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Vol. 65, No. 2	July 1973	**(completing Vol. 65)**
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of the disintegration and counting rates of ^{24}Na produced by the irradi
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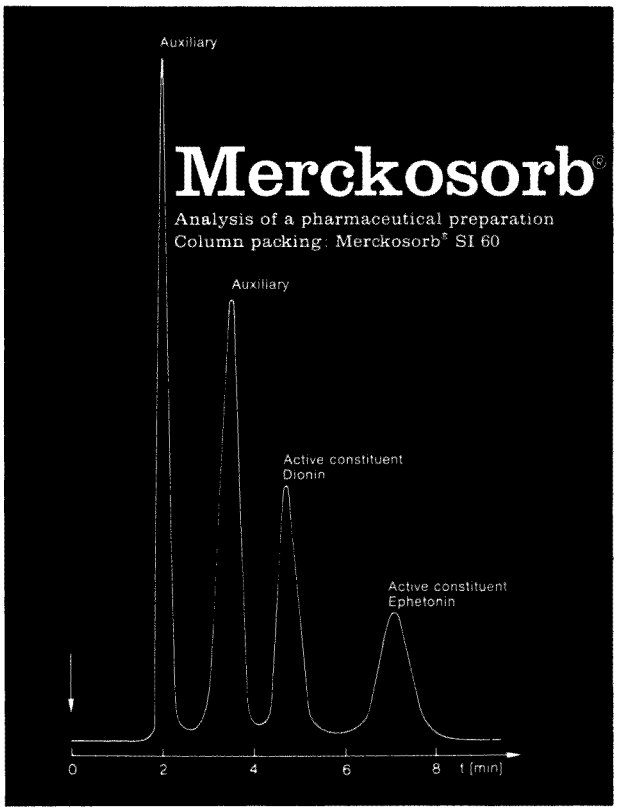

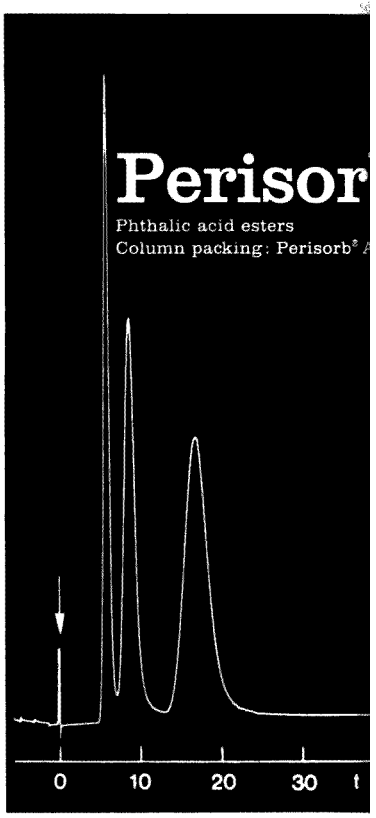

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ORRECTION FOR BACKGROUND ABSORPTION IN ATOMIC BSORPTION SPECTROMETRY WITH CARBON ATOMIZERS

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eceived 29th January 1973)

In atomic absorption spectrometry, an absorption band width of 0.003 nm typical (depending on wavelength and atomizer conditions) and the widths of ission lines from the hollow-cathode source are generally of the same order of gnitude. The resolution of atomic absorption spectrometry is usually conferred by e source while the monochromator isolates the resonance line of interest and ocks out nearby unabsorbed lines and low-level background radiation.

Although atomic absorption bands are very narrow, molecular absorption nds are wide (sometimes extending over 10 nm), and can easily interfere with e measurement of atomic absorption. Should such molecular absorption coincide th a resonance line of interest, it can result in direct error. With a flame omizer, a correction can usually be made by measuring a blank. Scattering the sample products also introduces a direct source of error. Molecular sorption and scatter constitute the principal components of the "background gnal".

he use of carbon atomizers

With the advent of non-flame atomizers the necessity of adequate back-ound correction becomes even more important. With the exception of the device eviously described[1], carbon atomizers are non-continuous, and operate by means a program of heat pulses which vaporize and atomize the sample. The high nsitivity attainable with these devices has been adequately demonstrated. However, the majority of these cases, smoke from residual fragments of organic molecules the matrix, undissociated salt particles, even undissociated solvent vapor generates vere background absorption. Carbon filament atomizers do not involve a ntinuous operation. Correction for background absorption as in flame atomizers not practical.

In addition the background absorption by the combustion products is often 0%. Correction by the measurement of a synthetic blank is also generally practical. The imprecision involved in the use of successive measurements of omic absorption and background absorption precludes that operation. In practice, e problem is solved by removing those species (*e.g.* the solvent) causing the ckground absorption before the atomic absorption is measured, or reducing eir absorption to a correctable level. This step can be a source of serious error used by loss of the element being determined.

The approach taken here is to burn the entire sample in a reducing

chamber. The combustion products including the free atoms enter the absorpti chamber where the atomic absorption and the residual background absorpti can be measured. The background can be reduced considerably, and sometin completely eliminated without using a pretreatment step (*e.g.* by use of dry and a steps). Measurement of atomic absorption and simultaneous correction for molecu absorption in a "one-shot" step is demonstrated.

PRESENT TECHNIQUES USED TO CORRECT FOR BACKGROUND ABSORPTION

Removal of absorbing species

This is recommended by users of the carbon rod filament and carbon r atomizer. The method involves removal of the species causing the backgrou absorption before the atomic absorption measurement. A power unit provides t necessary operating current to the carbon rod and three cycles are used to dry, a and atomize the sample. Should only one cycle be used, the atomic absorpti would be swamped by the very high background. The use of three cyc requires a very carefully regulated power supply. In the case of the rod atomiz the analysis can be carried out by either a step cycle in which the selected volta is constant over a preset period, or a ramp cycle in which the voltage progressively increased at a preselected rate to a chosen cut-off value. In th systems no attempt is made to measure simultaneously the background absorpti Recorder tracings for practical samples show a large non-specific absorption in t ashing cycle.

There are several disadvantages to such a system. It was recognized ea in the development of these devices[2,3] that the power supply must be v carefully regulated in order to prevent loss of sample during the preheat cycl Since the rod characteristics differ from shot to shot, this seems a diffic task. It is not safe to assume that sample loss in the preheat cycles will reproducible and corrected for by the calibration curve. It also seems unsafe assume equal losses during preheat cycles for different matrices, if calibration effected with samples whose matrix differs from the samples analyzed.

The recommended procedures also assume that the preheat cycles remove the background absorption and that the measured signal after ashing is complet due to atomic absorption. At the temperatures required to ash most orga residues, many elements (*e.g.* As, Hg, Cd, Pb) have appreciable vapor pressu and sample losses must occur. Results reported earlier indicate that sample los during the preheat cycles are sometimes significant[4,5]. In addition, there instances where the element of interest vaporizes more readily than the matrix.

Absorption measurement

An alternative to the absorption method is to remove the bulk of the mat by pretreating and then simultaneously measure the molecular background and t atomic absorption. A correction for the molecular background can then be ma In the earlier atomic absorption measurements this was achieved by the use adjacent non-resonance lines. This is sometimes inaccurate, because it is not alw easy to find a strong reference line sufficiently close to the resonance line, and ev if obtainable it may lie on a slope of the molecular absorption band and correct compensation may result.

Since first proposed by Koirtyohann and Pickett[6], a commonly employed chnique is to measure the absorption of a continuous source of radiation at the ime wavelength as the absorption line of the element of interest (*e.g.* H_2, D_2 mp). For the slit widths employed in most monochromators, the bandwidth of ie continuum radiation passed is typically two orders of magnitude greater than ie atomic absorption line. Thus the contribution to the measured molecular bsorption by atomic absorption is negligible. In practice then the procedure is to easure (*a*) the total absorption with the line source and (*b*) the molecular bsorption with the continuum source. The difference between the two values should eld a correct atomic absorption value. This can be done by consecutive measure-ent of these two signals, but as mentioned earlier it must be assumed that the recision of the sample treatment before and during atomization is reproducible. 1 the case of carbon atomizers this is often untrue. Ideally, then simultaneous easurement of (*a*) the molecular absorption and (*b*) atomic absorption plus olecular absorption signals is required. This was first described by L'vov[7] and is since been added to some commercial atomic absorption instruments. Ad-ntages of this approach are that corrections can be made for variations in omization from sample to sample. Ideally, the sample should be dried, ashed id atomized in one operation followed by simultaneous measurement of atomic id molecular signals. In actual practice, however, this system suffers from many f the difficulties of the previously described techniques.

ECHNIQUE USED WITH CARBON ATOMIZER SYSTEM

The r.f. carbon atomizer has been adequately described[8–12]. For the analysis solutions, the sample is injected into the carbon bed which is held at 1350° by heating. Sample evaporation, ashing and atomization occur in virtually one step id all the products issue into the absorption tube. In this way, rigorous sample etreatment is eliminated, and loss of sample is negligible. Organic solvents and ater are reduced to carbon monoxide and hydrogen on contact with the hot rbon bed, so that the major end products are the same irrespective of the solvent ed. Carbon monoxide and nitrogen do not absorb at wavelengths longer than 0 nm. Hydrogen absorption progressively increases below 210 nm but above 0 nm is very small.

The molecular absorption of various solvents over the wavelength range 4.9–422.6 nm is shown in Table I together with the measured "atomic" sorption. The molecular absorption was measured with a deuterium lamp and a ectral slit width of 0.4 nm on the Jarrell-Ash 0.5-m monochromator. Barnes mountable hollow-cathode lamps were used as line sources for atomic absorption easurements. As previously described[4], 5 μl of the solvent was injected onto the rbon bed. It was found that at a 100-ml min^{-1} flow rate of air across the bed, ganic materials were completely burned. At greater flow rates the molecular sorption was larger, probably because of incomplete dissociation of the solvent.

Typical absorption spectra for atomic lines and deuterium bands are shown Fig. 1. As can be seen, the molecular absorption at 184.9 nm (Hg line) is nificant and a correction is necessary when measuring the mercury atomic sorption. Similarly, there is a minor but discernible degree of molecular absorption

TABLE I

MOLECULAR AND ATOMIC ABSORBANCE VALUES FOR VARIOUS SOLVENTS AT RESONA LINES OF INTEREST

(Samples of 5 μl)

Wavelength (nm)		*Solvent*							
		Water	*Benzene*	*Toluene*	*Heptane*	*Formic acid*	*Acetone*	*MIBK*	*Butyl amine*
184.9	Molecular	0.349	0.013	0.012	0.011	0.003	0.002	0.002	0.087
(Hg)	Atomic	0.370	0.025	0.035	0.046	0.008	0.017	0.025	0.121
197.2	Molecular	0.228	0.023	0.025	0.026	0.012	0.015	0.010	0.080
(As)	Atomic	0.226	0.005	0.005	0.003	0	0.008	0.005	0.034
213.0	Molecula	0.100	0.022	0.020	0.012	0.016	0.009	0.012	0.028
(Zn)	Atomic	0.272	0.092	0.158	0.213	0.169	0.133	0.138	0.163
217.0	Molecular	0.022	0	0	0	0	0	0	0
(Pb)	Atomic	0.176	0.060	0.064	0.094	0.528	0.182	0.108	0.151
228.8	Molecular	0.027	0.008	0.012	0.007	0.007	0.005	0.007	0
(Cd)	Atomic	0.296	0.278	0.146	∞	0.177	0.190	0.243	0.005
232.0	Molecular	0	0	0	0	0	0	0	0
(Ni)	Atomic	0.005	0	0.005	0	0.005	0	0	0
253.7	Molecular	0	0	0	0	0	0	0	0
(Hb)	Atomic	0.003	0	0.005	0.008	0.003	0.003	0.003	0.002
285.2	Molecular	0	0	0	0	0	0	0	0
(Mg)	Atomic	0.111	0.106	0.119	0.122	0.005	0.078	0.102	0.070
328.0	Molecular	0	0	0	0	0	0	0	0
(Ag)	Atomic	0.013	0.004	0.008	0.005	0.003	0.006	0.006	0
422.6	Molecular	0	0	0	0	0	0	0	0
(Ca)	Atomic	0.008	0	0	0	0	0	0	0

at 213.8 nm (Zn) and 217.0 nm (Pb). However, no molecular absorption wa observed at longer wavelengths as illustrated by the data taken with calciur (422.6 nm). Molecular absorption from the organic solvents was negligible abov 217.0 nm. As expected the introduction of water led to a progressively highe absorbance below 217.0 nm. For completeness atomic absorption measurements wer also taken. Significant atomic absorption was recorded for zinc (213.8 nm), lea (217.0 nm), cadmium (228.8 nm) and magnesium (285.2 nm). This could be due t contamination of the solvents by these metals.

CONCLUSION

The advantages of the recommended technique are that sample pretreatmen always a subject of error, is completely eliminated and background absorption i greatly reduced, often to negligible values. In those cases where a backgroun occurs, simultaneous measurement of atomic absorption and molecular absorption i a truly "one-shot" step is feasible, owing to the relatively low molecular absorptior

It is believed that the procedure described eliminates errors arising from los of sample or inadequate removal of solvents, and therefore improves the accurac of the procedure.

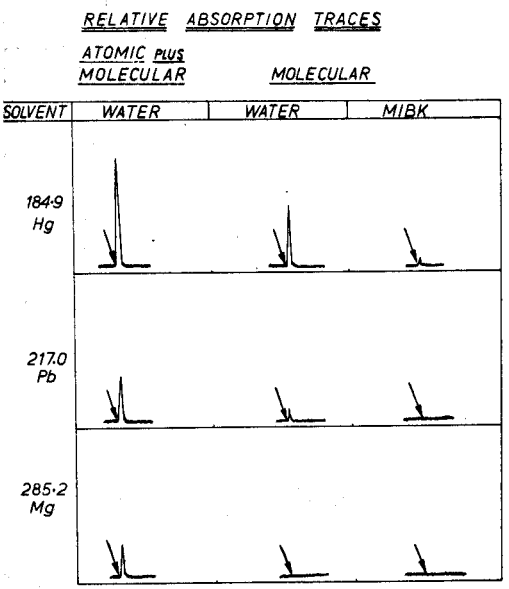

Fig. 1. Atomic and molecular absorption by solvents at typical atomic resonance lines. The arrows indicate the point of injection.

This investigation was supported by Research Grant R 800771, Air Pollution Control Office, Environmental Protection Agency.

SUMMARY

In atomic absorption, analytical errors arise in the pretreatment steps with carbon atomizers. A procedure is described wherein the entire sample is decomposed and atomized. The products are swept into an absorption tube where atomic absorption and molecular absorption measurements are made. Errors caused by sample loss during pretreatment or by incomplete solvent removal are eliminated.

RÉSUMÉ

En absorption atomique, avec atomiseur de carbone, des erreurs analytiques peuvent se produire au stade du prétraitement. On décrit une méthode où l'échantillon entier est décomposé et atomisé. Les produits sont envoyés dans un tube d'absorption où se font les mesures d'absorption atomique et d'absorption moléculaire. On élimine ainsi des erreurs causées par une perte lors du prétraitement ou par une séparation incomplète du solvant.

ZUSAMMENFASSUNG

Bei der Atomabsorption entstehen analytische Fehler bei der Probenvorbehandlung in Kohlenstoff-Atomisatoren. Es wird ein Verfahren beschrieben, bei dem die ganze Probe zersetzt und atomisiert wird. Die Produkte werden in ein

Absorptionsrohr überführt, in dem Atomabsorptions- und Molekülabsorptions messungen durchgeführt werden. Fehler, die durch Probenverlust während de Vorbehandlung oder durch unvollständige Lösungsmittelentfernung verursach werden, werden eliminiert.

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A COMPARATIVE STUDY OF THE DETERMINATION OF ZINC AND MOLYBDENUM BY ATOMIC ABSORPTION SPECTROMETRY WITH A CARBON FILAMENT ATOM RESERVOIR

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Until recently the most widely used method of atomization has been based on the premixed flame. Flames have several advantages and because of these they are unlikely to be replaced in the near future. However, although flames are very convenient in practice, they are not ideal atom reservoirs and can suffer from disadvantages of high background absorption and emission at the wavelength of measurement; thermal emission from analyte or concomitant elements at this wavelength (both of which can give rise to a high noise level) and the volume of sample solution available for analysis may be less than that required for conventional flame nebulization and the analyte concentration may be too low to allow further dilution. Furthermore, in some applications, *e.g.* analysis of radioactive materials, the use of flames requires many precautions. As a result many workers have devoted efforts towards the development of alternative methods of atomization. At the present time the most successful of these are the various forms of electrically heated furnaces and filaments which have been reviewed briefly by Kirkbright[1]. However, from the various accounts of work with non-flame cells it is not always possible to establish just what the advantages of the systems proposed are (with the exception of a superior limit of detection) or when such a system can or should be used in a real analytical situation. Furthermore, it is not obvious usually what types of interference one can expect because it is well known now that one can not always equate investigations using flames with similar studies using non-flame cells. This aspect was examined in a recent communication[2] with reference to the Massman furnace system which has been introduced recently as an accessory to an atomic absorption spectrometer[3].

In the present paper, the results of a comparative study concerning the determination of zinc and molybdenum by atomic absorption spectrometry with a filament atom reservoir similar to that designed by Alder and West[4], are described. These elements were selected because their determination has not been reported previously by this means and they show a wide difference in volatility which is likely to be a significant factor in the analytical utility of non-flame cells, especially with respect to chemical and physical interferences.

EXPERIMENTAL

The carbon filament atom reservoir was similar to that described earlier but with a separate cooling water supply to each filament support. A modificatio in the design of the shield gas box, in the form of an internal baffle, was made, whic provided a better protection to the ends of the filament from atmospheric oxidatio at high temperatures. The power supply to the filament was from a transforme capable of delivering 100 A at 13.8 V. The mains input to this was *via* a Varia transformer calibrated directly in terms of voltage applied to the filament.

The optical arrangement of radiation source, filament and detector was a follows. The radiation from the source was focused by a lens to a point directl above the filament. Another lens focused the radiation onto a plate in which wa cut a slit with the dimensions 1 mm × 3 mm. The monochromator entrance slit wa *ca.* 6 cm from the plate. This procedure, as opposed to focusing the light directly o the entrance slit, was adopted because it gave a better rejection of "white light from the heated filament. A stop (also in the form of a 3 mm × 1 mm slit) was situate behind the filament and further prevented an emission signal from the heate filament being detected. The height of the filament was variable, so that its positionin with respect to the light beam determined the height above the filament at whic analytical measurements were made.

A molybdenum hollow-cathode lamp was used for the determination of th metal and for zinc both a hollow-cathode lamp and an electrodeless discharg lamp were compared. The zinc discharge lamp was made by reaction of metallic zin and iodine, and was sealed under 4 torr of argon. This lamp was operated in ¾-wave cavity with a Beckman "Microgen" microwave generator. The hollow-cathod lamps were operated in the usual manner.

A Southern Analytical A1740 grating photometer was used with bypasse integration and background correction facilities; the output was taken directl from the photomultiplier tube to a storage oscilloscope (Telequipment DM 53, fitted with a K-type amplifier) on which the analytical signal was displayed an measured.

Sample solutions were prepared in the usual way and delivered to the filamer from a 1-μl pipette coated in "Repelcote".

The operating filament procedure was normal and essentially the same a that described by West *et al.*[5] with a regular timing procedure being observe Because of the very high temperature required to volatilize molybdenum, it wa necessary to allow 120 s between successive determinations to allow the filament t cool sufficiently. Atomic absorption was monitored at 213.9 nm and 313.3 nm fc zinc and molybdenum, respectively.

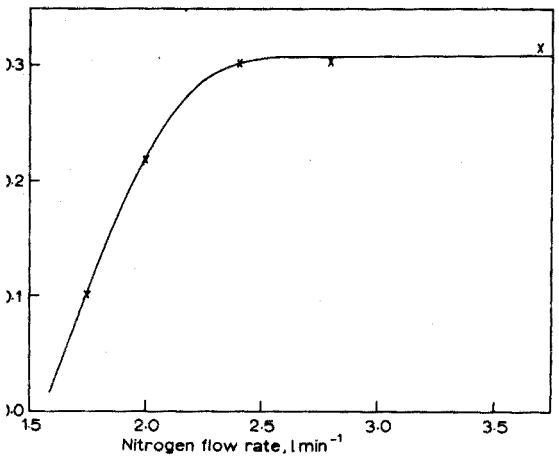
RESULTS AND DISCUSSION

Choice of sheathing gas

The use of both argon and nitrogen as shield gases was investigated; however no significant difference was found between the two gases either in the determinatio of zinc or molybdenum. In the case of zinc, the gas flow rate was relatively un important, the absorption varying only slightly over a wide range of flow rates. A

s flow rate of *ca.* 2 l min^{-1} was used for further studies of zinc.

