrane materials

Table I summarizes the membranes used in these investigations. The results obtained with different makes of membranes were qualitatively in good agreement with each other, when the membranes were treated properly.

Conditioning of the membranes

In order to obtain precise results, the membranes must be converted to a specific ionic form before use. In most cases, this was accomplished by soaking the membrane in a dilute solution containing the counter-ion with which the membrane was to be loaded. An efficient method was to drop the solution continuously over the membrane, by means of a glass vessel provided with a syphon outlet. In this way the membrane was soaked almost continually in fresh solution, while the exchanged products were carried away quickly. In most cases the membrane was equilibrated in this manner with the reference solution to be used in the actual titration. In some cases, an electric current was used to introduce the desired counter-ions into the membrane, as described by HELFFERICH[2a]. This is a rapid method, but has one disadvantage: when the electric current is too large or the transport of the counter-ions in the solution to the surface of the membrane is too slow, polarization effects can occur at the surface with the result that reaction products are formed which can penetrate into the membrane. In such cases, the membrane has still to be treated with a solution containing the desired counter-ion as described above.

Moisture content (% wt)	*Thickness (mm)*	*Transport number of counter-ion in the membrane when equilibrated with the stated solution*[c]		*Remarks*
30–40	1	0.94	1 *N* NaCl	Heterogeneous membrane, consisting of reinforced thermoplastic material with imbedded ion-exchanging particles
30–40	1	0.93	1 *N* NaCl	as C 20
40–45	0.6	0.90–0.95	0.6 *N* NaCl	Reinforced homogeneous membrane
38	0.23	0.99	1.5 *N* NaCl	Homogeneous membrane
31	0.23	0.99	1.5 *N* NaCl	Homogeneous membrane
30	0.15	0.99	1.5 *N* NaCl	Homogeneous membrane
15–20	0.05	Not determined		Homogeneous membrane, obtained by sulphonating polyethylene foil (Dutch Appl. 180, 986)

[c]The transport number of the counter-ions within the membrane ($\bar{t}_{c1}$) is frequently used to define the permselectivity (P) of the membrane:

$$P = n_{c1}(\bar{t}_{c1} - t_{c1})/1 - n_{c1}\, t_{c1}$$

(n_{c1} is the valence and t_{c1} the transport number of the counter-ion in the solution).

When precipitation titrations are carried out, a layer of precipitate forms at the surface or even inside the pores of the membrane. When the same membrane must be used for later titrations, such precipitates are very disadvantageous, because reproducible results cannot then be attained. In such cases, the precipitate can be removed by soaking the membrane in a solution containing a complexing agent for one of the ions in the precipitate. For instance, when silver halides had been precipitated, the membrane was first treated with a 5% solution of potassium cyanide, and then soaked for a few hours in a solution containing the counter-ion necessary to convert the membrane to the desired ionic form.

The reference solution

Because the permselectivity of the membrane is usually smaller than unity, it is not generally advisable for the reference solution to contain ions or molecules that can react with the ion to be determined or with the reagent. In most cases, a neutral solution is to be preferred. Moreover, the ionic strengths of the reference solution and of the solution to be titrated should be about the same, in order to avoid an unduly large membrane potential at the beginning of the titration.

The importance of the choice of the reference solution is demonstrated in Fig. 3, which shows the curves obtained when the same titration was carried out with several different reference solutions.

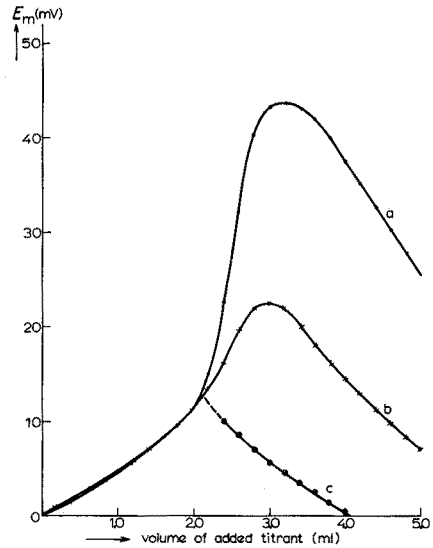

Fig. 3. Influence of the reference solution (Permaplex C 20 membrane). Titration of 20 ml of 0.01 *M* silver nitrate with 0.1 *M* sodium chloride. Addition of reagent 0.2 ml/cycle; waiting period 30 sec. Reference solutions: (a) 0.01 *M* potassium nitrate, (b) 0.1 *M* potassium cyanide, (c) 0.01 *M* potassium nitrate (titration performed in two separate steps, as described in Fig. 4a).

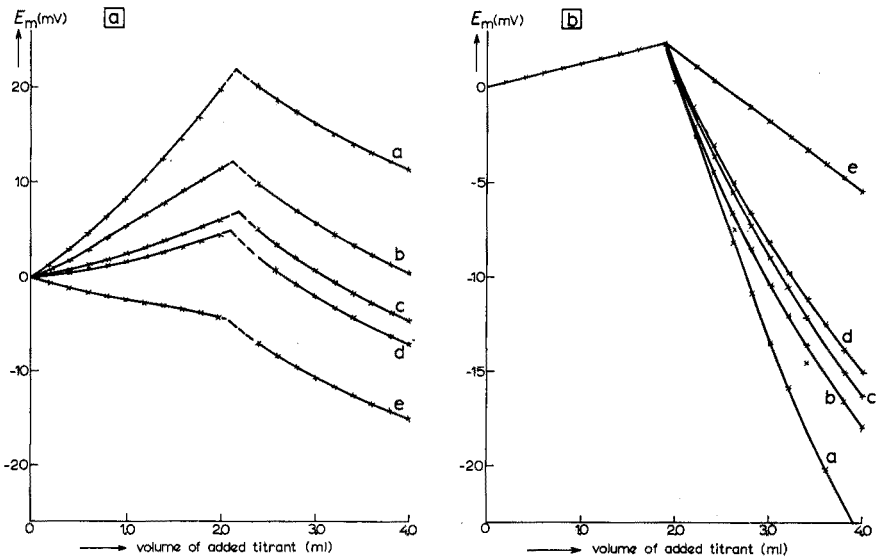

Fig. 4. Influence of different diffusion coefficients of counter-ions: (a) Li^+, (b) Na^+, (c) NH_4^+, (d) K^+ or Cs^+, (e) H^+, on the shape of the titration curves obtained in simple precipitation titrations with a cation-exchanging membrane (Permaplex C 20). (a) Titration of 20 ml of 0.01 *M* silver nitrate with 0.1 *M* chloride. Reference solution 0.01 *M* KNO_3. Waiting period 15 sec. The titrations were performed in two steps: (1) addition of 0.2 ml of reagent/cycle up to the equivalence point, and (2) addition of 0.2 ml of reagent/cycle to a pretitrated solution to which 110% of the required reagent had been added; in the second part a fresh membrane was used, which was inserted only after the pre-titration had been completed. (b) Titration of 20 ml of 0.01 *M* chloride with 0.1 *M* silver nitrate. Reference solution 0.01 *M* KNO_3. Addition of reagent 0.2 ml/cycle; waiting period 15 sec.

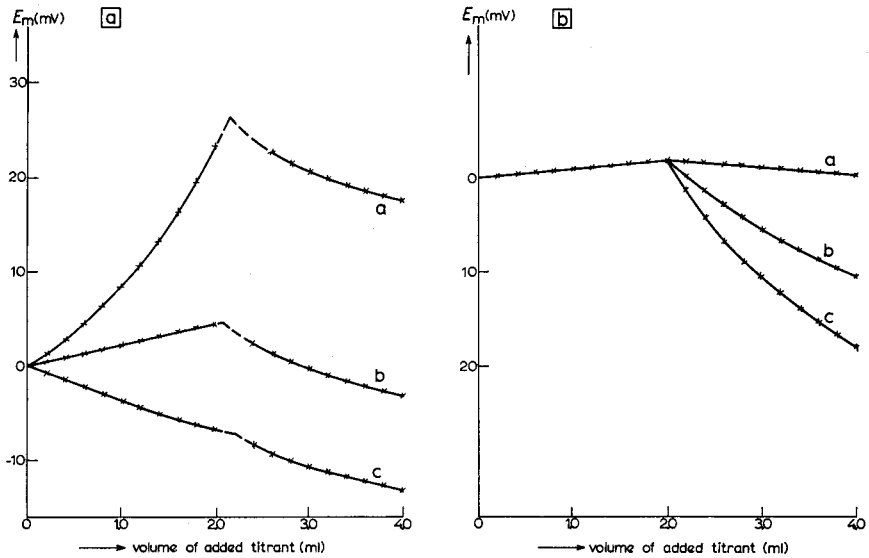

Fig. 5. Influence of different diffusion coefficients of counter-ions: (a) $(CH_3)_4$ N^+, (b) K^+, (c) H^+, on the shape of the curves obtained in simple precipitation titrations, using a homogeneous cation-exchanging membrane (X membrane; see Table I). (a) Titration of 20 ml of 0.01 *M* silver nitrate with 0.1 *M* iodide; for method and particulars see legend to Fig. 4a. (b) Titration of 20 ml of 0.01 *M* iodide with 0.1 *M* silver nitrate; for method and particulars see legend to Fig. 4b.

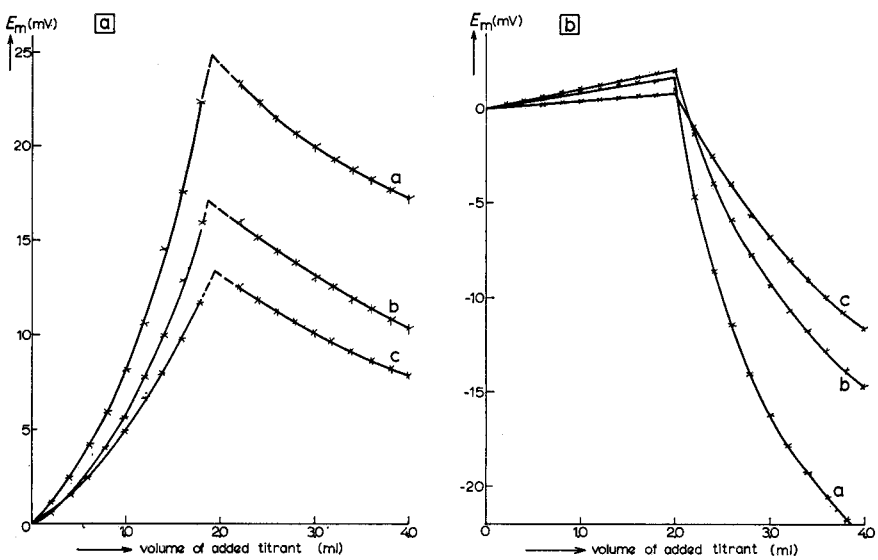

Fig. 6. Influence of different diffusion coefficients of counter-ions: (a) Li^+, (b) Na^+, (c) K^+, on the shape of the curves obtained in simple acidimetric titrations with Permaplex C 20 membrane. Reference solution 0.01 *M* KCl. (a) Titration of 20 ml of 0.01 *M* hydrochloric acid with 0.1 *M* hydroxide. (b) Titration of 20 ml of 0.01 *M* hydroxide with 0.1 *M* hydrochloric acid. Method as for Fig. 4b.

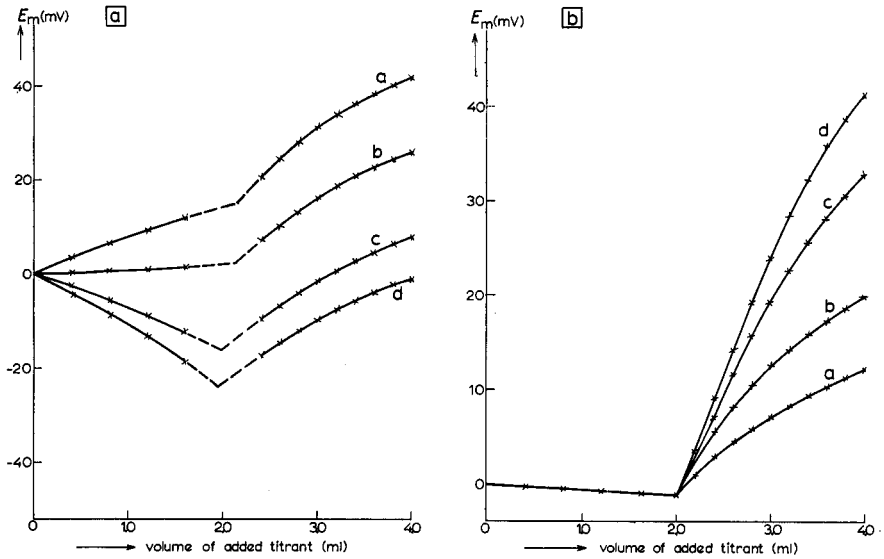

Fig. 7. Influence of different diffusion coefficients of counter-ions: (a) Cl^-, (b) Br^-, (c) I^-, (d) CNS^-, on the shape of the curves obtained in simple precipitation titrations with Permaplex A 20 membranes. Reference solution 0.01 *M* KNO_3. (a) Titration of 20 ml of 0.01 *M* potassium salt with 0.1 *M* silver nitrate. Method as for Fig. 4a. (b) Titration of 20 ml of 0.01 *M* silver nitrate with 0.1 *M* potassium salt. Method as for Fig 4b.

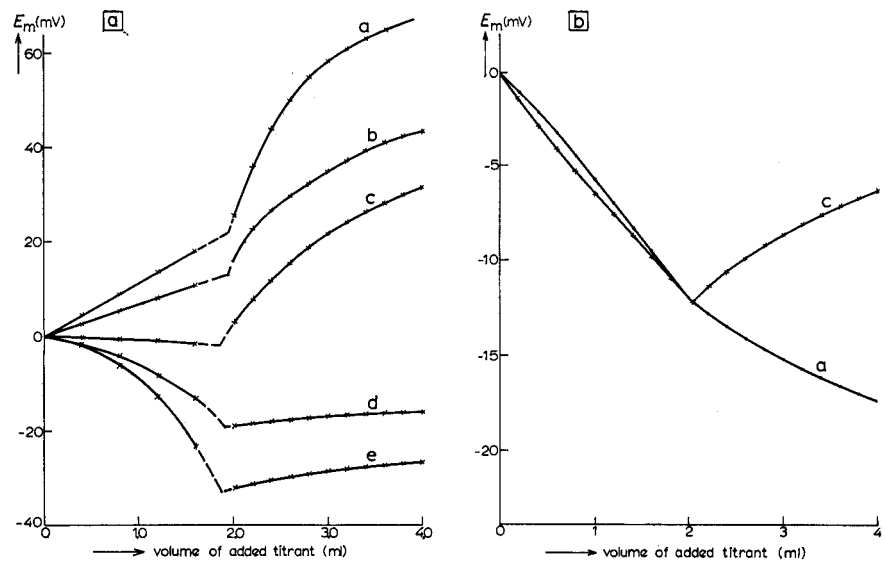

Fig. 8. Influence of different diffusion coefficients of counter-ions: (a) ClO_4^-, (b) NO_3^-, (c) Cl^-, (d) $HCOO^-$, (e) CH_3COO^-, on the shape of the curves obtained in simple acidimetric titrations with Permaplex A 20 membranes. Reference solution 0.01 *M* KCl. (a) Titration of 20 ml of 0.01 *M* potassium hydroxide with 0.1 *M* acid. Method as for Fig. 4a. (b) Titration of 20 ml of 0.01 *M* solutions of acid with 0.1 *M* potassium hydroxide. Method as for Fig. 4b.

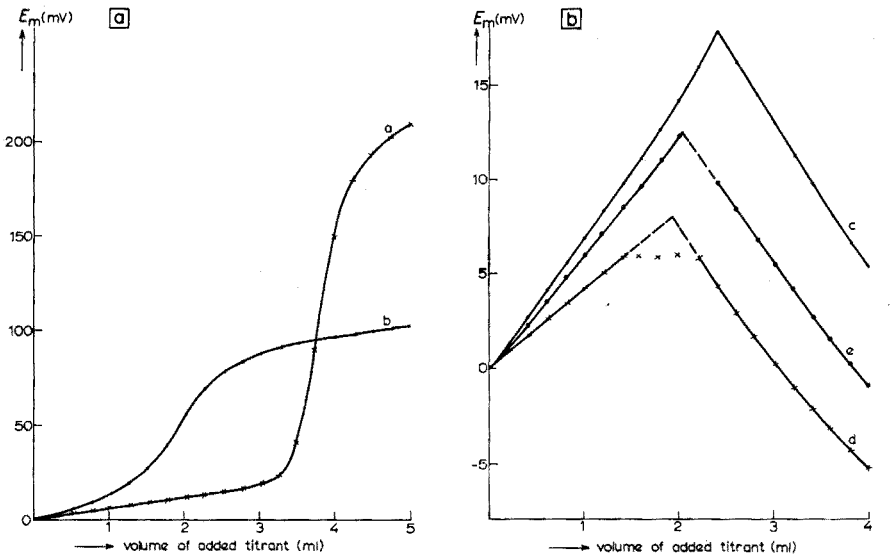

Fig. 9. Influence of the reference solution (Asahi CK 1 membrane). Titration of 20 ml of 0.01 *M* silver nitrate with 0.1 *M* sodium chloride. Method of titration as for Fig. 3. Reference solution: (a) 0.01 *M* KNO_3, (b) 0.1 *M* KCN, (c) 0.1 *M* $Na_2S_2O_3$, (d) 0.1 *M* NH_4Cl + 1 *M* NH_3, (e) 0.01 *M* KNO_3 (titration performed in two steps as in Fig. 4a).

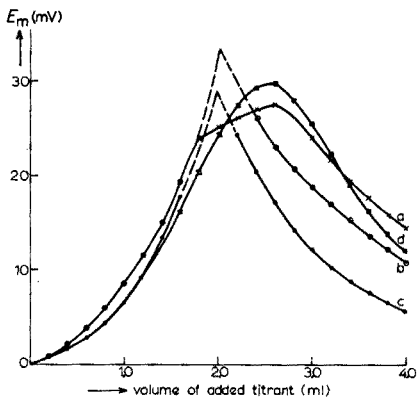

Fig. 10. Influence of the reference solution (Permaplex C 20 membrane). Titration of 20 ml of 0.01 *M* hydrochloric acid with 0.1 *M* sodium hydroxide. Method of titration as for Fig. 3. Reference solution: (a) 0.01 *M* KCl, (b) 0.01 *M* KCl (titration in two steps as in Fig. 4a), (c) 0.05 *M* CH_3COOH + 0.05 *M* CH_3COONa, (d) 0.01 *N* HCl.

Titrations examined

The following titrations were performed with cation-selective membrane electrodes:

(*1*) 0.01 *M* silver nitrate solutions with 0.1 *N* solutions of LiCl, NaCl, NH_4Cl, KCl, CsCl and HCl and the reverse titrations (Fig. 4);

(*2*) 0.01 *M* silver nitrate with 0.1 *M* solutions of tetramethylammonium iodide, potassium iodide or hydroiodic acid and the reverse titrations (Fig. 5);

(3) 0.01 *M* hydrochloric acid with 0.1 *M* LiOH, NaOH or KOH and the reverse titrations (Fig. 6).

The following titrations were performed with anion-selective membrane electrodes:

(1) 0.01 *M* silver nitrate with 0.1 *M* KSCN, KBr, KI or KCl and the reverse titrations (Fig. 7);

(2) 0.01 *M* potassium hydroxide with 0.1 *M* HCl, HNO_3, $HClO_4$, HCOOH and CH_3COOH and the reverse titrations (Fig. 8).

With regard to the titrations in which a counter-ion of the membrane used was initially present in the solution to be titrated, severe difficulties were encountered, because of the diffusion of the required counter-ion through the membrane to the reference side of the cell. In such cases, the titration curve did not resemble the theoretical shape and the end-point could not be determined reliably; examples are shown in Figs. 3, 9 and 10.

Interdiffusion of counter-ions during the titrations can cause the following phenomena: (*a*) negative titration errors; and (*b*) gradual end-points, because ions that diffuse out of the test solution into the membrane or even into the reference solution, will tend to diffuse back when the equivalence point has been reached. Which of these possibilities predominates depends largely on specific membrane qualities such as capacity, porosity and selectivity. Moreover, geometric factors such as the thickness of the membrane, the surface area available for diffusion and the ratio of this surface to the total surface of the membrane play some part. Some experiments were performed with a complexing or buffering agent in the reference solution to prevent the back-diffusion of the counter-ions to be determined. In this way, fairly normal titration curves could be obtained, depending on the make of the membrane used (see Fig. 9, curves c and d, and Fig. 10, curve c).

The theoretical shape was best approximated by performing the titration in two separate steps. The first step consisted of a rapid titration until the theoretical equivalence point was reached; the second step was carried out either with the same membrane after it had been restored to its initial condition, or with a fresh identical membrane. For the second part of the titration, a fresh portion of the test solution was pre-titrated to about 10% after the theoretical equivalence point and only then was the second membrane electrode placed in the solution (see Fig. 3, curve c, Fig. 9, curve e, and Fig 10, curve b). Of course, this method cannot be used when solutions of unknown concentration are titrated which implies that for practical purposes, titrations are possible only when the ion to be determined is a co-ion of the membrane used. The accuracy of the determination of the points of the titration curves is of the order of 0.25 mV when the ion to be titrated is a co-ion and 2 mV when it is a counter-ion.

From the titration curves, the following sequences of the diffusion coefficients of the counter-ions in the membranes can be derived:

$Li^+ < Na^+ < NH_4^+ < K^+ \sim Cs^+ < H^+$	(Figs. 4 and 6)
$N(CH_3)_4^+ < K^+ < H^+$	(Fig. 5)
$SCN^- < I^- < Br^- < Cl^-$	(Fig. 7)
$CH_3COO^- < HCOO^- < Cl^- < NO_3^- < ClO_4^-$	(Fig. 8)

For the alkali metal ions, this sequence is in general agreement with the theoretically

expected sequence based on the sequence of the size of the solvated ions[2b] and the electrical conductivity[3]. With regard to the anions thiocyanate, iodide, bromide and chloride, the same sequence of mobilities was also found by MOND AND HOFFMANN[4] for collodion membranes (the lyotropic series), disregarding the possible influence of the matrix and the fixed ionic groups.

CONCLUSIONS

The titration curves obtained in these simple precipitation and acidimetric titrations with only univalent ions present, are qualitatively in accordance with the theoretically expected curves[1]. The only exception is for anion-exchanging membranes when a strong acid is titrated with a strong base (Fig. 8b). In this case, the decrease in the membrane potential up to the end-point is too great, although the influence of the mobility of the counter-ions is definitely present. It can also be seen from Fig. 8a (curve e), that when a strong base is titrated with a weak acid, the change in the membrane potential after the equivalence point is small, owing to the relatively small change in ionic concentration after the neutralization.

Further work is in progress on the use of cation-selective membranes, and on the influence of several variable factors and the possible interference of neutral salts, as well as on actual analytical applications.

SUMMARY

Potentiometric titrations with ion-exchanging membrane electrodes for end-point detection are described for simple precipitation and acid–base reactions. When only monovalent ions are present, there is a qualitative agreement between the titration curves obtained and the theoretically calculated curves.

RÉSUMÉ

Des titrages potentiométriques sont exécutés, utilisant une électrode à membrane permsélective composée de matériel échangeurs d'ions. Dans quelques séries d'expériments nous avons trouvés des courbes de titrage qualitativement en rapport avec des courbes calculées.

ZUSAMMENFASSUNG

Potentiometrische Titrationen unter Verwendung von Ionenaustauscher-Membranelektroden zur Endpunktsbestimmung einfacher Fällungs- und Säure–Basen-Reaktionen werden beschrieben. Falls nur einwertige Ionen anwesend sind, ergibt sich eine qualitative Übereinstimmung zwischen den experimentell und theoretisch ermittelten Titrationskurven.

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DISSOCIATION CONSTANTS OF N,N'-BIS(2-CARBOXYETHYL)DITHIOOXAMIDE

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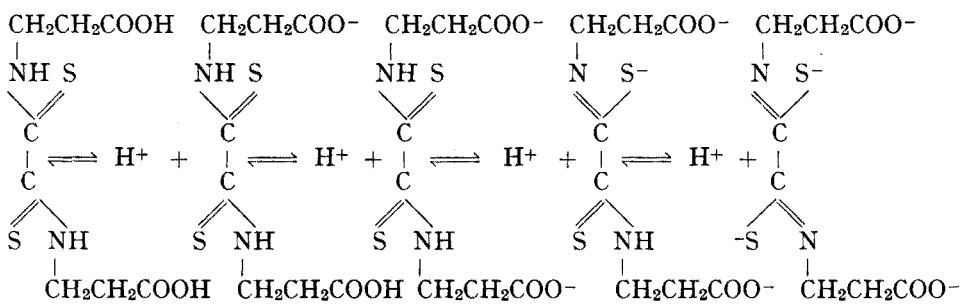
The dissociation constants of several dithiooxamide derivatives have previously been determined[1-3]. Although they show only slight differences, attributable to different electron-releasing or electron-withdrawing effects of the substituents, the derivatives act very differently in complex formation. In a study of the analytical applications of water-soluble nickel(II)–thiooxamide complexes[4], N,N'-bis(2-carboxyethyl)dithiooxamide (CEDTO) was used as a ligand. It was therefore considered desirable to determine the dissociation constants of this product, according to the following equilibria:



Or: $H_4X \overset{K_1}{\rightleftharpoons} H_3X^- + H^+ \overset{K_2}{\rightleftharpoons} H_2X^{2-} + H^+ \overset{K_3}{\rightleftharpoons} HX^{3-} + H^+ \overset{K_4}{\rightleftharpoons} X^{4-} + H^+$

Four dissociation constants must therefore be determined. From studies of similar derivatives it is known that K_1 and K_2 can be determined in the region of pH 3–6[5] and K_3 and K_4 in the region of pH 11–14[1-3].

For the estimation of K_1 and K_2, a potentiometric method was chosen, while K_3 and K_4 were determined by a spectrophotometric method.