The dependence of the molybdenum absorption on nitrogen gas flow rate is own in Fig. 1. At low gas flow rates, the absorption decreases, presumably because removal of molybdenum atoms as oxide species because of inefficient shielding m the surrounding atmosphere.



. 1. Dependence of molybdenum absorption on nitrogen gas flow rate.

The effect of hydrogen as a shield gas on the molybdenum absorption was vestigated also. This was achieved using both pure hydrogen and hydrogen/nitrogen :4) mixtures. Two major advantages were found when hydrogen was used: (*a*) a 3-fold increase in sensitivity, and (*b*) a considerable reduction in the "blank" sorption signal, without sample application. The former was probably due to the mplete removal of oxygen from the vicinity of the heated filament rather than an increase in temperature above the filament. The fact that the same increase sensitivity was found with hydrogen alone as with a mixture of hydrogen/nitrogen, uld seem to confirm this. In the absence of hydrogen, an absorption signal was vays obtained when the filament was heated, owing to volatilization of carbon the high temperatures attained. In the presence of hydrogen this absorption from rticulate carbon was not found, possibly because of its removal by hydrocarbon mation. In all subsequent measurements a sheathing gas flow rate of *ca.* 2.8 l min^{-1} s used for studies of molybdenum.

lament voltage

Increasing the voltage applied across the filament increased the rate of nperature rise of the filament and increased the magnitude of the absorption nal obtained. For zinc, the increase in absorption signal with voltage was approximately linear and provided a useful means of varying the sensitivity of the thod, *e.g.* 9.0 V over the 0.01–0.1 p.p.m. zinc range, 10.5 V over the 0.001–0.01 .m. zinc range, and 12.0 V for < 0.001 p.p.m. zinc.

The molybdenum absorption signal also varied with the voltage applied but ly with the maximum voltage possible (13.8 V) was a usable absorption signal

obtained; at this voltage the terminal filament temperature was *ca.* 3500° and gave an absorption signal of about 500 ms duration. Below this voltage the signal became progressively broader and flatter with no measurable absorption below *ca.* 10 V.

Height of observation

The variation in absorbance with height of observation above the filament is shown in Fig. 2. Both zinc and molybdenum exhibit a decreasing absorbance with increasing height above the filament, because of diffusion and expansion of the atomic cloud and condensation of atoms to molecular species with decreasing temperature. The reproducibility of the results also decreased with increasing height of observation, probably because of greater turbulence in the gas flow high above the filament.

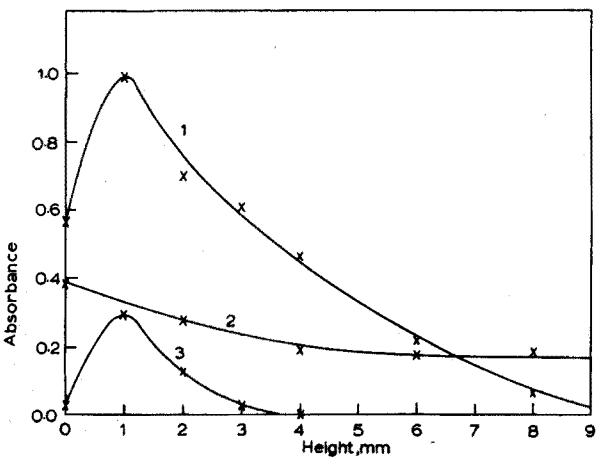


Fig. 2. Dependence of molybdenum and zinc absorption on height of observation above the filament. (1) Molybdenum with hydrogen/nitrogen sheathing gas (ratio 1:4); (2) zinc with nitrogen sheathing gas; (3) molybdenum (same quantity as curve 1) with nitrogen sheathing gas (same total flow as curve 1).

The decrease in the molybdenum absorption signal below 1 mm was due to radiation from the heated filament which was detected by the photomultiplier at low heights of measurement. The absorption profile for molybdenum with hydrogen/nitrogen (1:4) as sheathing gas shows that molybdenum atoms exist at a considerable height above the filament, compared with the absorption profile with nitrogen alone. The profile did not vary significantly with the hydrogen:nitrogen ratio which suggests that the effect is associated with the more effective removal of oxygen in the presence of hydrogen rather than an increase in filament temperature.

For the determination of zinc all measurements were made as close to the filament as possible; for molybdenum the filament height was adjusted until no emission signal was observed (*ca.* 1 mm above the filament).

Source operating conditions

The molybdenum absorption signal was not dependent on the current for

e hollow-cathode lamp, but the maximum allowable current was used (20 mA) that the photomultiplier EHT could be as low as possible to reduce noise. Noise ıs also reduced by placing a capacitor across the oscilloscope input terminals; is reduced the effective response time of the oscilloscope to *ca.* 75 ms f.s.d., but oduced negligible distortion of the signal which exhibited a rise time of *ca.* 200 ms.

The zinc electrodeless discharge lamp gave a better limit of detection for ıc than the hollow-cathode lamp as a result of a higher line intensity at 213.9 nm d a lower noise level in the system.

The spectrometer entrance slit width was optimized to give the highest signal--noise ratio, *viz.* 0.25 mm for zinc and 0.10 mm for molybdenum.

ılibration and limits of measurement

The variation of absorbance (measured from absorption peak height) with ncentration was studied for zinc and molybdenum over ranges down to 0.5 p.m. ($5 \cdot 10^{-10}$ g) and 50 p.p.m. ($5 \cdot 10^{-8}$ g) respectively, with a 1-μl volume of mple. Linear calibration curves were obtained for zinc over the range 0.0002–0.075 p.m. and for molybdenum over the range 0.03–10 p.p.m. Above the upper levels, ere was pronounced curvature towards the concentration axis owing to peak oadening. The use of a hydrogen/nitrogen (1:4) sheath gas gave a *ca.* 3-fold crease in molybdenum sensitivity (0.035 p.p.m. for 1% absorption) compared with trogen as sheath gas (0.10 p.p.m. for 1% absorption).

A computer programme was written to process the data obtained from the cillographic measurement of absorption peak height *vs.* concentration. On each ta card was punched the concentration (in p.p.m.) and up to five separate measure- ents of peak height (in cm) and the corresponding 100% transmission value (in cm). ıe absorbance value for each measurement was computed, and the mean absorbance lue for each concentration measurement found. The method of least squares was ed to compute the equation of the best-fit straight line, together with its correla- ın coefficient. Only data having a correlation coefficient >0.98 were assumed to linearly related. Knowing the equation of the best-fit straight line, the sensitivities the measurements were calculated, and after calculating the standard deviation the absorbance values, from the line, an estimate could be made of the limit of tection, *i.e.* that concentration in p.p.m. at which the standard deviation was ual to 50% of the signal after correction for the blank. The results obtained over number of concentration ranges are summarized in Table I.

The optimal working calibration ranges were 0.0005–0.05 p.p.m. zinc and l–10 p.p.m. molybdenum.

The reproducibility of a particular measurement was found by performing number of replicate determinations of a single sample solution. The standard viations at a number of different concentrations are listed in Table II.

The computer programme was slightly modified to accept data from solu- ns of unknown concentrations. The concentration of the solution and the error its computation, were found from the equation of the best line fit.

As a check on the accuracy of this method of analysis, a determination was ıde of the zinc and molybdenum concentrations in a solution containing a large ess of sulphate, phosphate and nitrate together with about 1000 p.p.m. of spended organic material. For application of flame atomic absorption spec-

TABLE I

COMPUTER PROCESSED DATA FOR ZINC AND MOLYBDENUM

Element	*Filament voltage (V)*	*Range (p.p.m.)*	*Coefficient in line*[a]		*Correlation coefficient*	*Sensitivity 1% absorption (p.p.m.)*	*Lim det (p.p*
			A	*B*			
Zn	9.0	0–0.5			Non linear		
	9.0	0–0.7	7.20	0.0081	0.996	0.0006	0.0(
	10.5	0–0.1	12.28	0.01 4	0.988	0.00036	0.0(
	12.0	0–0.001	33.18	0.0082	0.984	0.00013	0.0(
Mo	13.8	0–50			Non linear		
	13.8	0–10	0.031	0.031	0.986	0.14	1.0
	13.8	0–1.0	0.040	0.0014	0.992	0.10	0.08
	13.8[b]	0–1.0	0.126	0.0018	0.999	0.035	0.03

[a] Absorbance = A (concentration) + B.
[b] With H_2/N_2 (1:4) as sheathing gas. Other measurements were carried out using a nitrogen or argon sheat

TABLE II

ESTIMATION OF PERCENTAGE STANDARD DEVIATIONS FOR ZINC AND MOLY DENUM

Element	*Concentration (p.p.m.)*	*No. of detns.*	*Mean absorbance*	*% Standard deviation*
Zn	0.05	15[a] (20)[b]	0.498[a] (0.350)[b]	3.6[a] (4.4)[b]
	0.01[c]	10	0.134	8.2
	0.001[d]	15	0.034	9.7
Mo	10[e]	12	0.290	5.5
	1.0	12	0.112	2.4
	0.1	15	0.011	15.5

[a] Filament voltage 9.5 V.
[b] Filament voltage 9.0 V.
[c] Filament voltage 11.0 V.
[d] Filament voltage 12.0 V.
[e] Nitrogen only as sheathing gas.

trometry, it was necessary first to evaporate the solution to dryness and then as the residue to remove the organic material; after dissolution of the residue the zin and molybdenum concentrations were found to be 0.11 and 0.04 p.p.m., respectivel With the filament technique, no pretreatment of the sample was necessary (excep a 5-fold dilution of the zinc solution) although a 5-μl sample was used for th molybdenum determination to obtain a reasonable absorption signal. The concen trations found were 0.105 ± 0.005 p.p.m. zinc and 0.033 ± 0.004 p.p.m. molybdenun

Interferences

The effect of a number of cations and anions was investigated on the absorp tion of zinc at 0.05 p.p.m. and molybdenum at 1 p.p.m. Hydrogen/nitrogen (1:4

LE III

ERFERENCE STUDY FOR ZINC

aneous ion	*Concentration*[a]	*% Error*	*Extraneous ion*	*Concentration*[a]	*% Error*
	2000	−5	Mn^{2+}	200	−90
+	2000	−40		40	−40
	200	−5	Fe	2000	−100
+	2000	0	PO_4^{3-}	2000	0
+	100	−50	SO_4^{2-}	2000	0
	40	−30	Cl^-	2000	−10

lar excess over zinc.

LE IV

ERFERENCE STUDY FOR MOLYBDENUM

ıneous ion	Co^{2+}	W^{7+}	W^{7+}	W^{7+}	W^{7+}	Ni^{2+}	Bi^{3+}	Cl^-
ɔentration[a]	1000	1000	100	50	10	1000	1000	1000
r (%)	−10	−75	−30	−20	0	−5	−40	−10

lar excess over zinc.

used as sheathing gas for the molybdenum study. The results for zinc are marized in Table III. In general, for molybdenum, it was observed that two ɔrption peaks occurred when an extraneous ion was present; the first was due particulate or molecular absorption (confirmed by its occurrence over a wide ge of wavelengths) and the second was due to atomic molybdenum. The peaks ld be separated by first heating the filament at *ca.* 8.5 V for a few seconds n the first peak was observed and then increasing the voltage to a maximum, n only the second peak was observed. Except in the case of cobalt, no loss of ybdenum occurred during this procedure; it would appear that some co-ıtilization of molybdenum and cobalt occurs. No interference on molybdenum found from 1000-fold (molar) amounts of Na^+, Ca^{2+}, Mn^{2+}, Mg^{2+}, Cu^{2+}, $^+$, Zn^{2+}, V^{5+}, Sn^{2+}, phosphate, sulphate or nitrate. Interferences are listed in le IV.

Tungsten gave an interference with molybdenum which persisted after its ication to the filament. A single application of a 1000 p.p.m. tungsten solution ɔressed the molybdenum absorption for the lifetime of the filament. A single ication of a 100 p.p.m. solution interfered for some 20 determinations, the ybdenum absorption increasing linearly to its normal value during this period. ıgle application of a 50 p.p.m. solution gave an interference persisting for 2–3 rminations. It appears that tungsten, because of its great lack of volatility, is ɔved from the filament only slowly and that whilst it persists a suppression of nolybdenum absorption is observed.

The determination of molybdenum is therefore relatively free from inter-ıce effects because in the main the extraneous elements can be removed from ilament before volatilization and atomization of molybdenum occurs.

The interferences in the zinc determination are, on the other hand, quite

severe and it was not found possible to separate the peaks arising from the extraneou material and zinc. This investigation therefore suggests that this particular nor flame atom reservoir is better suited to the determination of relatively involatil elements. A similar conclusion was reached in a previous study[2] of the Massma system.

One of us (D.J.J.) wishes to thank Imperial Chemical Industries Limite Agricultural Division, Billingham, Teeside for the award of a research grant to carr out this work.

SUMMARY

A study is made of the operating parameters and interferences in the atom absorption determination of an element which is readily atomized (zinc) and a element which is difficult to atomize (molybdenum) with a filament atom reservoi This device seems better suited in real situations to the determination of involatil elements such as molybdenum and in this instance especially with a hydroger nitrogen-sheathed gas. There were numerous interferences in the case of zinc, bu only tungsten produced a significant effect in the determination of molybdenum.

RÉSUMÉ

Une étude est effectuée sur le dosage par absorption atomique, avec réservo atomique à filament de carbone, d'un élément facilement atomisé (zinc) et d'u élément difficilement atomisé (molybdène). Ce système convient surtout dans l cas d'éléments non volatiles, tel que le molybdène, spécialement avec un mélang gazeux hydrogène/azote. Les interférences sont nombreuses dans le cas du zinc pour le molybdène, seul le tungstène peut interférer.

ZUSAMMENFASSUNG

Die Arbeitsbedingungen und die Störungen bei der Atomabsorptionsbestim mung eines Elementes, das leicht atomisiert wird (Zink), und eines Elementes, da bei Verwendung eines Kohlefaden-Atomreservoirs schwer zu atomisieren ist (Mo lybdän), wurden untersucht. Diese Vorrichtung scheint sich für die Bestimmun von schwerflüchtigen Elementen wie Molybdän besser zu eignen und zwar in diesen Fall besonders bei Verwendung von Wasserstoff/Stickstoff als Schutzgas. Im Fal von Zink wurden zahlreiche Störungen beobachtet, jedoch wurde die Bestimmun von Molybdän nur durch Wolfram wesentlich beeinflusst.

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TUDE PAR SPECTROMÉTRIE INFRA-ROUGE DES COMPLEXES DES ERRES RARES AVEC L'OXYDE DE TRI-*n*-BUTYLPHOSPHINE À ÉTAT SOLIDE

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eçu le 9 février 1973)

Les composés organophosphorés neutres, tels que les oxydes de phosphine ı type R_3PO ou les trialkylphosphates du type $(RO)_3PO$, sont des agents com-exants qui réagissent comme bases de Lewis vis-à-vis d'un cation métallique agissant comme acide de Lewis.

Un grand nombre de complexes ont été préparés avec ces composés. Nous ous sommes particulièrement attachés à ceux formés avec l'oxyde de tri-*n*-butyl-osphine (TBPO). Ce sont surtout les métaux de transition[1–5] et les terres rares[6–11] ui ont été étudiés.

Dans le cas des terres rares, la réaction de complexation avec le TBPO est suivante:

$$Me^{3+} + 3\ TBPO \rightarrow (Me^{3+}) \cdot 3\ TBPO \qquad (1)$$

Nous avons étudié l'influence de la nature du cation central sur la fréquence : vibration du P=O dans les complexes $Me(NO_3)_3 \cdot 3$ TBPO.

ARTIE EXPÉRIMENTALE

réparation

L'oxyde de terre rare est dissous dans l'acide nitrique concentré. La solution t évaporée jusqu'à élimination totale de l'acide. Le nitrate de terre rare est ensuite cristallisé dans l'eau.

Le TBPO est préparé par oxydation à l'eau oxygénée de la tri-*n*-butylphos-hine dissoute dans le chloroforme. Le solvant est éliminé par distillation et le TBPO t distillé sous vide et sous courant d'azote (T.E. 134°/4 mm Hg).

A une solution de TBPO dans le toluène, on ajoute progressivement du nitrate terre rare solide. Il se forme une phase aqueuse résultant de la libération des olécules d'eau d'hydratation du nitrate de terre rare. Lorsque la phase aqueuse est turée par ce dernier, on décante les deux phases et le toluène est évaporé. Le mplexe est ensuite recristallisé dans l'éther de pétrole.

nalyse

Le phosphore est dosé par gravimétrie du phosphomolybdate ammonique[12].

Le métal est titré potentiométriquement par l'EDTA avec une électrode argent comme électrode indicatrice[13].

Les résultats des dosages sont résumés dans le Tableau I.

TABLEAU I

RÉSULTATS DES ANALYSES

Métal	*P théor. (% en poids)*	*P exp. (% en poids)*	*Me théor. (% en poids)*	*Me exp. (% en poids)*
La	9.48	9.50	14.18	14.30
Ce	9.47	9.39	14.29	14.32
Pr	9.46	9.40	14.35	14.45
Nd	9.43	9.35	14.65	14.41
Sm	9.37	9.42	15.18	15.52
Eu	9.36	9.22	15.31	15.97
Gd	9.31	9.40	15.76	15.94
Tb	9.29	9.21	15.90	16.01
Dy	9.26	9.29	16.20	16.43
Ho	9.24	9.14	16.40	16.65
Er	9.22	9.24	16.60	16.51
Tm	9.20	9.24	16.74	16.64
Yb	9.16	9.12	17.06	17.16

Spectrométrie

Les spectres infra-rouges ont été enregistrés sur un spectrophotomètre Perkin Elmer Modèle 125. Les complexes sont mélangés avec de la paraffine Uvaso Merck et placés entre deux lames de NaCl. Le domaine envisagé est celui s'étendant de 4000 cm^{-1} à 650 cm^{-1}

Les valeurs des fréquences de vibration des groupements nitrates et du P=O sont données dans le Tableau II. La précision des mesures est de l'ordre de 1 cm^{-1}

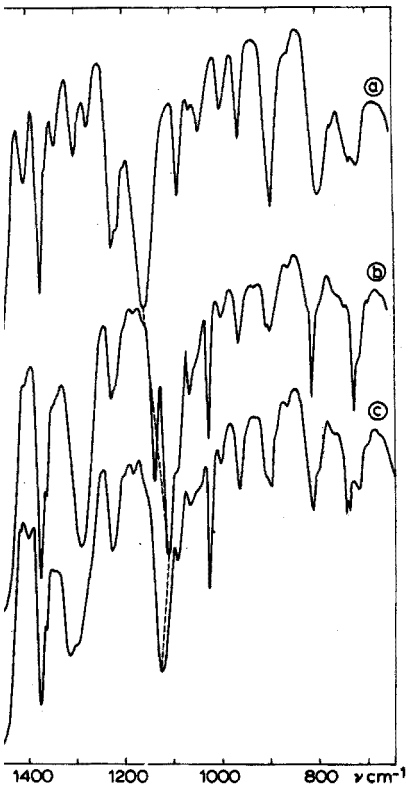
DISCUSSION

Quel que soit le cation coordonné, nous observons une diminution de l

TABLEAU II

SPECTRE INFRA-ROUGE

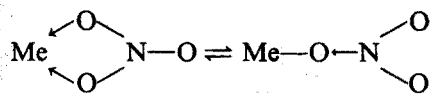
Métal	*ν P=O (cm^{-1})*	*ν Nitrates (cm^{-1})*
La	1114	1485, 1292, 1031, 819, 731
Ce	1114	1485, 1294, 1032, 819, 733
Pr	1114	1490, 1295, 1030, 819, 734
Nd	1117	1490, 1299, 1033, 819, 736
Sm	1118	1495, 1300, 1028, 818, 734
Eu	1118	1500, 1306, 1029, 818, 736
Gd	1115	1500, 1308, 1028, 820, 817, 742, 738
Tb	1120	1460, 1310, 1028, 820, 816, 742, 738
Dy	1124	1490, 1314, 1029, 820, 814, 743, 738
Ho	1125	1490, 1315, 1029, 820, 815, 746, 740
Er	1126	1490, 1316, 1029, 820, 816, 746, 741
Tm	1125	1490, 1316, 1030, 819, 811 746, 740
Yb	1127	1490, 1310, 1030, 824, 815, 747, 740



g. 1. (a) Spectre du TBPO; (b) spectre du $Ce(NO_3)_3 \cdot 3$ TBPO; (c) spectre du $Dy(NO_3)_3 \cdot 3$ TBPO.