METHOD

Estimation of K_1 and K_2

In its acid form CEDTO is a water-insoluble product, hence a reverse titration method was used and the starting product was the twice-dissociated form H_2X^{2-} as

its potassium salt. According to RICCI[6], the fundamental relation for the dissociation of a dibasic acid is:

$$D = a \cdot (1 + 2K_2/H)/\{1 + H/K_1 + K_2/H\} - b_s \quad (1)$$

where $D = H - OH$; H = concentration of hydrogen ion; OH = concentration of hydroxide ion; a = concentration of acid; b_s = concentration of strong monoacid base added; and K_1, K_2 are the dissociation constants.

For a reverse titration, a is replaced by c (salt concentration) and b_s by $2c - a_s$, where a_s is the concentration of strong monobasic acid added. Equation (1) then becomes:

$$D = c(1 + 2K_2/H)/\{1 + H/K_1 + K_2/H\} - 2c + a_s \quad (2)$$

and

$$K_2 = \frac{H(H - OH + c - a_s) + (H^2/K_1)(H - OH + 2c - a_s)}{OH - H + a_s} \quad (3)$$

$$K_1 = \frac{H(H - OH + 2c - a_s)}{(K_2/H)(OH - H + a_s) - H + OH - c + a_s} \quad (4)$$

With values of a_s such that $H \ll K_1$, approximate values for K_2 can be obtained from eqn. (3):

$$K_2 \cong H(H - OH + c - a_s)/(H - OH + a_s) \quad (3')$$

With values of a_s such that $H \gg K_2$, approximate values of K_1 can be obtained from eqn. (4):

$$K_1 \cong H(H - OH + 2c - a_s)/(OH - H - c + a_s) \quad (4')$$

By putting the approximate value of K_2 into eqn. (4), a new value of K_1 can be obtained; with this new value of K_1, an improved value of K_2 can be calculated from eqn. (3). This iteration is continued until constant values of K_1 and K_2 are obtained.

Estimation of K_3 and K_4

For the estimation of K_3 and K_4, a spectrophotometric method[1-3] was chosen. This method uses the general relationship:

$$(\varepsilon_1 - \varepsilon_n)(H^2/K_3) + \varepsilon_2 \cdot H + \varepsilon_3 \cdot K_4 - \varepsilon_n \cdot K_4 = \varepsilon_n \cdot H \quad (5)$$

where ε_1, ε_2 and ε_3 are the molar extinction coefficients of the species H_2X^{2-}, HX^{3-} and X^{4-} respectively. ε_n is the so-called apparent extinction coefficient which is obtained from the measured absorbance $E = \varepsilon_n \cdot l \cdot C_T$ where l = optical path length (cm) and $C_T = (H_2X^{2-}) + (HX^{3-}) + (X^{4-})$.

The value of ε_1 being measured directly at pH values below 9, four unknown parameters are left in (5): K_3, K_4, ε_2 and ε_3. Absorbance measurements at different pH values combined with a weighted least-squares treatment of the numerical data, give the best estimates for the unknown parameters. If $K_3 \gg K_4$, K_3 can be determined separately at pH values in the region 11–12 where eqn. (5) becomes:

$$(\varepsilon_1 - \varepsilon_n)(H/K_3) + \varepsilon_2 = \varepsilon_n \quad (6)$$

with only two unknowns: K_3 and ε_2.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Hilger-Uvispek spectrophotometer and a Beckman DK 1 recording spectrophotometer. pH values were measured with a Pye Dynacap pH and millivolt meter, using lithium glass and saturated calomel electrodes. pH values higher than 12 were calculated according to HARNED AND COOK[7]. Potentiometric titrations were carried out at $25 \pm 0.05°$, under dried nitrogen as an inert atmosphere. Apparatus and electrodes were the same as for the pH-measurements.

Reagents and solutions

CEDTO was prepared by a modified WALLACH'S reaction[8]. β-Alanine (22.3 g; Fluka puriss.) was dissolved in 25 ml of 10 *N* potassium hydroxide to obtain the potassium salt. This solution was added dropwise to a suspension of 15 g of dithiooxamide (U.C.B. p.a.) in 100 ml of ethanol at 40° and 3 ml of 13 *N* ammonia solution was added. The slurry was stirred for several hours at 40° and then the excess of DTO was filtered off. The filtrate was acidified with dilute hydrochloric acid to pH 2. The product in its acid form H_4X was precipitated. The crude product was filtered off and purified by recrystallisation from ethanol.

To obtain the product in its twice-dissociated form H_2X^{2-}, the acid was dissolved in ethanol and treated with a stoichiometric amount of strong potassium hydroxide solution. The potassium salt (K_2CEDTO) which was precipitated, was

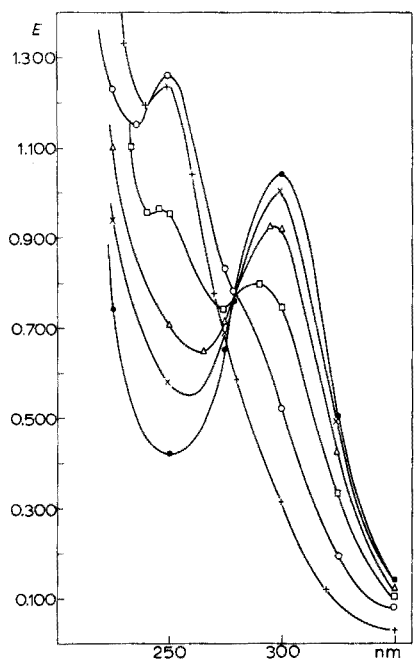


Fig. 1. Spectra of H_2X^{2-} at different pH values: (●) < 11.0, (×) 11.4, (△) 11.8, (□) 12.2, (○) 13.0, (+) 13.9.

filtered off and purified by recrystallisation from twice-distilled water. The product was dried in a desiccator over P_2O_5.

The compounds were analyzed with the following results: 37.03%C, 4.75%H (required for $C_8H_{12}O_4N_2S_2$, 36.35%C, 4.58%H); 27.51%C, 2.96%H, 22.51%K (required for $C_8H_{10}O_4N_2S_2K_2$, 28.22%C, 2.96%H, 22.97%K).

All solutions were made in calibrated glassware with twice-distilled water as a solvent. Buffer solutions for spectrophotometric determinations were prepared as described by KRATZ[9]. Constant ionic strength was obtained by adding potassium chloride as a neutral electrolyte.

Determination of K_1 and K_2

K_2CEDTO (0.1703 g) was dissolved in 100 ml of twice-distilled water. Enough potassium chloride was added to bring the solution to the ionic strength desired. The pH value of this solution was about 7.90. The titrant was 1.000 *N* hydrochloric acid. At a pH about 3.80, the acid CEDTO precipitated and the titration was stopped.

Determination of K_3 and K_4

The spectra of solutions containing 10^{-4} mole/l of H_2X^{2-} were recorded at different pH values, using buffer solutions[9] or solutions of calculated pH value[7]. As shown in Fig. 1, no change occurred beneath pH 11; then, the spectra changed rapidly. For the determination of K_3, the region of 260 nm was chosen, but for the simultaneous determination of K_3 and K_4 the region of 300 nm was better. The procedure was the same as that described earlier[1-3].

RESULTS

The results of the potentiometric determination of K_1 and K_2 are given in Table I. Ionic strengths less than 0.25 were not used, in order to prevent change of ionic strength during titration. The difference between pK_A values shows that the electrostatic interaction between the two carboxyl groups is almost negligible.

TABLE I

VALUES FOR K_1 AND K_2 BY POTENTIOMETRIC TITRATION

Ionic strength	pK_1	pK_2
0.25	3.73	4.65
0.50	3.75	4.71
1.00	3.76	4.74

The results of the spectrophotometric determination of K_3 and K_4 are summarized in Tables II and III. Table II gives the values of K_3, determined at different ionic strengths, by means of eqn. (6). Table III gives the values of K_3 and K_4 determined by means of eqn. (5) with a weighted least-squares treatment. This equation could only be used at ionic strength 1. Even at the highest pH values obtainable with lower ionic strength, the fourth dissociation was too weak for reliable measurement of K_4 to be obtained.

In Fig. 2, values of pK_3 are plotted against the square root of the ionic strength.

TABLE II

SPECTROPHOTOMETRIC DETERMINATION OF K_3

Wavelength (nm)	$\mu = 0.01$		$\mu = 0.05$		$\mu = 0.10$		$\mu = 0.25$		$\mu = 0.50$	
	$K_3(\cdot 10^{-11})$	pK_3	$K_3(\cdot 10^{-11})$	pK_3	$K_3(\cdot 10^{-11})$	pK_3	$K_3(\cdot 10^{-11})$	pK_3	$K_3(\cdot 10^{-11})$	pK_3
266	0.086	12.06	0.128	11.88	0.198	11.70	0.282	11.55	0.289	11.54
267	0.085	12.07	0.120	11.92	0.220	11.66	0.273	11.56	0.286	11.54
268	0.090	12.05	0.127	11.89	0.222	11.66	0.276	11.56	0.294	11.53
269	0.088	12.05	0.126	11.90	0.213	11.67	0.283	11.55	0.294	11.53
270	0.092	12.04	0.125	11.90	0.214	11.67	0.265	11.58	0.277	11.56
271	0.093	12.03	0.127	11.89	0.219	11.66	0.274	11.54	0.290	11.54
Mean	0.089	12.05	0.127	11.89	0.214	11.67	0.276	11.56	0.289	11.54

TABLE III

SPECTROPHOTOMETRIC DETERMINATION OF K_3 AND K_4

Wavelength (nm)	$\mu = 1.00$			
	$K_3(\cdot 10^{-11})$	pK_3	$K_4(\cdot 10^{-11})$	pK_4
295	0.405	11.39	0.795	14.10
296	0.402	11.40	0.703	14.15
297	0.403	11.40	0.647	14.19
298	0.397	11.41	0.610	14.21
299	0.392	11.42	0.629	14.20
300	0.384	11.42	0.545	14.26
Mean	0.397	11.41	0.655	14.19

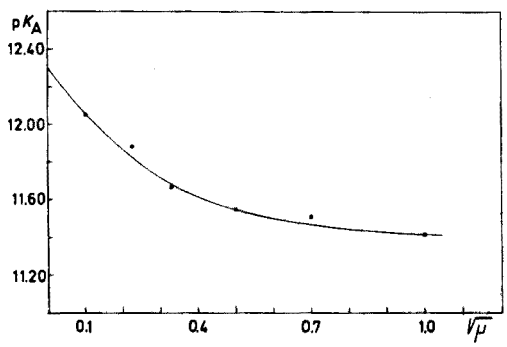


Fig. 2. Variation of pK_3 with ionic strength.

Extrapolation to zero ionic strength gives $pK_3^T = 12.32$. By means of the Debye–Hückel equation[10] for ionic strengths up to 0.05, thermodynamic pK_3 values were also obtained. Thus, pK_3^T was found to have the values 12.31 and 12.32 for ionic strengths 0.05 and 0.01, respectively; it can be seen that the values obtained by both methods are in good agreement.

CEDTO was used to study the complex formation with nickel(II) and other transition metal ions; this work will be described separately.

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SUMMARY

The dissociation constants of N,N'-bis(2-carboxyethyl)dithiooxamide have been determined by potentiometric and spectrophotometric methods. They were calculated by a modified RICCI formula and by a weighted least-squares treatment. The thermodynamic constant pK_3^T is 12.32. At ionic strength 1.00, $pK_1=3.76$, $pK_2=4.74$, $pK_3=11.41$ and $pK_4=14.19$.

RÉSUMÉ

Les constantes de dissociation du N,N'-bis(2-carboxyéthyl)dithiooxamide ont été déterminées par des méthodes potentiométriques et spectrophotométriques. Elles ont été calculées par la formule de RICCI modifiée et par la méthode des moindres carrés pondérée. La constante thermodynamique $pK_3^T=12.32$. Pour une force ionique 1, on trouve: $pK_1=3.76$, $pK_2=4.74$, $pK_3=11.41$, $pK_4=14.19$.

ZUSAMMENFASSUNG

Die Säurekonstanten von N,N'-Bis(2-Carboxyäthyl)dithiooxamid wurden durch potentiometrische und spektralphotometrische Methoden bestimmt. Zur Berechnung wird eine modifizierte Formel von Ricci verwendet sowie die Methode der kleinsten Quadrate. Die thermodynamische Konstante pK_3^T beträgt 12.32. Bei der Ionenstärke $\Gamma=1.00$ ist: $pK_1=3.76$; $pK_2=4.74$; $pK_3=11.41$; $pK_4=14.19$.

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THE ANALYSIS OF SILVER(II) OXIDE

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Most of the methods proposed for the analysis of silver(II) oxide are summarised in the review by McMILLAN[1]. The majority of the original authors appear to have used these methods to determine the ratio of silver to active oxygen present in the black residues obtained upon oxidation of silver salts, without any critical evaluation of the procedures.

The methods quoted in the literature for the analysis of silver(II) oxide are based on the following principles: (*i*) the oxidation of iron(II) in acid media[2–5]; (*ii*) the oxidation of oxalic acid in acidic media[2,3,6,7]; (*iii*) the oxidation of iodide ion to iodine[2,4,8–10]; (*iv*) oxidation of hydrogen peroxide[11]; (*v*) gasometric estimation through oxidation of hydrazine to nitrogen[8]; (*vi*) measurement of the volume of oxygen evolved on decomposition of the oxide in acid solutions[8]; (*vii*) thermogravimetric techniques[12–14]. Methods (*iv*) and (*v*) are subject to interference by silver(I) ion, while the difficulty of obtaining perfectly dry samples of silver(II) oxide leaves method (*vii*) open to doubt. The remaining 4 methods appear simpler and more direct and have been used by a number of workers to check the purity of silver(II) oxide samples.

The oxidation of iron(II) solutions with silver(II) oxide is usually carried out in dilute sulphuric acid media in the presence of excess iron(II) sulphate, the excess being back-titrated with potassium permanganate. Several papers have been published on this method but the results are conflicting. For example, it has been suggested that the presence of dilute sulphuric acid does[1,8] and does not[2] seriously influence the amount of silver(II) oxide found by reacting directly with the oxide, forming oxygen which does not react further with the iron(II). DUTTA[4] attempted to overcome this problem by using an acetate-buffered medium and the results quoted in his paper show a significant increase in the yield of active oxygen when compared with the acidified iron(II) method.

As with the iron(II) method, the determination of silver(II) oxide by oxidation of oxalate ions is usually carried out in sulphuric acid medium. It has been suggested[1] that the liberated carbon dioxide from the AgO–$H_2C_2O_4$ reaction dilutes the oxygen evolved from reaction with the acid, thus retarding the oxygen from further reaction with the solution, and giving low results.

The oxidation of iodide to iodine was first attempted in sulphuric or acetic media but erratic results were obtained[9,15]. To overcome this problem, JIRSA[8] proposed a variation on these methods whereby the silver(II) oxide sample was dissolved in neutral, saturated potassium iodide solution, the iodine formed by the reaction being liberated by the addition of sulphuric acid after complete solution of all solid material. Another variation of the method was proposed by DUTTA[4] who used

an acetate-buffered solution containing potassium iodide. The silver(II) oxide dissolved completely in this medium and the iodine formed was liberated without need of the addition of sulphuric acid.

The gasometric technique for the determination of silver(II) oxide based on the volume of oxygen evolved by decomposition in acid solution has been examined by JIRSA[8] and WATSON[12] but no experimental results are given in their papers. An impurity which is a possible source of error in this technique and which was apparently not considered by these experimenters is silver(I) carbonate. This impurity is produced by the effect of carbon dioxide and water vapour[16] in the atmosphere on silver(I) oxide impurity usually present in the oxide. NOYES *et al.*[17] have shown that silver(II) ion in concentrated acid solutions slowly evolves a stoichiometric amount of oxygen gas, but the reaction rate becomes rapid only when the solutions are diluted to below a 2 *M* acid concentration.

Because of the increasing interest in the use of silver oxides in chemical batteries, a critical review of the various methods seemed timely. This paper presents the results of an investigation of 5 of the published methods of analysis of silver(II) oxide. The aim of the project was to establish the best operating conditions for each method and to ascertain which technique was most precise. The precisions of the various methods were compared in terms of standard deviations.

EXPERIMENTAL

Reagents

The silver(II) oxide samples used in these analyses were prepared by alkaline oxidation of silver(I) oxide with persulphate as directed by HAMMER AND KLEINBERG[18]. The preparations were air-dried at 60–70° and lightly ground before storage in a desiccator over potassium hydroxide pellets. Several silver(II) oxide samples of low purity were prepared by intimately mixing a silver(II) oxide sample prepared as above with an appropriate amount of silver(I) oxide. These low-purity preparations were used for the comparison of the methods.

Sulphuric, perchloric, nitric, and acetic acid solutions were prepared by dilution of the A.R. grade concentrated acids. Iron(II) sulphate, potassium iodide, sodium thiosulphate, potassium iodate, potassium permanganate, and potassium dichromate solutions were prepared from the A.R. grade salts.

Cerium(IV) sulphate solution was prepared from A.R. grade cerium(IV) ammonium sulphate and its concentration checked against dried A.R. grade sodium oxalate. Ferroin indicator was a commercially prepared reagent solution.

Starch indicator was prepared by making a 5% solid solution of soluble starch in urea, as directed by CLARK[19]. This indicator was found to have good keeping properties.

Apparatus

The analyses in which iron(II) and iodide were used as reductants required only the usual items of volumetric glassware.

The volume of oxygen evolved from acid solutions was measured in a water-jacketed 5.00-ml gas burette with 0.01-ml divisions. The gas burette was connected to a jacketed reaction vessel of *ca.* 60 ml capacity through a short detachable capillary

tube and three-way stopcock (see Fig. 1). The acid solutions and a plastic boat containing the silver(II) oxide were admitted to the reaction vessel by removing the detachable capillary tube. The reaction mixture was stirred magnetically and temperature control was effected with the aid of a Braun Thermomix unit used in conjunction with a small refrigeration unit to maintain the circulating water from a reservoir near ambient temperature.

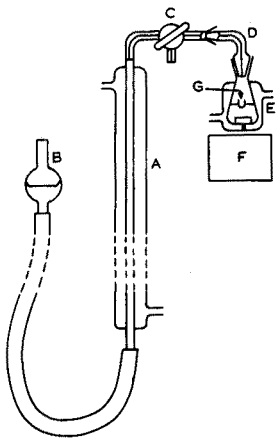

Fig. 1. Gas evolution measuring apparatus. (A) Water-jacketed gas burette. (B) Levelling bowl. (C) Three-way stopcock. (D) Removable capillary tube. (E) Water-jacketed reaction vessel. (F) Magnetic stirrer. (G) Plastic sample boat (floating).

Procedures

Titrimetric procedures. These consisted of adding an accurately weighed sample of the silver(II) oxide to a measured quantity of reductant in its appropriate solvent (sulphuric acid solution, acetate-buffer solution, or water) in a stoppered reaction flask. When the oxide had dissolved, the solution was acidified (where necessary) with sulphuric acid and the amount of iron(II) remaining, or the amount of iodine formed, titrated with the appropriate titrant.

The published procedures recommend the use of a small amount of silver(II) oxide (100–200 mg) and relatively "strong" solutions of titrant (usually 0.1 *N*). These conditions result in 0.1 ml of titrant being equivalent to approximately 1% of AgO, and greater sensitivity was sought by using 0.02 *N* titrant solutions.

Gasometric method. This consisted of accurately weighing a sample of the silver(II) oxide into a plastic boat which was floated on the surface of a measured volume of acid solution in the reaction vessel of the gasometric apparatus. When the system had attained thermal equilibrium the boat was sunk by starting the magnetic stirrer, and the volume of oxygen evolved from the stirred solution was measured in the gas burette.

In every case, the volumes of titrant used or the volumes of gas evolved were converted to the corresponding amounts of AgO, calculated from the stoichiometry of the reactions, and the results are presented as the percent by weight of AgO present in the original silver(II) oxide sample.

RESULTS

The iron(II)–sulphuric acid method

As described by previous authors, potassium permanganate was initially used to titrate the excess of iron(II) remaining after addition of the silver(II) oxide. However, difficulty was experienced with the determination of the end-point of the titration. With 0.005 *M* (0.025 *N*) titrant the permanganate colour was discharged slowly for some 2–5 ml before a "stable" end-point was reached. In addition, the brown coloration of the solution near the end-point made it difficult to detect a small amount of excess of permanganate.

Potassium dichromate (0.025 *N*) was tested as an alternative titrant, the silver ion being precipitated as the chloride before additon of sulphuric and phosphoric acids and titration to the diphenylamine indicator end-point. With this procedure the end-point occurred too early and was found to be unstable, usually fading in 1–2 min.

Cerium(IV) sulphate (0.02 *M*), on the other hand, was found to work exceptionally well at these concentration levels, when ferroin was used as the indicator. The end-point was clear and well defined, three drops of titrant being required to bring about the complete colour change from the first sign of fading in the red indicator colour. The low concentration of titrant used gave rise to an appreciable indicator blank (*ca.* 0.05 ml) and a measured amount of indicator (usually two drops) was added to each solution to give reproducible results.

TABLE I

EFFECTS OF EXPERIMENTAL CONDITIONS ON THE DETERMINATION OF AgO BY THE ACIDIFIED IRON(II) METHOD

(Volume of iron(II)–sulphuric acid solution = 100 ml)

Sample wt. (g)	*Sulphuric acid concn. (M)*	*pH*	*Initial Fe(II) concn. (M)*	*Temp. (°)*	*AgO found (%)*
0.12	0.0050	2.15	0.014	18	85.28
0.12	0.0075	2.05	0.014	18	97.15
0.12	0.0100	1.87	0.014	18	97.16
0.12	0.0125	1.78	0.014	18	96.90
0.12	0.0250	1.56	0.014	18	96.17
0.12	0.0375	1.39	0.014	18	95.37
0.12	0.0500	1.31	0.014	18	94.19
0.10	0.0075	2.1	0.014	18	97.24
0.11	0.0075	2.1	0.014	18	97.11
0.13	0.0075	2.1	0.014	18	97.09
0.14	0.0075	2.1	0.014	18	97.20
0.12	0.0100	1.9	0.007	18	95.67
0.12	0.0100	1.9	0.009	18	96.66
0.12	0.0100	1.9	0.020	18	97.36
0.12	0.0100	1.9	0.027	18	97.15
0.12	0.0100	1.9	0.014	1	97.37
0.12	0.0100	1.9	0.014	10	97.06
0.12	0.0100	1.9	0.014	20	97.06
0.12	0.0100	1.9	0.014	30	96.90
0.12	0.0100	1.9	0.014	45	96.79

The effects of sulphuric acid concentration, sample weight, reductant concentration, and temperature, are shown in Table I. The low result obtained with 0.005 *M* sulphuric acid was caused by the silver(II) oxide being incompletely reacted, even after continuous shaking for 3 h. Except for this result, the general trend was a decrease in the amount of AgO found with an increase in acid concentration. The amount of silver(II) oxide used appeared to have an insignificant effect (the 0.15% difference in results represents 0.075 ml of 0.02 *M* Ce^{4+} solution), while increased temperature produced a reduction in the amount of AgO found (possibly owing to a small amount of oxygen liberation). It appears that a certain excess of iron(II) is highly desirable, concentrations above 0.014 *M* giving fairly consistent results.

The iron(II)–acetate buffer method

For the reasons discussed above, 0.02 *M* cerium(IV) sulphate was substituted for potassium permanganate.

The effects of buffer solution composition, weight of sample, and iron(II) sulphate concentration are shown in Table II. The effect of pH or buffer solution composition follows a similar pattern to the sulphuric acid test in the previous method, namely, a decrease in pH gives rise to a decrease in the amount of AgO found. The pH of these buffer solutions was measured after the iron(II) sulphate solution, which was 0.25 *M* with respect to sulphuric acid, had been added. Solutions with a pH greater than 3 showed a distinct tendency to form a brown precipitate, and so solutions of pH 2.2 were used for subsequent tests. The effect of sample weight was insignificant as was the iron(II) sulphate concentration above 0.010 *M*.

The saturated potassium iodide method

The end-point in the titration of the liberated iodine formed, with 0.01 *M* sodium thiosulphate solution was readily detected with the starch–urea indicator of

TABLE II

EFFECTS OF EXPERIMENTAL CONDITIONS ON DETERMINATION OF AgO BY THE BUFFERED IRON(II) METHOD

Volume of iron(II)–buffer solution = 125 ml)

Sample wt. (g)	Buffer solution composition			Initial Fe(II) concn. (M)	Temp. (°)	AgO found (%)
	Ml 0.2 M HOAc	Ml 0.2 M NaOAc	pH			
.125	0	100	3.73	0.014	18	97.27
.125	10	90	3.10	0.014	18	97.04
.125	20	80	2.22	0.014	18	96.97
.125	30	70	1.92	0.014	18	96.80
.125	40	60	1.72	0.014	18	96.53
.125	50	50	1.51	0.014	18	96.04
.093	20	80	2.2	0.014	18	97.02
.103	20	80	2.2	0.014	18	96.92
.112	20	80	2.2	0.014	18	96.89
.133	20	80	2.2	0.014	18	97.08
.143	20	80	2.2	0.014	18	97.14
.125	20	80	2.2	0.009	18	96.75
.125	20	80	2.2	0.010	18	96.95
.125	20	80	2.2	0.012	18	97.13
.125	20	80	2.2	0.013	18	97.08

Clark. The colour change at the end-point was from a purple-brown to the pale yellow of the silver iodide, and some 3–4 drops of the sodium thiosulphate solution were required to effect this colour change from the first signs of permanent fading in the starch–iodine colour. Blank assays were run concurrently with the analyses to estimate the amount of iodine formed by atmospheric oxidation; usually a blank of 0.05–0.10 ml was observed.

The effects of sample weight, amount and concentration of reductant, and temperature are shown in Table III. In all cases except the 0.4 g weight of potassium iodide, the effects of these variables were insignificant. The effect of aerial oxidation

TABLE III

EFFECTS OF EXPERIMENTAL CONDITIONS ON THE DETERMINATION OF AgO BY THE SATURATED POTASSIUM IODIDE METHOD

(Volume of solution = volume of iodide solution)

Sample wt. (g)	*Amount KI (g)*	*Vol. KI solution (ml)*	*Temp. (°)*	*AgO found (%)*
0.055	4.0	4.0	18	96.11
0.081	4.0	4.0	18	96.02
0.091	4.0	4.0	18	96.17
0.105	4.0	4.0	18	96.15
0.114	4.0	4.0	18	96.06
0.123	4.0	4.0	18	96.04
0.132	4.0	4.0	18	96.29
0.152	4.0	4.0	18	96.28
0.201	4.0	4.0	18	96.26
0.123	0.4	0.4	18	94.05
0.123	0.8	0.8	18	96.29
0.123	1.5	1.5	18	96.24
0.123	3.0	3.0	18	96.24
0.123	7.5	7.5	18	96.44
0.125	4.0	4.0	18	96.81
0.125	4.0	5.0	18	96.83
0.125	4.0	6.0	18	96.80
0.125	4.0	8.0	18	96.86
0.125	4.0	12.0	18	96.86
0.125	4.0	20.0	18	96.62
0.125	4.0	29.0	18	96.72
0.125	4.0	4.0	3	96.75
0.125	4.0	4.0	10	96.58
0.125	4.0	4.0	15	96.69
0.125	4.0	4.0	20	96.69
0.125	4.0	4.0	25	96.74
0.125	4.0	4.0	30	96.81
0.125	4.0	4.0	45	96.76

TABLE IV

EFFECT OF STANDING TIME AT ROOM TEMPERATURE ON AN ACIDIFIED ASSAY SOLUTION

(4.0 g of potassium iodide, 0.125 g of AgO, and 5 ml of 1 *M* sulphuric acid solution)

Time (min)	1	2	5	10	20	40	60	120	240
% AgO found	96.54	96.76	96.63	96.69	97.19	98.12	98.88	100.37	104.32

on acidified solutions of an assay determination was studied (Table IV); it is obvious that these solutions must be titrated immediately upon acidification.

The potassium iodide–acetate buffer method

The presence of the acetate buffer had no apparent effect upon the performance of the sodium thiosulphate titrant and the starch–urea indicator, but did have a significant influence on the size of the blank, 0.20–0.40 ml of sodium thiosulphate solution (0.01 *M*) being required.

Table V presents the results of the examination of the effects of sample weight, amount of reductant, buffer solution composition and temperature. In all cases, the effects of these variables were insignificant in the range studied.

The oxygen evolution method

The effects of weight of silver(II) oxide, amount and concentration of acid solution used, and temperature on the volume of oxygen evolved from nitric acid solutions are shown in Table VI. Similar results were obtained from perchloric acid

TABLE V

EFFECT OF EXPERIMENTAL CONDITIONS ON THE DETERMINATION OF AgO BY THE BUFFERED POTASSIUM IODIDE METHOD

(Volume of solution = 10 ml buffer solution + 5 ml KI solution)

Sample wt. (g)	*Buffer solution composition*			*Amount KI (g)*	*Temp. (°)*	*AgO found (%)*
	Ml 1 M HOAc	*Ml 1 M NaOAc*	*pH*			
0.056	5.0	5.0	4.30	5.0	18	95.93
0.080	5.0	5.0	4.30	5.0	18	95.75
0.092	5.0	5.0	4.30	5.0	18	95.87
0.104	5.0	5.0	4.30	5.0	18	95.88
0.112	5.0	5.0	4.30	5.0	18	96.01
0.124	5.0	5.0	4.30	5.0	18	95.86
0.132	5.0	5.0	4.30	5.0	18	96.18
0.152	5.0	5.0	4.30	5.0	18	95.97
0.202	5.0	5.0	4.30	5.0	18	96.11
0.126	3.0	7.0	4.91	5.0	18	96.03
0.126	4.0	6.0	4.71	5.0	18	96.06
0.126	6.0	4.0	4.25	5.0	18	96.01
0.126	7.0	3.0	4.10	5.0	18	96.05
0.126	8.0	2.0	3.90	5.0	18	95.96
0.126	5.0	5.0	4.3	1.0	18	96.01
0.126	5.0	5.0	4.3	2.0	18	96.38
0.126	5.0	5.0	4.3	4.0	18	96.10
0.126	5.0	5.0	4.3	6.0	18	95.86
0.126	5.0	5.0	4.3	8.0	18	95.91
0.126	5.0	5.0	4.3	10.0	18	95.73
0.125	5.0	5.0	4.3	5.0	6	96.08
0.125	5.0	5.0	4.3	5.0	10	96.08
0.125	5.0	5.0	4.3	5.0	15	95.94
0.125	5.0	5.0	4.3	5.0	20	96.06
0.125	5.0	5.0	4.3	5.0	25	95.95
0.125	5.0	5.0	4.3	5.0	30	95.99
0.125	5.0	5.0	4.3	5.0	45	96.09

solutions. Sulphuric and hydrochloric acids proved unsuitable for this method as the reaction with sulphuric acid was too slow[20] while the reaction with hydrochloric acid produces some chlorine gas[8].

Each of the four variables had a significant effect on the yield of oxygen from the silver(II) oxide. The yield increased with weight of oxidant and acid concentration, but gave consistent results in the ranges 0.085–0.100 g AgO and 0.2–1.0 *M* nitric acid. At higher concentrations of nitric acid, the solution acquired the brown colour of the silver(II) nitrate complex which was slow to discharge, giving low results. The weight of silver(II) oxide taken was limited to a maximum of 0.1 g for 95–98% pure samples as the maximum volume of gas capable of being measured by the apparatus was 5.00 ml. The volume of acid solution and the temperature had a markedly significant effect on the yield of oxygen and for the purpose of obtaining consistent results it was decided to maintain a temperature within 1° of ambient, and to use as small a volume of acid solution as was convenient (25 ml).

The effect of concentration of dissolved air in the acid solutions on the yield of oxygen was examined; the results showed that a decrease of 2–3% in the yield of oxygen could be expected upon deaeration. Bubbling air through the acid solution for some hours before use, produced results which were indistinguishable from those

TABLE VI

EFFECTS OF EXPERIMENTAL CONDITIONS ON THE OXYGEN EVOLUTION METHOD

(Volume of acid solution = 25 ml)

Sample wt. (g)	*Nitric acid concn. (M)*	*Vol. HNO_3 soln. (ml)*	*Temp. (°)*	*AgO found (%)*
0.045	0.5	25	28	95.10
0.055	0.5	25	28	96.04
0.066	0.5	25	28	96.44
0.077	0.5	25	28	96.51
0.087	0.5	25	28	97.19
0.098	0.5	25	28	97.30
0.096	0.1	25	25	96.96
0.096	0.2	25	25	97.54
0.096	0.3	25	25	97.78
0.096	0.4	25	25	97.77
0.096	0.5	25	25	97.58
0.096	0.7	25	25	97.71
0.096	1.0	25	25	97.18
0.096	1.5	25	25	96.29
0.096	2.0	25	25	94.93
0.095	0.5	20	26	98.96
0.095	0.5	30	26	97.68
0.095	0.5	40	26	94.52
0.095	0.5	50	26	88.83
0.099	0.5	25	5	92.75
0.097	0.5	25	15	93.41
0.095	0.5	25	27	96.37
0.090	0.5	25	35	98.02
0.085	0.5	25	45	99.90
0.075	0.5	25	55	105.06

obtained from acid solutions which had been allowed to stand open to the atmosphere at room temperature for several days.

Comparison of methods

The results of the analysis of 6 samples of silver(II) oxide by the 5 methods examined above are shown in Table VII. The procedures used to obtain these results were those described in the *Recommended procedure* section.

The order of the methods with respect to the yield of AgO obtained was, in general, oxygen evolution > saturated potassium iodide > buffered potassium iodide > iron(II); the iron(II) methods gave similar results which were within 0.6% AgO of each other, and their relative positions varied. Low results were obtained with the iron(II) methods on low-purity samples. In all cases except one, the oxygen evolution method gave results which were at least 0.7% AgO higher than the corresponding results for the saturated iodide method, samples I, V and VI being higher by 1.75, 4.61 and 1.71% respectively. Samples I and V were analysed for carbon by a combustion method and were found to contain 0.06 and 0.08% C respectively. Assuming that the carbon is present solely in the form of carbonate, the volume of carbon dioxide in the gas evolved from the samples taken (0.095 and 0.140 g respectively) would correspond to 2.5 and 5.0% respectively of the total gas evolved. Correction for this CO_2 yields AgO values of 96.4% for sample I and 61.3% for sample V, both of which agree fairly well with the results of the other methods.

Standard deviations were calculated from the results of 26 determinations based on each of the 5 methods, using a 96% pure sample of silver(II) oxide. The standard deviations were found to be 0.11, 0.16, 0.14, 0.11, and 0.30% AgO for the acidified iron(II), buffered iron(II), saturated iodide, buffered iodide, and the oxygen evolution methods, respectively. These results indicate that the 4 titration methods have similar precisions, while the gasometric method is rather less precise.

DISCUSSION

In contrast to the predictions of McMillan[1] and Jirsa[8], the results show that silver(II) oxide samples can be analysed with reasonable accuracy and good precision by the oxidation of excess of iron(II) in the presence of sulphuric acid, provided that the acid concentration and temperature are kept reasonably low, and the silver(II) oxide sample is better than 80% pure. With low-purity samples, results may be 2–4% AgO lower than those obtained by other methods. The replacement of the acid with acetate buffer of pH 2–2.5 produces consistent results regardless of sample purity. The results, however, are, in general, 0.8–1.0% lower than those obtained by other methods. The methods involving iron(II) as reductant were rapid and convenient; shaking for only 1–2 min was required to dissolve the solid silver(II) oxide sample, and the colour change with ferroin indicator was well defined. On the debit side, it was found necessary to add measured amounts of indicator, and there was some difficulty in ascertaining the approach to the end-point (common when a colour change is from a highly coloured to a feebly coloured solution). In some solutions, small amounts of silver(I) sulphate were formed and if it appeared before equivalence-point, a recurring end-point resulted since the precipitate contained occluded iron(II) ions which were only released upon solution of the solid. The buffered iron(II)

solutions were found to be more prone to the formation of this precipitate, possibly owing to the higher ionic strength of these solutions compared to the acidic solutions. As one drop (0.05 ml) of titrant corresponds to *ca.* 0.1% AgO, the end-point had to be approached cautiously and care was required to ensure that all the silver(I) sulphate precipitate was completely dissolved.

The two iodide methods proved highly satisfactory, giving results which were of good precision and, presumably, of good accuracy. As no "standard" method of analysis of silver(II) oxide is currently available, the absolute accuracy of these and the other methods could not be checked. These methods gave results which were within 0.1–0.3% AgO of each other, regardless of sample purity, the buffered iodide method tending to give a slightly lower result. They were as rapid and convenient as the iron(II) methods and had the added advantages of no indicator blank, apparent insensitivity to a wide range of experimental conditions, and direct proportionality of the titre with the amount of AgO present in the sample. With the starch–urea indicator the end-points were sharp, even in the presence of large amounts of yellow silver iodide. The high concentration of iodide, together with the low concentration (0.01 *M*) of titrant used, necessitated the use of blank assays as atmospheric oxidation of the iodide was significant. These blank determinations only provide an approximation of the amount of iodine formed in assays as the blank titrations occupied only 20% of the time required for the titration of an actual determination. Aerial oxidation during titration may, in part, contribute to some of the 0.5% increase in AgO yield between the iron(II) and iodide methods.

The oxygen evolution method was found to be completely inferior to the iron(II) and iodide methods, since the magnitude of the results depends upon the experimental conditions and the technique is subject to interference from carbonates present in the sample. The anomalous behaviour of low sample weights and large volumes of acid solutions (*cf.* Table VI) may be due to supersaturation of the solvent with the evolved oxygen. The time required for a complete analysis of one sample of silver(II) oxide (20–25 min) was more than double that required for any of the titration methods, which makes the method unsuitable for the rapid routine work.

In view of their speed, convenience, and insensitivity to large changes in experimental conditions, the iodide methods of JIRSA[8] (saturated iodide) and DUTTA[4] (buffered iodide) with the modifications shown in the following section are considered to be the best methods for the analysis of the silver(II) oxide content of silver oxide samples. The oxygen evolution method should be considered only where the apparatus is readily available, and errors of up to 5% can be tolerated.

RECOMMENDED PROCEDURES

The experimental details of these procedures were determined from the results shown in Tables I–VI.

Acidified iron(II) method

Procedure. Pipette 25.00 ml of 1.5% (w/v) iron(II) sulphate in 0.04 *N* sulphuric acid into a 250-ml stoppered flask and dilute to 100 ml with distilled water. Add an accurately weighed aliquot of the silver(II) oxide sample (0.12–0.13 g), stopper the flask and shake vigorously until all the black oxide has dissolved. Add 5 ml of 18 *M*

TABLE VII

COMPARISON OF METHODS AS DESCRIBED IN THE RECOMMENDED PROCEDURES SECTION

Method	*Sample I*	*Sample II*	*Sample III*	*Sample IV*	*Sample V*	*Sample VI*
Acidified Fe(II)	96.69	97.30	53.98	79.16	58.64	96.51
Buffered Fe(II)	96.10	97.00	56.64	79.93	59.15	96.27
Saturated KI	97.10	97.69	57.40	80.27	61.16	97.04
Buffered KI	96.85	97.46	57.28	80.48	60.89	96.88
O_2 evolution	98.85	98.40	58.18	79.87	66.27	98.75

sulphuric acid and a carefully measured portion of ferroin indicator (2 drops). Titrate with 0.02 *M* cerium(IV) ammonium sulphate solution (containing 30 ml of 36 *M* sulphuric acid per l and standardized against sodium oxalate) to a pale blue colour. If a precipitate of silver(I) sulphate is present at the end-point, shake the flask until all is dissolved and titrate to the end-point if the solution is red.

Treat a blank iron(II) solution in a similar fashion but omit adding the silver(II) oxide. The difference in blank and assay titres is equivalent to the amount of AgO present in the sample. (1.00 ml 0.0200 *M* $Ce(SO_4)_2$ solution ≡ 2.4774 mg AgO.)

Buffered iron(II) method

Stock buffer solution. Mix together 160 ml of 1 *M* acetic acid, 640 ml of 1 *M* sodium acetate, and 100 ml of 2.5 *M* sulphuric acid and dilute to 1 l with distilled water.

Procedure. To 25.00 ml of 1.5% (w/v) iron(II) sulphate in 0.025 *M* sulphuric acid add 25 ml of stock buffer solution and dilute to 100 ml with distilled water. Introduce an accurately weighed aliquot of the silver(II) oxide sample (0.12–0.13 g) and proceed as in the acidified iron(II) method.

Saturated potassium iodide method

Procedure. To 5 ml of saturated potassium iodide solution (100 g A.R. KI dissolved in water to give 100–110 ml of solution) in a 150-ml stoppered flask add an accurately weighed aliquot of the silver(II) oxide sample and shake until the yellow precipitate has completely dissolved. Dilute the solution with 20 ml of distilled water and add 5 ml of 1 *M* sulphuric acid to liberate the iodine. Titrate immediately with 0.01 *M* sodium thiosulphate solution until most of the brown iodine colour has been discharged. Add a pinch of starch–urea indicator[19] and titrate to the disappearance of the purple-brown colour.

Prepare and treat a blank solution similarly without adding the silver(II) oxide. The assay titre with blank correction is equivalent to the amount of AgO present in the sample. (1.00 ml 0.0100 *M* $Na_2S_2O_3$ solution ≡ 2.4774 mg AgO.)

Buffered potassium iodide method

Procedure. Dilute 5 ml of saturated potassium iodide solution (as above) with 10 ml of acetate buffer solution (equal volumes of 1 *M* acetic acid and 1 *M* sodium acetate) in a 150-ml stoppered flask. Add to this mixture an accurately weighed aliquot of the silver(II) oxide sample and proceed as in the saturated iodide method.

Oxygen evolution method

Reagent. 0.5 *M* Nitric or perchloric acid solution. Dilute the A.R. grade concentrated acid with distilled water which has been allowed to equilibrate with the atmosphere for several days.

Procedure. The apparatus is shown in Fig. 1; add 25 ml of 0.5 *M* acid solution to the reaction vessel E and stir by means of the magnetic stirrer F to equilibrate thermally with the circulating water from the reservoir. Weigh accurately into a plastic boat an aliquot of the oxide sample, and float the boat on the acid surface. Connect the reaction vessel to the gas burette by replacing the detachable capillary tube D and allow several minutes for the system to attain thermal equilibrium. Level the liquid in the gas burette A, and sink the boat by starting the stirrer. Measure the volume of gas evolved from the continually stirred solution after 10 min.

Convert the volume of gas evolved to that of the dry gas at normal temperature and pressure and compute the amount of AgO present in the sample. (1.00 ml O_2 at 273.2°K and 760 mm ≡ 22.120 mg AgO.)

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SUMMARY

Five methods for the analysis of silver(II) oxide have been critically examined and modified procedures are proposed. The effects of varying temperature, solution composition, and amount of oxide have been studied for methods based on (*a*) the oxidation of iron(II) sulphate in the presence of sulphuric acid or acetate-buffered media; (*b*) the oxidation of iodide ion in neutral saturated solution or in acetate-buffered solution, and (*c*) the oxidation of water to yield oxygen from strong acid solutions.

RÉSUMÉ

Cinq méthodes sont proposées pour le dosage de l'oxyde d'argent(II). On a examiné l'influence de la température, de la composition de la solution et de la teneur en oxyde pour les procédés basés sur: (*a*) l'oxydation du sulfate de fer(II) en présence d'acide sulfurique ou en milieu tampon acétique; (*b*) l'oxydation des iodures en solution saturée neutre ou en milieu tampon acétique et (*c*) l'oxydation de l'eau avec dégagement d'oxygène en solution acide fort.

ZUSAMMENFASSUNG

5 Methoden zur Analyse von Silber(II)oxid wurden kritisch untersucht und modifizierte Verfahren vorgeschlagen. Für die folgenden Methoden wurde der Einfluss der Temperatur, die Zusammensetzung der Lösung und die Menge des Oxids untersucht: (*a*) Oxydation von Eisen(II)sulfat in schwefelsaurer Lösung oder in acetatgepufferter Lösung; (*b*) Oxydation von Jodid in gesättigter, neutraler Lösung oder in acetatgepufferter Lösung; (*c*) Oxydation von Wasser unter Bildung von Sauerstoff in sauren Lösungen.

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ATOMIC FLUORESCENCE SPECTROSCOPY OF BERYLLIUM

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Recently, it has been demonstrated that several elements can be determined by atomic fluorescence. Early attempts to obtain atomic fluorescence signals from beryllium were not successful. These employed an air–propane or air–hydrogen flame and irradiation from a 150-W xenon arc lamp[1] or an air–hydrogen flame and irradiation from a hollow-cathode lamp[2].

In the present work a study was made using a high-intensity beryllium hollow-cathode lamp as source and oxy–acetylene or nitrous oxide–acetylene flame as atomizer. Atomic fluorescence from beryllium at the resonance line 2349 Å was observed with the sensitivities of 10 p.p.m. in oxy–acetylene flames and 0.5 p.p.m. in nitrous oxide–acetylene flames.

A newly designed atomizer burner was constructed for nitrous oxide–acetylene flames for use in atomic fluorescence studies. The calibration curve for beryllium determination in this flame was linear over the range 0.5 p.p.m. to 10.0 p.p.m. The intensity reversed and approached zero at higher concentrations of beryllium.

EXPERIMENTAL

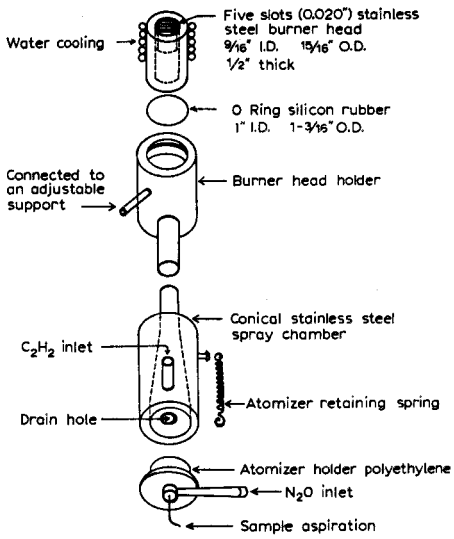
Apparatus

A Techtron AA3 atomic absorption spectrophotometer was used for fluorescence intensity measurements. For oxy–acetylene flame studies a large-bore Beckman total-consumption burner (No. 4090) was used and for nitrous oxide–acetylene flame a newly designed burner (as described in the following section) was used. A high-intensity beryllium hollow-cathode lamp (Atomic Spectral Lamps, Australia) was used as radiation source. The lamp and detector were modulated at 60 counts /sec.

Burner assembly construction. A burner with a cylindrical burner head with multiple slots (Fig. 1) was built for use with the nitrous oxide–acetylene flame. The burner head was water-cooled to prevent flash-back which could occur when the acetylene flow rate was reduced. It was found that nitrous oxide–acetylene mixture could be safely burned with multiple slots as wide as 0.020–in in a burner made of 0.5-in thick stainless steel. A stainless steel spray-chamber was used because of its rigidity, and because of the high thermal conductivity which further helped to prevent flash-back. The burner was carried in a support which could be moved in the vertical or both horizontal planes. This enabled easy optical alignment of the burner and also enabled studies to be made of intensity of fluorescence signal from various portions of the flame.

Five slots were cut in the burner head. It was positioned so that the slots were

parallel to the optical axis of the monochromater. The maximum fluorescence signal was obtained using this alignment. If the slots were perpendicular to the optical axis of the monochromater the intensity of the fluorescence emission was about 70% that of the former case, and if it was positioned at 45° angle to both entrance slit and source the signal intensity was about 85%.



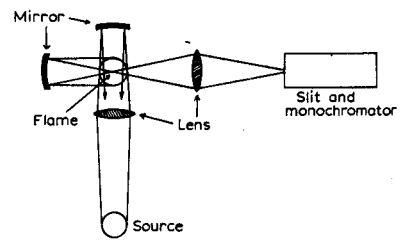


Fig. 1. Schematic diagram of atomizer burner assembly for nitrous oxide–acetylene flame.

Fig. 2. Optical arrangement for atomic fluorescence studies.

The burner produced a stable rose-red inner cone in the nitrous oxide–acetylene flame. The burner should be useful for atomic fluorescence studies of refractory metals such as aluminium, beryllium, silicon, titanium, tungsten and vanadium which are not appreciably atomized with other flames.

Optical system. The optical arrangement used is shown in Fig. 2. This optical arrangement was similar to that used by ARMENTROUT[3] except that an additional concave mirror was used to focus fluorescence emission onto the entrance slit increasing the detectible fluorescence intensity about two-fold. To obtain the most sensitive results, the lamp source was situated as closely as possible to the flame (about 1.5 in from the lens) with a condensing lens immediately in front of the window of the hollow cathode.

Reagents

A stock solution containing 1.0 g Be/l was prepared by dissolving 19.7 g of analytical-grade beryllium sulfate tetrahydrate in 1 l of distilled water. Standard solutions were made by appropriate dilution of stock solution immediately before measurement.

For the studies of effect of organic solvents, 100 p.p.m. of beryllium in each organic solvent was prepared by dissolving 0.691 g of beryllium acetylacetonate in 100 ml of each organic liquid; the solutions were then diluted as required.

In the interference studies, sodium or potassium salts were used for anionic interference and chlorides, nitrates or sulfates for cationic interference studies. Concentrated acids were used to study the effect of the addition of acids.

Procedure

With aqueous solutions containing 500 p.p.m. of beryllium for oxy–acetylene flame and 5 p.p.m. of beryllium for nitrous oxide–acetylene flame, the optimum operating conditions listed in Table I for each flame were established, the burner height and fuel ratio being adjusted to obtain maximum fluorescence intensity. Fluorescence measurements were made at 3 cm above the burner top for oxy–acetylene flame and at the rose-red inner cone of the flame about 1.5 cm from the burner head for the nitrous oxide–acetylene flame. Under these conditions, the sample feed rates were about 1.15 l/min and 4.8 l/min for oxy–acetylene and nitrous oxide–acetylene flames respectively.

TABLE I

OPERATING CONDITIONS

Metal	*Wavelength (Å)*	*Lamp current (mA)*	*Booster current (mA)*	*Slit (mm)*	*Oxygen (l/min)*	*Acetylene (l/min)*	*Nitrous oxide (l/min)*	*Sensitivity (p.p.m.)*
Be	2349	25	400	0.3	2.3	3.5		10
						5.3	29	0.5

Under the above conditions, working curves for beryllium at 2349 Å in oxy–acetylene and nitrous oxide–acetylene flames were determined by measuring the relative fluorescence intensities of a number of standard aqueous solutions varying in concentration from 1000 to 0.5 p.p.m.

RESULTS AND DISCUSSION

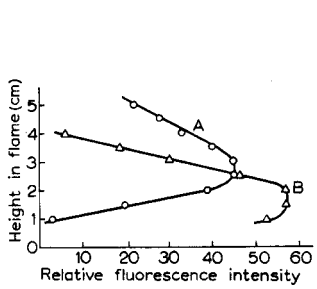
Atomization profile

The position of the burner was varied by means of the positioning mechanism. The operating conditions were as listed in the procedure and the concentration of beryllium in the oxy–acetylene flame was 700 p.p.m. and 10 p.p.m. in the nitrous oxide–acetylene flame. The base of the flame was taken as the zero position. The burner was moved downward in 0.5-cm steps and the fluorescence signal was recorded at each increment. The fluorescence signal was maximal at about 2.5–3.0 cm from the base of the flame in oxy–acetylene flame and 1.5–2.0 cm from the flame base in the nitrous oxide–acetylene flame (Fig. 3). In the nitrous oxide–acetylene flame, the fluorescence signal was observed only in the rose-red cone of the flame. Apparently the sharp maximum in both flames indicated that beryllium oxide was formed very rapidly even though fuel-rich reducing flames were used.