équence du P=O par rapport à celle du P=O libre (ν(P=O) libre = 1164 cm^{-1}) ig. 1). Dans le spectre du TBPO, c'est la seule bande qui subisse une modification nportante. Il est donc évident que c'est par l'intermédiaire de l'oxygène du P=O ue la liaison coordinative s'établit.

De plus, le spectre infra-rouge nous montre que les groupements nitrates nt eux aussi coordonnées. Néanmoins, contrairement aux complexes formés entre s nitrates de terres rares et le triisopropylphosphate[11] d'une part, le tributylphosate[9] d'autre part, il semble qu'un brusque changement dans le mode de coornation des ions nitrates apparaisse au niveau du gadolinium (Tableau II). En effet, vibration non dégénérée γ_2, qui absorbe à 820 cm^{-1}, se dédouble pour les comexes suivants; c'est aussi à partir du gadolinium que se produit le dédoublement la raie dégénérée des nitrates située à 740 cm^{-1}. Nous supposons qu'il s'agit du ssage partiel des ions nitrates bidentés aux nitrates monodentés (2).



(2)

Ce changement résulterait de la contraction lanthanique, le cation central evenant trop petit pour pouvoir s'entourer d'un grand nombre d'atomes d'oxygène. ette conclusion semble d'ailleurs se confirmer par l'étude de la vibration P=O.

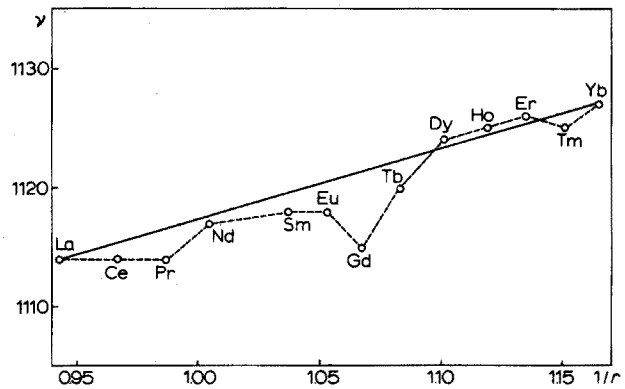


Fig. 2. $\nu_{P=O} = f(1/r)$.

A première vue, nous devrions nous attendre à une diminution monotone la fréquence du P=O avec une augmentation du nombre atomique Z, l'attracti électrostatique augmentant avec la diminution du rayon ionique. Or, en moyen nous observons une augmentation de la fréquence avec cependant une brusc diminution de la fréquence du P=O au niveau du gadolinium et des variations n monotones entre le lanthane et l'europium d'une part, et entre le gadolinium l'ytterbium d'autre part (Fig. 2). Ces variations non monotones ont été interprét théoriquement[14] par la détermination des paramètres d'interaction électronique

Pour expliquer ces phénomènes, nous devons tenir compte de la contracti lanthanique, des effets dûs aux forces d'attraction et de répulsion, du changeme de nombre de coordination des terres rares, changement qui est une conséquence la contraction lanthanique et du "back-bonding"[15,16].

Avant toute chose, rappelons que chaque fois que Z augmente d'une uni un électron supplémentaire vient se placer dans la couche 4 f. Ces électrc peuvent avoir une légère influence sur les doublets électroniques libres des oxygèn en effet, les orbitales 4 f sont fortement allongées et, lorsqu'elles contiennent ou deux électrons, elles créent en certains endroits de l'environnement du cati des densités de charges négatives. De plus, la saturation progressive de la couche produit un effet d'écran. La charge apparente n'est plus égale à 3+ et, par cc séquent, l'attraction des doublets électroniques libres de l'oxygène n'augmente p aussi vite. Cet effet écran augmente surtout lorsqu'on passe des configurations à f^7. De f^8 à f^{14} il aurait même tendance à se stabiliser par suite de la présence deux électrons sur la même orbitale (valeur de m). Ces deux électrons vont repousser, ce qui va produire un élargissement de l'orbitale et par suite diminu l'importance de l'effet d'écran.

La présence de ces charges négatives et de cet effet d'écran va produire "back-bonding" induit, c'est-à-dire, un incrément de "back-bonding" qui vi s'ajouter au "back-bonding" intrinsèque de la molécule de TBPO.

Pour mieux comprendre les phénomènes, divisons les traces rares en tr groupes:

(a) les terres cériques (La, Ce, Pr, Nd, Sm, Eu)

(b) le gadolinium

(c) les terres yttriques (Tb, Dy, Ho, Er, Tm, Yb)

Dans les complexes des terres cériques, la fréquence de vibration du P=O ugmente lentement: si le rayon ionique diminue, le champ électrique au voisinage e l'ion augmente et par conséquent l'attraction des doublets de l'oxygène par le étal augmente, ce qui doit entraîner normalement une diminution de la fréquence u P=O par affaiblissement de cette liaison. Comme nous observons en moyenne ne augmentation de la fréquence, il faut bien, pour les terres cériques, trouver un ffet opposé plus important. Chaque fois que Z augmente d'une unité, un électron ıpplémentaire vient se placer dans la couche 4 *f*. L'augmentation progressive du ombre d'électrons dans cette couche va avoir pour effet d'augmenter l'effet d'écran t de créer un champ électrique négatif qui va refouler les doublets libres de l'oxygène ers le phosphore:

$$Me^{3+}—\overset{\diagdown}{\underset{\diagup}{O}}=P\overset{\diagup}{\underset{\diagdown}{<}} \rightarrow Me^{3+}—|O\overset{\cdots}{=}P\overset{\diagup}{\underset{\diagdown}{<}} \qquad (3)$$

Le cas du gadolinium est beaucoup plus complexe: essayons tout d'abord expliquer pourquoi le nombre de coordination diminue à ce niveau. Le rayon nique devenant de plus en plus petit, si nous supposons que le cation central est ıtouré de neuf atomes d'oxygène pour les terres cériques, ce nombre devient trop and à partir d'un certain moment et automatiquement une partie des atomes t refoulée hors de la sphère de coordination.

Il est intéressant de noter le parallélisme qui existe entre les complexes formés vec les nitrates de terres rares et le TBPO d'une part et le triisopropylphosphate autre part.

La modification du nombre de coordination du cation central, au niveau du ıdolinium peut s'expliquer qualitativement par l'action conjuguée des forces attraction qui sont du type purement électrostatique et des forces de répulsion ıi sont plutôt du type forces de Van der Waals.

La force d'attraction est due à la charge 3+ du cation central, charge qui tire tous les oxygènes voisins.

Les forces de répulsion, qu'elles soient dues aux interactions entre les doublets es neuf atomes d'oxygène qui entourent le métal, ou à l'encombrement stérique causé ar la grande dimension des chaînes butyles, augmentent beaucoup plus vite que s forces d'attraction lorsque la distance interatomique diminue. Nous devons par ınséquent nous attendre à ce que ce soit ces forces de répulsion qui régissent la ıodification du nombre de coordination. Nous avons dit précédemment que nous ıpposions que ce changement se faisait par le passage des ions nitrates bidentés aux itrates monodentés (2). Si, au lieu de neuf atomes d'oxygène autour du métal, il y en a plus que six, les forces de répulsion doivent diminuer et c'est l'attraction ectrostatique qui l'emporte.

La liaison métal–oxygène du TBPO se renforce au détriment de la liaison =O qui s'affaiblit. Si la liaison P=O s'affaiblit, sa fréquence de vibration doit iminuer. McRae et Karraker[11] constatent le même phénomène de répulsion avec triisopropylphosphate (T2PP) qui forme des complexes du type $Me(NO_3)_3 \cdot 3\,T2PP$ vec les terres cériques et des complexes du type $Me(NO_3)_3 \cdot 2\,T2PP \cdot H_2O$ avec les rres yttriques. La fréquence du P=O du T2PP est plus faible avec ce dernier complexe par suite de la diminution des forces de répulsion, la molécule d'eau étant plus etite que la molécule de T2PP[11].

Si nous comparons les résultats obtenus avec le tributylphosphate (TBP le T2PP[11] et le TBPO, nous constatons que le comportement du complexe gadolinium est différent dans les trois cas. Si nous examinons les résultats obter par Ferraro *et al.*[9] pour les complexes $Me(NO_3)_3 \cdot 3$ TBP, par McRae et Karrake pour $Me(NO_3)_3 \cdot 3$ T2PP et par nous-mêmes pour $Me(NO_3)_3 \cdot 3$ TBPO, nous cc statons que dans un graphique présentant la fréquence de vibration du P=O fonction de l'inverse du rayon ionique, *r*, la fréquence de vibration du P=O pas au niveau du gadolinium, par un maximum avec le TBP, se situe sur la dro joignant la fréquence du P=O pour le complexe du lanthane à celle du lutétiu avec le T2PP et passe par un minimum avec le TBPO. Les deux premiers auteurs constatent aucun changement au niveau des nitrates, contrairement à notre c Nous devons par conséquent admettre que non seulement la nature du cati central est primordiale, mais également la nature des substituants R dans les co posés du type R_3PO. Le TBPO étant un ligand beaucoup plus basique que deux autres, il doit se trouver beaucoup plus près du cation central et par cc séquent subir beaucoup plus fortement les effets d'encombrement autour de cation.

Si maintenant nous examinons ce qui se passe avec les terres yttriqu nous constatons que la fréquence du P=O recommence à augmenter lentement.

Théoriquement, d'après ce que nous avons dit précédemment à propos "back-bonding", nous devrions observer une constance de la fréquence. Puisq ce n'est pas le cas, c'est que le phénomène de répulsion dont nous venons parler agit fortement dans ce cas. Ceci nous paraît tout à fait normal vu que ions métalliques deviennent très petits. La répulsion devient telle que, à partir thulium, nous observons le même phénomène que McRae et Karraker[11], à sav le remplacement de la grosse molécule de TBPO par la petite molécule d'eau si abandonne le complexe à l'air. Ce départ de la molécule de TBPO se fait progressiv ment lorsqu'on passe du terbium à l'ytterbium. Le TBPO s'écartant de plus en pl du cation central, la fréquence de vibration du P=O associé tend vers celle du P= libre.

CONCLUSIONS

Les complexes formés entre les nitrates de terres rares et l'oxyde de tri-butylphosphine ont été étudiés par spectrométrie infra-rouge. Le TBPO est fi au métal par l'intermédiaire de l'oxygène. Les groupements nitrates sont éga ment coordonnés. A cause de la contraction lanthanique, nous observons u modification importante dans le mode de liaison des nitrates. Ils sont bident pour les complexes des terres légères et monodentés pour les lourdes. Ceci se marq par un dédoublement des raies caractéristiques des groupements nitrates et p la fréquence particulière du P=O dans le complexe du gadolinium. De plus, il exis au sein de la molécule de complexe, une série de forces d'attraction et de répulsic forces qui jouent un rôle très important dans les complexes des terres yttriques p suite de la petite dimension du cation central.

Nous remercions l'Institut pour l'Encouragement de la Recherche Scientifiq dans l'Industrie et l'Agriculture pour l'octroi de la bourse de recherche qu'il no a accordée et grâce à laquelle nous avons pu réaliser ce travail.

UMÉ

L'oxyde de tri-*n*-butylphosphine (TBPO) réagit avec les nitrates de terres s pour former des complexes de formule générale $Me(NO_3)_3 \cdot 3$ TBPO. Ces mplexes ont été étudiés par spectrométrie infra-rouge. Le mode de coordination nitrates n'est pas le même au long de la série lanthanique. Ils sont bidentés pour terres rares légères et monodentés pour les terres lourdes. La fréquence de ation du P=O n'augmente pas de façon monotone lorsque *Z* augmente, mais a une cassure au niveau du gadolinium. Ce fait est expliqué par une influence 'back-bonding", par la diminution du rayon ionique et par la valeur du nombre coordination.

MARY

Tri-*n*-butylphosphine oxide (TBPO) reacts with rare earth nitrates to form mplexes of general formula $Me(NO_3)_3 \cdot 3$ TBPO. These complexes were studied infrared spectrometry. The coordination of the nitrates is not the same along lanthanide series. They are bidentate for the light rare earths and monodentate the heavy earths. The P=O frequency does not vary monotonously when *Z* eases; there is a break for gadolinium. This is explained by an influence of back-ding, the decrease of the ionic radius and the coordination number.

SAMMENFASSUNG

Tributylphosphinoxyd reagiert mit den Nitraten von Seltenen Erden, um mplexe von allgemeiner Formel $Me(NO_3)_3 \cdot 3$ TBPO zu bilden. Diese Komplexe l durch Infrarotspektrometrie studiert worden. Die Koordination der Nitrate ist mt diesselbe für alle Seltenen Erde. Sie sind für die leichten Seltenen Erde durch i Sauerstoffe und für die schweren Seltenen Erde durch einen Sauerstoff fest-unden. P=O Schwingungsfrequénz variiert nicht auf einförmige Weise, wenn Z immt, aber es gibt eine Brechung für Gadolinium. Diese Tatsache erklärt sich ch einen Einfluss der "Zurück-Bindung", durch das Verkleinern des ionischen bmessers, und durch die Koordinationszahl.

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N IMPROVED SPECTROPHOTOMETRIC DETERMINATION OF IIOBIUM WITH THIOCYANATE

PPLICATION TO FERROUS ALLOYS

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The determination of the earth acids, niobium and tantalum, is attended y serious difficulties. These elements lose their individual character when they re found together or in combination with elements such as titanium and zirconium[1]. his is invariably the case when dealing with minerals such as columbite and yrochlore. The principal cause of difficulty appears to be the formation of hetero-olyacid systems of variable composition and properties. The polyacids which con-ain niobium and tantalum appear to be too stable or inert to be broken down by ost analytical reagents. Thus, if a precipitate or a color is to be formed by niobium, ntalum and certain other elements are carried along in the analysis and these in-uence the result.

The use of thiocyanate for the determination of niobium in natural and anufactured products has been termed recently a "classical" photometric method[2]. fter the initial use by Russian workers[3–6] of thiocyanate and tin(II) chloride for ie determination of niobium, Freund and Levitt[7], Hume *et al.*[8], and Bacon and filner[9] studied critically the conditions under which a determination should be ade. These authors showed that tantalum causes a reduction in the color produced y niobium even though it itself contributes slightly to the absorbance of the sample.

It has not been possible hitherto to apply the thiocyanate method to samples ontaining fluoride owing to a reduction in the absorbance caused by this ion. This as been a disadvantage because the most favored method of isolating niobium om interfering elements involves ion exchange applied to a solution containing ydrofluoric acid[10]. In the present paper, a procedure which greatly reduces the fect of tantalum on the niobium absorbance is reported. This entails a preliminary eatment with hydrofluoric acid with the subsequent addition of aluminium ion. he proposed method may be applied readily to fluoride-containing solutions. This ould be of advantage when large quantities of tantalum or other interfering ele-ents are separated by the ion-exchange method.

XPERIMENTAL

eagents and materials

Various stock solutions of niobium and tantalum were employed depending n the nature of the experiment. Fluoride-free solutions were prepared by treating ie pentoxides of 99.5% purity (Research Inorganic/Organic Chemical Co.) with

an excess of molten potassium pyrosulfate and dissolving the melt in 1 *M* tarta acid. Stock solutions containing 700 mg Nb l^{-1} and 164 mg Ta l^{-1}, respective were diluted with 1 *M* tartaric acid as required. A solution of niobium in 1.1 hydrofluoric acid was prepared by dissolving the oxide or the metal (99.95% purit Research Inorganic/Organic Chemical Co.) in the concentrated acid, then adjusti the acidity, and diluting with water. A solution of tantalum was prepared by d solving tantalum sheet (99.99% purity; Research Inorganic/Organic Chemical C and adjusting the final concentration of hydrofluoric acid to 1.1 *M*. These fluoric containing stock solutions of niobium and tantalum contained 2.03 g l^{-1} a 8.66 g l^{-1}, respectively.

Solutions containing 15 wt.% of tin(II) chloride were prepared by dissolvi the anhydrous salt in concentrated hydrochloric acid and diluting to give a soluti that was 4 *M* in hydrochloric acid. For use in the final procedure, aluminium sulfa was also added to this solution to make it 0.1 *M* in $Al_2(SO_4)_3$. The 20 wt potassium thiocyanate solution was prepared fresh every two weeks.

A solution which was 1 *M* in tartaric acid and 9 *M* in hydrochloric acid w used to adjust the final hydrogen ion concentration to 4.0 *M*. Peroxide-free dieth ether was used for extraction of the coloured species.

Basic procedure

The extraction of the coloured niobium complex into ether has the advanta that the colour due to certain other ions, *e.g.*, Ni^{2+}, Cr^{3+}, remains in the aqueo phase and so does not interfere. This is useful in the analysis of steel. The concentr tions of added reagents were the same as recommended previously[8] but certa modifications of procedure were introduced and these are discussed below. T following procedure was ultimately adopted.

Samples of niobium which contain interfering elements such as tantalu should be prepared by heating in the presence of 20–40% hydrofluoric acid a stored at a hydrofluoric acid concentration not less than 0.1 *M* and a tartaric ac concentration of 1.0 *M*. At the commencement of the determination, and no soon an aliquot is taken of a size such that, upon dilution, the concentration of hydr fluoric acid in the colour development step is about 0.01 *M*. In addition, t aliquot ideally should contain 10–60 μg of niobium. This is placed in a sm separatory funnel to which previously 6 ml of tin(II) chloride–aluminium sulfa solution have been added. Next are added in order, 10 ml of hydrochloric aci tartaric acid solution and 10 ml of potassium thiocyanate solution. The solution finally brought to a fixed volume by the addition of 4 *M* hydrochloric acid wh necessary; 28 ml was normally used in the present study, *i.e.*, a 2-ml sample aliqu was taken and the final addition of 4 *M* hydrochloric acid was dispensed wi Within 5 min, a precisely measured 10.0-ml portion of peroxide-free ether w added and the yellow complex was extracted. The aqueous phase was allowed run into a second separatory funnel where it was extracted with a second 10- portion of ether. The ether extracts were transferred to a glass-stoppered 25- volumetric flask and made up nearly to the mark. After 1 h the volume was ma up to 25 ml and the absorbance was determined at 385 nm in a 1-cm cell. Bo a Beckman Model DU and a Bausch and Lomb Spectronic 20 were used in t present study.

SULTS AND DISCUSSION

uilibria in the colour formation reaction

Previous work has demonstrated that the intensity of colour formed depends the concentration of reagents added to the aqueous sample[8]. In the work scribed here, the absorbance of a sample depended also upon the ratio of ether aqueous volumes, the colour intensity increasing with a decrease in this ratio. As e effect (Table I) was very pronounced, it was important to determine whether e volume ratio after making up the ether phase to a fixed volume in a volumetric sk was alone significant or whether the ratio of volumes used during extraction is also important. It was found that the volume ratio during extraction was indeed tical and that the subsequent dilution of the ether phase in making up to a fixed lume was significant only in the way prescribed by Beer's law. This observation ggests that the coloured thiocyanatoniobium complex is incompletely formed the aqueous phase and that the equilibrium involved in its formation is important both the aqueous and the ether phases. Apparently, a small ether-to-aqueous lume ratio favors extraction not only of the coloured species but also the other rticipants in the reaction such as thiocyanic and chloroniobic acids. It is well cognized that niobium, which forms the compound $H[Nb(OH)_2Cl_4]$ in 10 *M* drochloric acid, is extractable into ether[11].

BLE I

FECTS OF RATIO OF ETHER TO AQUEOUS VOLUMES

lume of aqueous se (ml)[a]	*Volume of first ether extract (ml)*[b]	*Absorbance*[c]
	10	0.508
	20	0.367
	40	0.144
	10	0.303

ne quantities of reagents added to the 14-ml sample were one half those given in the Basic procedure.
n all cases, two extractions were made with a final ether volume of 50 ml.
ne quantity of Nb taken was 81 μg.

ecision and accuracy

As the volume of ether used in extraction was critical, the ether was delivered m a burette directly into the separatory funnel. Failure to measure the ether volume within 0.1 ml resulted in a significant reduction in precision. It was found visable to perform the determination in a room the temperature of which was ntrolled. High room temperatures can lead to erratic results. This may be due to poration of ether, but it has been noted that the polymerization of thiocyanate avoured at higher temperatures and the polymer absorbs at 385 nm.

The reproducibility of the procedure as applied to aliquots of the fluoride-ntaining stock solutions was determined by examining the results of nine analyses samples containing 40.6 μg of niobium. The standard deviation was 2.6%. Six weeks er, a further nine determinations were done on the same stock solution but with

fresh reagents. The mean value of the absorbance in these determinations was 0. higher than in the first set and the standard deviation was 2.4%. The precision co pares favorably with that obtained by Hume *et al.*[8] who reported a stand deviation of 2.9%.

Aluminium salt had to be included whenever the samples contained fluor ion. This caused a small decrease in sensitivity but did not affect the reproducibil

The determination of niobium in the presence of tantalum was examined a similar way. Fluoride-free aliquots containing 340 μg of tantalum were mi with 28-μg aliquots of niobium. The reproducibility of colour development w these solutions was very poor and depended on the time between mixing of aliquots and the colour formation. Moreover, the results were quite low, as cussed in the next section. However, when the fluoride-containing stock soluti were employed, the standard deviation amongst twenty-two 40.6-μg samples niobium containing 480 μg of tantalum was 0.012 or 2.0%. The accuracy of such de minations is discussed below.

Effect of tantalum on the accuracy

The chemical behaviour of tantalum is similar to that of niobium in m respects, so that it is to be expected that tantalum will be carried along with niobi in most of the reactions of analytical importance. Analytical separation of the t elements is usually very difficult or incomplete. Precipitation with tannin[12] i lengthy and tedious operation. Solvent extraction gave poor results in this laborat and in the hands of others also[13]. Ion exchange of hydrofluoric acid contain solutions[10] appears to be the only fully reliable technique which can be appl generally to analytical samples.

The thiocyanate method for niobium, modified by the inclusion of tartr has been applied to samples containing considerable tantalum[7,8]. In our har however, satisfactory results were obtained only if the samples had been prepa freshly by mixing aliquots of niobium with aliquots of tantalum. A solution prepa by mixing an aliquot containing 340 μg of tantalum with one containing 28 μg niobium gave a result which was low by 14% when analyzed after the solution l been allowed to age for 0.5 h. The solution had remained clear so that the effect not due to the formation of a hydrolytic precipitate.

In an actual analysis, the sample would presumably have the properties of aged mixture and could be expected to yield a low result. Tantalum, and to a les extent niobium, is prone to form a polyacid in solution. Nelson and Tobias[14] h identified one such polyacid anion as $Ta_6O_{19}^{8-}$. Upon aging of a mixed niobi and tantalum solution, the dissolved species are presumably converted to heterop acids in which the niobium and tantalum are distributed in a statistical way. Bridg of the metal atoms probably occurs by means of oxo groups. The effect is appare less severe or less rapid in the presence of tartrate[7,8] and the present study shown that fluoride ion can eliminate it entirely.

The effect of tantalum, in the manner outlined above, is to lower the spec absorbance of the thiocyanate–niobium complex. The function of the alumini ion appears to be two-fold. It serves to bind the fluoride ion as described below it possibly enters into the niobium–tantalum heteropoly system as well. In this la function, it appears to swamp the effect of tantalum because it is present in suc

e amount. This conclusion is based on the fact that the absorbance due to bium is somewhat reduced in the presence of aluminium salt and that interference to tantalum is less quenched when the concentration of aluminium ion is too

The choice of 0.1 *M* for the concentration of aluminium sulfate in the stock gent solution was empirical, being that concentration which resulted in the t interference from 475 μg or less of tantalum. When the concentration of minium sulfate was increased to 0.25 *M*, there was a positive error of *ca.* 0.04 orbance units caused by 475 μg of tantalum. This error is the result of the intrinsic orbance of the thiocyanate–tantalum complex. The error did not increase with easing tantalum concentration; rather it was a maximum at a weight ratio of talum to niobium of about 8 : 1, decreasing slowly to zero at a ratio of 30 : 1.

It is evident that there is a compensation of errors at work. It is important to ne conditions within which the compensation may be relied upon. The choice 0.1 *M* for the concentration of aluminium sulfate in the stock solution makes ossible to keep the error small up to a tantalum content of *ca.* 500 μg and where weight ratio of tantalum to niobium does not exceed 25:1. Table II shows orbance data obtained within these conditions.

LE II

ECT OF NIOBIUM : TANTALUM RATIO

bium n)	*Tantalum taken (μg)*	*Absorbance*	*% Mean error*
	0	0.648	—
	238	0.664	+2.5
	475	0.639	−1.3
	0	0.266	—
	475	0.274	+3.0

uence of other elements

Interference by other elements is reported to be less for the ether extraction hod than for the "homogeneous" method[7]. Of particular concern in the analysis errous alloys are Mo, W, V, Ti and Fe, all of which produce an enhancement of absorbance. Fortunately, these elements, with the exception of iron, do not mally occur in high concentrations in niobium-stabilized steels which may con- up to *ca.* 2% niobium.

Nickel and chromium are the principal alloying constituents in stainless steel. as verified that these elements do not interfere in amounts up to 150 times the ght of niobium taken. Large amounts of uranium gave rise to a yellow colour this was not extracted into ether. Interference from iron was slight and entirely ligible if the sample to be analysed was ferroniobium. The inclusion of 4 mg of n(II) in the form of the sulfate caused an increase in the blank absorbance of .2. A similar increase occurred when the same quantity of iron(II) was added a 40-μg niobium sample. Such a quantity of iron would be encountered in the

analysis of a niobium-stabilized stainless steel and could lead to an error of up +2%. This is a large improvement over the error encountered in the procedure Bacon and Milner[9] and makes it possible to determine niobium in certain al steels without prior separation.

Analysis of ferroniobium and stainless steel

The procedure was applied to the British Chemical Standards ferroniobi No. 362 and austenitic stainless steel, No. 337. The methods of sample preparat were as follows.

Ferroniobium. A sample of ferroniobium weighing about 150 mg was pla in a Teflon beaker and 5 ml of concentrated hydrofluoric acid, 4 ml of concentra hydrochloric acid and a few drops of nitric acid were added. The mixture v heated gently and nitric acid was added from time to time as required. Dissolut was complete in about 1 h. To the cool solution, 25 ml of concentrated hydroflu acid were added and the volume was made up to 250 ml with 1 *M* tartaric acid. A 5 aliquot of this solution was diluted to 100 ml with 1 *M* tartaric acid. An aliquot (2 of this solution was used for the determination following the Basic procedure.

Stainless steel. A sample of steel weighing about 200 mg was placed i Teflon beaker and a solution consisting of 0.5 ml of concentrated hydroflu acid, 5 ml of concentrated hydrochloric acid and 1 ml of concentrated nitric a was added. The mixture was heated gently and further nitric acid was adde dissolution was not complete in about 0.5 h. The volume of the cooled solution v made up to 100 ml with 1 *M* tartaric acid and a 2-ml aliquot of this solution v used for the determination following the Basic Procedure.

TABLE III

DETERMINATION OF NIOBIUM IN STANDARD FERRONIOBIUM AND STAINLESS STEEL

Sample	*Niobium found (%)*
B.C.S. 362[a]	62.(5) 62.(0) 62.(5)
B.C.S. 337[b]	1.02 1.03 1.03 1.04 1.04

[a] The certified value was 62.7%. The values found have been rounded off to the nearest 0.5%.
[b] The certified value was 1.02±0.02%.

The results of determinations carried out in the way described are given Table III. A blank determination was carried out on a 2-ml aliquot of 1 *M* tart acid. A good-quality tartaric acid gave a blank absorbance of 0.003. All of analyses were quite satisfactory. The average of the results for the steel sam was about 1% high. A slightly high result is to be expected owing to the influenc the iron. Upon subtracting the absorbance corresponding to the iron conten each sample as determined by means of an iron blank, the following correc percentages of niobium were obtained: 1.01, 1.02, 1.01, 1.03, 1.02. The mean va is in exact agreement with the certified value and the precision is very good should be borne in mind that such accuracy is possible only for steels which relatively free of interfering elements.

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IMARY

The selectivity of the spectrophotometric determination of niobium with cyanate has been improved by treating the sample with hydrofluoric acid and equently adding aluminium ion. The procedure can be used in the presence latively large quantities of tantalum and iron. Accurate and rapid analyses of niobium and niobium-stabilized stainless steel were carried out without the ssity of a prior separation of niobium.

JMÉ

La sélectivité du dosage spectrophotométrique du niobium, au moyen de cyanate, peut être améliorée par traitement de l'échantillon à l'acide fluorhydri- et addition d'aluminium. Cette méthode peut être utilisée en présence de quan- relativement grandes de tantale et de fer. Elle permet une analyse exacte et de de ferroniobium et d'acier inox au niobium, sans qu'il soit nécessaire de éder à une séparation préalable du niobium.

AMMENFASSUNG

Die Selektivität der spektrophotometrischen Bestimmung von Niob mit cyanat wurde verbessert, indem die Probe mit Fluorwasserstoffsäure behan- und anschliessend mit Aluminiumionen versetzt wurde. Das Verfahren kann iegenwart relativ grosser Mengen von Tantal und Eisen angewendet werden. Analyse von Ferroniob und niob-stabilisiertem Edelstahl konnte genau und ell ausgeführt werden, ohne dass das Niob vorher abgetrennt werden musste.

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?ECTROPHOTOMETRIC DETERMINATION OF MICROGRAM MOUNTS OF AMINO ACIDS WITH CHLORANIL

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Charge-transfer complexes formed between molecules usually have charac-ristic spectra and high molar absorptivities[1]. Recently, these attributes have been ilized for the spectrophotometric determination of sulphur dioxide[2], nitrate ions[3] ıd oxygen[4], by complexing with *o*-xylene, with toluene (by nitrotoluene formed ' reaction with nitrate ions) and with N,N-dimethylaniline, respectively. All ese methods are highly selective, rapid and, apart from that for oxygen, sensitive. rks and Slifkin[5,6] have reported that some amino acids form n–π charge-ınsfer complexes with chloranil (2,3,5,6-tetrachloroquinone) in aqueous 50% hanol buffered at certain pH values. As a result of complex formation, the loranil absorbance ($\lambda_{max} = 295$ nm) decreases and a new band ($\lambda_{max} \approx 350$ nm) ows, which is attributed to the molecular complex. Chloranil complexes with ıino acids are quite strong compared to many other molecular complexes. The ıparent stability constant with glycine[5], for example, is *ca.* 200 at pH 8. The esent paper describes the use of chloranil for the spectrophotometric deter-ination of microgram amounts of various amino acids in aqueous solution.

:PERIMENTAL

?agents

Chloranil was used as a saturated ethanolic solution

Borate buffer solution, pH 9. A $5 \cdot 10^{-2}$ *M* sodium borate solution was used.

Amino acid standard solutions. Aqueous 100 p.p.m. solutions were prepared. little ethanol was added for those acids which were difficultly soluble in water.

ocedure for determination of a typical amino acid

Calibration. To a series of 10-ml graduated flasks add exactly 0.0, 0.2, 0.4,), 0.8 and 1.0 ml of the 100 p.p.m. amino acid solution, followed by exactly ml each of the chloranil and borate buffer solutions. Make up to volume with ıter, and place in a water bath at $65 \pm 1°$ for the time required for maximal lour development (Table I), or other suitable time. Measure the absorbance of : solution at 350 nm in 1-cm cells against a solution of reagents containing no ıino acid as a blank.

ıknown amino acid concentrations

Take an appropriate volume (less than 6 ml) of nearly neutral amino id solution through the above procedure.

TABLE I

Amino acid	*Maximal apparent molar absorptivity at 350 nm*	*Time for maximal reaction (min)*	*Apparent molar absorptivity at time*		
			0 min	*5 min*	*10 min*
Glycine	6,200	15	2,000	5,700	
Alanine	17,000	35	3,300	7,300	12,400
Valine	20,500	15	3,800	15,600	18,100
Leucine	21,000	25	3,200	13,700	17,900
iso-Leucine	20,500	25	2,100	17,400	19,200
nor-Leucine	17,600	35	2,400	9,500	14,500
Phenylalanine	18,000	15	6,300	10,300	14,300
Serine	15,700	35	1,060	8,500	13,700
Threonine	12,100	25	1,190	6,200	11,200
Lycine	28,100	10	12,000	26,800	28,100
Arginine	18,700	25	2,600	11,500	16,000
Aspartic acid	5,600	40	270	1,300	2,700
Glutamic acid	11,500	50	1,030	4,100	6,300
Cystine	18,300	40	2,200	8,300	12,200
Cysteine	5,500	35	2,300	2,900	4,000
Methionine	15,500	35	1,800	5,700	10,100
Tyrosine	16,000	45	1,800	6,700	10,400
Proline	11,200[a]	15		10,200	11,100
Hydroxyproline	8,700[b]	15		7,100	8,400
Tryptophan	15,500	45	2,000	6,300	11,000
Histidine	11,600	40	780	4,400	7,700
2-Amino-n-butyric acid	15,800	40	625	5,400	10,000
Ornithine	25,600	25	3,400	17,500	23,700
NH_4Cl	650	15	135	350	590
Tyrosinase		20			

[a] 13,300 at 362 nm. [b] 9200 at 362 nm.

RESULTS

Selection of optimal conditions-

Preliminary experiments with chloranil and $5 \cdot 10^{-3}$ *M* glycine showed t the expected spectral shift occurred only in alkaline solutions; chloranil in (1- aqueous ethanol solutions of sodium acetate at an apparent pH of 5 gave spectral change at room temperature, nor did similar Britton–Robinson or Micha phosphate buffer solutions of pH 5 or 7, on addition of glycine. Micha phosphate buffer solution, pH 8, gave some complex formation but a Britt Robinson buffer, pH 11, gave much greater absorbance, at *ca.* 360 nm. In last solution, however, chloranil is unstable and becomes less sensitive towa amino acids with time. Borate buffer, pH 9, also gave high sensitivity, and decomposition of chloranil, but the stability of the chloranil solution remai inadequate. In all further experiments, therefore, the chloranil was dissolved ethanol, in which it was stable, and mixed with the amino acid and pH borate buffer solution at the beginning of each run.

The absorbance of the glycine complex increased considerably with

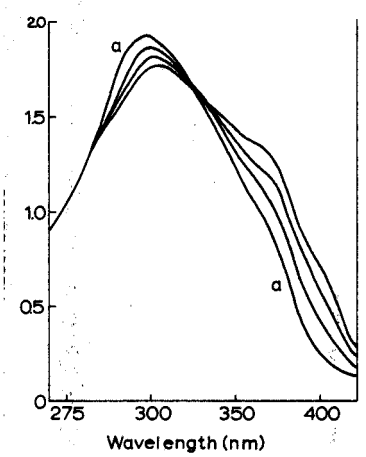
reasing chloranil concentration. A final chloranil concentration of $1 \cdot 10^{-3}$ *M* was ound to give maximal sensitivity with $1.3 \cdot 10^{-4}$ *M* (10 p.p.m.) glycine, and was sed in all subsequent experiments. It should be appreciated that this relatively arge concentration of chloranil itself gives rise to a significant absorbance at 50 nm and lower wavelengths. Thus a double-beam spectrophotometer or a ingle-beam instrument with extensive backing off facilities is necessary to eliminate he effect of this large background absorbance. In the double-beam instrument sed, this results in the spectra having plateaux at wavelengths below 350 nm, /hen the energy falling on the detector drops below the response limit.

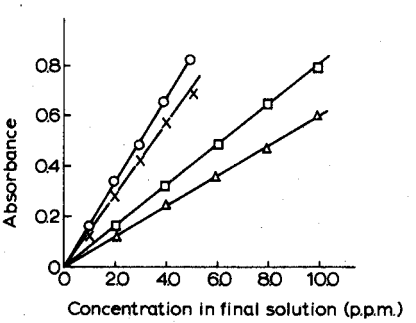
Unlike most molecular complexes, amino acid–chloranil complexes form lowly. Although there is significant immediate complex formation, an extended eriod is required for maximal development of the 350-nm absorbance peak Fig. 1). Reaction rates increased markedly when the solutions were heated, and temperature of 65° was selected for subsequent experiments. This achieves a easonable reaction rate without causing noticeable evaporation of ethanol.

leaction of different amino acids

Twenty-four amino acids were tested for reactions with chloranil in (1+1) queous ethanol, at an apparent pH of 9.0 in borate buffer, at 65°. All but ,4-dihydroxyphenylalanine formed complexes. The absorbance maximum of the omplex was at 350 nm in all cases, apart from proline and hydroxyproline, /hich gave peaks at 362 nm. This accords with previous studies of a very estricted selection of amino acids[5].

The rate of reaction differed significantly for the various amino acids. 'or 10 p.p.m. of amino acid, the time required to develop maximal absorbance t 350 nm by reaction at 65° ranged from 10 min for lysine to 50 min for lutamic acid. The change in apparent molar absorptivity with time for all the





ig. 1. Spectrum of a solution $4.0 \cdot 10^{-4}$ *M* in glycine and $5.0 \cdot 10^{-4}$ *M* in chloranil in pH 7.0 iosphate buffer at room temperature, on mixing (*a*) and at 10 min intervals thereafter.

ig. 2. Calibration graphs for glycine (○), serine (×), lycine monohydrochloride (□), and cystine △).

amino acids is given in Table I. The maximal apparent molar absorptivi differs markedly for the various amino acids (Table I), ranging from 28,1(for lycine to 4,000 for cysteine. Therefore separate calibration graphs for ea amino acid will be necessary.

In addition to the amino acids, three other compounds were investigat for reaction with chloranil (Table I). Ammonium chloride reacted weakl Tyrosinase, chosen as an example of a protein, gave a similar spectral peak the amino acids, as has been observed with other proteins[5,6]. A solution co taining 42 p.p.m. of tyrosinase gave a maximal absorbance of 0.46 when su jected to the recommended procedure. Urea gave no response, as would l expected from its electronic structure. Amines react with chloranil in the san way as amino acids[5], and no doubt could be determined in a similar way the amino acids.

When the recommended procedure is used, and sufficient time allow for maximal development of the spectral peak, all the amino acids give rectiline calibration graphs, up to absorbances of at least 0.8 (the maximum studied Four typical examples are shown in Fig. 2. The coefficients of variation were the range normally expected for spectrophotometric measurements; a value 2.5% was obtained for 5 determinations of 10 p.p.m. of cysteine. The sensitivi of the method is high for many of the amino acids, and all except 3,4-dihydrox phenylalanine can be determined without difficulty in the p.p.m. range.

DISCUSSION

The method described provides a sensitive and reproducible means of dete mining amino acids. The nature of the reaction, however, is not clearly unde stood; in particular the reason for the unusual slow formation of the compl is not known. It is possible that chloranil is converted to another produc which is the real complexing agent. In this respect, it is interesting to obser that a chloranil solution in ethanol is yellow, but it slowly becomes purp when added to the pH 9.0 buffer solution. The nature of the purple compone has not been established with certainty, but it has been suggested that it mig be trichlorohydroxyquinone[7]. It is not chloranilic acid[7]. As the purple colo develops equally in the blank and test solution, it has no effect on the amir acid determinations. If the active complexing agent is trichlorohydroxyquinon the reaction time for maximal absorbance production would be expected to l the same regardless of the amino acid. This was found not to be the cas Perhaps the amino acid exerts a catalytic effect on the hydrolysis of chloran as a result of complex formation.

The proposed method compares favourably in many respects with oth spectrophotometric methods for the determination of amino acids. It appea to be more sensitive than the ninhydrin method[8-10], and appreciably mo sensitive than methods based on *o*-diacetylbenzene[11], 3,5-dibromosalicylaldehyde[1 peri-naphthindan-2,3,4-trione hydrate[13] and sodium 2-naphthoquinone-4-su phonate[10]. It also has the advantage that all but one of the "natural" amir and imino acids can be determined, with no interference from urea, and on a weak response from ammonium ions. The reagents used are readily availabl

l the procedure is simple to carry out. An extended reaction time is often essary to achieve maximal sensitivity, but Table I shows that absorbance asurements after a few minutes are quite possible, although this would result a 30–70% reduction in sensitivity. Such a procedure would be well suited to omated analytical procedure, however.

The authors thank Professor R. Belcher for his interest and encouragement. F.A.-S. thanks the University of Riyadh, Saudi Arabia, for financial support.

MMARY

Amino acids form molecular complexes with chloranil at pH 9.0 having parent molar absorptivities at 350 nm ranging from 4,000 to 28,000. A spectrophotometric method for the determination of μg amounts of amino acids is cribed, based on such complex formation. There is no interference from urea l only a weak interference from ammonium ions.

SUMÉ

Les acides aminés forment des complexes moléculaires avec le chloranile, pH 9.0, avec des coefficients d'absorption molaires à 350 nm allant de 4,000 28,000. Une méthode spectrophotométrique, basée sur la formation de ces nplexes, est décrite pour le dosage des acides aminés, en quantité de l'ordre μg. On n'observe pas d'interférence avec l'urée; seuls les ions ammonium erfèrent légèrement.