Sensitivity

The limits of detection are listed in Table I together with the optimum operating conditions. The limit of detection was chosen as that solution concentration which

resulted in a fluorescence signal, the magnitude of which was equal to two-thirds of the background noise level. The sensitivities for beryllium were 10 p.p.m. with oxy–acetylene flame and 0.5 p.p.m. with nitrous oxide–acetylene flame. These values are comparable with the best atomic absorption sensitivity data reported for this element with the same flames[4], for which a 10% diethylene glycol diethyl ether in water was used to enhance the sensitivity of beryllium, a 5-fold enhancement of absorption by beryllium being reported. A similar solvent containing 10% diethylene glycol diethyl ether in water was studied for comparison in the present work. It was found that the sensitivity was 4 p.p.m. in oxy–acetylene flame, but no significant sensitivity enhancement was detected in nitrous oxide–acetylene flame. It should be noted that the sample feed rate (4.8 l/min) with the nitrous oxide–acetylene flame was 4 times larger than the feed rate (1.15 l/min) with the oxy–acetylene flame.



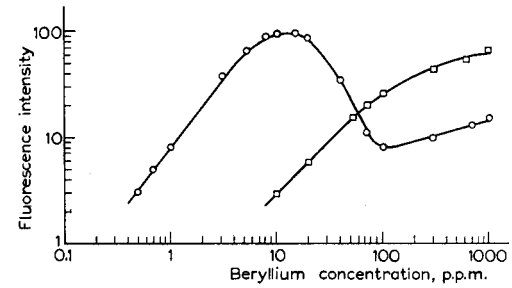


Fig. 3. Flame profile of atomic fluorescence for beryllium at wavelength of 2349 Å. (A) In oxy–acetylene flame; (B) in nitrous oxide–acetylene flame.

Fig. 4. Calibration curves for beryllium fluorescence intensities at 2349 Å. □ (A) In oxy–acetylene flame; ○ (B) in nitrous oxide–acetylene flame.

Calibration curve

Figure 4 shows the relationship between fluorescence intensity and the concentration of beryllium in aqueous solution. The 2349 Å line was studied with the oxy–acetylene and nitrous oxide–acetylene flames for sample atomization. The shape of calibration curves had already been discussed by WINEFORDNER AND VICKERS[5]. The relationship is linear at low metal concentrations and curved at high concentrations. It can be seen from Fig. 4 that this type of relationship was also obtained when an oxy–acetylene flame was used. But when a nitrous oxide–acetylene flame was used the beryllium fluorescence signal went through a maximum and approached zero. This relationship is markedly similar to that observed in molecular fluorescence and may be caused by the same phenomena, *i.e.* self absorption or quenching. This may present an important problem to the determination of this metal by atomic fluorescence spectroscopy.

Effect of flame composition

It was thought the shape of the fluorescence/concentration working curve for beryllium in nitrous oxide–acetylene flame might be varied by changing the flame composition. Therefore, a change in fuel ratio from optimized condition was made. The flame was optimized at a flow rate of 5.3 l/min producing a red inner cone. The inner cone disappeared when the acetylene was decreased to 4.8 l/min and the flame

turned to light yellow when the acetylene flow rate was increased to 5.8 l/min. The relative fluorescence intensities and working curves are shown in Fig. 5. It can be seen that the fluorescence intensity was very sensitive to flame composition but the general shape of working curve remained the same.

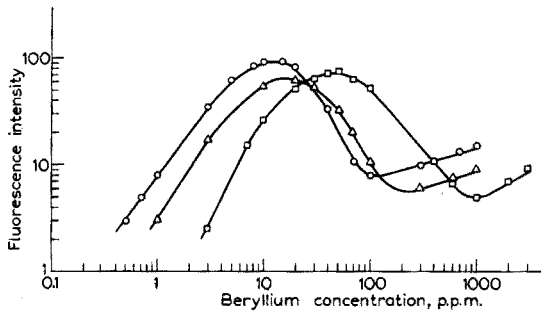


Fig. 5. Calibration curves for beryllium fluorescence intensities with varying fuel ratio in nitrous oxide–acetylene flame.

	Flame composition	
	N_2O (l/min)	*C_2H_2 (l/min)*
□	29	4.8
○	29	5.3
△	29	5.8

TABLE II

INTERFERENCE EFFECTS OF OTHER IONS AND COMPOUNDS ON THE ATOMIC FLUORESCENCE OF BERYLLIUM[a]

Interfering species	*Intensity of signal*		*Difference (%)*	
	O_2/C_2H_2	*N_2O/C_2H_2*	*O_2/C_2H_2*	*N_2O/C_2H_2*
None	36	52	—	—
Al^{3+}	34	50	− 6	−4
Co^{2+}	34	50.5	− 6	−3
Cu^{2+}	38	53	+ 6	+2
Mn^{2+}	34.5	51	− 4	−2
Hg^{2+}	34.5	52	− 4	0
Ti^{4+}	39	53	+ 8	+2
Zr^{4+}	37.5	53	+ 4	+2
$B_4O_7^{2-}$	38	51	+ 6	−2
Br^-	33	52	− 8	0
Cl^-	32	52	−11	0
PO_4^{3-}	34	51	− 6	−2
HPO_4^{2-}	32	51	−11	−2
SO_3^{2-}	32	52.5	−11	+1
SO_4^{2-}	34	52.5	− 6	+1
HAc	41	55	+14	+6
HCl	41	50	+14	−4
HNO_3	42	51	+17	−2
$HClO_4$	41	52	+14	0
H_2SO_4	42.5	48	+18	−8

[a] No significant interference was found from the following ions and compounds: Sb^{3+}, Ba^{2+}, Bi^{2+}, Cd^{2+}, Ca^{2+}, Ce^{4+}, Cs^+, Cr^{3+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, Li^+, Mg^{2+}, Ni^{2+}, Pd^{2+}, K^+, Ag^+, Na^+, Sr^{2+}, Th^{4+}, Sn^{4+}, Zn^{2+}, NH_4^+, $HAsO_4^{2-}$, CO_3^{2-}, HCO_3^-, F^-, I^-, MoO_4^{2-}, NO_3^-, SeO_3^{2-}, SiO_3^{2-}, TeO_3^{2-}, SCN^-, WO_4^{2-}, UO_4^{2-}, VO_3^{2-}, acetate, EDTA, citrate, oxalate, tartrate, and detergent (Dreft).

Study of interferences

The interfering effect of foreign ions on the fluorescence signal of beryllium was examined under the conditions indicated in Table I. The results are shown in Table II. The concentrations of beryllium were 300 p.p.m. for the oxy–acetylene flame and 5 p.p.m. for the nitrous oxide–acetylene flame, and that of interfering ion, 300 p.p.m. for both flames. Hydrolysis of the interference salt was prevented where necessary by the addition of sufficient acid to maintain a clear solution. The effect of various acids was examined by making a 5% acid solution.

In general, it was noted that the signal interference by the interfering species is larger in the oxy–acetylene flame than in the nitrous oxide–acetylene flame. No significant interference (±5%) was observed from ions and compounds studied in the nitrous oxide–acetylene flame except acetic acid and sulfuric acid. Both aluminium(III) and cobalt(II) ions caused more suppression of the beryllium signal than any other cations in both flames. In oxy–acetylene flame, cations such as copper(II) and titanium(IV) enhanced the signal by 6 and 8% respectively, while anions such as Br^-, Cl^-, PO_4^{3-}, HPO_4^{2-}, SO_3^{2-}, and SO_4^{2-} produced an interference greater than 5%. The interferences from anions were eliminated by adding EDTA to the solution (Table III).

TABLE III

ANIONIC INTERFERENCES

Interfering anion	*Intensity of signal*	
	Be (300 p.p.m.)	*Be (300 p.p.m.) + EDTA (4000 p.p.m.)*
None	36	37
Br^-	33	37
Cl^-	32	37
PO_4^{3-}	34	37
HPO_4^{2-}	32	36.5
SO_3^{2-}	32	37
SO_4^{2-}	34	37.5

When an oxy–acetylene flame was used all acids enhanced the fluorescence intensities for beryllium by about the same extent. When a nitrous oxide–acetylene flame was used no similar enhancement was observed. However, in the latter flame acetic acid slightly enhanced the signal but sulfuric acid slightly reduced the fluorescence intensity.

The effect of organic solvents

The relative fluorescence intensities of the beryllium 2349 Å line were investigated in a series of different organic liquids. The results are listed in Table IV. It was observed that different organic solvents affect the intensity of beryllium fluorescence signal differently. As already known, organic solvents in many cases enhance the intensity of both flame emission and absorption for a given metal as compared to aqueous solution. This was also found to be true of some of the solvents studied for beryllium fluorescence. However, more than half of the solvents studied reduced the signal intensity compared to aqueous solution. It is interesting to note that solvents

TABLE IV

RELATIVE FLUORESCENCE INTENSITY OF BERYLLIUM AT 2349 Å IN DIFFERENT ORGANIC SOLVENTS

Solvent	*Oxy–acetylene flame*		*Nitrous oxide–acetylene flame*	
	Feed rate (ml/min)	*Relative intensity (Be 50 p.p.m.)*	*Feed rate (ml/min)*	*Relative intensity (Be 3 p.p.m.)*
Water	1.15	25	4.8	26
Methanol	1.8	49	5.1	58
Ethanol	1.0	42	4.6	47
n-Propanol	0.55	39	4.1	40
Isopropanol	0.5	40	4.0	42
n-Butylaldehyde	1.75	24	5.05	17
Isobutylaldehyde	0.85	33	4.5	27
MIBK	1.7	22	5.05	34
Acetic acid	0.9	36	3.6	54
Ethyl acetate	2.3	24	5.2	20
Bis(2-ethoxy-ethyl)ether	0.8	34	4.2	40
n-Butylamine	2.0	23	5.0	7
Di-*n*-butylamine	1.05	29	4.75	40
Tri-ethylamine	3.35	12	5.6	2
Nitropropane-2	1.25	27	4.9	50
Nitrobenzene	0.55	22	3.7	25
Aniline	0.3	27	3.35	18
Pyridine	1.05	23	4.5	24
Dimethyl sulfoxide	0.5	30	3.85	27
Thiophene	1.5	10	4.9	12
Tri-*n*-butylphosphate	0.25	36	3.3	25
n-Butylchloride	2.25	15	5.2	3
Chloroform	1.25	2	4.8	2
Heptane	3.1	14	5.45	3
Heptene-2	3.1	8	5.45	2
Cyclohexane	1.15	20	4.8	2
Cyclohexene	1.65	14	4.9	5
Benzene	1.7	8	5.0	10
Toluene	1.85	9	5.1	18
1-Chloronaphthalene	0.35	13	3.5	21

which enhanced the fluorescence intensities of beryllium in nitrous oxide–acetylene flame also enhanced the fluorescence signal in oxy–acetylene flame. The variation in the intensity of fluorescence signal between different organic solvents can be explained by several factors[6]: (*a*) the effect of solvent on the efficiency of producing atomized species from the sample, (*b*) the change in sample feed rate with solvents of different viscosities and specific gravities, (*c*) the effect of surface tension on drop size and atomization efficiency, and (*d*) reduction of intensity by absorption or quenching by the solvent or its combustion product. This problem needs further study. Essentially the enhancement of fluorescence signals by organic solvents is due to the high combustibility of organic solvents so that the atom population is increased.

Studies on the other atomic lines and other flames

No detectable fluorescence was observed for the beryllium lines at 2495, 2651, 3131 and 3321 Å using a beryllium solution of 100 p.p.m. concentration. Oxy–hydrogen, air–hydrogen, and air–acetylene flames were also tested at the resonance line 2349 Å but yielded no fluorescence signal.

CONCLUSIONS

An investigation of the atomic fluorescence signal of beryllium has shown that beryllium can be determined with a high-intensity beryllium hollow-cathode lamp as source and oxy–acetylene or nitrous oxide–acetylene flame as atomizer. The sensitivity is 10 p.p.m. in oxy–acetylene flame and 0.5 p.p.m. in nitrous oxide–acetylene flame. No significant interference was found in the presence of 300 p.p.m. of certain cations and some anions. The interferences from several anions were effectively overcome by adding EDTA to the sample solutions.

The authors wish to thank Mr. R. REISS of Aztec Instruments for the loan of a beryllium high-intensity hollow-cathode lamp and a power supply. They also wish to express their appreciation to Mr. E. T. KEEL who constructed the burner assembly for nitrous oxide–acetylene flame.

SUMMARY

The atomic fluorescence of beryllium has been observed. A high-intensity beryllium hollow-cathode lamp was used as the source. Oxy–acetylene and nitrous oxide–acetylene flames were studied. A newly designed burner assembly for nitrous oxide–acetylene flames used for atomic fluorescence studies is described. The sensitivity for beryllium at 2349 Å was 10 p.p.m. in the oxy–acetylene flame and 0.5 p.p.m. in the nitrous oxide–acetylene flame. The analytical calibration curves for both flames are presented. No significant interference was found from the cations studied. Some anionic interferences were removed by EDTA. The effects of some organic solvents were investigated.

RÉSUMÉ

On examine la fluorescene atomique du béryllium. Comme source on utilise une lampe à cathode creuse béryllium de haute intensité. On examine également les 2 flammes: oxy–acétylène et oxyde nitreux–acétylène. Un brûleur de conception nouvelle est décrit, pour flammes oxyde nitreux–acétylène. Sensibilité pour le béryllium: à 2349 Å, 10 p.p.m. avec flamme oxy–acétylène et 0.5 p.p.m. avec flamme oxyde nitreux–acétylène. Les courbes d'étalonnage analytique sont données pour les 2 flammes. On n'observe aucune interférence appréciable des cations étudiés. Quelques interférences anioniques sont éliminées par addition d'EDTA. On examine également l'influence de quelques solvants organiques.

ZUSAMMENFASSUNG

Die Bestimmung von Beryllium mit der Flammenabsorptionsanalyse wurde untersucht. Als Quelle wurde eine hochintensive Beryllium-Hohl-Kathodenlampe verwendet. Die Sauerstoff-Acetylen- und die Stickstoffoxid–Acetylen-Flammen wurden untersucht. Ein neu entwickelter Brenner für Stickstoffoxid–Acetylen-Flammen wird näher beschrieben. Die Empfindlichkeit für Beryllium bei 2349 Å beträgt in der Sauerstoff–Acetylen-Flamme 10 p.p.m., in der Stickstoffoxid–Acetylen-Flamme 0.5

p.p.m. Es werden Eichkurven für beide Flammen angegeben. Während eine Anzahl der untersuchten Kationen keine bedeutenden Störungen ergaben, konnten Störungen durch Anionen durch ÄDTE beseitigt werden. Die Einflüsse einiger organischen Lösungsmittel wurden untersucht.

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DETECTION OF GASEOUS ORGANIC COMPOUNDS BY THEIR INFRA-RED EMISSION STIMULATED BY A LASER BEAM

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Gaseous organic molecules can be detected by infra-red absorption, but compared to many other techniques the method lacks sensitivity and is not easily handled. Frequently infra-red gas cells one meter long are used and it is often necessary to use a multi-pass optical system in order to obtain a reasonable absorption spectrum or intensity measurement.

In air pollution studies, LOW AND CLANCY[1] have detected sulfur dioxide and carbon dioxide in the smoke effluents from chimney stacks by the infra-red radiation from these compounds. The radiation was very weak. Frequently fifty or more scans of the smoke were necessary in order to accumulate a signal of sufficient intensity for measurement. The gases were thermally warm when they issued from the chimney. It is therefore quite probable that the origin of excitation was thermal.

Based on the model of a photon proposed earlier[8,9], it was suggested that a strong, coherent electromagnetic field would exist in the vicinity of a laser beam. Such a field may interact with nearby molecules in which there was a dipole, causing vibration of the molecule followed by relaxation. Such relaxation may be accompanied by the emission of infra-red radiation.

In the present work a study was made of the use of a carbon dioxide laser beam to excite a wide variety of organic gases and vapors. It was hoped that these would reach higher vibrational levels without decomposition of the molecule, and therefore emit characteristic molecular infra-red radiation[5].

In previous work by BORDÉ *et al.*[2-4] it was observed that, when a carbon dioxide laser beam was focussed on certain unsaturated hydrocarbon molecules, decomposition of the molecules occurred at the focal point with the emission of radiation in the visible and UV regions of the spectrum.

EXPERIMENTAL

Apparatus

Laser. The radiation source was a carbon dioxide gas laser (Perkin-Elmer Model 6200). Wavelength 10.6 μ, quasi-continuous radiation at 60 W. The diameter of the beam was about 1 cm. The plasma tube current used was 45 ± 1 mA.

Infra-red spectrophotometer. A Beckman model IR-10 was used in the single-beam mode. The infra-red source on the IR-10 was disconnected. The entire cell compartment was lined with Transite ($\frac{1}{4}$ in thick). A suitable hole was cut in the Transite to allow radiation to reach the entrance slit of the monochromator.

Sample cell. The sample cell used (Fig. 1) was made primarily of glass. Several materials were tested for use as windows at positions 1, 2, and 3, *viz.* potassium bromide, silver chloride and Irtran-2 (Eastman Kodak Co.). Of these, Irtran-2 was the most satisfactory because it was unaffected by normal laboratory conditions. Potassium bromide was greatly affected by atmospheric moisture and, therefore, without rigorous care, could not be used in the atmosphere for extended periods. Silver chloride was light-sensitive; over a period of several hours, the windows darkened and thus absorbed an increasing proportion of the incident laser beam. This increased the heating effect of the laser with the result that the windows melted (m.p. AgCl = 455°). The Irtran-2 windows used, diameter 25 mm, thickness 0.5 mm or 1.0 mm, had low transmission at wavelengths longer than 16 μ. This prevented the observation of emitted radiation in this spectral region.

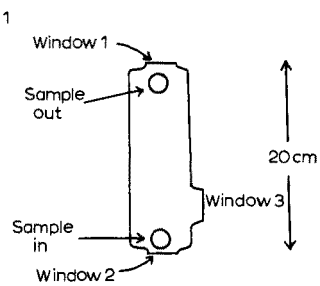


Fig. 1. Cell for flowing gas samples.

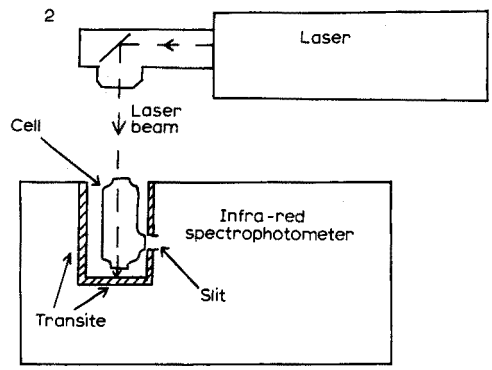


Fig. 2. Schematic diagram of experimental arrangement.

Several adhesives were used to fix these windows in position. The two chief requirements for this were: (*1*) that the adhesive should be unaffected by the passage of the laser beam. With the 10-mm diameter beam passing through 25-mm diameter windows, it was difficult to avoid the beam striking the adhesive directly occasionally. This should not destroy the adhesive. (*2*) The adhesive should provide a reasonably leakproof seal. Both of these criteria were satisfied by Sauereisen Insa-lute adhesive cement (Sauereisen Cements Co., Pittsburgh 15, Penn.) which is reported to be resistant to *ca.* 1100°. However, there was a tendency for the use of this adhesive to result in cracking of the windows. An epoxy resin, *e.g.* Araldite (Ciba, A.R.L. Ltd, Duxford, Cambridge, England) or Eccobond (Emerson and Cuming, Canton, Mass.) was satisfactory if it was protected from direct incidence of the laser beam by an infra-red reflecting material, *e.g.* aluminum foil.

Optical system. The experimental arrangement used is shown in Fig. 2. The cell was clamped vertically in the cell compartment of the spectrophotometer with window 3 adjacent to the monochromator entrance slit. The laser was placed on a table above the spectrophotometer. The laser beam passed vertically downwards through the cell via windows 1 and 2, and was subsequently absorbed by the Transite sheet below. The optimum mutual alignment of the laser and spectrophotometer was

achieved by adjustment to obtain maximum response for the peak at 10.6 μ attributable to reflection of the laser beam within the cell compartment. Some of the emitted radiation stimulated by the passage of the laser beam through the gaseous sample entered the monochromator entrance slit and thus reached the detector. The infra-red emission spectrum of the sample was then recorded in the single beam mode. To obtain maximum sensitivity over the full wavelength range, the spectrophotometer slit was used in the fully open position.

Reagents

The reagents used were as follows (the source and grade are given in brackets): methane (Matheson, C.P.), ethane (Matheson, C.P.), propane (Matheson, C.P.), *n*-pentane (Eastman Organic, practical), isopentane (Harleco-Leddon Co., fluorimetric), *n*-hexane (Matheson, Coleman and Bell, Research), *n*-heptane (Matheson, Coleman and Bell, Research), ethylene (Matheson, C.P.), acetylene (Airco, Purified).

Experimental procedure

Gaseous samples were passed directly through the cell at a steady rate up to 2 l/min. When the compound under investigation was liquid, a stream of dry nitrogen was bubbled through the sample and then passed through the cell. The volume of sample used was about 150 ml. For each sample the flow rate was optimised. After switching on the laser, a few minutes were allowed for the system to reach equilibrium. The readout signal of the emission spectrum was adjusted to a suitable value by means of the SB 100% control. Spectra were recorded over the range 2.5–16 μ in 35 min. Heating of the cell, which would cause emission characteristic of the cell material, was avoided by directing an airstream at the cell wall opposite window 3. Under these conditions there was virtually no background radiation. Care was taken to flush the system thoroughly with air or nitrogen between experiments to remove traces of the previous sample and, thereby, to prevent memory problems.

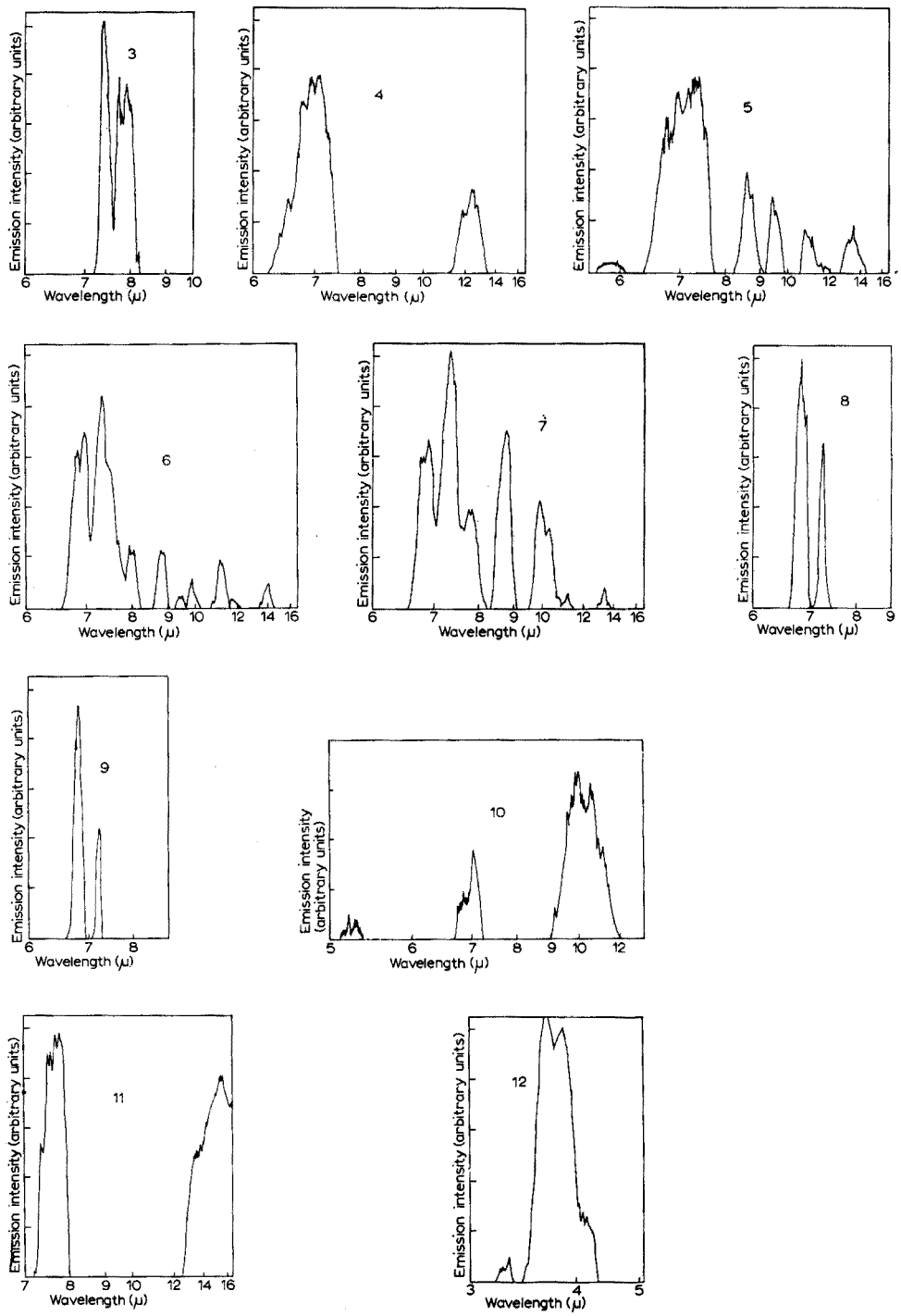
RESULTS

Emission spectra

Figures 3–11 show the spectra recorded as described above for methane, ethane, propane, *n*-pentane, isopentane, *n*-hexane, *n*-heptane, ethylene and acetylene respectively, in the region 5–16 μ. The relative intensity of the spectra can be judged by the relative sensitivity settings shown in Table I. It should be noted that the emission signal was fairly intense from all compounds. No extra signal amplification other than that provided by the instrument was necessary.

As discussed above, the use of Irtran-2 window 3 prevented detection of emitted radiation at wavelengths above 16 μ. The optical system was less sensitive in the region 2.5–5 μ than in the region 5–16 μ, but emission was detected at wavelengths less than 5 μ from some compounds. As an example, Fig. 12 illustrates the emission of propane at below 5 μ at approximately twelve times higher instrumental sensitivity than was used to obtain the spectrum shown in Fig. 5.