SAMMENFASSUNG

Aminosäuren bilden mit Chloranil bei pH 9.0 Molekülkomplexe, deren einbare molare Extinktionskoeffizienten bei 350 nm im Bereich 4,000 bis 28,000 gen. Für die Bestimmung von Aminosäuren in μg-Mengen wird eine spektrophotometrische Methode beschrieben, die auf einer solchen Komplexbildung beruht. rnstoff stört nicht, und von Ammoniumionen wird nur eine schwache Störung ursacht.

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HE CHLOROFORM EXTRACTION OF NICKEL WITH OXINE FROM ERCHLORATE AND SULFATE SOLUTIONS

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eceived 12th January 1973)

In a previous paper[1], it was confirmed that zinc is extracted with oxine -hydroxyquinoline; HOx) into chloroform from perchlorate solutions as a binuclear mplex, $Zn_2(Ox)_3(HOx)_3ClO_4$, but extracted from neither nitrate nor chloride lutions. Though this type of extractable metal–oxine complex had not been oposed before, the authors were convinced that some other metals should be tracted in a similar manner. The work described below shows that nickel can be tracted in this way from perchlorate solutions at low pH values, whereas a fferent species is extracted from perchlorate solutions at high pH or from sulfate lutions.

:PERIMENTAL

aterials and apparatus

All the materials and apparatus used were essentially the same as described eviously[1], except that radio-tracer was not used.

:traction of nickel

The extraction procedure was essentially as previously described[1]. Minor)difications were as follows. Nickel was also extracted either from sulfate solution from a mixed solution of perchlorate and sulfate with an ionic strength of 0.1 less otherwise stated. A small amount of phosphate was used (10^{-3} *M*) at I 6–8 to buffer the aqueous phase. The aqueous phase at equilibrium was nsferred to another glass tube, and acidified to about 0.1 *M* with hydrochloric id; nickel was then determined by atomic absorption spectrometry at 232.0 nm. e organic concentration of nickel was calculated as the difference between : initial aqueous concentration and the final one.

)lation of nickel–oxine complexes

The organic extracts from the perchlorate solutions were prepared, and the :kel–oxine complexes were isolated essentially as previously described[1]. The)lation from the sulfate solution was also carried out with 0.1 *M* nickel sulfate d 1 *M* sodium sulfate solutions instead of the respective perchlorate solutions.)out 50% of the nickel was obtained as nickel–oxine complexes in all cases. The)lated complexes from the perchlorate solutions were pale green at pH 3.80 and :enish yellow at pH 9.20, and the one from the sulfate solution was yellowish :en irrespective of pH.

Analysis of isolated nickel–oxine complexes

The isolated nickel–oxine complexes from the perchlorate solutions we analyzed for nickel, perchlorate and oxine as previously described[1]. The compl isolated from the sulfate solution (200 mg) was dissolved in 10 ml of 4 hydrochloric acid, diluted to 100 ml with water and analyzed for nickel, oxine ai sulfate. Sulfate was tested semi-quantitatively by adding a barium chloride solutio

Analysis of nickel–oxine complexes in organic extracts

A portion (10 ml) of the organic extract from perchlorate solution wa shaken with an equal volume of 0.03 *M* sulfuric acid for 20 min. The extrac from the sulfate solution was treated with 0.1 *M* hydrochloric acid. Each back extract was transferred to a suitable volumetric flask and diluted to an appropriat concentration with water. Nickel was determined by atomic absorption spectrometr Then to an aliquot of the back-extract by sulfuric acid were added 1 ml of 0.0 *M* EDTA, 0.1 *M* sodium hydroxide and a phosphate buffer solution to adjust th pH about 6. After most of the oxine had been removed by pre-extraction wit monochlorobenzene, perchlorate was determined by the method of Uchikawa Sulfate in the back-extract by hydrochloric acid was tested as described above.

RESULTS

Absorption spectra of extracted nickel–oxine complexes

Figure 1 shows the absorbance (400 nm) of the extracted nickel–oxin complexes from the perchlorate and the sulfate solutions as a function of pH where C and C° are the initial aqueous and organic concentrations of the specie shown by the subscripts, respectively. Charges are omitted for simplicity. Th absorbance by excess of oxine was negligible at 400 nm. The absorbance–pl curves of the perchlorate system differ significantly from those of the sulfat system, showing the important roles of the inorganic anions which have bee regarded as inert.

For $C^{\circ}_{HOx} = 0.1$ *M* and $C_{ClO_4} = 0.1$ *M*, the absorbance–pH curve rises at abou

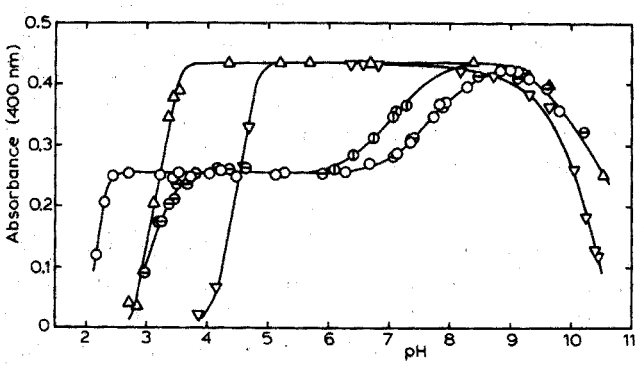
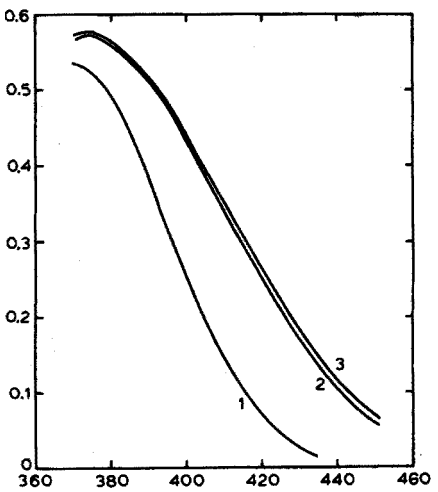


Fig. 1. Absorbance of nickel–oxine complexes in the organic extracts as a function of pH. C_t $1.00 \cdot 10^{-4}$ *M*. Perchlorate system: C°_{HOx}, (○), (◐) 0.1 *M*, (⊖) 0.01 *M*; C_{ClO_4}, (○), (⊖) 0.1 *M* (◐) 0.02 *M* (sodium sulfate was used to adjust ionic strength to 0.1). Sulfate system: C°_{HOx}, (△) 0.1 *M*, (▽) 0.01 *M*; C_{SO_4}, 0.1 *M*.

H 2, reaches a contant value at pH 2.6–6.0, increases again as far as pH 9 and ıen decreases. Since nickel was found to be completely extracted throughout the H region 2.6–9.0, the increase at pH 6–9 must be due to a change in the ıtractable nickel–oxine complex. The rising part of the absorbance–pH curve for $C^{\circ}_{HOx} = 0.01$ *M* and $C_{ClO_4} = 0.1$ *M* is located at higher pH than that for $C^{\circ}_{HOx} = 0.1$ *M* ıd $C_{ClO_4} = 0.1$ *M*, and they are not parallel to each other. However, the experimental ɔints for both cases fall on the same curve above pH 3.8; this suggests that at the ıwer pH where the absorbance–pH curves rise, the extracted nickel species depended ı the oxine concentration, whereas at the higher pH, this species was independent of ıe oxine concentration. The rising parts of the absorbance–pH curves at pH 6–9 tered only when the perchlorate concentration was changed.

The absorbance–pH curves for the sulfate system are quite ordinary. The H regions for maximal absorbance agreed with those for complete extraction. ;owever, a pH change of 1.3 is caused by a change of oxine concentration from 01 *M* to 0.1 *M*, which suggests rather complicated extraction stoichiometries.

The absorption spectra of the nickel–oxine complexes extracted with 0.1 *M* xine in chloroform are given in Fig. 2. The absorption maxima appear at about 70 nm, but could not be clearly observed because of the large absorbance of free xine. The absorption spectrum for the perchlorate system at high pH (pH 9.19) grees with that for the sulfate system, but not with that for the perchlorate system t low pH (pH 5.23).



g. 2. Absorption spectra of nickel–oxine complexes in the organic extracts measured against reagent ınk. The extracts from the perchlorate solutions at (1) pH 5.23, (2) pH 9.19 and from the lfate solution at (3) pH 5.55. C°_{HOx}, 0.1 *M*; C_{Ni}, $1.00 \cdot 10^{-4}$ *M*.

nalysis of nickel–oxine complexes

The results of the determination of the molar ratio of perchlorate to nickel r the extracts from the perchlorate solutions are given in Table I. The molar ıtio for the acid extracts (pH < 6) was 1:2, which is the same result as for zinc[1]. owever, perchlorate was not bound to nickel at pH 9. No sulfate was detected ı the extracts from sulfate solution.

TABLE I

COMPOSITION OF EXTRACTED COMPLEXES

$C^{o}_{HOx}(M)$	pH^{a}	$[Ni]_{o}(M)$	$[ClO_4]_{o}(M)$	$[ClO_4]_{o}/[Ni]_{o}$
0.100	4.00	$1.00 \cdot 10^{-4}$	$5.18 \cdot 10^{-5}$	0.518
0.100	9.02	$1.00 \cdot 10^{-4}$	$8.0 \cdot 10^{-6}$	0.080
0.100	9.10	$1.00 \cdot 10^{-4}$	$1.12 \cdot 10^{-5}$	0.112
0.010	3.20	$6.35 \cdot 10^{-4}$	$3.16 \cdot 10^{-5}$	0.498
0.010	3.84	$1.00 \cdot 10^{-4}$	$5.08 \cdot 10^{-5}$	0.508
0.010	9.03	$1.00 \cdot 10^{-4}$	$4.3 \cdot 10^{-6}$	0.043

[a] pH after extraction.

The results of the determination of the molar ratios of oxine to nickel a perchlorate (or sulfate) to nickel for the isolated complexes are given in Table Nickel and oxine were found to combine in the ratio 1:3 for all cases examir The molar ratio of perchlorate to nickel agrees with that shown in Table I. Th results indicate that the extracted complexes are $[Ni_2(Ox)_3(HOx)_3ClO_4]_n$ at pH and $[Ni_2(Ox)_4(HOx)_2]_m$ (n and $m = 1,2,3,\ldots$) at high pH in the perchlo system, and that the latter species is extracted for the sulfate system irrespec of pH.

TABLE II

COMPOSITION OF ISOLATED COMPLEXES

Anion (X)	pH^{a}	$(HOx)/(Ni)^{b}$	$(X)/(Ni)^{b}$	*Solvent*[c]
Perchlorate	2.60	2.92	0.509	CCl_4
	3.80	2.82	0.506	CCl_4
	9.20	3.07	0.086	CCl_4 and n-C_6H_{14}[d]
Sulfate	6.95	2.96	n.d.[e]	n-C_6H_{14}

[a] pH after extraction. [b] Molar ratio. [c] Solvent used to precipitate complex. [d] (1 + 1) mixture. [e] Su was not detected (below 0.03).

Distribution of nickel

In the perchlorate system, the two-phase equilibrium constant of the extract of nickel at low pH, K_p, may be given by

$$K_p = \frac{[Ni_{2n}(Ox)_{3n}(HOx)_{3n}(ClO_4)_n]_o[H]^{3n}}{[Ni]^{2n}[HOx]_o^{6n}[ClO_4]^n}$$

where the subscript o indicates the organic phase, and charges are omitted simplicity. Correspondingly, the distribution ratio of nickel, D, is given by

$$D = \frac{2n[Ni_{2n}(Ox)_{3n}(HOx)_{3n}(ClO_4)_n]_o}{[Ni]_T}$$

where the subscript T indicates the total aqueous concentration of nickel equilibrium, which may be given by

$$[\mathrm{Ni}]_T = [\mathrm{Ni}]\left(1 + \sum_{i=1} \beta_i [\mathrm{Ox}]^i\right) \tag{3}$$

ere β_i is the stability constant of nickel–oxine complex, $\mathrm{Ni(Ox)}_i$, as given by

$$\beta_i = \frac{[\mathrm{Ni(Ox)}_i]}{[\mathrm{Ni}][\mathrm{Ox}]^i} \tag{4}$$

en eqns. (2), (3) and (4) are introduced into eqn. (1), the following equation ılts

$$K_p = \frac{D[\mathrm{H}]^{3n}\ (1 + \sum_{i=1} \beta_i [\mathrm{Ox}]^i)^{2n}}{2n[\mathrm{Ni}]_T^{2n-1}[\mathrm{HOx}]_o^{6n}[\mathrm{ClO_4}]^n} \tag{5}$$

The distribution data are given in Table III. The distribution ratios at

ILE III

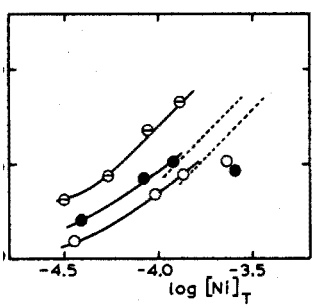
TRIBUTION DATA

og C_{Ni}:log C^o_{HOx}:pH (log D):Symbol mark[a]

hlorate system (log C_{ClO_4} = −1.00)
4.00: −1.00:2.03(−0.34), 2.10(0.00), 2.11(−0.04), 2.20(0.29), 2.29(0.66): ⊖
3.70: −1.00:2.21(0.46), 2.30(0.83), 2.42(1.24): ⌽
3.30: −1.00:2.11(0.35), 2.22(0.75), 2.30(1.01), 2.40(1.33): ●
3.00: −1.00:1.89(−0.68), 1.95(−0.39), 2.04(0.10), 2.07(0.23), 2.14(0.59), 2.29(1.10), 2.35(1.35): ○
4.00: −2.00:3.01(−0.21), 3.20(0.21), 3.31(0.41), 3.48(0.69): △
3.52: −2.00:2.95(−0.15), 3.05(0.12), 3.21(0.45), 3.42(0.85): ⧋
3.30: −2.00: 3.00(0.05), 3.10(0.31), 3.21(0.52), 3.36(0.73): ▲
3.00: −2.00:2.89(−0.14), 3.01(0.09), 3.15(0.38), 3.25(0.55), 3.26(0.57), 3.41(0.80), 3.56(1.04): ▽

ate system (log C_{SO_4} = −1.48)
-4.00: −1.00:2.84(−0.33), 2.92(−0.14), 2.99(0.04), 3.05(0.23), 3.13(0.46), 3.20(0.68), 3.33(0.91): ⊖
-3.52: −1.00:2.85(−0.16), 2.96(0.24), 3.02(0.41), 3.10(0.62), 3.17(0.78), 3.26(1.04), 3.40(1.29): ◐
-3.30: −1.00:2.83(−0.18), 2.93(0.21), 2.99(0.40), 3.14(0.80): ●
-3.00: −1.00:2.64(−0.91), 2.72(−0.45), 2.82(−0.08), 2.91(0.26), 3.05(0.65), 3.11(0.81), 3.21(1.06): ○
-4.00: −2.00:4.27(−0.16), 4.39(0.09), 4.47(0.34), 4.55(0.50), 4.81(1.05): △

mbol mark used in Figs. 4 and 5.



3. Distribution ratio of nickel as a function of $\log[\mathrm{Ni}]_T$. Perchlorate system: (⊖) C^o_{HOx} 0.1 *M*, 2.20, (●) C^o_{HOx} 0.01 *M*, pH 3.20. Sulfate system: (○) C^o_{HOx} 0.1 *M*, pH 3.00.

pH 2.20 ($C^{\circ}_{HOx}=0.1$ *M* and $C_{ClO_4}=0.1$ *M*) and 3.20 ($C^{\circ}_{HOx}=0.01$ *M* and $C_{ClO_4}=0.$ *M*) taken from the log*D*–pH plot of the data in Table III by interpolation wer plotted as a function of $[Ni]_T$ in Fig. 3. The $[Ni]_T$ was calculated by

$$[Ni]_T = \frac{C_{Ni}}{1+D} \qquad (6$$

When C°_{HOx} is 0.1 *M*, $\partial \log D/\partial \log [Ni]_T$ is unity at $[Ni]_T > 10^{-4.3}$ *M* or $[Ni]_0 > 10^{-3.}$ *M*, indicating that $n=1$, or the extracted complex is a binuclear one. But whe C°_{HOx} is 0.01 *M*, $\partial \log D/\partial \log [Ni]_T$ is about 0.7 at $[Ni]_T < 10^{-3.9}$ *M*, suggestin that some mononuclear complex is also present. Unexpectedly, the distribution rati of nickel decreased, when $[Ni]_T = 10^{-3.5}$ *M* for the latter case; it was considere that the relatively higher C_{Ni} for the lower C°_{HOx} micht result in the formation of som other complex less soluble in chloroform, which reduced the distribution ratio (nickel. Thus a very large amount of oxine as well as nickel was required for th extraction of nickel as the binuclear complex.

In order to determine the K_p value, the function $F_1 = 0.5 \log D - 0.5 \log [Ni]_T$ - $1.5\,pH - 3 \log [HOx]_o - 0.5 \log [ClO_4]$ was plotted against pOx ($-\log[Ox^-]$). Th distribution data for the perchlorate system in Table III are plotted in Fig. 4. Th equilibrium concentrations, $[HOx]_o$ and pOx, were calculated as previously de

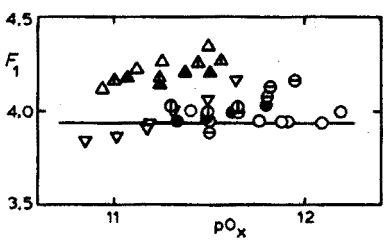


Fig. 4. Determination of K_p. Refer to Table III for symbols.

scribed[1,3]. According to eqn. (5), when the extractable complex is the binuclear on and nickel(II) is the only predominant species in the aqueous phase, the plot shoul give a straight line parallel to the horizontal pOx axis. The experimental points fo $C^{\circ}_{HOx}=0.1$ *M* and $C_{Ni}=10^{-3}$*M* fall on a straight line, but for smaller C°_{HOx} the deviate from the line and tend to approach it from above until they meet it at lowe pOx values. For $C^{\circ}_{HOx}=0.01$ *M*, the points meet the line only for $C_{Ni}=10^{-3}$ *M*. Th upward deviation of the experimental points may be due to dissociation of th binuclear complex in the organic phase, because the deviation increases with de creasing C_{Ni}. However, the experimental points for $C^{\circ}_{HOx}=0.01$ *M* and $C_{Ni}=10^{-}$ *M* tend to lie below the other points for $C^{\circ}_{HOx}=0.01$ *M*, as expected from Fig. 3 Thus the horizontal line in Fig. 4 corresponds to eqn. (7):

$$K_p = \frac{D[H]^3}{2[Ni]^2[HOx]_o^6[ClO_4]} \qquad (7$$

The K_p value was calculated to be $10^{7.58}$ from the line.

In the sulfate system the two-phase equilibrium constant of the extractio of nickel at low pH, K_s, is given by

$$K_s = \frac{[Ni_{2m}(Ox)_{4m}(HOx)_{2m}]_o[H]^{4m}}{[Ni]^{2m}[HOx]_o^{6m}} \quad (8)$$

ıe distribution ratio of nickel is given by

$$D = \frac{2m[Ni_{2m}(Ox)_{4m}(HOx)_{2m}]_o}{[Ni]_T} \quad (9)$$

Ni(II) and $NiSO_4$ are the only dominant species in the aqueous phase, $[Ni]_T$ ll be given by

$$[Ni]_T = [Ni](1+\beta_s[SO_4]) \quad (10)$$

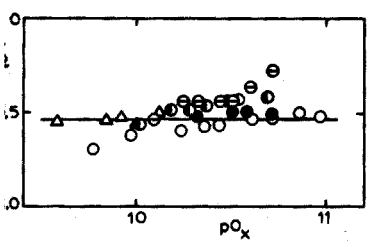
ıere β_s is the stability constant of $NiSO_4$.

When eqns. (9) and (10) are introduced into eqn. (8), the following uation results

$$K_s = \frac{D[H]^{4m}(1+\beta_s[SO_4])^{2m}}{2m[Ni]_T^{2m-1}[HOx]_o^{6m}} \quad (11)$$

The distribution data for sulfate system are also given in Table III. For $_{Ox}=0.01$ M and $C_{Ni} > 10^{-3.5}$ M the distribution ratio could not be determined, cause a yellow precipitate of nickel–oxine complex appeared in the extraction stem.

The distribution ratios at pH 3.00 ($C^o_{HOx}=0.1$ M) taken from the log D–pH ɔt of the data in Table III by interpolation were plotted as a function of $[i]_T$ also in Fig. 3. It can be seen that $\partial \log D/\partial \log [Ni]_T$ is 0.7 at $[Ni]_T < 10^{-3.8}$ M, dicating that the extracted complex is essentially the binuclear complex, $Ni_2(Ox)_4$-$HOx)_2$. The distribution ratio at $[Ni]_T = 10^{-3.64}$ M was much smaller than expected.



g. 5. Determination of K_s. Refer to Table III for symbols.

The function $F_2 = 0.5 \log D - 2pH - 0.5 \log [Ni]_T - 3 \log [HOx]_o$, was plotted ainst pOx (Fig. 5). According to eqn. (11) when the extracted complex is Ni_2-$Ox)_4(HOx)_2$, the plot should give a straight line parallel to the horizontal pOx is. The experimental points, as in the perchlorate system (Fig. 4), tend to approach e line from above until they meet it at low pOx values. The points for $C^o_{HOx}=0.1$ M ıd $C_{Ni}=10^{-3}$ M deviate downward from the horizontal line at low pOx as was pected from Fig. 3. From the horizontal line the following equation can be ɔtained

$$\frac{K_s}{(1+\beta_s[SO_4])^2} = 10^{-1.38} \quad (12)$$

The β_s value at 20° at zero ionic strength was evaluated as $10^{2.28}$ by int polation of the β_s values at varied temperatures[4]. When the activity coefficients ionic strength 0.1 were taken[5] as $\gamma_{Ni}=0.405$, $\gamma_{SO_4}=0.355$, and $\gamma_{NiSO_4}=1$ was assum the β_s value at 20° was calculated to be $10^{1.44}$. The K_s value was found to $10^{-0.82}$.

Effect of pH on the complexes in the organic phase

The nickel–oxine complex extracted from the perchlorate solution at pH has the same absorption spectrum and composition as that from the sulf solution. It was therefore assumed that the following equilibrium existed betwe the two binuclear complexes in the organic phase and that the complex on left-hand side of eqn. (13) had lower absorbance at 400 nm than that on the ri hand side.

$$Ni_2(Ox)_3(HOx)_3ClO_4(o) \rightleftharpoons Ni_2(Ox)_4(HOx)_2(o)+H^+ + ClO_4^- \quad ($$

Thus

$$K_o = \frac{[Ni_2(Ox)_4(HOx)_2]_o[H][ClO_4]}{[Ni_2(Ox)_3(HOx)_3ClO_4]_o} \quad ($$

where o refers to the organic phase. The concentrations of the complexes equilibrium may be calculated from the observed absorbance by eqns. (15) a (16)

$$[Ni_2(Ox)_3(HOx)_3ClO_4]_o = \frac{d_{max}-d}{d_{max}-d_{min}} \cdot \frac{C_{Ni}}{2} \quad ($$

$$[Ni_2(Ox)_4(HOx)_2]_o = \frac{d-d_{min}}{d_{max}-d_{min}} \cdot \frac{C_{Ni}}{2} \quad ($$

where d_{min} and d_{max} are the minimal and maximal absorbances of the orga extracts from the perchlorate solutions at the pH of the optimal extracti respectively, and d is the absorbance of an extract at an arbitrary pH. Consequen eqn. (14) can be rewritten as

$$K_o = \frac{d-d_{min}}{d_{max}-d}[ClO_4][H] \quad ($$

A plot of $\log(d-d_{min})/(d_{max}-d)$ against pH–$\log[ClO_4]$ is shown in Fig. a straight line with unit slope being obtained as expected by eqn. (17). The K_o w graphically determined to be $10^{-8.75}$ at 390 or 400 nm.

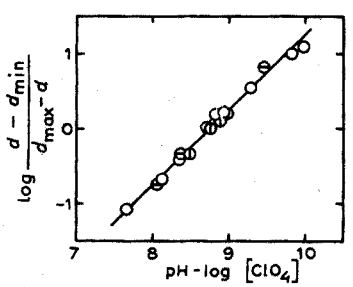


Fig. 6. Determination of K_o. Refer to Fig. 1 for symbols.

The K_o value can also be obtained from eqns. (1) and (8) as $K_o = K_s/K_p = 10^{-8.40}$, which is in good agreement with the K_o value determined by the ctrophotometric method.

CUSSION

The solvent extraction of nickel with oxine solution in chloroform may be racterized by the important roles of inorganic anions. Not only perchlorate but many common inorganic anions such as iodide, bromide, chloride, nitrate, etc. e found to be held in the nickel–oxine complexes extracted from the solutions taining these anions at low pH. These complexes gave the same absorption ctra in the wavelength region of 370–480 nm as that containing perchlorate, ich suggests that these extractable complexes have a common structure. Thus, se anions might be thought to combine with the nickel–oxine complex cation electrostatic force to form the ion-association complexes, $[Ni_2(Ox)_3(HOx)_3^+, X^-]$, where X^- is an anion mentioned above.

The cationic nickel–oxine complex is supposed to dissociate in the aqueous se:

$$Ni_2(Ox)_3(HOx)_3^+ \rightleftharpoons Ni_2(Ox)_4(HOx)_2 + H^+ \qquad (18)$$

ce the neutral complex on the right-hand side of eqn. (18) is also extractable, en there is some weakly hydrated anion in the aqueous phase, nickel will be racted as the ion-association complex at low pH, but as the neutral complex at h pH. However, when there are only strongly hydrated anions as in the sulfate tem, nickel will be exclusively extracted as the neutral complex. Thus, it seems sonable to assume that nickel was extracted as the neutral binuclear complex ier from the perchlorate solution at high pH or from the sulfate solution.

The two-phase equilibrium constant, K_p, for zinc was $10^{1.10^1}$. The rather ge difference between the K_p values could not be explained only by the small erence in the stability constants of the monomeric oxine complexes in aqueous ution[6]. It was shown that nickel was extracted from nitrate or chloride ution as the ion-association complexes, while zinc was extracted from neither ution. This striking contrast, which may be due to a difference in the affinity the cationic complexes of these metals for water, was thought to result in the ge difference in the K_p values.

The K_o value could be determined by distribution measurements as well as spectrophotometry. The latter method is thought to be more reliable, because distribution method for K_s required the β_s value, which was calculated from rature values after making several assumptions. Furthermore, the K_p and K_s ues needed more complicated experimental procedures and calculations than the ctrophotometric K_o values. However, the nickel–oxine complexes in the organic se seemed to be exclusively binuclear at higher pH values even for $C_{Ni} = 10^{-4}$ judging from the unaltered absorption spectra on changing C^o_{HOx} (0.01–0.1 M) d C_{ClO_4} (0.01–0.1 M).

The authors are grateful to Professor Jun'ichi Kobayashi for his helpful vice.

SUMMARY

Nickel–oxine complexes extracted from perchlorate and sulfate solutions with chloroform were isolated and their compositions were determined. They were $Ni_2(Ox)_3(HOx)_3ClO_4$ from perchlorate solution at low pH and $Ni_2(Ox)_4(HOx)_2$ from perchlorate solution at high pH or from sulfate solution. The extraction equilibria, $2Ni^{2+}+6HOx(o)+ClO_4^- \rightleftharpoons Ni_2(Ox)_3(HOx)_3ClO_4(o)+3H^+$, $2Ni^{2+}+6HOx(o) \rightleftharpoons Ni_2(Ox)_4(HOx)_2(o)+4H^+$ and $Ni_2(Ox)_3(HOx)_3ClO_4(o) \rightleftharpoons Ni_2(Ox)_4(HOx)_2(o)+H^++ClO_4^-$, were proposed and the equilibrium constants were determined to be $10^{7.58}$, $10^{-0.82}$ and $10^{-8.75}$, respectively, at ionic strength 0.1 and 20°.

RÉSUMÉ

Les complexes nickel–oxine, en solutions perchlorique ou sulfurique ont été extraits par le chloroforme, puis isolés et analysés. Ce sont $Ni_2(Ox)_3(HOx)_3ClO_4$ en solution perchlorique à pH bas et $Ni_2(Ox)_4(HOx)_2$ en solution perchlorique à pH élevé ou en solution sulfurique. Les équilibres d'extraction sont proposés. Les constantes d'équilibre trouvées sont respectivement $10^{7.58}$, $10^{-0.82}$ et $10^{-8.75}$, à force ionique de 0.1 et à 20°.

ZUSAMMENFASSUNG

Nickel–Oxin-Komplexe, die aus Perchlorat- und Sulfatlösungen mit Chloroform extrahiert worden waren, wurden isoliert und deren Zusammensetzungen bestimmt. Bei Verwendung von Perchloratlösungen mit niedrigem pH-Wert wurde $Ni_2(Ox)_3(HOx)_3ClO_4$ erhalten, bei Perchloratlösungen mit hohem pH-Wert oder Sulfatlösungen bildete sich $Ni_2(Ox)_4(HOx)_2$. Folgende Extraktionsgleichgewichte wurden vorgeschlagen:

$$2Ni^{2+}+6HOx(org)+ClO_4^- \rightleftharpoons Ni_2(Ox)_3(HOx)_3ClO_4(org)+3H^+$$

$$2Ni^{2+}+6HOx(org) \rightleftharpoons Ni_2(Ox)_4(HOx)_2(org)+4H^+$$

und $Ni_2(Ox)_3(HOx)_3ClO_4(org) \rightleftharpoons Ni_2(Ox)_4(HOx)_2(org)+H^++ClO_4^-$.

Die zugehörigen Gleichgewichtskonstanten wurden bei Ionenstärke 0.1 und 20° zu $10^{7.58}$, $10^{-0.82}$ und $10^{-8.75}$ ermittelt.

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'RACTION OF BORIC ACID WITH ALIPHATIC 1,3-DIOLS AND 1ER CHELATING AGENTS

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ived 10th December 1972)

The 1,3-diols have been suggested for boron recovery from alkaline brines by rett[1] and for extraction of boric acid from acidic solutions by George[2]. In a ious paper[3] 2-ethylhexanediol-1,3 (EHD) and 2,2-diethylpropanediol-1,3 PD) were thoroughly studied for the extraction of boric acid from aqueous tions. A separate study of the concentration dependence of the diol association also performed[4] in order to elucidate the mechanism of the boron distribution.

In a search for more efficient extracting agents than EHD and DEPD, r hydroxy compounds, as well as species containing other chelating groups, were nined. A number of compounds were investigated in a screening test to establish possible ability as boric acid extractants. Besides other 1,3-diols, 1,2- and 1,4-droxy, diketo, ketohydroxy, aminohydroxy and diamino compounds were ıded. Depending on their extraction potential, an approximate order of edence may be arranged. The most promising reagents were subjected to more iled study.

ERIMENTAL

ıents

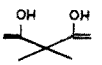
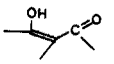
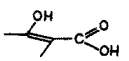
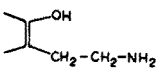
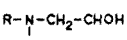
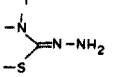
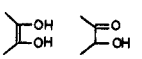
2,2-Diethylpropanediol-1,3 (DEPD; J. T. Baker Chemical Co, Philipsburg, A.) was recrystallized from benzene (m.p. 63.5–64.5°). 2,2-Diphenylpropanediol-DPPD; EGA-Chemie KG, Steinheim, W. Germany) was recrystallized from nol (m.p. 107–108°). 2-Ethylhexanediol-1,3 (EHD; Kebo AB, Stockholm, Sweden) redistilled at 239.5–240.5°. The chloroform (Merck A. G., Darmstadt, W. Germany) washed twice with redistilled water to remove ethanol. Sodium chloride, hydroric acid and hexane were of analytical grade and the boric acid was of Merck apur quality. If not otherwise stated, all other chemicals were used as received. ionic strength was kept at 0.5 *M* or 0.9 *M* with sodium chloride. The exnents were carried out at 25 ± 1°.

ıratus

For the measurements in the ultraviolet and visible region a Beckman DB, nicam SP 500 and a Shimadzu MPS-50 L spectrophotometer were used. investigations in the infrared region were made with a Perkin-Elmer 337 i.r.-trophotometer and the n.m.r. spectra were obtained with a Varian A60 spectro-r.

TABLE I

SURVEY OF PRESUMPTIVE EXTRACTANTS FOR BORIC ACID

Extractant	*Active group*	*pH*
I. Poor boric acid extractants (practically no boric acid extracted)		
1. Phenylethanediol-1,2	–CHOH–CH_2OH	2
2. Propanediol-1,3	–CHOH–C–CH_2OH	4.5
3. Poly(2,2-dimethylpropanediol-1,3-succinate)	–CHOH–C–CH_2OH	2
4. 2,2'-Dihydroxybiphenyl		2
5. Catechol		2
6. *o*-Hydroxyacetophenone		4.5
7. 4,4'-Methylene-bis(3-hydroxy-2-naphthoic acid)		2
8. Benzoylacetone	-CO-CO-	2
9. 1,2-Cyclohexanedione	-CO-CO-	2
10. 2-Pyridylmethylacetate	-O-CO-	2
11. 2-Pyridineethanol	$-N-CH_2-CH_2OH$	2
12. α-(1-Aminoethyl)benzylalcohol hydrochloride		2
13. D(–)-N-Methylglucamine	$HOCH_2-(CHOH)_4-CH_2(NH)CH_3$	2
II. Poor boric acid extractants (small, but detectable amounts of boric acid were extracted)		
14. Hydrocinnamoin	–CHOH–CHOH–	2
15. 2-Amino-2-methylpropanediol-1,3	–CHOH–C–CH_2OH	2
16. Butanediol-1,3	–CHOH–C–CH_2OH	2
17. 1,3-Dihydroxypropanone	CH_2OH–CO–CH_2OH	2
18. 1-(Diethylamino)-2-propanol		2
19. 3-Methyl-2-benzothiazolinonhydrazone hydrochloride		
20. 2,2'-(Benzyliminodiethanol)	$R-N/(CH_2)_2OH/_2$	2
21. 9-*o*-Hydroxyphenyl-2,3,7-trihydroxy-6-fluorone		4.5
22. Benzylsalicylate	-CO-COH	2
23. Isopentylsalicylate	-CO-COH	4.5
24. *o*-Aminophenol		2
25. 2-Aminobenzyl alcohol		2

BLE I *(continued)*

'ractant	*Active group*	*pH*
Medium extraction properties		
1,2-Cyclohexanediol	-CHOH-CHOH	4.5
2-Pyridyl-2-propanediol-1,3	-CHOH-C-CHOH-	2
2-Ethyl-2-methylpropanediol-1,3	-CHOH-C-CHOH-	2
2,4-Pentanediol	-CHOH-C-CHOH-	2
1,3-Diphenylpropanedione-1,3	$-CO-CH_2-CO-$	2
2-Benzylaminoethanol	$R-NH(CH_2)_2-OH$	2
1,4-Butanediol	$CH_2OH-(CH_2)_2-CH_2OH$	2
Benzoin	-C(OH)-CO-	2
1,2-Naphthalenediamine		2
Good extraction properties		
2,2-Diphenylpropanediol-1,3	–CHOH–C–CHOH–	2
2-Ethyl-2-butylpropanediol-1,3	–CHOH–C–CHOH–	2
2-Methylpentanediol-2,4	–CHOH–C–CHOH–	2
3-Methylpentanediol-2,4	–CHOH–C–CHOH–	2
3-Methyl-5-ethylnonanediol-2,4	–CHOH–C–CHOH	2
2,2,4-Trimethylpentanediol-1,3	–CHOH–C–CHOH–	2

alytical methods

Boron in aqueous solutions was determined by the curcumin procedure scribed by Uppström[5]. The boron content in organic solvents was determined after ıporation to dryness[3], or, for chloroform, directly in the organic phase, as it has been)wn that rosocyanin, the reaction product of curcumin and boric acid is ıdily formed in the chloroform phase[6].

The following method was used to determine boric acid in chloroform samples. sample of 2 ml of chloroform solution in a stoppered tube was cooled in an ice ter bath, and 3 ml of a mixture of concentrated sulphuric acid and glacial acetic acid 1) and 3 ml of curcumin solution (0.125 g dissolved in 100 ml of glacial acetic id) were added. The tube was chilled again and then repeatedly shaken vigorously. ter 10 min, 20 ml of buffer solution (180 g of ammonium acetate, 90 ml of ethanol d 135 ml of glacial acetic acid dissolved and diluted to 1 l with water) and ıl of chloroform were added slowly with continuous cooling, and finally the solution s centrifuged.A reddish or reddish brown colour of the chloroform phase indicated ıt the original chloroform solution contained boron. If the chloroform sample s coloured by the boron extracting agent, the organic phase was shaken with an :aline solution to strip off the boric acid. The boron content was then determined the aqueous phase as usual.

Diol concentrations were determined by an evaporation-weighing procedure described earlier[4]. The concentration of DPPD was determined spectrophoto-:trically at 259 nm, with chloroform as reference solution.

Procedure for preliminary screening

A certain amount (0.5 g or 1 ml) of the extractant was dissolved in a few ml chloroform in a stoppered tube and an equal volume of 0.01 *M* boric acid solutic (I=0.5 *M*, pH=2 or 4.5) was added. After 2 min of shaking, the phases we separated by centrifugation. The organic layer was analyzed for boron as describe above.

INVESTIGATION OF POSSIBLE EXTRACTANTS FOR BORIC ACID

The compounds investigated are listed in Table I. The extractants are divide into four groups according to their extraction ability, which was estimated rough based on earlier experience[3]. The first group contains the least effective compoun and the fourth those which are as powerful as DEPD. The partition of boric ac between aqueous solution and chloroform is negligible[3].

Comparison of chelating groups

From Table I it is evident that compounds with hydroxy groups in aliphat 1,3-positions are superior to all other tested structures for extraction of boric aci Hermans[7] and other workers[8] have shown that boric esters are more readily form with 1,3-diols than 1,2-diols. This depends probably on the formation of unstraine six-membered rings in the reaction between 1,3-diols and trigonal planar boric aci whereas the 1,2-diols preferably form unextractable ionic complexes with t tetrahedral borate ion[9]. The 1,2-cyclohexanediol is a mixture of the *cis–tra* conformations and according to Dale[10] only the *cis* form may form any complexe Dale has also shown that *cis*-cyclohexanediol-1,3 can form a boric ester althou it was not possible to extract it from aqueous solution. This was explained by t fact that *cis*-diols normally exist in a diequatorial conformation in polar solvents a have to become diaxial to react. Dimeric species may be formed both with 1, diols (I, Fig. 1) and 1,4-diols (II, Fig. 1) according to Steinberg and Hunter[1] However, the 3:2 complex with 1,3-diols seems to be partially hydrolyzed to the 1 complex in the presence of water. Of the diketo compounds, 1,2-cyclohexanedio extracted no boric acid, but keto groups in the 1,3-positions had some effect as show by 1,3-diphenylpropanedione-1,3. George[2] made some unsuccessful attempts to isola keto-coordinated boric acid chelates from aqueous solutions. Of the amines tested on 1,2-naphthalenediamine showed some extraction ability.

The results of this survey indicated that the investigation should be continue with diols containing the propanediol-1,3 skeleton.

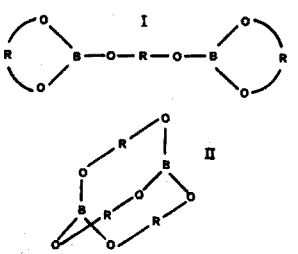


Fig. 1. Species formed by the reaction between aliphatic diols (R) and trigonal boric acid (B) accordi to Steinberg and Hunter[11].

EXTRACTION PROPERTIES OF 2,2-DIPHENYLPROPANEDIOL-1,3

ibution measurements and results

In previous work, it seemed that the favourable extraction of boric acid with liols was due mainly to the formation of the boron–diol complex in the nic phase. Furthermore, the most efficient diols seemed to be those with large tion coefficients. Of the diols available, 2,2-diphenylpropanediol-1,3 (DPPD) d be expected to have an advantageous distribution and was regarded as very nising. In addition it was easy to determine the diol by u.v. measurements. It was fore chosen for a start.