Comparison of the emission spectra obtained with the infra-red absorption spectra of these compounds[6,7] showed that most of the major peaks of the two spectra occurred at similar wavelengths. Based on this observation, it seemed reasonable to



Figs. 3–12. IR emission spectra of: (3) methane, (4) ethane, (5) propane, (6) *n*-pentane, (7) isopentane, (8) *n*-hexane, (9) *n*-heptane, (10) ethylene, (11) acetylene, (12) propane, 2.5–5 μ.

TABLE I

VAPOR PRESSURES OF SAMPLES AND INSTRUMENTAL SENSITIVITY SETTINGS

Figure no.	*Compound*	*Vapor pressure of compound at room temperature*	*Relative sensitivity of read-out*	*Spectral range recorded (μ)*
3	Methane	Atmospheric	15	5–16
4	Ethane	Atmospheric	4	5–16
5	Propane	Atmospheric	1	5–16
6	*n*-Pentane	400 mm of Hg	4	5–16
7	Isopentane	600 mm of Hg	4	5–16
8	*n*-Hexane	120 mm of Hg	12	5–16
9	*n*-Heptane	35 mm of Hg	12	5–16
10	Ethylene	Atmospheric	3	5–16
11	Acetylene	Atmospheric	4	5–16
12	Propane	Atmospheric	12	2.5– 5

deduce that the emitted bands could be assigned to the same energy transitions as those assigned in IR absorption spectroscopy. Thus, methane (Fig. 3) showed emission in the 7.2–8.4 μ region which was attributable to CH-bending. Ethane (Fig. 4) exhibited emission in the 11.4–13.3 μ region attributable to CH-rocking and at 6.3–7.5 μ attributable to CH-bending motions. The spectra of propane (Figs. 5 and 12) showed C–C stretching emission bands in the 8.3–12.5 μ range in addition to CH-bending and rocking bands. Furthermore, the emission observed in the 3.2–4.2 μ region was compatible with CH-stretching bands.

When the emission spectra of *n*- and isopentane (Figs. 6 and 7) were compared with their absorption spectra (Sadtler Index nos. 6406 and 691), a good correlation between peak positions and intensity was noted after due allowance had been made for the use of an unprogrammed slit in the spectrophotometer. Thus the ratio of the peak heights at 7.3 and 6.9 μ was greater for isopentane than for *n*-pentane in both emission and absorption spectra. The relative heights of the C–C stretching peaks at 8.8 and 9.9 μ were also greater for the branched compound whereas the peak at 11.1 μ predominated in both the absorption and emission spectra of *n*-pentane. Furthermore, it was noted that the CH-rocking peak occurred at a longer wavelength for *n*-pentane compared to isopentane in both instances.

Figures 8 and 9 show that the emission spectra of *n*-hexane and *n*-heptane consisted essentially of only CH-bending peaks in the 6.7–7.5 μ region.

The emission spectrum of ethylene is given in Fig. 10. The positions of the maxima at 5.2, 7.0 and 10–11 μ are the same in the absorption and emission spectra. The absorption of the laser beam by ethylene was so great that, in order to obtain this emission spectrum, it was necessary to dilute the ethylene with nitrogen. A dilution ratio of 1:8, ethylene: nitrogen, was used.

Figure 11 indicates that the emission spectrum of acetylene contained the CH-bending peaks at 7.5 and 7.7 μ. These coincided with the absorption spectrum as did the CH-rocking vibrational peaks in the region 13–16 μ.

Sensitivity

The calculation of the sensitivity of detection of the gases examined was based on two assumptions. First, only gas which was directly in front of the entrance slit of the monochromator contributed to the detected signal. Secondly, only gas molec-

ules in the laser beam and its immediate vicinity were excited and emitted radiation. The second assumption may be unsound, but was nevertheless used in the preliminary calculations.

Based on these assumptions, the volume of gas which contributed to the signal was contained in a cylinder 1 cm in diameter (the diameter of the laser beam) and 1.8 cm long (the length of the entrance slit) and was equal to 1.4 ml. Therefore for a normal gas, 1.4/22,400 gmols of the gas were responsible for the emission signal. For methane, this was *ca.* 1 mg. As can be seen from Fig. 3, the most intense emission band was 8.2 μ and was 100 units. Based on the noise level of the instrument operated under these conditions it should be possible to detect a signal 2 units high. This would be equivalent to 20 μg of methane.

Similar calculations for the other compounds studied, taking into account the instrumental sensitivity available, gave the detection limits listed in Table II.

TABLE II

CALCULATED DETECTION LIMITS FOR COMPOUNDS STUDIED (IN μg)

Methane	20
Ethane	12
Propane	5
n-Pentane	15
Isopentane	20
n-Hexane	14
n-Heptane	5
Ethylene	1.2
Acetylene	33

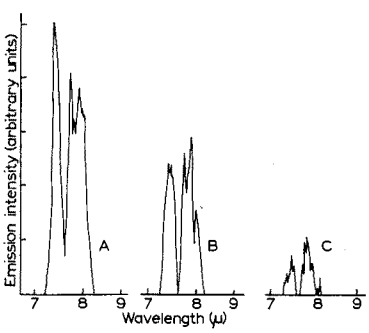


Fig. 13. Emission spectra obtained from varying concentrations of methane. Total flow rate *ca.* 250 ml/min. Sensitivity constant. (A) 100% methane; (B) 60% methane, 40% nitrogen; (C) 20% methane, 80% nitrogen.

The relationship between emission intensity and concentration

A preliminary study of the relationship between gas concentration and emission intensity was carried out as follows. While a constant total gas-flow rate was maintained, methane was diluted successively with increasing proportions of nitrogen. It was noted that, over the concentration range examined (20–100% methane, 80–0% nitrogen), the emission signal in the range 7.2–8.2 μ varied approximately linearly with the methane concentration. The present experimental set-up did not permit the investigation of a wider concentration range. The spectra obtained are illustrated in Fig. 13.

It was observed that the emission intensity from hexane and heptane was lower than from pentane, propane, etc. It seems clear that the lower emission intensity observed was related to the lower vapor pressure of these compounds and, therefore, to their lower concentration in the gas cell.

Relationship between emission intensity and absorption of radiation

The absorption spectra of the compounds examined show that certain of these absorb at 10.6 μ, the wavelength of the laser beam. These include propane and *n*-pentane. However, it is also apparent that other molecules, such as methane and ethane, do not absorb significantly at 10.6 μ.

The emission spectra recorded for these two groups of molecules showed that those molecules which absorbed radiation at 10.6 μ emitted more strongly than those which did not appreciably absorb the laser beam radiation.

However, it should be noted that even those molecules which apparently did not absorb this radiation, emitted IR radiation quite strongly. This observation has certain important theoretical implications which will be discussed later.

Interferences

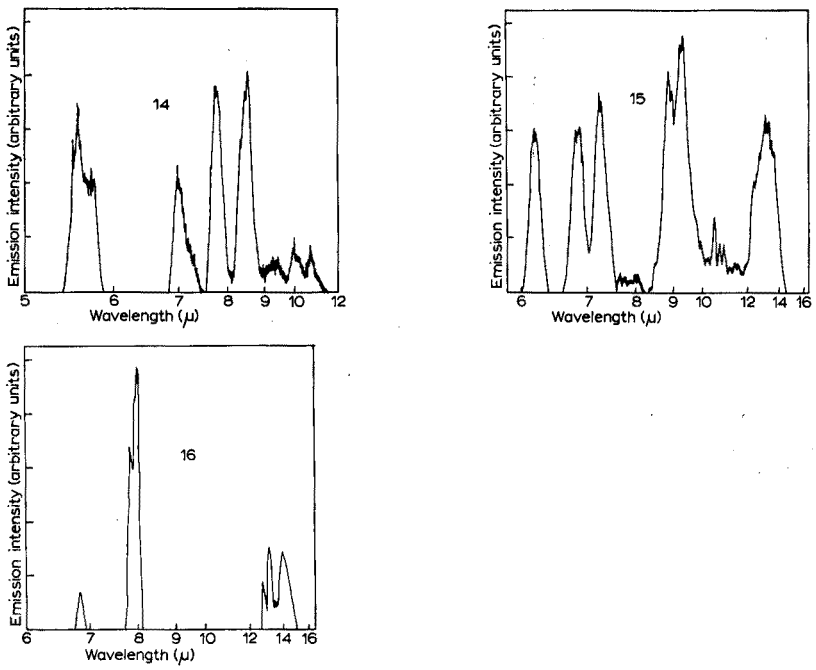
It is important to know whether the presence of two or more compounds together will affect the intensity of the IR emission due to a given concentration of each component of the mixture. This was investigated using nitromethane vapor and propane as sample gases. These were selected because nitromethane showed strong emission at 6.3 μ, where propane showed no emission, while nitromethane showed little or no absorption at 10.6 μ where propane absorbed relatively strongly. The intensity of the nitromethane emission at 6.3 μ when the vapor was present at *ca.* 20 mm pressure in an atmosphere of nitrogen, A, was compared with the intensity of the same peak when the cell contained the same concentration of nitromethane and *ca.* 350 mm each of nitrogen and propane, B. The emission intensity was found to be considerably greater in B, *i.e.* the presence of propane enhanced the emission due to nitromethane.

The cause of this effect, which was not unexpected, was probably that the presence of propane increased the absorption of the laser beam by the cell contents. The energy thus acquired could then be redistributed between propane and nitromethane. The nitromethane, therefore, gained, in total, more energy than when it was present alone. Consequently the emission intensity was also greater. The significance of this observation in analytical applications of this technique is that any two compounds may mutually interfere. In quantitative studies, therefore, this possibility must always be considered and checked.

DISCUSSION

The work described in this paper has shown that infra-red emission spectra have been readily obtained from organic compounds in the vapor phase and that these spectra may be correlated with molecular deformations in the same way as absorption spectra. Preliminary results with different classes of compounds, showed that emission peaks were also observed at the frequencies compatible with C–H, C–O, C=O, O–H, C–N, N–H, C–Cl, and other bond vibrations. These are illustrated in the

emission spectra of acetic acid, *n*-butylamine and methylene chloride, Figs. 14–16. As mentioned above, the spectra obtained to-date have been uncorrected in that the use of the manual slit in the spectrophotometer resulted in spectra related to the sensitivity of the detecting system at all wavelengths. This was maximal in the range 5.5–10 μ.



Figs. 14–16. IR emission spectra of (14) acetic acid, (15) *n*-butylamine, (16) methylene chloride.

It is interesting to note that, although the only incident radiation used was at 10.6 μ, emission was observed at appropriate frequencies over the range 3.2–15.4 μ, where the energy of emitted photons was both higher and lower than the energy of photons absorbed. In fact, for propane (and also for other compounds not discussed herein) the energy of photons emitted in the CH-stretching region was more than 3 times that of the absorbed photons.

The experiments carried out to date have indicated that this technique has considerable analytical promise particularly in the area of the detection and determination of atmospheric pollutants. If, as it appears, infra-red emission spectra can be obtained from any substance which shows infra-red absorption, their detection will become a problem of achieving sufficient instrumental sensitivity to record the weak emission signals.

Further studies will be made to increase analytical sensitivity and to study the fine structure of the spectra. Before this can be done, however, it is necessary to overcome the present experimental difficulty of slowness of instrumental response to small signals. Although this effect, which results in a delay of several seconds between the incidence and the recording of a small signal emission at high instrumental sensitivity, has been tolerable in the work to date, it will be unacceptable when the fine structure of the bands is examined.

EXCITATION OF SPECTRA

The mechanism of excitation of the molecules which results in infra-red emission is not clearly understood at present. Several explanations are possible and, of course, any or all of these processes may contribute to the total signal observed. Some of the possible methods of excitation are as follows:

(*1*) The gas molecules absorb the laser beam directly. Inter- or intra-molecular rearrangement of the energy acquired is then followed by fluorescence. This process appears probable for ethylene, for example. which absorbs strongly at 10.6 μ, but does not account for the emission observed from methane, ethane, etc., which do not absorb at 10.6 μ.

(*2*) The molecules are thermally heated indirectly by the cell windows and walls which become heated during operation. Irtran-2 windows absorb a small proportion of radiation at 10.6 μ. Furthermore, window 2 (see Fig. 1) is *ca.* 1 cm above the Transite sheet which is strongly heated by absorption of the laser beam. It is likely that a portion of this energy could be transferred to the lower part of the cell and, therefore, be available for excitation of the sample. This process could contribute to the emission of methane, etc.

(*3*) The laser heats suspended particles in the cell which in turn heat the gas molecules. Under the experimental conditions used, attempts were made to keep the gases clean. It is pertinent to note that when cigarette smoke was introduced into the cell, a strong scatter peak was observed at 10.6 μ. This indicated that small particles in the laser light path could be detected by scattering. However, under normal operating conditions, when all reflected radiation from the beam was eliminated then no peak at 10.6 μ was observed. It seems logical to deduce from these results that under normal conditions there were no particles detectable in the gas stream. From this it follows that no interaction was observed between the laser beam and particles in its path. It is therefore unlikely that this mechanism provided a source of heat and therefore a source of excitation of the molecules.

(*4*) The laser beam interacts with the gas molecules without prior absorption. The basis of this proposal is that the laser provides a coherent beam of radiation. This must produce a coherent electro-magnetic field which could interact with the dipoles of the molecules. Any such interaction would involve vibration of the components of the molecules. This is equivalent to causing vibrational excitation. The subsequent relaxation may be accompanied by the emission of radiant energy, in this instance infra-red. Definite conclusions cannot be drawn concerning this possibility without further studies.

It is important to understand the processes by which infra-red emission is stimulated before the maximum possible analytical applications of this technique can be realized. The present work is being directed towards this goal and it is hoped to report the results of these studies in a later communication.

The authors wish to express their appreciation to the Army Research Center, Edgewood Arsenal, Maryland, for financial support.

SUMMARY

Excitation by a carbon dioxide laser has been used to obtain the infra-red

emission spectra of a number of gaseous aliphatic hydrocarbons. The experimental set-up is described and the spectra obtained are correlated with bond vibrations and are shown to be similar to infra-red absorption spectra. The future requirements of this technique are discussed and its analytical possibilities are indicated.

RÉSUMÉ

On propose l'utilisation d'un laser CO_2 pour obtenir des spectres d'émission dans l'infra-rouge d'un certain nombre d'hydrocarbures aliphatiques gazeux. Les spectres obtenus sont similaires aux spectres d'absorption dans l'infra-rouge. On envisage le développement de cette technique et ses possibilités d'applications analytiques.

ZUSAMMENFASSUNG

Eine Anzahl gasförmiger aliphatischer Kohlenwasserstoffe wurde mit einem CO_2-Laser zur Aussendung von Infrarotspektren angeregt. Die experimentelle Anordnung wird beschrieben. Es konnte gezeigt werden, dass die Emissions-Spektren denen der Absorptions-Spektren ähnlich sind. Zukünftige Erfordernisse dieser Technik werden diskutiert und ihre analytischen Möglichkeiten aufgezeigt.

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SHORT COMMUNICATIONS

m-Chloroperbenzoic acid as a reagent for the determination of unsaturation in natural and cyclized rubber

Perbenzoic acid has been used extensively for the determination of the total unsaturation in various types of organic compounds[1-6]. For example, KOLTHOFF AND LEE[1] used this reagent to determine the internal and external double bonds in synthetic rubbers. LEE *et al.*[3] found that perbenzoic acid was superior to reagents such as ozone, iodine chloride, and phenyliodochloride in the determination of unsaturation in cyclized rubber. The instability of perbenzoic acid and its commercial unavailability are well known, hence perbenzoic acid has not found general use as an analytical laboratory reagent.

In recent work carried out in our laboratories, *m*-chloroperbenzoic acid, a new solid peracid, was found to react rapidly and quantitatively with several types of unsaturated compounds. Moreover, *m*-chloroperbenzoic acid is a very stable solid and is available commercially for analytical purposes. The results of this work and a comparison of the stability of equivalent *m*-chlorobenzoic acid and perbenzoic acid solutions are reported in this communication.

Reagents

m-*Chloroperbenzoic acid* (technical grade, 85.4%, FMC Corp., Inorganic Chemicals Div.) was used without purification. An approximately 1 *N* (0.5 *M*) solution was prepared in 9:1 chloroform-benzene (analytical grade). The solution was filtered twice to remove residual matter. The titer was determined before use by a simple iodimetric titration with 0.1 *N* sodium thiosulfate. The solution was stored at 5–10°.

Squalene. Eastman Chemical Co., white label, 99% by vapor phase chromatography.

Natural rubber. Number 1 ribbed smoked sheet was masticated for several hours on a rubber mill to reduce the viscosity and to render the sample more soluble in benzene solvent.

Cyclized rubber. Several types of cyclized rubber were separated from commercial mixtures by precipitation in methanol. The samples were purified by dissolving in benzene and precipitating twice from methanol. In addition, laboratory samples were prepared by the procedure given below.

Laboratory cyclization procedure. Natural rubber (5 g) was dissolved in 100 ml of benzene. To this mixture were added 2,2-methylenebis(4-methyl-6-*tert*-butylphenol) antioxidant to prevent gel formation, and 0.25 ml of (anhydrous) tin(IV) chloride as catalyst. After refluxing for 2 h at 80°, the solution was treated with dilute hydrochloric acid to remove tin residues. The product was precipitated twice from methanol and dried *in vacuo* at 50° to give 4.7 g (95% yield) of a white powdery solid.

The product was identified by the infrared spectrum which was similar to the one described by GOLUB AND HELLER[7]. The band at 830 cm^{-1}, present in uncyclized rubber and attributed to C–H aplanar deformations of the trialkyl-substituted double bonds was not present in the cyclized rubber.

Recommended procedure

The unsaturated compound (0.04–0.10 g) was dissolved in 25 ml of benzene. *m*-Chloroperbenzoic acid (5 ml of 0.5 *M*) was added, and the mixture was gently shaken for 2 h at room temperature. (The results showed little change with reaction times greater than 2 h.) Aqueous potassium iodide solution (10 ml of 10%), 7 ml of acetic acid, and 40 ml of distilled water were then added and the liberated iodine was titrated with 0.1 *N* thiosulfate solution.

Results and discussion

The oxidation properties of the *m*-chloroperbenzoic acid were tested on the known unsaturated compounds: squalene and isoprene. The results of seven determinations with squalene are given in Table I and are within ± 2% of the theory. However, with isoprene, no quantitative result could be obtained because only about one-half the double bonds were epoxidized, even after reaction times of 16 h. This was not unexpected for complete epoxidation of conjugated double bonds is reported to be difficult[8].

TABLE I

DETERMINATION OF THE UNSATURATION IN SQUALENE BY *m*-CHLOROPERBENZOIC ACID

Sample wt. (mM)	*Reagent consumed (mM)*	*Number of double bonds*	
		Found[a]	*Theory*
0.2049	1.247	6.08	6.00
0.3196	1.893	5.92	6.00
0.2663	1.568	5.89	6.00
0.2328	1.412	6.06	6.00
0.1854	1.132	6.10	6.00
0.3285	1.996	6.07	6.00
0.3720	2.280	6.12	6.00

[a] The standard deviation calculated from these data is ± 0.084.

TABLE II

DETERMINATION OF THE UNSATURATION IN CYCLIZED RUBBERS BY *m*-CHLOROPERBENZOIC ACID

Rubber sample	*Quantity (mM)*	*Reagent consumed (mM)*	*Alkene function*[a] (%)(–C = C–)
Laboratory-cyclized natural rubbers	1.059	0.278	9.2
	4.496	1.167	9.2
Commercial cyclized polyisoprenes			
T–7	1.490	0.735	17.4
	1.510	0.797	17.3
T–11	4.440	2.098	16.6
	4.480	2.033	16.1
M–7	0.960	0.368	13.5
	0.979	0.413	13.6
	3.200	1.231	13.6
M–28	1.496	0.685	16.2
	1.476	0.672	16.1

[a] The alkene function is calculated on the basis of the following formula:
(% –C = C–) = (meq *m*-chloroperbenzoic acid consumed) (24.02) (100)/2 (sample weight) (1000)

The unsaturation values of three samples of natural rubber were determined as a further indication of the reliability of this reagent. Unsaturation values of 102.7, 97.0 and 102.6% of the theory were obtained. The results of a comparison of several different lots of cyclized natural rubber and cyclized polyisoprene are given in Table II. The agreement between duplicate samples was excellent.

Solid *m*-chloroperbenzoic acid was found to be a very stable compound showing little or no decomposition after standing for many months at room temperature. Chloroform–benzene solutions of the acid slowly decomposed but could be used reliably for one month provided that the solution was stored at 5 to 10°. Figure 1 compares

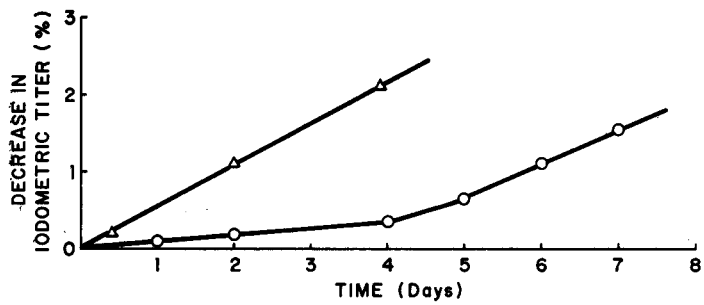

Fig. 1. Stability of solutions of perbenzoic acid and *m*-chloroperbenzoic acid in 90% chloroform–10% benzene at 25°. Triangles: 0.06 *N* perbenzoic acid (Ref. 2). Circles: 0.92 *N* *m*-chloroperbenzoic acid (this work).

the stability of perbenzoic acid and *m*-chloroperbenzoic acid solutions prepared in a solvent mixture of 9:1 chloroform-benzene. After 4 days, the titer of the perbenzoic solution had decreased more than 2% while that of the *m*-chloroperbenzoic solution had changed by less than 0.5%. After 14 days, the titer of the latter solution had changed by only 2%. Thus, the superior stability and the reproducible unsaturation values attainable with *m*-chloroperbenzoic acid make it a more suitable replacement for perbenzoic acid.

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Indirect determination of sodium and potassium in mixtures by extraction of their dipicrylaminates into nitrobenzene

Methods for the indirect determination of sodium and potassium in their mixtures have been recently reviewed by KORENMAN in his monograph[1]. The principal requirement in an indirect determination is the uniform change of a measurable quantity with the sodium to potassium ratio if their total amount is constant. The main disadvantage of most indirect methods is their low accuracy because of low sensitivity to changes in the sodium to potassium ratio; the values of the measured quantity for the pure sodium and potassium salts rarely differ by a factor of more than two. In this communication, a method is given based on the different extractability of sodium and potassium dipicrylaminates from alkaline aqueous solutions (pH > 8) into nitrobenzene. Under the same conditions, the distribution ratio for potassium exceeds that of sodium by a factor of about one hundred[2].

The method is based on colorimetric determination of the dipicrylaminate C in the aqueous phase. Calcium dipicrylaminate is used as the reagent because of its very low extractability. If the aqueous phase contains sodium and potassium, these are extracted into nitrobenzene, and the concentration of dipicrylaminate ions is thus lowered, the effect being about hundred times larger for potassium than for sodium. For solutions with varying molar ratio of sodium to potassium (G_K/G_{Na}) but with the same total amount of the two elements ($G_K + G_{Na}$), the concentration of dipicrylaminate ions in the equilibrium aqueous phase (C_{DPA}) will be a direct function of the molar ratio.

Reagents and apparatus

Nitrobenzene was purified by vacuum distillation. Calcium dipicrylaminate was prepared by reaction of aqueous calcium hydroxide solution with an excess of dipicrylamine; the excess of dipicrylamine was filtered off, and crystallization of the filtrate yielded solid calcium dipicrylaminate.

The extinction (E) of the aqueous phase was measured by a FEK-M colorimeter (U.S.S.R.) with a blue filter (λ_{max} = 460 nm) and 2-cm glass cells. The Lambert–Beer law was obeyed in the concentration range $10^{-6} - 2 \cdot 10^{-5}$ N dipicrylaminate[3]. The extinction coefficient of the dipicrylaminate anions was not influenced by the cations present, and amounted to $2.3 \cdot 10^4$ mole/cm with the above-mentioned filter.

Construction of calibration curves

Several calibration curves (E *vs.* log G_K/G_{Na}) were obtained for various values of $G_K + G_{Na}$ and of the ratio $(G_K + G_{Na})/G_{DPA}$. The construction of calibration curve 2 of Fig. 1 is described here as an example. Samples (3.0 ml) containing sodium and potassium in different ratios (total $G_K + G_{Na} = 3 \cdot 10^{-5}$ mole being kept constant) were prepared by mixing different volumes of sodium chloride and potassium chloride of the same concentration (10^{-2} M). All samples were made alkaline by the addition of 0.1 ml of $4 \cdot 10^{-2}$ M calcium hydroxide and their volumes were adjusted to 6 ml. The solutions were then equilibrated for 30 min with 2 ml of $6.8 \cdot 10^{-3}$ M calcium dipicrylaminate in nitrobenzene. After centrifugation, 5 ml of the aqueous phase was diluted with 10 ml of water and the extinction was measured.

Results and discussion

Typical calibration curves are shown in Fig. 1. Their steep sections, applicable for the determination, cover a wide range of G_K/G_{Na} values. It is seen that with increasing ratio $(G_K + G_{Na})/G_{DPA}$, the calibration curves are shifted towards lower values of G_K/G_{Na}.

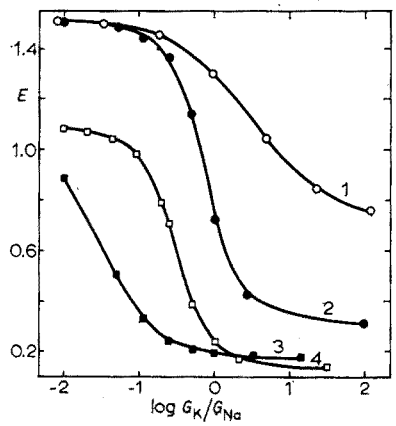

Fig. 1. Typical calibration curves. (1) $G_K+G_{Na} = 1.2\cdot10^{-5}$ mole, $(G_K+G_{Na})/G_{DPA} = 1.05$; (2) $G_K+G_{Na} = 3\cdot10^{-5}$ mole, $(G_K+G_{Na})/G_{DPA} = 2.20$; (3) $G_K+G_{Na} = 2.05\cdot10^{-5}$ mole, $(G_K+G_{Na})/G_{DPA} = 3.42$; (4) $G_K+G_{Na} = 3\cdot10^{-4}$ mole, $(G_K+G_{Na})/G_{DPA} = 21.7$.

It may be mentioned that the dependence of C_{DPA} on G_K/G_{Na} can also be calculated theoretically by using the values for the extraction constants for sodium and potassium found previously[2]. This can be done under the simplifying assumption that the extraction of calcium is negligible compared with that of sodium and potassium. It is assumed that the ions Na^+, K^+, and DPA^- are present in the aqueous phase; while in the organic phase, where dissociation also takes place owing to the high dielectric constant of nitrobenzene, ionic and molecular species, namely Na^+, K^+, DPA^-, NaDPA, and KDPA are expected to appear. Considering the simplifications involved, the agreement found between calibration curves calculated in this way and the experimental ones, is very satisfactory so far as the general shape and position are concerned.

In a sample of unknown composition, the total molarity of sodium and potassium must first be determined. According to the expected sodium : potassium ratio, the concentration of dipicrylaminate in nitrobenzene and the total concentration of ions to be determined by extraction must then be suitably chosen so as to yield an appropriate calibration curve. A suitable range of the dipicrylaminate concentration is $10^{-3} - 10^{-2}$ mole/l, while the total concentration should correspond to values of $(G_K + G_{Na})/G_{DPA}$ between about 1 and 20. If the determined ratio G_K/G_{Na} happens to occur outside the steep part of the calibration curve, another curve must be employed according to these preliminary results.

The accuracy of determining G_K/G_{Na} is high, corresponding to a standard mean deviation of about 3% within the steep parts of the calibration curves. Moreover, the method is rather insensitive to small errors in the determination of the total amount of $G_K + G_{Na}$. For the verification of the method, 3 samples of known composition were analyzed (Table I).

The advantages of the described method are its rapidity as well as its modest requirements in laboratory equipment. Only a small amount of sample is necessary for the determination. Elements whose dipicrylaminates are only slightly extractable,

TABLE I

RESULTS OF ANALYSES OF TEST MIXTURES

Taken			*Found*		
Na(mg)	*K(mg)*	$G_{Na}+G_K$*(mmole)*	*Na(mg)*	*K(mg)*	$G_{Na}+G_K$*(mmole)*
0.3450	0.5865	0.0300	0.3474	0.5760	0.0298
0.0276	1.0320	0.0276	0.0294	1.0290	0.0276
5.7300	0.6960	0.2670	5.7330	0.6909	0.2670

and among these are frequently occurring admixtures like Fe, Ca, Mg, do not interfere with the determination when present at low concentrations. On the other hand, elements which are easily extracted as dipicrylaminates (Cs, Rb) are less likely to be found as admixtures. The fact that the calibration curve must be selected according to the values of the ratio G_K/G_{Na} appears to be a certain disadvantage.

Some experiments were also made with lithium dipicrylaminate instead of the calcium salt. In some cases, this led to more favorable calibration curves, but the tolerance for foreign cations was decreased.

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The detection of traces of barium or strontium by induced precipitation

Induced precipitation is a term used to describe a number of co-precipitation phenomena, and has found much application in analysis[1]. However, there appear to be only two examples in which the induction of precipitation by traces of an inductant has been used for the detection of the inductant. In one[2], traces of zinc ions speed up the appearance of the precipitate of cobalt mercurithiocyanate; in the other[3], barium ions induce lead sulphate to precipitate from a saturated solution of the latter in ammonium acetate. As little as 0.2 μg of zinc and 0.4 μg (at a dilution of $1:10^5$) of barium can be detected by these reactions. The zinc test probably involves the formation of microscopic particles of zinc mercurithiocyanate upon which the

cobalt mercurithiocyanate precipitates, so that the slow nucleation of the latter salt is avoided. The mechanism of the barium test, however, is obscure.

A modified test for barium and strontium has been developed from that described above, and a definite mechanism is postulated. If ethanol is added to a lead sulphate–ammonium acetate solution so that the solution becomes supersaturated, the appearance of a visible turbidity in the solution is delayed. However, when traces of barium or strontium are present, the turbidity appears much more quickly. A test for the detection of barium or strontium was developed on this basis.

Reagent solution

Lead sulphate in ammonium acetate solution. Dissolve analytical-reagent grade ammonium acetate (500 g) in the minimal quantity of distilled water, and shake with lead sulphate (*ca.* 60 g) for 12 h. Filter through a Whatman No. 40 filter paper and dilute to 1 l. Leave to stand for 2 weeks before use.

Detection of barium or strontium

To two test tubes add 2 ml of the lead sulphate solution and 1 ml of test solution or water (as a blank). Inject 2 ml of absolute ethanol from a syringe, first into the blank and then into the test solution. The appearance of a precipitate in the test solution at least 30 sec before that in the blank (which usually took 3 min) indicates the presence of barium or strontium.

Sensitivity

Barium: 0.1 μg, dilution $1:10^7$ in test solution.
Strontium: 0.2 μg, dilution $1:5\cdot10^6$ in test solution.

Discussion

This induced precipitation reaction allows the detection of barium or strontium at concentrations at which precipitates of their sulphates would be invisible. There was no interference from 1-mg amounts of Ag^+, Cd^{2+}, Cl^-, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, I^- or Pb^{2+}. Up to 0.1 mg of calcium or fluoride could also be tolerated; above this limit calcium also induced precipitation, whereas fluoride inhibited the induction.

For reproducible results, the ethanol had to be added rapidly from a syringe into the bulk of the solution. Other methods of addition tended to produce temporary ethanol–water interfaces at which precipitation occurred rapidly but irregularly, so that the test became less sensitive and reliable. It was also necessary to age the lead sulphate–ammonium acetate solution; fresh solutions showed much less delay in precipitation. These observations tend to confirm the mechanism of the induction. The traces of barium present are sufficient to exceed the supersolubility product required for heteronucleation to occur[4], so that microscopic barium sulphate crystals are produced. These must form more rapidly than those of the lead salt that precipitates, so that crystal growth of the lead salt then occurs on the barium sulphate particles, resulting in the more rapid appearance of precipitate than in the absence of barium. The final precipitate contained lead, sulphate and appreciable amounts of ammonium. Excessive supersaturations at water–ethanol interfaces would accelerate the nucleation of the lead salt so that no induction by barium would be apparent.

Ageing of solutions of barium chloride is known to result in the production of larger (and thus fewer) barium sulphate particles[5], indicating that the process of ageing involves the disappearance of potential heteronuclei from the solution, possibly fragments of the barium chloride lattice which dissolve only slowly. In the present example it would again appear to be true that time must be allowed for the bulk of potential heteronuclei—in this instance minute lead sulphate clusters—to disperse completely from the lead sulphate–ammonium acetate solution before the inducing effect of barium becomes apparent. It is interesting that KRUMHOLZ AND SANCHEZ[2] found that the zinc-induced precipitation occurred more *rapidly* if the cobalt-mercury-(II)-thiocyanate solution was aged for 3 to 4 days, but this could have been a result of slow reactions between the components to produce a species suitable for precipitation.

Attempts to relate the rate of production of turbidity to the concentration of barium present showed that the reproducibility of the addition of the reagents, especially of the ethanol, is critical. Indeed, in non-equilibrium systems in which precipitation processes are involved, the method and order of addition of reagents is of prime importance, whereas the concentration of reagents is likely to be a minor consideration. This is directly opposite to most methods of trace analysis. Although there appeared to be some trend to more rapid induction with increasing barium concentration, at the present time it has not been possible to formulate an experimental procedure for the determination of barium based on this reaction. Nevertheless, the great sensitivity of the present qualitative test shows that induced precipitations show considerable promise for trace analysis.

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The ultraviolet spectrophotometric determination of vanadium by the molybdovanadophosphoric acid method

Many spectrophotometric methods for vanadium have been proposed[1]. The tungstovanadophosphoric acid[2,3] and peroxyvanadic acid[4-6] methods have been used extensively. In a systematic study of molybdoheteropoly complexes a mixed heteropoly acid, molybdovanadophosphoric was investigated. As the result of this study a sensitive ultraviolet method for the determination of vanadium has been developed.

A survey of the literature reveals that methods for vanadium using heteropoly chemistry have been reported previously, but almost exclusively utilizing the tungstovanadophosphoric acid complex. The majority of this spectrophotometric work has been done in the aqueous phase using the yellow tungstovanadophosphoric acid[2,3,7-13] with some work done on the extraction of the tungstovanadophosphoric acid into organic media[14-16]. There have also been reports of vanadium being determined by utilization of both the 5-molybdovanadic acid[17] and the 3-tungstovanadic acid[18]. There has been only one paper on the colorimetric determination of vanadium using the molybdovanadophosphoric acid[19].

Experimental

Reagents. Standard vanadium solution (15.05 μg of vanadium/ml). Dissolve 0.3460 g of reagent-grade ammonia vanadate in 500 ml of distilled water, add 28 ml of concentrated hydrochloric acid and dilute to 1 l with distilled water. Transfer a 50-ml aliquot of this solution to a 500-ml volumetric flask and dilute to the mark with distilled water. Store in a polyethylene bottle.

Stock phosphate solution (0.66 mg of phosphorus/ml). Dissolve 0.2891 g of reagent-grade potassium dihydrogen phosphate in distilled water and dilute to 1 l. Store in a polyethylene bottle.

Stock molybdate solution. Dissolve 2.60 g of reagent-grade ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 100 ml of distilled water. Store in polyethylene bottle.

Mixed reagent. Combine 50 ml of stock phosphate solution with 12.50 ml of stock 2.5 *N* hydrochloric acid solution (stored in a polyethylene bottle). Add 20 ml of molybdate solution and dilute to 1 l with distilled water. Store in a polyethylene bottle. (Prepare a new solution after about 2 weeks.)

Dilute hydrochloric acid solution (1.0 N). Store in polyethylene bottle.

Chemicals used for diverse ion study were reagent grade.

Apparatus. Spectrophotometric measurements were made using a Cary 14 spectrophotometer. All measurements were made in 1.000-cm silica cells.

General procedure. Weigh or measure by volume into a 25-ml volumetric flask an amount of sample containing not more than 95 μg of soluble vanadium(V). Add 10.0 ml of the mixed reagent and swirl to mix. Add 2.0 ml of 0.1 *N* hydrochloric acid solution, dilute to the mark with distilled water and mix well. Allow to stand for 10 min before measuring the absorbance at 323 nm against a reference solution prepared in a similar manner except for addition of the sample solution.

Results

Ultraviolet absorption spectrum. The absorbance maximum for molybdovanadophosphoric acid is at 323 nm in contrast to an absorbance maximum for the tungsto-

vanadophosphoric acid which is at approximately 365 nm[10]. The sensitivity for the ultraviolet spectrophotometric determination of vanadium by the molybdovanadophosphoric acid method is 0.0046 μg V per cm^2. The sensitivity for the tungstovanadophosphoric acid ranges from 0.019–0.045 μg per cm^2 depending on the wavelength selected for measurement. Typical ultraviolet absorption spectra for the molybdovanadophosphoric acid solutions are shown in Fig. 1.

Vanadium concentration. The optimum concentration range for the general procedure is 0.9–3.8 p.p.m. of vanadium. Conformity to Beer's law was observed for this range. The molar absorptivity at 323 nm was found to be 11,400 l/mole-cm.

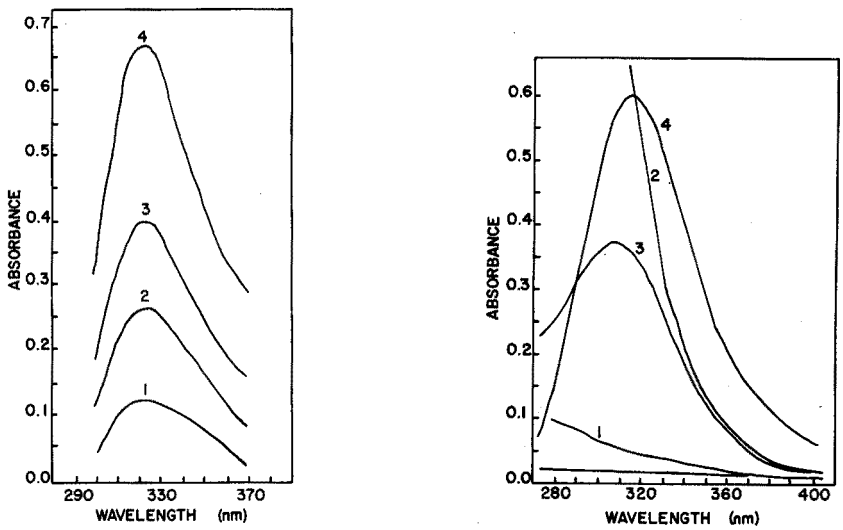

Fig. 1. Ultraviolet absorption spectra for molybdovanadophosphoric acid. Reference: blank solution. (1) 0.6 p.p.m. V, (2) 1.2 p.p.m. V, (3) 1.8 p.p.m. V, (4) 3.0 p.p.m. V.

Fig. 2. Spectral evidence for formation of molybdovanadophosphoric acid. Reference: water. Absorption spectra of: (1) ammonium vanadate soln., (2) ammonium molybdate soln., (3) molybdophosphoric acid reagent, (4) molybdovanadophosphoric acid.

Composition of molybdovanadophosphoric acid. Figure 2 is evidence for the formation of molybdovanadophosphoric acid in acid solution. Curve 1 represents a solution of ammonium vanadate measured against water in the reference cell. Curve 2 represents a solution of ammonium molybdate measured against water. Curve 3 represents a mixture of ammonium molybdate solution and a solution of phosphate to form the molybdophosphoric acid. Curve 4 represents the absorption spectrum of a mixture of the molybdate, vanadate, and phosphate, or molybdovanadophosphoric acid.

The composition of the molybdovanadophosphoric acid has been determined and a ratio of 11:1:1 was found for the molybdenum:vanadium:phosphorus ratio. This stoichiometric ratio has been used as the basis of an indirect ultraviolet spectrophotometric method[20] and indirect atomic absorption spectrometric method[21] for the determination of vanadium by measurement of the molybdate present in molybdovanadophosphoric acid isolated by extraction with a (1:4) mixture of 1-pentanol and diethyl ether.

Acidity. It was observed that when the pH of the solution was decreased to 0.0–0.3, the absorbance of the molybdovanadophosphoric acid reached a maximum. It was also noticed, by monitoring of the blank solution, that the excess of molybdophosphoric acid is decomposed at a rapid rate and, after about 10 min, the absorbance of the blank solution is decreased to a fraction of its original value.

Reagent concentration. The concentrations of the reagents chosen for the molybdate–phosphate reagent were based on a study of the effect of one solution variable while the other 3 variables were held constant. Molybdate, vanadate, phosphate and acidity were the variables investigated. A volume of 10 ml is recommended.

It was found that about 3 weeks after preparation, the mixed reagent began to give lower absorbances than were obtained with the freshly prepared reagent. Hence, a lifetime of two weeks was assigned to the mixed reagent, after which it was discarded and fresh reagent prepared.

Stability. A solution of this heteropoly complex formed according to the recommended general procedure was subjected to a time/stability study. It was found that for at least an 80-min period, no change in absorbance at the wavelength of absorbance maximum occurred.

Effect of diverse ions. A study was made to determine the permissible amounts of various ions that may be present without interfering with the determination of 2.17 p.p.m. of vanadium. No attempt was made to determine the effects of ion concentration larger than 500 p.p.m. Errors of less than $\pm 1.4\%$, twice the relative standard deviation, of the mean absorbance value were considered negligible. Table I summarizes the results of this study. Owing to the formation of competing heteropoly complexes, silicate and tungstate interfere. Iron(II) and iron(III) interfere, presumably because they cause the complexes to be kinetically unstable, the iron(II) causing reduction to the heteropoly blue and iron(III) probably complexing the phosphate ions. The titanium(IV) interferes by causing the wavelength of maximum absorbance to shift, whereas chromate gives a very large positive error by exhibiting its own ultraviolet absorptivity in this wavelength region.

TABLE I

TOLERANCE OF DIVERSE IONS

Ion	*Added as*	*Permissible amount (p.p.m.)*	*Ion*	*Added as*	*Permissible amount (p.p.m.)*
Al^{3+}	$Al(ClO_4)_3$	500	Sn^{4+}	$SnCl_4$	50
Ca^{2+}	$Ca(ClO_4)_2$	500	Ti^{4+}	$H_2Ti(SO_4)_2$	10
Cd^{2+}	$Cd(ClO_4)_2$	500	Zn^{2+}	$Zn(ClO_4)_2$	500
Co^{2+}	$CoCl_2$	500	AsO_3^{3-}	H_3AsO_3	500
Cr^{3+}	$Cr(ClO_4)_3$	250	AsO_4^{3-}	Na_3AsO_4	10
Cu^{2+}	$Cu(ClO_4)_2$	500	$C_2H_3O_2^-$	$NaC_2H_3O_2$	500
Fe^{2+}	$Fe(ClO_4)_2$	0	Cl^-	NH_4Cl	500
Fe^{3+}	$Fe(ClO_4)_3$	0	ClO_4^-	$KClO_4$	500
K^+	$KClO_4$	500	CrO_4^{2-}	K_2CrO_4	0
Mg^{2+}	$Mg(ClO_4)_2$	500	MoO_4^{2-}	Na_2MoO_4	10
Mn^{2+}	$Mn(ClO_4)_2$	500	NO_3^-	KNO_3	500
NH_4^+	NH_4Cl	500	PO_4^{3-}	Na_3PO_4	0
Na^+	$NaClO_4$	500	SO_4^{2-}	K_2SO_4	500
Ni^{2+}	$Ni(ClO_4)_2$	500	SiO_3^{2-}	Na_2SiO_3	5
Pb^{2+}	$Pb(ClO_4)_2$	500	WO_4^{2-}	Na_2WO_4	0

Precision. An estimate of the precision of this method was ascertained from the results of 11 samples, each containing 2.17 p.p.m. of vanadium. These samples gave a mean absorbance value of 0.468 at 323 nm. The standard deviation was 0.003 absorbance unit, or a relative standard deviation of 0.64%. In a series of determinations, about 15 min is required for each determination.

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Direct complexiметric titration of indium, thallium and thorium with EDTA using iron-N-benzoyl-N-phenylhydroxylamine as indicator

FLASCHKA AND ABDINE[1,2] were the first to use organometallic chelates as indicators in titrations of various metal ions with EDTA. A metal (M) which forms a weakly coloured or colourless chelate with an organic reagent is titrated with EDTA in the presence of a coloured metal (M′) chelate formed from the same reagent, as indicator. The success of this method depends mainly on two factors: (*a*) the stability of the M–EDTA complex should be greater or nearly equal to that of the M′–EDTA complex at the appropriate pH values, and (*b*) the stability of the M′–chelate should be greater than that of the M–chelate. FLASCHKA AND ABDINE used copper–PAN indicator in this type of direct titration for determinations of cadmium, lead, indium, gallium, etc. with EDTA in acid solution. Later, HARA[3] recommended zinc dithizonate as the indicator for the titration of iron and indium.

In the present investigation, it was observed that N-benzoyl-N-phenylhydroxylamine (BPHA) formed a strongly coloured complex with iron(III) and colourless complexes with indium, gallium, thorium, etc. The iron–BPHA complex could thus be used as indicator in the EDTA titration of small amounts of indium, thallium(III) and thorium in the pH interval 1.5–6.0, the optimum range being 2.0–4.0. The end-point, indicated by a change of colour from reddish-violet to colourless, was very sharp. The interference of large amounts of aluminium, mercury, chromium, manganese, zinc, nickel, cerium, uranium, calcium and magnesium were avoided by this direct titration.

Reagents and chemicals

Standard indium solution. Extra pure indium sulphate was dissolved in water containing dilute sulphuric acid and the indium content of the solution was determined by the oxide method.

Standard thallium solution. Pure thallium(III) oxide was dissolved in nitric acid and diluted. The thallium content was determined by precipitating the metal as thallium(I) chromate.

Standard thorium solution. Pure thorium nitrate was dissolved in water containing dilute nitric acid and diluted. The thorium content was determined by weighing as thorium oxalate.

Indicator solution. 2.5 ml of 0.001 *M* iron(III) solution and 5 ml of ethanolic 1% BPHA solution were used for each titration.

All other chemicals used were of A.R. quality.

Procedure

Transfer an aliquot of the standard indium, thallium or thorium solution to a 200-ml conical flask, dilute to 50 ml with distilled water, and adjust the pH of the solution to 2.0–3.0 by addition of 10% sodium acetate solution or dilute hydrochloric acid. Then add indicator solution (2.5 ml of iron solution and 5 ml of BPHA solution). The solution should turn reddish violet; if there is any precipitate, add 10–15 ml of ethanol to dissolve it. Titrate with standard 0.01 *M* EDTA solution to a colourless end-point, deducting 0.2 ml as the indicator correction.

Results and discussion

The limits for the titrimetric determination of indium and thallium were found to be 2.5 mg and 9.2 mg respectively; thorium could be titrated at higher concentrations (35 mg or more). The results are recorded in Table I.

Effect of pH. In order to study the effect of pH, the solutions were adjusted to pH values in the range 1.0–5.0 with sodium acetate solution or hydrochloric acid, and to higher pH values with 10% sodium potassium tartrate solution and ammonium hydroxide (3 *N*). After addition of indicator, the solution was titrated and finally, the pH values of the solutions were again measured. The titration of the specified metal ions could be carried out smoothly between pH 1.5–6.8, the optimum range being 2.0–4.0. Below pH 1.5 the end-point was not sharp and above 6.8 there was no colouration after the addition of the indicator.

Effect of foreign ions. In studying the effect of diverse ions, the solution containing the required metal ion and the interfering ion was adjusted to pH 2.0 by

TABLE I

DETERMINATION OF INDIUM, THALLIUM, THORIUM

Metal taken (mg)		*Volume of 0.012155 M EDTA required (ml)*	*Metal found (mg)*	*Error (mg)*
In	1.08	0.78	1.09	+0.01
In	2.16	1.55	2.16	0.00
In	2.16	1.54	2.15	−0.01
Tl	2.33	0.94	2.33	0.00
Tl	3.35	1.35	3.35	0.00
Tl	4.66	1.85	4.69	+0.03
Tl	9.32	3.70	9.24	−0.08
Th	5.30	1.88	5.30	0.00
Th	10.60	3.75	10.57	−0.03
Th	15.90	5.65	15.84	−0.06
Th	26.50	9.40	26.51	+0.01
Th	31.80	11.30	31.88	+0.08

adding 10% sodium acetate solution or dilute hydrochloric acid, before the titration was done as described above. Titrations of 5.30 mg of thorium(IV), 2.33 mg of thallium(III) or 2.16 mg of indium(III) could be carried out without interference in the presence of aluminium (50 mg), chromium(III) (8 mg), manganese(II) (25 mg), zinc (100 mg), uranium(VI) (12 mg), nickel (7.0 mg), mercury(II) (150 mg), cerium-(III) (45 mg), calcium (100 mg) or magnesium (120 mg). When the titration was carried out in the presence of chromium(III), the colour changed from violet to light green colour at the end-point. In the presence of nickel the pH of the solutions was adjusted to 1.5–1.8, as nickel–EDTA complex was stable at higher pH. Trace amounts of titanium(IV), molybdenum(VI) and vanadium(V) interfered with the titration of indium, thallium and thorium.

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Sodium-*p*-(mercaptoacetamido)benzene sulfonate as an iodometric and iodimetric reagent

Mercaptoacetamides are strong reducing agents and are readily oxidized by mild oxidizing agents such as iodine solution. FEIGL[1] suggested that this property could be used for the titrimetric determination of certain metals with thionalide. UBEDA AND CAPITAN[2] reported the use of *p*-(mercaptoacetamido)acetanilide for the indirect iodometric determination of Ag(I), Cu(II), and Hg(II). However, when this indirect iodometric method was applied to the determination of silver(I), mercury(II), cobalt(II) and nickel(II) using mercaptoacetamidobenzene, definite end-points were not obtained[3]. GUPTA AND SOGANI[4] prepared the sulphonic acid derivative of mercaptoacetamidobenzene which is highly soluble in water and can be titrated directly with iodine. This reagent, sodium-*p*-(mercaptoacetamido)benzenesulfonate (MABS), was used for the iodometric determination of copper(II)[5]. Further investigation showed that it is very suitable as a reagent for the iodometric and iodimetric determination of those oxidizing and reducing agents which are commonly determined using sodium thiosulfate as titrant.

The standard (oxidation) potential of the reaction $2\ RSH \rightleftarrows RS\text{–}SR + 2\ H^+ + 2\ e^-$ (RSH represents the reagent (MABS) molecule) has been determined to be +0.63 V. The corresponding value for $2\ S_2O_3^{2-} \rightleftarrows S_4O_6^{2-} + 2$ e reaction is −0.170 V[6]. The net change in free energy of reagent–iodine reaction is, therefore, much larger as compared to thiosulfate–iodine reaction. Thus, the former reaction is more favorable.

The reagent–iodine reaction is as follows:

$$2\ RSH + I_2 \rightleftarrows RS\text{–}SR + 2\ H^+ + 2\ I^-$$

The equivalent weight of the reagent is equal to its molecular weight.

Glacial acetic acid can be used in place of hydrochloric acid for liberating iodine by the action of permanganate or dichromate on potassium iodide.

A method has been developed for the determination of iron(II) by oxidizing the latter with a known excess of standard permanganate, masking the iron(III) produced with sodium fluoride, and determining the excess of permanganate iodometrically. The procedure has been extended to the determination of iron(II) and iron(III) in a mixture and also to the determination of peroxydisulfate. Determinations were simultaneously carried out with sodium thiosulfate and the results have been included in Table I.