Solutions containing different concentrations of DPPD in chloroform –0.2 *M*) were equilibrated with known volumes of sodium chloride solutions 0.5 or 0.9 *M*). A shaking time of 10 min was found to be satisfactory. The unt of diol was measured in the aqueous phase. The results are shown in Table II. distribution values given there were plotted against the concentration of the diol ie aqueous phase (Fig. 2). If it is assumed that only dimers and no polymeric ies are formed, the following reactions are valid:

$$A(aq) \rightleftharpoons A(org) \qquad K_e \qquad (1)$$

$$2A(aq) \rightleftharpoons A_2(org) \qquad K_{dim} \qquad (2)$$

the distribution D is expressed as:

$$D = ([A]_{org} + 2[A_2]_{org})/[A] \qquad (3)$$

om eqns. (1) and (2):

$$D = K_e(1 + 2K_{dim}K_e[A]) \qquad (4)$$

best straight lines fitted to the experimental data give by extrapolation to concentration the distribution constant K_e of the monomer in the different media. The distribution values show a slight increase with increasing concentra- of diol, thus indicating the formation of dimers. The values obtained for K_e and are shown in Table II. The partition of DPPD and other 1,3-diols is compared ig. 3 and Table III. The results show that the tendency to dimerize (K_{dim}) and merize (K_9) varies considerably, while the distribution constant of the monomer largely depends on the size of the hydrocarbon part.

LE II

PARTITION OF DPPD BETWEEN SODIUM CHLORIDE SOLUTION AND OROFORM

ith	*Partition constants for a concentration of DPPD of*				K_e	K_{dim}
	0.01 M	*0.03 M*	*0.1 M*	*0.2 M*		
	126	129	141	161	123	0.92
	146	154	163	196	144	1.02

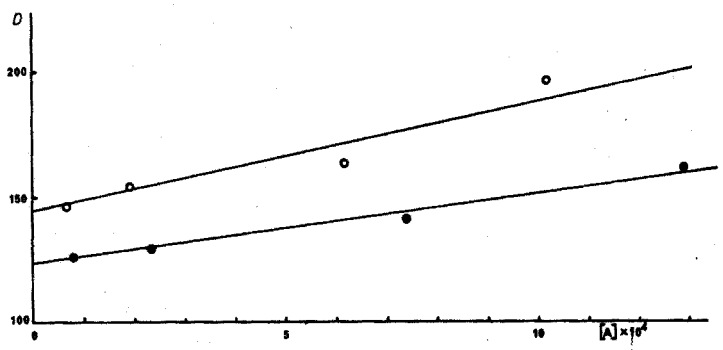


Fig. 2. Distribution values for 2,2-diphenylpropanediol-1,3 (DPPD) between chloroform and (NaCl (●) or 0.9 *M* NaCl (○) plotted against the concentration of the diol in the aqueous p Extrapolation to zero concentration gives the distribution constant, K_e, of the monomer (Tabl

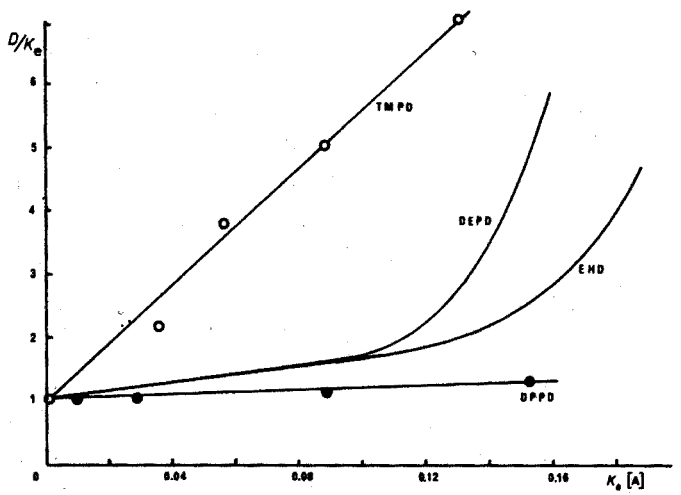


Fig. 3. The distributions of 2,2,4-trimethylpentanediol-1,3 (TMPD) (○) and DPPD (●) between chlor and 0.5 *M* NaCl plotted as D/K_e against $K_e[A] = [A]_{org}$. The curves for DEPD and EHD determined previously[4]. The equilibrium constants derived from the data are given in Table III.

TABLE III

PARTITION CONSTANTS FOR SOME 1,3-DIOLS

Diol	*No. of C atoms*	K_e	K_{dim}	K_9
2,2-Diethylpropanediol-1,3, DEPD	7	1.0	3.63	$1.02 \cdot 10^6$
2-Ethylhexanediol-1,3, EHD	8	5.0	3.63	$1.86 \cdot 10^5$
2,2-Diphenylpropanediol-1,3, DPPD	15	123	0.98	Low
2,2,4-Trimethylpentanediol-1,3, TMPD	8	1.6	23	Low

traction of boric acid. Treatment of data and results

Solutions containing 0.1 *M* or 0.01 *M* DPPD in chloroform were equilibrated r 10 min with aqueous boric acid solutions of different concentrations. The nic strength was kept at 0.5 *M* with sodium chloride and pH 2 in all experiments. The ases were separated by centrifugation, and the boron content was determined in e organic and/or in the aqueous phase and the concentration of DPPD in the ueous phase. The results are given in Table IV.

BLE IV

E DISTRIBUTION OF BORIC ACID AND DPPD BETWEEN CHLOROFORM AND SODIU LORIDE SOLUTION FOR DIFFERENT TOTAL CONCENTRATIONS OF BORIC ACID AND DPP

=0.5 *M*; pH 2)

PD	$B(OH)_3$							
	0.0005 M	*0.001 M*	*0.005 M*	*0.01 M*	*0.05 M*	*0.1 M*	*0.4 M*	*0.8 M*
0.1 *M*	0.613	0.539	0.438	0.428	0.562	0.534	0.223	0.130
0.01 *M*	0.082	0.030	0.031	0.029	0.061	0.047	0.018	0.012
0.1 *M*	128	128	128	132	156	200	404	588
0.01 *M*	120	115	123	120	148	174	345	420

The following equilibria were considered for the calculation of the complex formation constants between boric acid and DPPD, denoting $B(OH)_3 = B$, DPPD = A, $]_{aq} = b$, $[A]_{aq} = a$.

$$B + A \rightleftharpoons BA(org) \qquad K_{11} \tag{5}$$

$$B + A \rightleftharpoons BA \qquad K'_{11} \tag{6}$$

$$BA \rightleftharpoons BA(org) \qquad K_{11}/K'_{11} \tag{7}$$

$$A \rightleftharpoons A(org) \qquad K_e \tag{1}$$

$$B \rightleftharpoons B(org) \qquad K_{DB} \tag{8}$$

he distribution constants of boron and diol are thus

$$D_B = \frac{[B]_{org} + [BA]_{org}}{[B] + [BA]} \approx \frac{[BA]_{org}}{[B]} = K_{11}\,a \tag{9}$$

ice $K_{DB} = 4.07 \cdot 10^{-5}$ (ref. 3) and $[B] \gg [BA]$; and

$$D_A = \frac{[A]_{org} + 2[A_2]_{org} + [BA]_{org}}{[A] + [BA]} \tag{10}$$

or B = 0

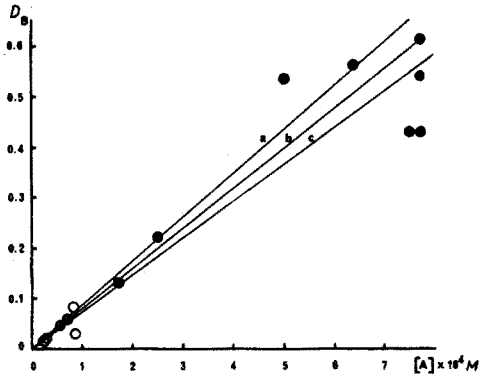
$$D_A^0 = ([A]_{org} + 2[A_2]_{org})/[A] \tag{11}$$

$$D_A = \frac{D_A^0 a + K_{11} ab}{a + K'_{11} ab} = \frac{D_A^0 + K_{11} b}{1 + K'_{11} b} \tag{12}$$

By rearrangement of eqn. (12),

$$(D_A - D_A^0)/b = K_{11} - D_A K'_{11}$$

In Fig. 4 the distribution values (D_B) for boric acid are plotted against concentration of DPPD in the aqueous phase. The slope of the line will t give a value of K_{11} according to eqn. (9). However, the experimental uncertaint as shown in the spread of the points, allow no accurate determination of constant and the calculations were based on three plausible drawings of straight line, a, b, c in Fig. 4. In Fig. 5 the values for $(D_A - D_A^0)/b$ are plot against the corresponding values for D_A. The values for K_{11} obtained in Fi are also indicated. The regression line in Fig. 5 seems to give a somewhat hig value of K_{11}, thus showing the uncertainty in the evaluation. Approximate val of K_{11} and K'_{11} are given in Table V.



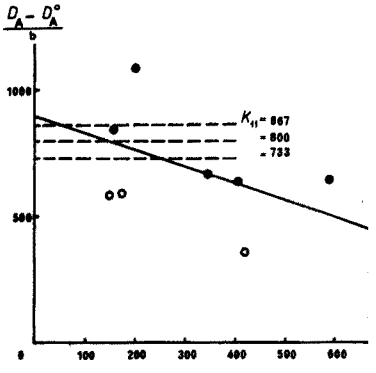


Fig. 4. Distribution values for boric acid plotted against the concentration of DPPD in the aqu phase. Owing to the scatter of the points, three different plausible lines are shown. The slope of a gives a value of K_{11} (eqn. 5). The values for the lines a, b and c are 867, 800 and 733, respectively (*cf.* Fi

Fig. 5. Values of $(D_A - D_A^0)/b$ according to eqn. (13), are plotted against D_A. The intercept of regression line gives K_{11}. The values of K_{11} given in Fig. 4 are indicated.

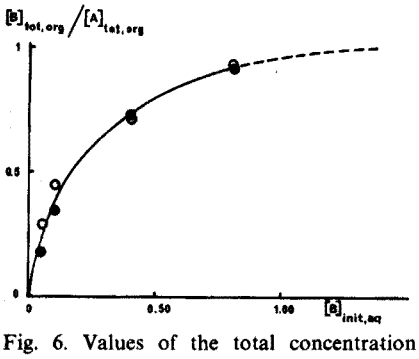


Fig. 6. Values of the total concentration of boron in the organic phase divided by the t initial concentration of DPPD in the organic phase are plotted against the initial concentratio boron in the aqueous phase. The data indicate a limiting value of 1.

BLE V

NSTANTS FOR THE EQUILIBRIA BETWEEN 1,3-DIOLS AND BORIC ACID IN THE STEM CHLOROFORM: 0.5 *M* SODIUM CHLORIDE AT pH 2

	K_1	K_2	$K_{11}(\beta_1)$	$K_{12}(\beta_2)$	K'_{11}
PD[3]	$2.04 \cdot 10^5$	83.1	8.3	$10^{2.82}$	—
D[3]	$6.16 \cdot 10^5$	35.3	126	$10^{4.36}$	—
PD	$1.70 \cdot 10^5$	Negl.	850 ± 50	~ 0	0.59 ± 0.13
PD	—	—	~ 500	—	—

A plot of total concentration of boric acid in the chloroform phase against the tial boric acid concentration in the aqueous phase is shown in Fig. 6. The ference between the two concentrations of DPPD is small. This plot shows the mation of a 1:1 species in the organic phase quite clearly, and there was therefore reason to include a B_2A_3 complex (I in Fig. 1) in the expression for D_B (eqn. 9). e equilibrium constant for

$$B(org) + A(org) \rightleftharpoons BA(org) \quad (14)$$

$$K_1 = K_{11} K_{DB}^{-1} K_e^{-1} \quad (15)$$

e value obtained is given in Table V together with previous results[3].

The boric acid extraction is surprisingly small with DPPD in comparison EHD and DEPD. The partition coefficient of the diol is thus less important than pected. Other factors such as polymerization properties or structural differences of diols, *e.g.* the formation of internal hydrogen bonds, must be considered.

MPARISON OF 1,3-DIOLS FOR THE EXTRACTION OF BORIC ACID

traction ability and molecular size

The above results initiated a comparative investigation of the available -diols and a first study was made on their extraction ability for boric acid in ation to their molecular size. Solutions of 0.1 *M* diol in chloroform or hexane re equilibrated with equal volumes of 0.005 *M* boric acid (I = 0.5 *M*, pH 2) for 20 n. The phases were then separated and analyzed for their boron content. In some es the solubility of the diol in chloroform or hexane was less than 0.1 *M*. wever, the total concentration of diol in the chloroform(hexane)–aqueous system ld be held at 0.1 *M*, for the remaining quantity (insoluble in the organic phase) s dissolved in the aqueous phase. Data for the experiments are given in Table VI. e boric acid distribution constants are plotted against the number of carbon ms in the diols in Fig. 7.

The most efficient extractants seem to be those containing eight or nine bon atoms, but differences depending on the structures are obvious. The general ture is the same for both organic solvents, chloroform being the superior dium for all extractants except 3-methyl-5-ethylnonanediol-2,4. Chloroform n form hydrogen bonds not only through self-association, but also with the ol as well as with boric acid and the boric acid–diol complex. The solvation

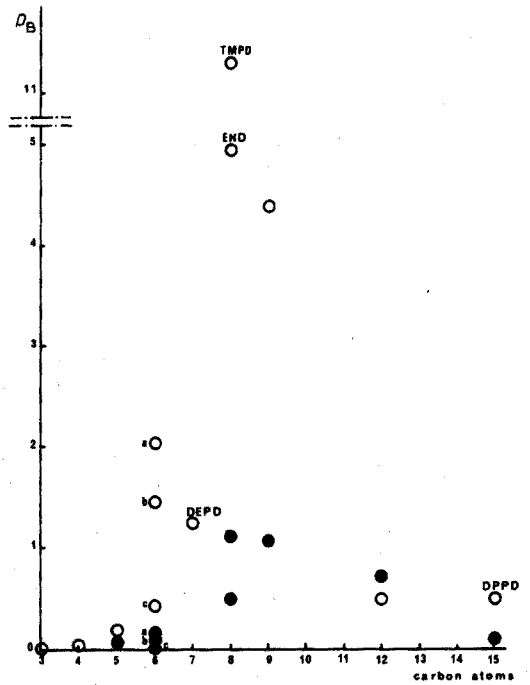


Fig. 7. Boron distribution values for the different 1,3-diols investigated related to their number carbon atoms. Chloroform (○); hexane (●). The notations are given in Table VI. Observe that value for TMPD is very high.

TABLE VI

DISTRIBUTION DATA FOR 0.005 *M* BORIC ACID IN AQUEOUS SOLUTION EXTRACTI BY 0.1 *M* 1,3-DIOLS IN CHLOROFORM OR HEXANE

Diol	*No. of C atoms*	*Notation in Fig. 7*	$D_{B(OH)_3}$ *in*	
			Chloroform	*Hexane*
Butanediol-1,3	4	—	<0.015	—
2,4-Pentanediol	5	—	0.19	0.06
3-Methylpentanediol-2,4	6	a	2.04	0.13
2-Methylpentanediol-2,4	6	b	1.45	0.06
2-Ethyl-2-methylpropanediol-1,3	6	c	0.43	0.00
2,2-Diethylpropanediol-1,3	7	DEPD	1.24	—
2-Ethylhexanediol-1,3	8	EHD	4.94	0.48
2,2,4-Trimethylpentanediol-1,3	8	TMPD	11.30	1.12
2-Ethyl-2-butylpropanediol-1,3	9	—	4.38	1.06
3-Methyl-5-ethylnonanediol-2,4	12	—	0.51	0.72
2,2-Diphenylpropanediol-1,3	15	DPPD	0.51	0.09

is, however, much weaker than in the aqueous phase and does not impede the compl formation. The solvent interference caused by hexane is still weaker; most di have a lower solubility in hexane than in chloroform. The boric acid–diol chel

ot so easily formed in the aqueous phase, although an ester formation may ntaneously take place with higher concentrations of suitable diols and boric l, as was first reported by Hermans[7]. Both the boric acid and the diol are ngly solvated by water molecules and for a small diol like butanediol-1,3 solvation seems almost completely to hinder any interaction with boric acid. s was also found in an investigation of boric acid extraction with EHD and anediol-1,3. The distribution values remained the same whether butanediol was sent or not.

omparison with Hermans' results

From cryoscopic measurements, Hermans[7] was able to show that the ester ned from 2,4-dimethylpentanediol-2,4 and boric acid was not completely rolyzed in water at a concentration as low as 0.035 *M*. The compound was found to be soluble in most organic solvents. The cryoscopic data can used to calculate a formation constant for the equilibrium

$$B(OH)_3 + R(OH)_2 \rightleftharpoons B(OH)RO_2 + 2\,H_2O \qquad (16)$$

LE VII

CULATION OF FORMATION CONSTANT FOR 2,4-DIMETHYLPENTANEDIOL-1,3- ATE FROM RESULTS OF HERMANS[7]

rity	*Dissociation (%)*	α	$K=(1-\alpha)/C\alpha^2$
12	74.3	0.743	3.01
14	74.7	0.747	3.22
18	85.6	0.856	5.65

The results are given in Table VII. The solubility in water of the diol–borate found to be 0.282 *M*[7]. If the equilibrium constant for eqn. (16) is $K=3$ in the rated solution, the molar ratio (α) of boric acid and diol is calculated to be . The concentration of ester in the aqueous phase is thus 0.099 *M*. If the bility of the diol–borate ester in chloroform is about 3 *M*, the distribution ficient obtained is $K_D = 3/0.099 \approx 30$. If the K_e value for the distribution of the monomer does not differ too much from that of DEPD (both diols have n carbon atoms) an approximate value of the ester formation constant in roform can be calculated from the following equilibria.

$$B(OH)_3 + R(OH)_2 \rightleftharpoons B(OH)RO_2 + 2\,H_2O \qquad K \qquad (17)$$

$$B(OH)RO_2 \rightleftharpoons B(OH)RO_2(org) \qquad K_D \qquad (18)$$

$$B(OH)_3 \rightleftharpoons B(OH)_3(org) \qquad K_{DB} \qquad (8)$$

$$R(OH)_2 \rightleftharpoons R(OH)_2(org) \qquad K_e \qquad (19)$$

$$B(OH)_3(org) + R(OH)_2(org) \rightleftharpoons B(OH)RO_2(org) + 2\,H_2O \qquad K_1 \qquad (20)$$

The value of K_1 is $K_1 = KK_D/(K_{DB}K_e) = 2 \cdot 10^5$. This estimate of K_1 is of same order as has been experimentally found for some other diols (see Table V), wl is a strong indication that boric acid is extracted in the form of an ester, B(OH)R with 1,3-diols. N.m.r. studies support this conclusion (see below).

Formation of diol polymers

The diol with the highest boric acid distribution value in Table VI is 2, trimethylpentanediol-1,3 (TMPD). This was investigated to see if any dimeric polymeric species were formed in the organic phase. Solutions with diffe concentrations of TMPD were equilibrated with equal volumes of 0.5 *M* sod chloride at pH 2 for 20 min, and the distribution of TMPD was determined. distribution constant (D) of the diol is plotted against the initial concentratio Fig. 8. In Fig. 3 the values for D/K_e are plotted against K_e [A], where [A] is diol concentration in the aqueous phase. The corresponding results for DE EHD and DPPD are also found in Fig. 3.

There seems to be no simple relation between the tendency to polymeriza and the extraction ability for boric acid, as can be seen from the opposite res

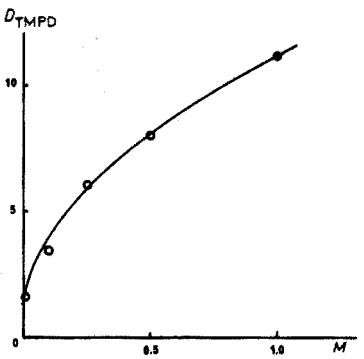


Fig. 8. Distribution values of TMPD between chloroform and water are plotted against the i concentration of TMPD in the organic phase. Extrapolation to zero concentration gives the distrib constant $K_e = 1.6$ of the monomer.