Experimental

Preparation of solutions. Prepare the reagent as described by GUPTA AND SOGANI[4]. Dissolve 7.17 g of it (MABS) in 250 ml of oxygen-free water, standardize it with iodine and dilute suitably to obtain a 0.05 *N* solution. Fresh solutions were used. Prepare a 0.05 *N* sodium thiosulfate solution and store in a colored bottle[7]. The following solutions were standardized using the primary standard or reagent indicated: potassium permanganate (sodium oxalate A.R.); dichromate (iron wire); iodate, bromate, chloramine-T, cerium(IV) sulfate (arsenious oxide); peroxydisulfate, Mohr's salt, tellurite (permanganate), ferrocyanide (chloramine-T), ferric alum (dichromate). Each of these solutions was suitably diluted to give 0.05 *N* solution.

Solutions of potassium chlorate were prepared directly from A.R. grade

TABLE I

SUMMARY OF APPLICATIONS AND COMPARATIVE STUDY OF REAGENT WITH SODIUM THIOSULFATE

Desired constituent	*Conditions*	*Average vol. (ml) of*		*Relative standard deviation (reagent) (%)*	*Reference to p. no. in ref. 8*
		0.05 N reagent solution	*0.05 N sodium thiosulfate solution*		
Arsenite	Neutral soln.[a]	20.00	20.00	0.25	p. 356
Bleaching powder	HAc	16.35	16.35	0.56	p. 364
Bromate	2 ml 4 *N* HCl	19.95	20.00	0.35	p. 350
Cerium(IV)	Excess H_2SO_4	20.05	20.10	0.65	p. 354
Chloramine-T	4 ml HAc	20.00	20.05	0.25	p. 392[b]
Chlorate	40 ml HCl	20.05	20.15	0.75	p. 362[c]
Dichromate	HAc (4 ml)	20.05	20.05	0.25	p. 351
Ferricyanide	2 ml 4 *N* HCl and 1.0 g $ZnSO_4 \cdot 7H_2O$	19.25	19.35	0.50	p. 372
Hydrogen peroxide	50 ml 2 *N* H_2SO_4 Molybdate catalyst	14.20	14.20	0.65	p. 363
Iodate	3 ml *N* H_2SO_4	20.00	20.00	0.25	p. 349
Iron(II)	Procedure II	20.05	20.05	0.25	
Iron(III)	Cu_2I_2 catalyst	20.00	20.05	0.50	p. 372
Iron(II) and (III)					
Iron(II)	Procedure II	20.05	20.00	0.35	
Iron(III)	Cu_2I_2 catalyst	19.95	19.95	0.65	p. 372
Nitrite	Excess chloramine-T detd.	20.45	20.50	0.56	p. 393
Permanganate	HAc (2 ml)	20.00	20.00	0.25	p. 353[b]
Peroxydisulfate	Excess Fe(II) detd.	19.95	19.90	0.50	p. 299[d]
Sulfide	Excess I_2 detd.	28.30	28.35	0.50	p. 371
Sulfite	Excess I_2 detd.	20.25	20.25	0.40	p. 370
Tellurite	Excess CrO_4^{2-} detd.	19.95	20.00	0.50	p. 324

[a] $CaCO_3$ used for $NaHCO_3$.
[b] Acetic acid used for HCl.
[c] Diluted to 300 ml before titration. Procedure B.
[d] Procedure A.

reagent. Solutions of bleaching powder, hydrogen peroxide, potassium ferricyanide, nitrite, sulfite, and hydrogen sulfide were used to obtain the comparative results. The 25% potassium iodide, 100% ammonium thiocyanate and 1% starch solution were prepared from reagent-grade chemicals.

The 0.1 *N* iodine solution was prepared by method A of VOGEL[8]. A Sargent potentiometer (E.H. Sargent, Chicago) was used for all potential measurements. Platinum and saturated calomel electrodes were used as indicator and reference electrodes, respectively. The potentiometer was standardized with a standard saturated cadmium cell ($E = 1.0186$ V) provided in the instrument by the manufacturers.

Procedure for estimation of formal (reduction) potential ($E°$) for the reaction $RS\text{–}SR + 2\,H^+ + 2\,e \rightleftarrows 2\,RSH$

Pipet 20 ml of iodine solution into a 150-ml beaker and dilute to *ca.* 40 ml with oxygen-free water. Standardize the potentiometer *vs.* the standard cell. Dip the reference and the indicator electrodes in the solution and stir with a magnetic stirrer. Gradually add from a 10-ml microburet the 0.1 *N* reagent solution and read the voltage. Determine the pH of the solution at the end of the titration. The pH was 1.6.

Figure 1 shows the potentiometric titration graph. First and second derivative graphs were also plotted and from the latter, the volume of the reagent required to reach the equivalence point was found to be 19.976 ml. From Fig. 1, the value of equivalence potential corresponding to this volume was found to be 0.245 V. From these data, the formal reduction potential for this reagent (MABS) was calculated to be −0.63 V.

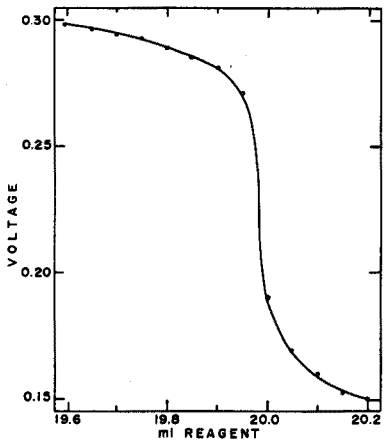

Fig. 1. Potentiometric titration graph of iodine with MABS.

Iodometric and iodimetric determinations

Procedure I. Take 20 ml of solution of the species under determination and follow the procedure as described by VOGEL[8], except for the determination of iron(II). The important conditions for each determination are mentioned in Table I. Carry out all determinations in an atmosphere of carbon dioxide generated in the titration flask by adding a little A.R. sodium carbonate to the acidic solution. Use starch solution as indicator and add 1 ml of 10% ammonium thiocyanate solution near the end-point in all determinations except in the case of iron(II) and iron(III). Titrate with standard MABS solution.

Procedure II (determination of iron(II)). Add exactly 20 ml of 0.05 *N* iron(II) solution to a 250-ml iodine flask, followed by *ca.* 20 ml of 8 *N* sulfuric acid and exactly 40 ml of 0.05 *N* permanganate solution. Add 5 ml of 5% sodium fluoride solution to mask iron(III) produced in the reaction. Add about 0.1 g of sodium carbonate. When the effervescence ceases, add 10 ml of 25% potassium iodide solution. Stopper the flask, mix the contents and keep in the dark for 10 min. Titrate the liberated iodine using starch as indicator.

Discussion

Table I shows that MABS gives almost the same results as sodium thiosulfate with various oxidizing and reducing agents (19 in all) which can be determined iodometrically and iodimetrically except in the cases of chlorate and cerium(IV). In these two cases, sodium thiosulfate gives slightly higher results. This may be due to the slight decomposition of thiosulfate at high acid concentrations. The reagent is quite stable in highly acidic solution and the results with it are, therefore, more acceptable.

Again, the reagent is stable in the solid state and its fresh solutions can be used as a primary standard, whereas sodium thiosulfate tends to dehydrate.

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Rapid extraction of gold with mesityl oxide

Mesityl oxide [$(CH_3)_2C=CH.COCH_3$] can be utilized for the rapid solvent extraction of gold(III) at micro levels[1], extraction being quantitative from 5 *M* hydrochloric acid. After the organic phase has been stripped with 1 *M* ammonium hydroxide, the gold can be determined colorimetrically in the aqueous phase by reduction with tin(II) chloride[2].

Several oxygen-containing solvents have been used for the solvent extraction of gold; ethyl acetate[3] allows extraction from 10% hydrochloric acid, and methyl isobutyl ketone[4] has also been used. The bromo-aurate complex can be extracted with butyl acetate[5], dichloromethane[6] or trioctyl phosphine oxide in chloroform[7]. The gold azide complex[8] can be extracted with butanol and measured colorimetrically at 330 nm but the color is unstable. The complex with ethyl violet[9] is extractable with benzene and measurable at 550 nm. The gold–thiocyanate complex with triphenylisopropyl phosphonium salt can be extracted with benzene[10] and the gold–tetraphenyl arsonium chloride complex with chloroform[11]. 2-Thenoyltrifluoroacetone allows the solvent extraction and simultaneous spectrophotometric determination of gold at tracer concentrations[12].

These existing methods for the solvent extraction and determination of gold either involve too many steps or are not applicable at micro levels. So far no systematic studies have been made of the solvent extraction of gold with mesityl oxide. In the present communication, the effects of acidity, salting-out agents, other ions, etc., on the system are described, as well as the optimum conditions for the determination of gold by this method.

TABLE I

DISTRIBUTION RATIO AS THE FUNCTION OF ACIDITY

(Gold(III) = 220.8 μg)

Concn. of mesityl oxide (%)	*Initial HCl (M)*	*Percentage extraction*	*Distribution ratio*
19 (1.65 *M*)	2	47.3	2.2
	3	52.6	2.7
	4	68.4	5.4
	5	71.5	6.2
50 (4.35 *M*)	2	57.8	3.4
	3	78.9	9.3
	4	84.2	13.3
	5	86.8	16.4
75 (6.52 *M*)	2	71.5	6.2
	3	84.2	13.3
	4	89.4	21.0
	5	97.3	90.0
100 (8.70 *M*)	0.5	47.3	2.2
	1.0	57.8	3.4
	2.0	76.3	8.6
	3.0	89.4	21.0
	4.0	94.7	44.6
	4.5–5.5	100.0	>100

TABLE II

EFFECT OF LITHIUM CHLORIDE AND MAGNESIUM CHLORIDE AS SALTING-OUT AGENT

Salting-out agent	*HCl (M)*	*Percentage extraction*	*Distribution ratio*
LiCl			
2 *M*	1	68.4	5.4
	2	78.9	9.3
	3	92.1	29.1
	4	97.3	90.0
4 *M*	1	81.5	11.0
	2	84.2	13.3
	3–4	100.0	>100
6 *M*	1	84.2	13.3
	2	86.8	16.4
	3	94.7	44.6
	4	89.4	21.0
$MgCl_2$			
1 *M*	1	68.4	5.4
	2	78.9	9.3
	3	92.1	29.1
	4	100.0	>100
2 *M*	1	76.3	8.6
	2	92.1	29.1
	3–4	100.0	>100
3 *M*	1	86.8	16.4
	2	89.4	21.0
	3	100.0	>100

Reagents

The stock solution of gold was prepared by dissolving 1 g of gold chloride (Johnson, Matthey and Co., London) in 250 ml of water containing 1% hydrochloric acid. The solution was standardized gravimetrically and then diluted to give a concentration of 110.4 μg Au/ml. Mesityl oxide (Fluka AG; b.p. 125–132°) was used.

Procedure

A 2-ml aliquot containing 220.8 μg of gold was mixed with an appropriate volume of hydrochloric acid, diluted to 25 ml and transferred to a 250-ml separatory funnel. Salting-out agents or foreign ions were added before the dilution step. The solution was then shaken for 10 min with 10 ml of 100% mesityl oxide and the layers were allowed to settle. The aqueous layer was carefully withdrawn and the organic phase was stripped by shaking consecutively with 10-ml and 5-ml portions of 1 *M* ammonium hydroxide for 10 min. The aqueous extracts were combined and the gold was determined colorimetrically by the tin(II) chloride method[2].

Results and discussion

Effect of acidity and mesityl oxide concentration. The concentration of hydrochloric acid was varied from 0.5 to 5.5 *M*, and that of mesityl oxide from 19 to 100% (1.65–8.70 *M*) by diluting it with methyl isobutyl ketone. The distribution ratio was calculated as usual. The results (Table I) showed that pure mesityl oxide was necessary for quantitative extraction. The optimum concentration of hydrochloric acid was 4.5–5.5 *M*.

Effect of salting-out agent. The addition of lithium or magnesium chloride to the aqueous phase showed no appreciable effect on the extraction of gold from varying concentration of hydrochloric acid. At low acidity, the distribution ratio increased because of the increase in the chloride concentration, and at high acidity the distribution ratio was further increased by the salting-out agent because of the change in the dielectric constant of the aqueous phase (Table II). Aluminium chloride could not

TABLE III

EFFECT OF FOREIGN IONS

(Gold(III) = 220.8 μg)

Foreign ions	*Added as*	*Tolerance limit (μg)*	*Foreign ions*	*Added as*	*Tolerance limit (μg)*
Tl^{+}	$TlNO_3$	5000	Ce^{3+}	$Ce_2(SO_4)_3$	5000
Pb^{2+}	$Pb(NO_3)_2 \cdot 2H_2O$	5000	Be^{2+}	$Be(NO_3)_2$	2500
Cd^{2+}	$CdCl_2 \cdot 5H_2O$	200	Ba^{2+}	$BaCl_2 \cdot 2H_2O$	5000
Co^{2+}	$CoCl_2 \cdot 6H_2O$	2000	CH_3COO^{-}	CH_3COONH_4	2000
Sb^{3+}	$SbCl_3 \cdot 3H_2O$	None	Citrate	Citric acid	1000
Bi^{3+}	$Bi(NO_3)_3 \cdot 5H_2O$	2000	Tartrate	Tartaric acid	2000
Pt^{4+}	$H_2PtCl_6 \cdot 6H_2O$	1000	Malonate	Malonic acid	None
OsO_4^{3+}	Na_3OsO_4	130	Ascorbate	Ascorbic acid	2000
Cr^{3+}	$Cr_2(SO_4)_3 \cdot 18H_2O$	None	Oxalate	$H_2C_2O_4 \cdot 2H_2O$	1000
Mn^{2+}	$MnCl_2 \cdot 6H_2O$	None	$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	None
Ni^{2+}	$NiSO_4 \cdot 7H_2O$	200	HPO_4^{2-}	Na_2HPO_4	200
Th^{4+}	$Th(NO_3)_4 \cdot 4H_2O$	1000	SO_4^{2-}	$Na_2SO_4 \cdot 10H_2O$	10000
Zr^{4+}	$Zr(NO_3)_4$	1000	$EDTA^{4-}$	Disodium salt	2000
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	500			

be used as the salting-out agent as it was precipitated as the hydroxide during the stripping.

Time of extraction. The solution must be shaken for at least 10 min to obtain 100% extraction. Shaking for 5 min gave 73% extraction whereas shaking for 8 min gave 87% extraction when the hydrochloric acid concentration was 5 *M*.

Interfering ions. The results in Table III show the effect of various ions when the extraction was made from 5 *M* hydrochloric acid medium. The tolerance limit was set at the amount required to cause 2% error in the gold recovery. Gold could be extracted satisfactorily in the presence of large amounts (1:20) of thallium(I), lead(II), cerium(III), barium and sulphate. Cobalt(II), bismuth(III), beryllium, acetate, tartrate, ascorbic acid and EDTA could be tolerated at ratios of 1:10, but mercury, antimony, chromium, manganese, malonate and thiosulphate interfered seriously.

From 12 experiments the average recovery of gold was $99.5 \pm 0.5\%$. Each determination took a total of 40 min. The method has the advantage of allowing separation and determination of gold in a minimal time.

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Determination of sodium with *m*-chlorophenyl-α-methoxyacetic acid*

A procedure was described some years ago for determining sodium by precipitating it as the sodium acid salt of α-methoxyphenylacetic acid[1]. Since then the following four substituted α-methoxyphenylacetic acids have been found which form sodium acid salts much less soluble than the one formed from the parent acid[2]: *m*-chlorophenyl-α-methoxyacetic acid; *p*-chlorophenyl-α-methoxyacetic acid, 3,4-dichlorophenyl-α-methoxyacetic acid, and α-methoxy(2-naphthalene)acetic acid. Accordingly, it seemed desirable to study these as precipitants for sodium.

The determination of sodium with any of these acids involves the precipitation of the sodium acid salt of the acid, and the separation of this from the excess reagent by filtration and washing with acetone, in which the precipitate is insoluble. The sodium acid salt is soluble in boiling water and can be titrated with standard base.

The advantages of using the α-methoxyphenylacetic acids over the traditional uranyl acetate reagents include less interference from potassium, no interference from small amounts of lithium, and the use of a simple titrimetric procedure in the final step[1]. The advantage of the *m*-chlorophenyl-α-methoxyacetic acid, recommended here, over the previously described α-methoxyphenylacetic acid is that the solubility of the sodium hydrogen di(*m*-chlorophenyl-α-methoxyacetate) is less than that of sodium hydrogen di(α-methoxyphenylacetate) by a factor of ten under the analytical conditions employed; accordingly, the correction factor previously used may be reduced by a factor of ten or omitted.

Preliminary investigations

Preliminary studies were carried out on the 4 acids to see which was best as a precipitant for sodium. Solubility data alone are insufficient criteria because the sodium acid salt precipitates relatively slowly; also required are favorable kinetics in the rate of precipitation of the sodium acid salt, especially in the presence of other ions and with low concentrations of sodium.

The preparation of the reagents was patterned after that of the previously described α-methoxyphenylacetic acid reagent. Typically, 8 mmoles of the organic acid was dissolved in a little 100% ethanol and partially neutralized with 3 mmoles of methanolic 1 *N* tetramethylammonium hydroxide. The solution was then diluted to 10 ml with 100% ethanol, allowed to stand overnight near 0°, and filtered to remove any sodium acid salt that had formed.

Tests were carried out by adding 3 volumes of reagent to dilute sodium chloride test solutions. The *m*-chlorophenyl-α-methoxyacetic acid reagent would detect 0.25 mg of sodium ion per ml within 18 min at 0°. Under the same conditions the *p*-chlorophenyl-α-methoxyacetic acid reagent required an hour; the reagents prepared from the other two acids were less sensitive.

Consideration was given to replacement of the ethanol solvent and the tetramethylammonium hydroxide base with less expensive substitutes, but none were found which did not adversely affect the performance of the reagent. The solvents considered included methanol, isopropyl alcohol, and dimethyl sulfoxide. Trimethylamine was studied as a replacement for the tetramethylammonium hydroxide, and in the qualitative tests the reagents prepared with it were only slightly inferior to the

* Abstracted from the B.S. thesis of J.S.F., University of Maryland, 1966.

reagent prepared with tetramethylammonium hydroxide. However, in the quantitative work, it was found that the sodium was precipitated less completely with the reagents prepared using trimethylamine. A series of reagents was prepared to determine the optimum ratio of free acid to tetramethylammonium salt in the reagent, and the 5:3 ratio proved to be best.

Experimental

Preparation of m-*chlorophenyl-α-methoxyacetic acid.* The synthesis of this acid involves two steps. Benzaldehyde is chlorinated to *m*-chlorobenzaldehyde[3], which then reacts with bromoform and methanolic potassium hydroxide to form potassium *m*-chlorophenyl-α-methoxyacetate; this is converted to the insoluble sodium acid salt and isolated as such[2]. The salt is dissolved in sodium hydroxide solution and the solution is acidified with hydrochloric acid. The insoluble *m*-chloro-α-methoxyphenylacetic acid is extracted with chloroform, and obtained in a sufficiently pure form by evaporation of the solvent.

Sodium reagent. Dissolve 16 g (0.08 mole) of *m*-chlorophenyl-α-methoxyacetic acid and 0.03 mole (12 ml of 2.5 *N*) of methanolic tetramethylammonium hydroxide (Southwestern Analytical Chemicals, Austin, Texas) in sufficient 100% ethanol to make 100 ml. Allow to stand at room temperature for several hours and then at 0° overnight. Sufficient sodium is probably present to saturate the reagent and cause a precipitate to form. Filter the cold solution, which is ready for use after warming to room temperature.

Glassware. Borosilicate glass beakers, flasks, and filter funnels were used. There was no indication that the glassware gave up any measurable amount of sodium to the various solutions.

Analytical procedure. The sodium salt to be analyzed should be present as the carbonate, halide, or nitrate, dissolved in water to give a solution containing *ca.* 15 mg of sodium/ml.

Weigh the sample, containing *ca.* 2 meq of sodium, into a 50-ml Erlenmeyer flask and add 3 ml of water by pipet. If the sample contains carbonate, add one drop of methyl orange indicator followed by 6 *N* hydrochloric or nitric acid dropwise to the end-point. Add 13 ml (*ca.* 65% more than the theoretical requirement) of reagent slowly from a buret while swirling the flask. After all the reagent has been added, swirl the flask for another minute, capped with a 10-ml beaker, and allow to stand for about 30 min at room temperature. The sodium acid salt precipitates and causes the contents of the flask to set to a mushy solid. Place the flask in a cold room near 0° overnight along with the filter and acetone that are going to be used.

Filter the cold reaction mixture on a 15-ml coarse sintered glass funnel held in a micro belljar; pour as much as possible of the mixture into the funnel while suction is applied. Tamp down the precipitate with a stirring rod flattened at one end, and then wash five times with 5-ml portions of cold acetone, using a major part of each portion to rinse the Erlenmeyer flask first. Pour the washings into the funnel with the suction off, and use the remaining part of the 5-ml acetone to wash off the outside of the neck of the flask into the funnel. Stir the precipitate gently and then drain under suction. Repeat the wash process five times in all. Remove the funnel from the belljar, and wash the outside with distilled water.

Dissolve any precipitate remaining in the 50-ml Erlenmeyer flask with boiling

distilled water and transfer to the funnel. Stir the precipitate and allow the solution to drip by gravity into a 250-ml Erlenmeyer flask. Add further boiling water until all the precipitate has dissolved. After the filtrate has cooled, titrate with 0.05 *N* sodium hydroxide in the presence of phenolphthalein indicator. If any of the sodium acid salt should crystallize, reheat the solution. The conversion factor for meq of base to mg of sodium is 22.99.

Results

Sodium salts, with and without other salts present, were analyzed to establish the accuracy of the method. With samples containing *ca.* 45 mg of sodium, either as the chloride or nitrate, the mean value obtained averaged 0.15 mg less than theory and the standard deviation was 0.08 mg. The 0.15-mg average difference between theoretical and found values compares very favorably with the corresponding 1.5 mg difference observed with the reagent based on the parent α-methoxyphenylacetic acid. Ammonium, potassium, and magnesium salts have no effect, even when present in large amounts.

TABLE I

DETERMINATION OF SODIUM IN MIXTURES

Comp. of mixture (mg) dissolved in 3 ml of H_2O	*Theoretical sodium (mg)*	*Found sodium (uncorrected) (mg)*
114.8 NaCl	45.15	45.02
107.1 Na_2CO_3 + HNO_3	46.45	46.23
107.7 Na_2CO_3 + HCl + 17 LiCl	44.12	44.41
104.8 Na_2CO_3 + HCl + 65 LiCl	45.04	45.72
117.0 NaCl + 21 KCl	46.02	46.00
117.5 NaCl + 43 KCl	46.20	46.06
118.0 NaCl + 614 KCl	46.41	46.31
106.4 Na_2CO_3 + HCl + 27 RbCl	46.05	46.03
106.1 Na_2CO_3 + HCl + 15 CsCl	46.03	45.91
108.3 Na_2CO_3 + HCl + 25 NH_4Cl	46.98	46.84
102.4 Na_2CO_3 + HCl + 59 $MgCl_2$	44.42	44.19
105.5 Na_2CO_3 + HCl + 94 $MgCl_2$	45.77	45.88
113.2 NaCl + 15 $CaCl_2$	44.50	45.13
105.8 Na_2CO_3 + HCl + 16 $BaCl_2$	45.90	46.16
103.4 Na_2CO_3 + HCl + 56 $BaCl_2$	44.80	45.85
88.1 NaCl + 11.3 Na_2CO_3 + H_2SO_4	39.55	35.67

Interferences of lithium, barium and sulfate. The common alkali and alkaline earth cations were examined to see if their presence would interfere with the sodium determination (Table I). Calcium, barium and lithium caused the sodium results to be high by 0–4% depending on the amount of interfering ion present. None of these elements forms a precipitate with the reagent in the absence of sodium, but each appears to be capable of replacing some of the sodium ions in a growing crystal lattice of sodium hydrogen di(*m*-chlorophenyl-α-methoxyacetate), so that more than the theoretical amount of the acid salt is precipitated. If the amount of the barium or lithium chloride is around 15% of the amount of the sodium chloride, the observed result for

the sodium analysis is about 0.5% high; with calcium, the result is about 1.4% high. If 7 times this amount of barium or lithium is present, the result is high by 4%.

Sulfate ions cause low results; thus analysis of sodium sulfate gives results 12–17% less than the theoretical amount of sodium. The accuracy of all wet analytical methods for sodium is less in the presence of sulfate, largely because of the insolubility of most sulfates in non-aqueous solvents. The addition of a lead acetate solution to precipitate the sulfate before adding the sodium reagent was found to reduce the sodium error to less than 5%. However, the results were somewhat variable and it would probably be better to eliminate the sulfate from the sample before attempting to carry out an accurate sodium analysis.

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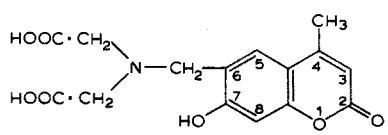
A structural study of the methyleneiminodiacetic acid derivatives of some 7-hydroxycoumarins

Interest in the metallofluorescent properties of the methyleneiminodiacetic acid derivatives of hydroxycoumarins has led us to a study of a number of such compounds as possible analytical reagents for complexiметry and fluorimetry. EGGERS[1] first described the synthesis of a methyleneiminodiacetic acid derivative of 4-methylumbelliferone to which he assigned structure (I). He gave no practical details for the preparation and purification of this compound other than the statement that the substance was obtained by condensation of 4-methylumbelliferone with iminodiacetic acid and

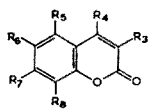


(I)

paraformaldehyde in a water–acetic acid medium; no evidence was provided to support the substitution of the methyleneiminodiacetic acid group in the 6-position of the coumarin system. WILKINS[2] independently described a compound obtained by

TABLE I

N.M.R. PARAMETERS OF SOME 7-HYDROXYCOUMARIN DERIVATIVES

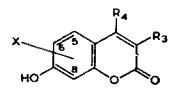


Substituents						*Chemical shifts (τ)*						*Coupling constants (Hz)*			
R_3	R_4	R_5	R_6	R_7	R_8	*3*	*4*	*5*	*6*	*7*	*8*	J_{34}	J_{56}	J_{58}	J_{68}
H	H	H	H	OH	H	3.75	2.09	2.46	3.15	—	3.24	9.4	9.0	0.0	2.5
H	Me	H	H	OH	H	3.90	7.64	2.46	3.12	—	3.28	1.2[a]	8.7	0.5	2.4
H	H	Me	H	OH	H	3.82	1.98	7.60	3.45	—	3.37	9.9	0.0	0.0	2.3
H	H	H	H	OH	Me	3.80	2.08	2.62	3.11	—	7.80	9.5	8.5	0.0	0.0
H	H	H	OH	OH	H	3.84	2.14	3.00	—	—	3.24	9.45	—	0.0	—
H	CH_3	H	H	OH	OH	3.86	7.62	2.91	3.17	—	—	1.1[a]	8.75	—	—
H	CH_3	OH	H	OH	H	4.14	7.47	—	3.75	—	3.65	1.2	—	—	2.5
H	CH_3	H	OH	OH	H	3.88	7.65	2.93	—	—	3.20	1.1[a]	—	0.0	—
H	CH_3	H	OMe	OMe	H	3.81	7.61	2.90	6.12[b]	6.13[b]	3.00	1.1[a]	—	—	—
CO_2H	H	H	H	OH	H	—	1.29	2.20	3.11	—	3.21	—	8.6	0.0	1.8
H	CO_2H	H	H	OH	H	3.42	—	1.98	3.13	—	3.22	—	9.3	0.0	2.5
H	CH_2CO_2H	H	H	OH	H	3.72	6.12[c]	2.42	3.17	—	3.23	—	9.0	0.0	2.7
CH_3COO·	H	H	H	OH	H	7.44[d]	1.45	2.24	3.17	—	3.25	—	8.5	0.0	2.3
H	Ph	H	H	OH	Me	3.89	2.46	2.86	3.09	—	7.76	—	9.0	—	—

[a] HC=C·Me coupling.
[b] Shift of OMe group.
[c] Shift of $-CH_2-$ group.
[d] Shift of acetyl group.

TABLE II

N.M.R. PARAMETERS OF "COMPLEXAN" DERIVATIVES OF 7-HYDROXYCOUMARINS



X = $-CH_2N(CH_2CO_2H)_2$

	Substituents					*Chemical shifts (τ)*							*Coupling constants (Hz)*	
											Substituent X			
	R_3	R_4	R_5	R_6	R_8	*3*	*4*	*5*	*6*	*8*	$-CH_2-N\langle$	$\rangle N-CH_2\cdot CO_2H$	J_{34}	J_{56}
I	H	H	H	H	X	3.82	2.09	2.52	3.22	—	5.89	6.52	9.8	8.55
II	H	Me	H	H	X	3.86	7.63	2.41	3.17	—	5.89	6.54	—	9.6
III	H	CO_2H	H	H	X	3.58	—	2.07	3.14	—	5.88	6.50	—	8.3
IV	$CH_3CO\cdot O$	H	H	H	X	7.47[a]	1.41	2.25	3.15	—	5.88	6.49	—	9.0
V	H	Me	H	OH	X	3.88	7.65	2.97	—	—	5.84	6.46	*ca.* 1	—
VI	H	CO_2Et	H	H	X	3.41	—[b]	2.15	3.13	—	5.87	6.48	—	8.7
VII	H	H	H	X	Me	3.79	2.09	2.73	—	7.82	6.08	6.54	9.0	—
VIII	H	Me	H	X	OH	3.90	7.64	3.02	—	—	6.10	6.63	*ca.* 1	—
IX	H	H	Me	H	X	3.84	1.95	7.50	3.36	—	6.02	6.67	10.0	—

[a] Shift of acetyl group.

[b] CO_2Et shifts: $-OCH_2-$ 5.58τ; $-C\cdot CH_3$ 8.63τ; J_{HH} = 7.0 Hz.

a similar condensation to which he gave the trivial name "Calcein blue". In neither case was the reported new substance characterised in any conventional way and only its fluorescence characteristics were examined in any detail. DIEHL[3] recognised these deficiencies in the earlier work on Calcein blue and reported the preparation of a pure Calcein blue containing one methyleneiminodiacetic acid group occupying the 8-position of the coumarin ring. No details of how this configuration was arrived at were given although reference was made to a M.S. Thesis[4] on the preparation and properties of Calcein blue.

Similar problems have been encountered in the present work, not only in characterising the "complexan" derived from 4-methyl-7-hydroxycoumarin, but also those from a number of other hydroxycoumarins. In general, these compounds are obtained by reacting the hydroxycoumarin dissolved in glacial acetic acid with an aqueous 40% solution of formaldehyde and iminodiacetic acid. An examination of these derivatives and their parent coumarins by the techniques of nuclear magnetic resonance have enabled definite configurations to be assigned to these new compounds which may have a bearing on the interpretation of their analytical reactions.

Nuclear magnetic resonance studies

The chemical shifts and coupling constants, obtained from the analysis of the ^1H spectra*, of a number of 7-hydroxycoumarin derivatives are shown in Table I. The chemical shifts of the ring protons fall into characteristic ranges, and J_{34} and J_{56} are both of the magnitude expected[5] for *ortho* HH coupling in aromatic systems. Similarly, the *meta* J_{68} is approximately 2 Hz, while the *para* J_{58} is very small or zero.

The use of the chemical shift ranges and coupling constants permits unambiguous assignment of the methyleneiminodiacetic acid substituent to position 8 or, if position 8 is already substituted, to position 6 (Table II). This is especially evident in compound I as the ^1H spectrum shows two AB spectra, with J_{HH} values of 9.8 and 8.55 Hz, which can only arise from H_3H_4 and H_5H_6. In compounds II, III, IV and VI, which have a substituent in position 3 or 4, the presence of an AB spectrum with J_{AB} of 8–9 Hz must also arise from H_5H_6. The only case at all open to doubt is that of compound IX, since the shift of the single isolated proton of the carbocyclic ring falls into the range of either H_6 or H_8. In view of the consistency of the other results, the signal has been assigned to H_6 and the substituent group X to position 8. The preparation, purification and metallofluorescent reactions of these new substances will be described at a later date.

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1 J. H. EGGERS, *Talanta*, 4 (1960) 38.
2 D. H. WILKINS, *Talanta*, 4 (1960) 182.
3 H. DIEHL, *Anal. Chem.* 39 (1967) 30A.
4 G. M. HUITINK, *M.S. Thesis*, Iowa State University, Ames, Iowa, 1965.
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(Received May 1st, 1968)

* All the spectra were recorded in dimethylsulphoxide - D_6 solution on a Perkin-Elmer R10 Spectrometer at 60 MHz.

Thermogravimetric analysis and gas chromatography of rare earth chelates of trifluoroacetylpivaloylmethane

Eleven chelates of the ligand trifluoroacetylpivaloylmethane (1,1,1-trifluoro-5,5-dimethylhexan-2,4-dione; H(TAPM)) with tripositive rare earth metal ions have been synthesized by the method reported for 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-octan-4,6-dione chelates by SIEVERS *et al.*[1]. Trifluoroacetylpivaloylmethane was obtained by Claisen condensation[2] of ethyl trifluoroacetate and pinacolone. It was found that these new chelates are also useful for the gas chromatography of rare earth metals.

Thermogravimetric analysis[1]

A Shimadzu thermobalance was used; a nitrogen atmosphere was maintained over the sample, the nitrogen flow rate being held constant at 100 ml/min. The sample heating rate was 2°/min, and the sample sizes were 100 mg.

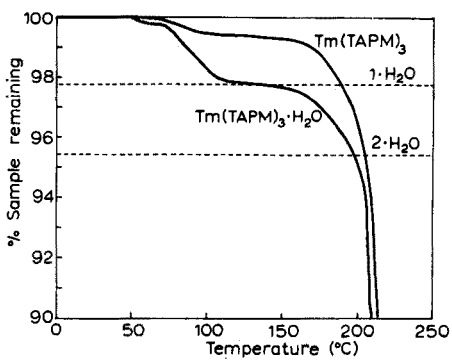


Fig. 1. Thermogravimetric curves of $Tm(TAPM)_3$ and $Tm(TAPM)_3 \cdot H_2O$.

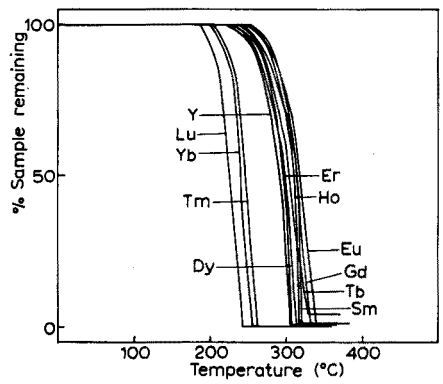


Fig. 2. Thermogravimetric curves of rare earth TAPM chelates.

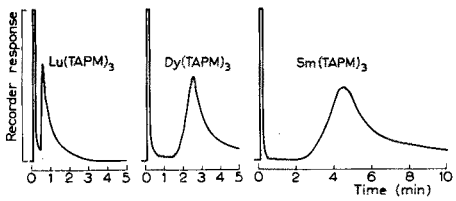
In Fig. 1 the thermogravimetric curves for $Tm(TAPM)_3$ and $Tm(TAPM)_3 \cdot H_2O$ are shown. It can be seen that the thermogram for the hydrated thulium chelate showed a 2.3% weight loss at about 100°, which corresponds to the volatilization of the water present. On the other hand, the thulium chelate which had been dried *in vacuo* over P_2O_5 showed very little weight loss at 100° and had no broad peak at 3350 cm^{-1} in the infrared spectrum. All the complexes obtained were monohydrates which could be easily dehydrated *in vacuo* over P_2O_5. The thermogravimetric curves obtained for the anhydrous TAPM chelates are shown in Fig. 2. It was found that the TAPM chelates volatilized at quite low temperatures without decomposition and could be chromatographed in the vapor phase.

Gas chromatography[3]

The gas chromatographic data were obtained on a Shimadzu Model GC-2C chromatograph. The stainless-steel column (3 mm i.d. × 150 cm long) was packed with 1.5% (w/w) Silicone Gum SE-30 on Chromosorb W (60–80 mesh). The carrier gas was helium at a flow rate of 127 ml/min. The column was maintained at 200° and the injection port at 300°. One μl of a 5% solution of the anhydrous TAPM chelates in benzene (which had been dried over calcium hydride) was injected with a micro-

syringe. For identification purposes, the eluted substances were trapped at the exit port and were shown to be identical with the original chelates by infrared spectroscopy.

Typical examples of the chromatograms obtained are shown in Fig. 3. The retention times, melting points and colors of the anhydrous TAPM chelates are shown in Table I.



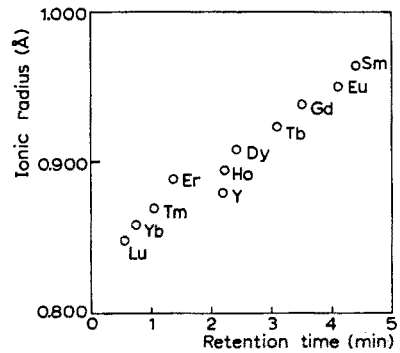


Fig. 3. Gas chromatograms of $Lu(TAPM)_3$, $Dy(TAPM)_3$ and $Sm(TAPM)_3$.

Fig. 4. Gas chromatographic retention times as a function of ionic radius.

TABLE I

PROPERTIES AND RETENTION TIMES OF ANHYDROUS TAPM CHELATES

Metal ion	*M.p. (°)*	*Color*	*Retention time (min)*
Sm(III)	115–119	White	4.40
Eu(III)	154–162	White	4.10
Gd(III)	115–119	White	3.50
Tb(III)	169–172	White	3.10
Dy(III)	147–152	White	2.42
Ho(III)	117–120	Beige	2.23
Er(III)	166–169	Pink	1.35
Yb(III)	162–164	White	0.75
Tm(III)	163–165	White	1.03
Lu(III)	164–166	White	0.56
Y(III)	181–183	White	2.20

A plot of the retention time *vs.* the ionic radius of the corresponding six-coordinate, tripositive metal ion (Fig. 4) showed that the retention time tends to decrease with decreasing ionic radius, in a similar fashion to that reported for other ligands of this type[1,3].

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1 C. S. SPRINGER, JR., D. W. MEEK AND R. E. SIEVERS, *Inorg. Chem.*, 6 (1967) 1105.
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BOOK REVIEWS

J. RAMÍREZ–MUÑOZ, *Atomic-Absorption Spectroscopy and Analysis by Atomic-Absorption Flame Photometry*, Elsevier Publishing Co., Amsterdam–London–New York, 1968, xii+493 pp., price Dfl. 80,—.

Atomic-absorption spectroscopy has been known as an analytical technique since the first publication in 1953 by A. WALSH of the Australian C.S.I.R.O. of a description of an apparatus for this purpose. Since then the technique has gained in popularity to a tremendous extent and has now become far more commonplace than the author indicates in his introduction. Indeed, the seeds of its successor-technique of atomic-fluorescence spectroscopy were planted several years ago now, and the new child already bids fair to overshadow its parent technique of atomic-absorption. The author has paid scant attention to this new arrival but the lack of assessment of the atomic-fluorescence technique may partly arise from the fact that literature references beyond 1964–65 are not very prominent and are mainly collected separately in the reference section.

However, there is little doubt that the coverage of literature on atomic-absorption spectroscopy of this book is comprehensive up to the stated period and there is a wealth of detailed information available that is not readily found anywhere else in the literature. The author dissects the technique and looks at the individual parts of the technology as under a microscope. Thus, there are extensive detailed chapters on the flame, the burner, nebulizer and optical systems, and on the selection of the atomic line, and extensive discussions of the various ways of defining sensitivity and on the limitations of the technique. In the experimental part of the text, there are four chapters devoted to (i) experimental process, (ii) preparation of standard solutions, (iii) preparation of samples, and (iv) experimental measurements and calibration. The applications section (40 pp.) constitutes a remarkably small part of the text in contrast to other books on atomic-absorption spectroscopy (two of which are mentioned by the author). It is this different emphasis which makes this book outstanding in its own way and it is a testimonial to Dr. RAMÍREZ–MUÑOZ's treatment that he has discussed all other matters relating to the technique in such fine detail.

Whilst the reviewer does not agree with some of the opinions expressed and conclusions drawn by the author, he has no hesitation in concluding that this is a most interesting and worthwhile treatise on atomic-absorption spectroscopy which should be read carefully by all who are concerned with the technique. It is not a laboratory manual such as may be useful for an analytical chemist searching for a procedure but rather one for the expert himself who wishes to know more about his subject.

T. S. WEST (London)

G. W. C. MILNER AND G. PHILLIPS, *Coulometry in Analytical Chemistry*, Pergamon Press, Oxford, 1967, x+207 pp., Hard cover 30 s; Flexi cover 21 s.

This book, which is aimed mainly at the undergraduate, is of interest to all those active in the field of electroanalytical techniques. The book contains a collection of reprints of papers in which important ideas in coulometry were first developed. It forms part of a planned series of such volumes on analytical chemistry. In addition to the reprints, the present book offers a brief but lucid introduction to coulometry (124 pp.). The theoretical bases and equipment of both controlled current and controlled potential coulometry are described in adequate detail, and various applications are tabulated.

The reprinted papers range from the classical paper of L. SZEBELLÉDY AND Z. SOMOGYI to recent publications by R. G. MONK AND G. C. GOODE, W. M. MACNEVIN AND B. B. BAKER, and L. MEITES AND S. A. MOROS. Particular attention is given to the development of instrumentation from the papers by A. HICKLING, and J. J. LINGANE AND S. L. JONES, to those of G. L. BOOMAN, and J. BARD AND E. SOLON.

The volume is interesting both from the practical and historical points of view and can be warmly recommended.

P. ZUMAN (Prague)

Handbuch der Analytische Chemie, Herausgegeben von W. FRESENIUS UND G. JANDER, *Teil III. Band IV a α. Elemente der vierten Hauptgruppe. I. Kohlenstoff, Silicium*, Bearbeitet von H. GRASSMANN UND W. PRODINGER, Springer-Verlag, Berlin, 1967, viii+563 S., Geheftet DM 153,–; Gebunden DM 158,–.

The major part of this volume describes the analytical chemistry of carbon (444 pp.); surprisingly, silicon is only allotted one-quarter of this number of pages.

The section on carbon has been compiled by H. GRASSMANN and covers the ground extensively. There are some omissions, but these are to be expected. Besides the determination of the element, various compounds of carbon are dealt with adequately, *e.g.*, carbon dioxide, carbon monoxide, phosgene, cyanides, cyanates, thiocyanates and some of the simpler organic compounds. One notable omission is the excellent method of OBERLIN AND MERING for the determination of forms of elemental carbon.

The section on silicon by W. PRODINGER is equally comprehensive as far as it goes, but it is more confined in its scope than the section on carbon. Also one looks in vain for informed comment on the troublesome question of determining free and bound silica.

This volume maintains the good standards set by previous volumes and it is recommended as a valuable reference book to all those interested in the determination of silicon and carbon and their simpler compounds.

R. BELCHER (Birmingham)

G. CHARLOT, *Chimie Analytique Générale. Tome I. Solutions Aqueuses et Non Aqueuses*, Masson et Cie, Paris, 1968, 264 pp., prix 39 F.

Le tome premier de cet ouvrage qui doit en comprendre trois, est composé de 5 parties: Equilibres en milieu homogène, Equilibres en milieu hétérogène (séparations), Equilibres non réalisés (réactions lentes), Analyses quantitatives et Solvants variés.

Dans l'esprit de l'auteur, il s'agit de préparer l'étudiant à un genre de pensée telle qu'il puisse aborder les chapitres les plus variés de la chimie générale. On obtient ce résultat en ramenant les phénomènes les plus complexes à un ensemble de réactions simples.

Cet ouvrage a aussi pour but de développer le raisonnement et d'apporter les bases nécessaires à ceux qui se spécialiseront en chimie analytique. Une série d'exercices, avec les réponses (mais malheureusement sans la marche à suivre), choisis avec soin, complète chaque chapitre et l'illustre de façon remarquable.

La plupart des chapitres sont illustrés par une série d'essais, c'est-à-dire par des expériences simples de laboratoire, extrêment démonstratives du sujet traité. On y voit l'effet du pH, des potentiels redox, des couples et composés peu solubles sur les équilibres. Toutes les opérations de la chimie analytique et minérale sont ainsi mises en évidence.

Un précieux instrument de travail pour tous les étudiants et pour ceux qui désirent acquérir les bases fondamentales modernes de la chimie analytique et minérale.

D. MONNIER (Genève)

Chemical Principles in Practice, Edited by J. A. BELL, Addison–Wesley Publishing Company, Reading, Mass., xi+273 pp., price *ca.* 30 s (paperback).

This book describes a course in general chemistry suitable for first- or second-year undergraduates. It starts conventionally with descriptions of general techniques and a brief section on gravimetric analysis, and then proceeds in rapid succession through synthesis and analysis of a cobalt complex, vacuum techniques, calorimetry, distribution equilibria, ionic equilibria, electrochemical cells and redox reactions, atomic and molecular properties, nuclear magnetic resonance, reaction rates and mechanisms, and the N-solution problem. Details are given for 33 experiments and there are eight useful appendices.

The experiments have been extracted from published work or have been contributed by teachers in various American Universities. All are aimed at making the student really think about his practical work. There is much in this book which will prove valuable to teachers at universities or advanced technical colleges.

A. M. G. MACDONALD (Birmingham)

A. G. WALTON, *The Formation and Properties of Precipitates*, Chemical Analysis, Vol. 23, Interscience Publishers–J. Wiley and Sons, New York, 1967, xi + 232 pp., price 88 s.

This volume, number 23 in the well-known Interscience series of monographs on analytical chemistry and its applications, deals essentially with the theoretical and experimental aspects of precipitation from solution. The text is divided into six main chapters which deal in turn with nucleation, precipitation and crystal growth, coprecipitation, surface properties, morphology of precipitates, and complex precipitation systems; this last chapter is contributed by Dr. H. FÜREDI, Zagreb.

Unlike most accounts of precipitation phenomena, which are largely qualitative in nature, Dr. WALTON has based his text on recent experimental and theoretical developments which allow a much more quantitative treatment of the mechanism of precipitate formation. Apart from its obvious interest to analytical chemists, this book is also directed to physical chemists, physiologists and geophysicists who are concerned with the formation and properties of precipitates.

This is a very worthwhile book which presents a realistic view of the problems of precipitation from solution and how some of these problems can be solved. In an area of study too often ignored by analytical chemists, Dr. WALTON has provided a most interesting and valuable account of present theory and experimental practice.

W. I. STEPHEN (Birmingham)

W. POETHKE, *Praktikum der Gewichtsanalyse*, Verlag Theodor Steinkopff, Dresden, 1967, ix+218 pp., kld. 11,70 MDN.

Cet ouvrage, sur la pratique de l'analyse pondérale, est une réédition revue et complétée de la 8ème datant de 1951. Il s'adresse plus spécialement aux étudiants et à ceux qu'intéressent des données générales en ce domaine.

La première partie (44 pp.) rappelle d'une façon concise les opérations de base de la gravimétrie qu'il est indispensable de connaître avant tout travail pratique (mise en solution, évaporation, filtration, etc.). L'auteur présente ensuite le matériel nécessaire (balance, électrolyseur, échangeur d'ions) et des exemples de calcul gravimétrique. Il n'aborde aucun problème théorique proprement dit.

Le domaine des applications est divisé en trois grandes rubriques: (a) mode opératoire pour le dosage de plus de 20 cations (divisés en 5 groupes) et 13 anions; (b) marche à suivre pour la séparation des cations et des anions les plus importants; (c) exemples d'analyses complexes (alliages, minerais, silicates).

Le non spécialiste trouvera donc dans cet ouvrage l'essentiel, avec des exemples pratiques bien décrits, qui lui permettra de se familiariser avec cette méthode classique d'analyse quantitative.

W. HAERDI (Genève)

Encyclopedia of Industrial Chemical Analysis. Vol. 4. Ablative Materials to Alkaloids, Edited by F. D. SNELL AND C. L. HINTON, Interscience Publishers–J. Wiley and Sons, Inc., New York, 1967, xiii+650 pp., price 425 s (subscription price 310 s).

This is the first volume of this Encyclopedia to deal with the analysis of specific substances or materials, the description of general techniques having been completed in Vol. 3.

The volume under review starts badly with Ablative Materials; the chapter is analytical science in its broadest sense and contains little information on actual analytical procedures, presumably because such information is still "classified". However, this is followed by a sensible chapter on Abrasives and, in all, 26 different topics are discussed in a very useful way. The chapter on Acetone may serve to indicate the scope of the treatment: a brief introduction contains data on its usage, properties, manufacture and specifications, and then identification, assay by the iodoform method, determination of properties, determination of impurities and determination in mixtures are discussed in turn with full procedural detail for selected methods; 71 references are given.

The present volume will be of greatest interest to workers in the synthetic fibre field, for about 250 pages are devoted to such analyses or related topics. The analysis of acetate fibres, acrylamide polymers, acrylic and modacrylic fibres (150 pp.!), and acrylonitrile polymers is covered. The various chapters deal not only with definite compounds, such as Acrolein and Adipic acid, but also with classes of material such as Adhesives, Aerosols and Alcoholic Beverages (distilled). The authors have been well chosen from the large American chemical companies. The coverage in this volume is well balanced.

Any industrial analytical laboratory which has to cope with many different kinds of material should find this Encyclopedia a worthwhile investment. And European laboratories may find it valuable in assessing their own methods against current American practice. The editors have assumed an enormous task in seeing this Encyclopedia through to Z, but if the standard of this volume can be maintained, they will have provided a great service to industrial analysis.

A. M. G. MACDONALD (Birmingham)

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PUBLICATIONS RECEIVED

D. W. Moss, *Enzymes*, Contemporary Science Paperbacks 15, Oliver and Boyd, Edinburgh–London, 1968, vii+110 pp., price 7s 6d.

C. T. GREENWOOD AND E. A. MILNE, *Natural High Polymers*, Contemporary Science Paperbacks 18, Oliver and Boyd, Edinburgh–London, 1968, vii+128 pp., price 7s 6d.

R. DOLIQUE, *L'Arsenic et ses Composés*, "Que sais-je?" Le point des connaissances actuelles no. 1290, Presses Universitaires de France, Paris, 1968, 128 pp.

Progress in High Temperature Physics and Chemistry, Vol. 2, Edited by C. A. ROUSE, Pergamon Press, Oxford, 1968, iii+176 pp., price 75 s.

This volume contains reviews on High-temperature Exploding Wires (F. D. BENNETT), Diagnostics in Field-free Plasmas with Medium-dispersion Optical-spectrographic and Source-monitoring Equipment (R. HEFFERLIN), Calculation of Stellar Structure (C. A. ROUSE), and Shock-tube Chemistry (R. A. STREHLOW).

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ANNOUNCEMENT

INTERNATIONAL SYMPOSIUM ON ANALYTICAL CHEMISTRY, BIRMINGHAM, JULY 21st–25th, 1969

This symposium is organised by the Midlands Section of the Society for Analytical Chemistry and held under the patronage of the International Union of Pure and Applied Chemistry. A preliminary announcement has already been made in the press, and plans for the Scientific and Social Programmes are now well advanced.

Seven plenary lectures will be given by: Prof. I. P. ALIMARIN (Moscow), Prof. F. FEIGL (Rio de Janeiro), Prof. W. KEMULA (Warsaw), Prof. H. MALISSA (Vienna), Dr. W. SCHÖNIGER (Basle), Prof. P. W. WEST (Baton Rouge), Prof. C. L. WILSON (Belfast). A further 60–65 ordinary lectures will be presented on many different fields of analytical chemistry by well-known scientists from all over the world.

The programme will include social activities, together with organised entertainment for the wives of delegates. A comprehensive exhibition of scientific equipment is also being arranged. Accommodation for delegates and their guests will be available in the University Halls of Residence, but delegates will also be free to make their own private arrangements.

This Symposium coincides with the 60th birthday of Prof. R. BELCHER, and his many friends and colleagues are particularly invited.

Everyone interested in attending sould write to the undersigned, who will pass on further information as it becomes available, and, towards the end of this year, supply a registration form.

The Symposium Secretary, D. M. PEAKE, 61 Lodge Road, Walsall, Staffordshire, England.

Potential delegates who have already written to the Symposium Secretary for information need not make any further application at this stage.

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(contents, continued from page 3 of cover)