TABLE VIII

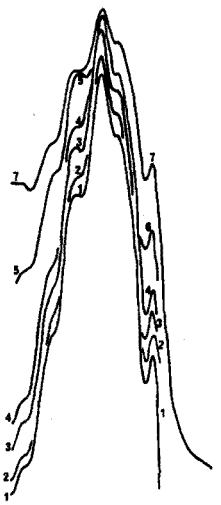
PREDICTED BORIC ACID EXTRACTION ABILITY OF 1,3-DIOLS BASED ON i.r. MEASUREMENTS OF VON RAGUÉ SCHLEYER COMPARED TO THE EXPERIMEN RESULTS OBTAINED BY DISTRIBUTION MEASUREMENTS

Diol	*Predicted order*	*Experimental order*	D_B *for 0.1 M diol in chloroform*
2-Ethylhexanediol-1,3	1	2	4.94
2,2,4-Trimethylpentanediol-1,3	2	1	11.30
2-Ethyl-2-butylpropanediol-1,3	3	3	4.38
2,2-Diethylpropanediol-1,3	4	4	1.24
2,2-Diphenylpropanediol-1,3	5	5	0.51

EHD and DEPD. The low polymerization degree for DPPD may be explained by formation of stronger intramolecular hydrogen bonds. In work on intramolecular drogen bonding in 2-substituted propane-1,3-diols, von Ragué Schleyer[12] tested the orpe–Ingold hypothesis that geminal groups on a carbon atom would bring the ends a carbon chain closer together, thus favouring ring closure. Ring opening is also arded, as it would involve separation of the ends. Only equivalently tetra-substituted bon atoms would be expected to possess exactly tetrahedral angles. Experimental dence was found that the C–C–C angle could be altered as much as 5° by substi- nts in the 2-position. All other parameters being neglected, the intramolecular drogen bond strength due to the 2-positioned groups, according to von Ragué leyer[12], can be used to predict the order of extraction ability for diols with re than six carbon atoms. In Table VIII are listed the orders predicted and perimentally found.

r., INFRARED AND ULTRAVIOLET INVESTIGATIONS OF THE 1,3-DIOL–BORIC ACID ELATES

Some studies were made on the 1,3-diol–boric acid chelates to find out if they associated by hydrogen bonds only, or if ester formation takes place at m temperature. A certain amount of DPPD, which was the only available diol t could be studied in the near ultraviolet region, was dissolved in chloroform and tated with different concentrations of boric acid in aqueous solutions. The spectra m samples of the aqueous phase are drawn in Fig. 9. The peaks found for



. 9. 0.1 *M* DPPD in chloroform was shaken with increasing amounts of boric acid in the aqueous se: 0.0, 0.001, 0.005, 0.01, 0.05, 0.1, and 0.5 *M*. The corresponding ultraviolet spectra of the eous phase are denoted 1, 2, ..., 7.

TABLE IX

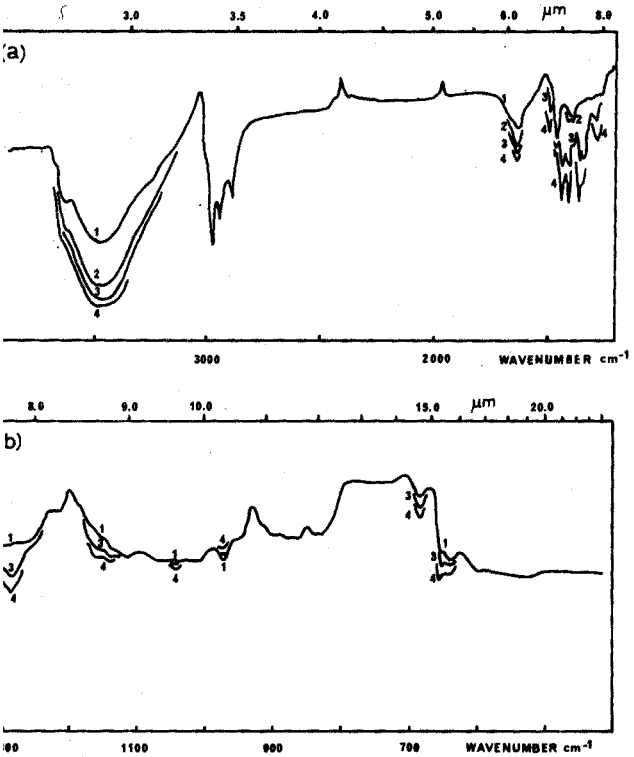
CHANGING PEAK FREQUENCIES IN THE INFRARED SPECTRA OF 2-ETHYLHEXANEDIOL- AND 2,2-DIPHENYLPROPANEDIOL-1,3 (DPPD) IN CHLOROFORM SOLUTIONS SHAKEN WI AQUEOUS SOLUTIONS OF DIFFERENT BORIC ACID CONCENTRATIONS

EHD			*DPPD*		
Frequency	*Change*[a]	*Assignment*[13]	*Frequency*	*Change*[a]	*Assignment*
3665	+		3590	(+)	Free OH-stretch
3620	(+)	Free OH-stretch	3470	+	Bonded OH-stretch
3460	+	Bonded OH-stretch	1630	+	C⋯O stretch in enolize
1630		C⋯O stretch in enolized β-keto-ester	1605	+	ester As above
1490	+	$-CH_2-$ bending	1495	+	$-CH_2-$ bending
1460	+		1450	+	Asym. planar B–O stret
1440	+	Asym. planar B–O stretch	1410	+	Asym. planar B–O stret
1405	+	Asym. planar B–O stretch or OH in plane deformation			OH in plane deformatio
			1365	+	Symm. B–O stretch
1286	+	Symm. planar $B–O_2$ stretch	1345	+	Symm. B–O stretch
1045	+	C–O stretch	1295	+	B–O stretch
975	–		1285	+	B–O stretch
685	+		1145	+	C–O stretch
657	+	BO_3 out of plane deformation	1055	–	C–O stretch
			950	(+)	
			654	+	BO_3 out of plane defor

[a]Direction of change: + increase; – decrease.

DPPD remained unchanged on addition of boric acid, but an hyperchromic eff was evident. As the number of conjugated bonds in the diol remain unaltered by t complex formation, no peak shift was expected.

Infrared spectra were measured for EHD and DPPD. The diols were dissolv in chloroform and shaken with different concentrations of boric acid in aquec solution (I=0.5 *M*, pH 2). The results are summarized in Table IX and t spectra are shown in Figs. 10 and 11. It seems that for both diols, a broadeni of the OH-stretching peak and a relative decrease of the free OH-peak occurs the boric acid concentration is increased. This should mean that a switch fr intra- to intermolecular bonds occurs. The peak changes at 1630 and 1605 cm^{-1} mi indicate the loss of hydrogen and formation of a CO–O–B bond, *i.e.* enolized β-ke ester. Lehmann *et al.*[14,15] made an extensive investigation of the infrared spectra alkoxyboranes and the peak assignments in Table IX are in accord with their resul The typical frequencies found for C–O and B–O vibrations in borate esters a present and it is highly probable that ester formation occurs between these 1,3-di and boric acid in chloroform at room temperature. The results of Werner a O'Brien[16] are also in good agreement. This conclusion is supported by n.m investigations made on DPPD, TMPD, and propanediol-1,3. Borate esters of DPI and propanediol-1,3 were prepared as described by Watt[17]. Spectra were made chloroform solutions containing only the diols, on the same solutions shaken w boric acid, and finally on the borate esters dissolved in chloroform. Spectra DPPD shaken with boric acid and of the DPPD–borate ester were identical a



0. Infrared spectra of EHD for different boron concentrations. The diol was dissolved in chloroform shaken with increasing amounts of boric acid in aqueous phase: 0.0, 0.005, 0.05, and 0.1 *M*. corresponding spectra of the organic phase are denoted 1, 2, 3 and 4.

rent from the spectrum of the diol alone. The CH_2-peak for the aliphatic part e diol shifted from 4.2 p.p.m. to 4.45 for the ester. The propanediol borate ester ved a quite different spectrum from that of the diol alone, but could not be oduced by shaking the diol solution with boric acid. This was expected because anediol-1,3 is one of the compounds with poor extraction properties (Table I). propanediol borate is also readily hydrolyzed when exposed to atmospheric sture Spectra of TMPD alone and TMPD shaken with boric acid are shown ig. 12.

USSION

In previous work[3], a guess was made that if the hydrocarbon residue of the atic 1,3-diol was increased compared to those investigated (DEPD and EHD 7 and 8 carbon atoms, respectively), increased values for $[A]_{org}$ and K_e could xpected but hardly any great changes in the boron distribution ratio $D_B = + K_1[A]_{org} + K_1K_2[A]^2_{org}$). Surprisingly, the D_B values decreased with increased of the 1,3-diol (Fig. 7). Since the main reaction for the boron extraction with s having $K_e \geqslant 1$ is

$$B(aq) + A(org) \rightleftharpoons BA(org) \qquad K_{11}/K_e \tag{21}$$

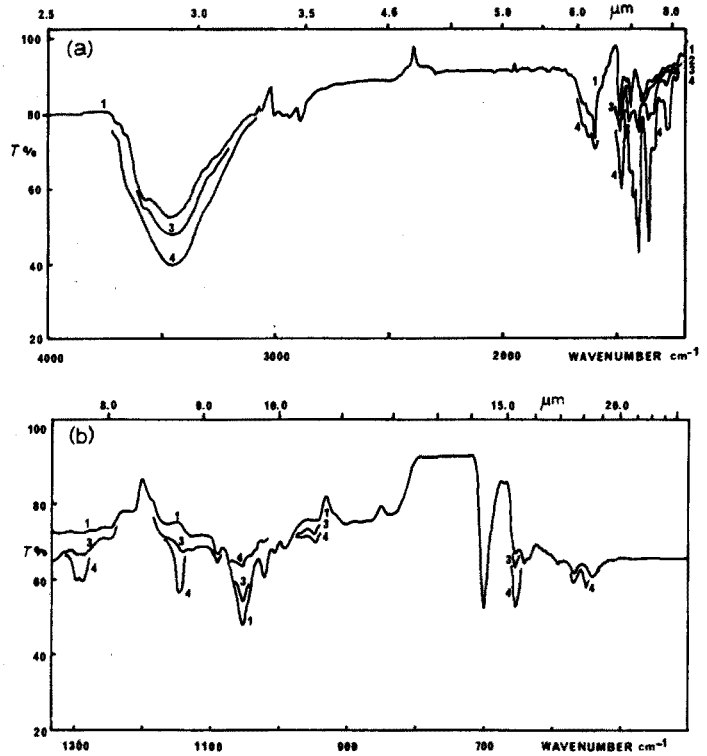
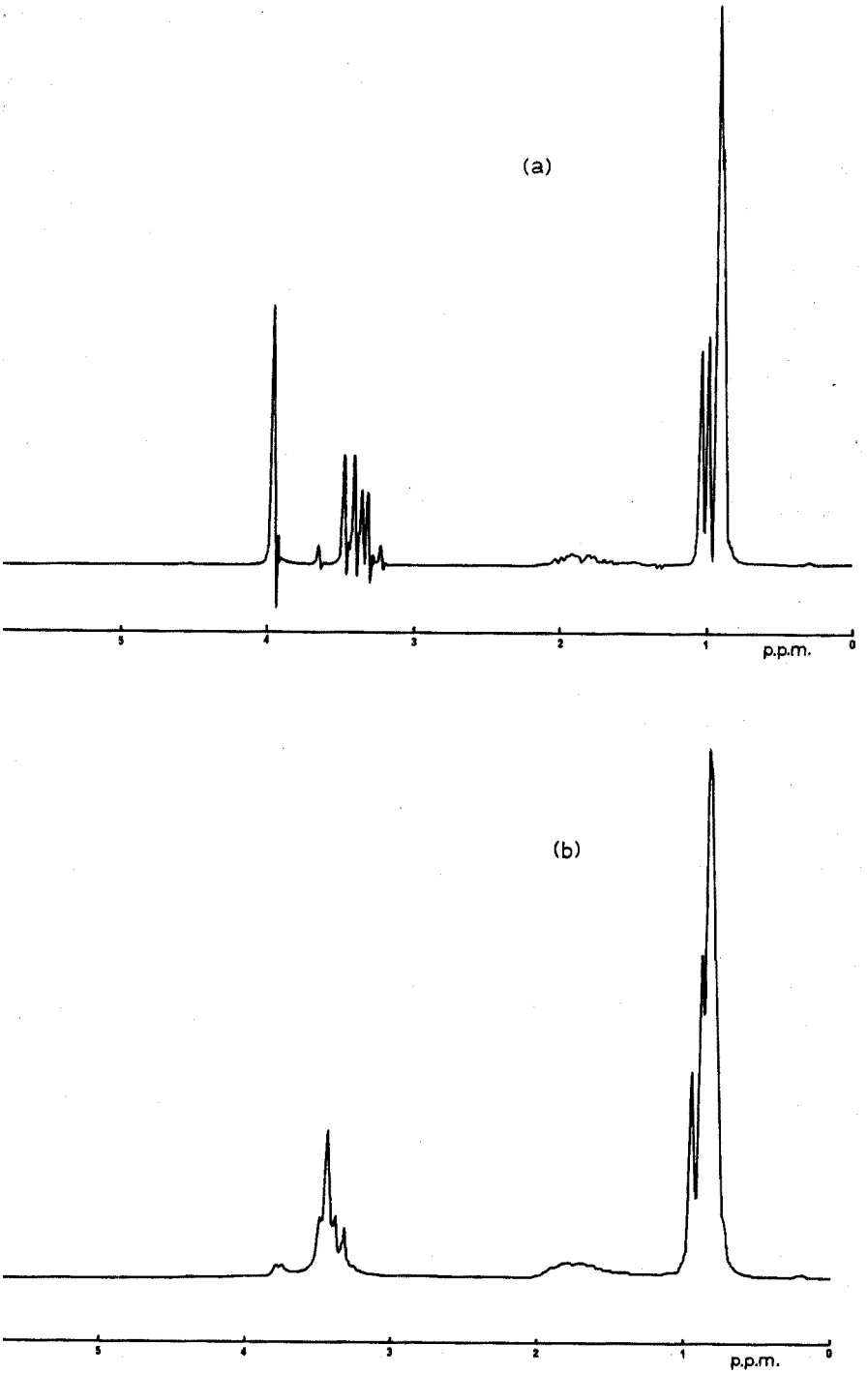


Fig. 11. Infrared spectra of DPPD for different boron concentrations. The diol was dissolved in chlorofo and shaken with increasing amounts of boric acid in the aqueous phase: 0.0, 0.005, 0.05, 0.1 The corresponding spectra of the organic phase are denoted 1, 2, 3, 4. No significant difference co be seen between spectra 1 and 2.

those diols having large values of K_{11}/K_e will have good extraction qualities. Fro Tables III and V the following values of K_{11}/K_e may be calculated:

2,2-Diethylpropanediol-1,3, DEPD	8.3
2-Ethylhexanediol-1,3, EHD	25.2
2,2,4-Trimethylpentanediol-1,3, TMPD	313
2,2-Diphenylpropanediol-1,3, DPPD	6.9

From Table VI, it can be seen that values of D_B for 0.1 *M* solutions of the dio are 1.24, 4.94, 11.30 and 0.51, respectively. 2,2,4-Trimethylpentanediol-1,3 is thus far the most powerful extracting agent, probably because it forms an ester wi boric acid much more readily than the other diols. One explanation could be th the two geminal methyl groups stabilize the six-membered ester ring. TMPD h also a large dimerization constant (Table III). Thus the total number of carbon ato is of minor importance. However, the diols with less than 6 carbon atoms fo compounds which generally are too easily hydrolyzed or too hydrophilic, a can not be considered for extraction use. The species formed between alipha 1,3-diols and boric acid in the organic phase must be regarded as esters; this



. N.m.r. spectrum of TMPD in $CDCl_3$ (a) and of TMPD in $CDCl_3$ shaken with boric acid at emperature (b).

supported by the i.r. and n.m.r. spectra. The solubility of the compounds formed the organic phase is of course also important for extraction.

Some years ago only few aliphatic 1,3-diols were commercially availal but owing to new methods for synthesis, *e.g.* as described by Klein and Medlik the range may be considerably enlarged. EHD has been adapted to different analyti procedures for the determination of boron[19–21], but will probably be replaced the more effective TMPD in the future.

The search for still more efficient extraction systems should probably directed toward combinations of suitable amines and hydroxy compounds. T aromatic 1,2-diols have not been investigated here, although they have promis extraction properties[22]. In unpublished work, Storm[23] found a boric acid distri tion value $D_B = 1.1$ for 1 *M* pyrocatechol between chloroform and aqueous ph and $D_B = 8.13$ for 1 *M* 2,3-dihydroxynaphthalene between hexanol and an aque phase.

The authors are indebted to Professor David Dyrssen, head of the dep ment, for valuable discussions and helpful criticism. We also wish to thank I Reine Torberntsson, who measured the n.m.r. spectra.

SUMMARY

Some 40 compounds have been investigated with reference to their b acid extraction properties. Preliminary tests showed that aliphatic 1,3-diols v at least 6 carbon atoms possess superior extraction qualities compared to diketo hydroxyketones, hydroxyamines and other species investigated. The 1,3-d were then further studied with attention to size and steric configuration. The extract equilibria involved were thoroughly investigated for 2,2-diphenylpropanediol (DPPD). The constants derived showed that this diol, in spite of its large hydroph groups, has a smaller reaction constant than the previously investigated 2,2-dietl propanediol-1,3 (DEPD) and 2-ethylhexanediol-1,3 (EHD). It was found that extraction capacity has a maximum for 1,3-diols with 8–9 carbon atoms. The lar boron distribution was obtained with 2,2,4-trimethylpentanediol-1,3 (TMP which seems to form a very stable ester with boric acid in chloroform at ro temperature. The ester formation is supported by n.m.r. and i.r. spectra. The ef of geminal substituents in the 2-position is discussed.

RÉSUMÉ

Une étude est effectuée sur l'extraction de l'acide borique au moyen diols-1,3 aliphatiques et d'autres agents chélatants; 40 composés ont été exami Des essais préliminaires ont montré que les diols-1,3 aliphatiques possèdan atomes de carbone au moins étaient supérieurs, comparés aux dicétones, hydrc cétones, hydroxyamines et autres composés. Les équilibres d'extraction ont spécialement étudiés pour le diphényl-2,2-propanediol-1,3 (DPPD). Les vale trouvées montrent que malgré ses groupements hydrophobes importants, ce di une constante de réaction plus petite que celle du diéthyl-2,2-propanediol (DEPD) et de l'éthyl-2-hexanediol-1,3 (EHD) précédemment examinés. Le pou

xtraction est maximum pour les diols-1,3 avec 8 et 9 atomes de carbone. La tribution de bore est la plus grande avec le triméthyl-2,2,4-pentanediol-1,3 MPD); il forme un ester très stable avec l'acide borique, dans le chloroforme, à la ıpérature ambiante.

SAMMENFASSUNG

Etwa 40 Verbindungen wurden hinsichtlich ihrer Eigenschaften für die Extktion von Borsäure untersucht. Vorausgehende Versuche ergaben, dass aliphahe 1,3-Diole mit wenigstens 6 Kohlenstoffatomen bessere Extraktionseigenschafals Diketone, Hydroxyketone, Hydroxylamine und andere untersuchte Verdungen besitzen. Die 1,3-Diole wurden dann bezüglich ihrer Grösse und sterischen nfiguration weiter untersucht. Eine gründliche Untersuchung der Extraktionschgewichte bei 2,2-Diphenylpropandiol-1,3 (DPPD) ergab, dass dieses Diol trotz ıer grossen hydrophoben Gruppen eine kleinere Reaktionskonstante als das ıer untersuchte 2,2-Diäthylpropandiol-1,3 (DEPD) und 2-Äthylhexandiol-1,3 ID) hat. Die Extraktionskapazität hat ein Maximum bei 1,3-Diolen mit 8–9 hlenstoffatomen. Die grösste Borverteilung wurde bei 2,2,4-Trimethylpentandiol-(TMPD) beobachtet, das mit Borsäure in Chloroform bei Raumtemperatur einen r stabilen Ester zu bilden scheint. Die Annahme der Esterbildung wird durch i.r.- und i.r.-Spektren gestützt. Der Einfluss geminaler Substituenten in der 2-llung wird diskutiert.

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ELATING ION-EXCHANGERS CONTAINING 4-(2-PYRIDYLAZO)-ORCINOL AS THE FUNCTIONAL GROUP

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ived 5th March 1973)

The value of 4-(2-pyridylazo)naphthol (PAN) and 4-(2-pyridylazo)resorcinol R) as wide-range spectrophotometric reagents for metals is now firmly blished[1–4]. The incorporation of these heterocyclic azo dyestuffs into a resin ix to produce a chelating ion-exchanger is the subject of this paper. In line previous work on 8-hydroxyquinoline resins[5], two methods of producing chelating exchangers were considered: (*a*) condensation of the ligand with aldehyde, and (*b*) coupling of a polystyrene diazotate to the ligand in line solution.

On theoretical grounds, PAN is unsuitable for either reaction owing to deactivating influence of the azo group on the naphthol. However, in the of PAR, azo deactivation of the aromatic ring should be more than t by the presence of the two phenolic groups in the 1 and 3 positions, ving condensation with formaldehyde to give a linear polymer linked via 2 and 6 positions. These two positions should also be available for coupling diazotized poly(aminostyrene) with the 6 position being preferred. Conently, PAN was rejected and attempts were made to incorporate PAR into ndensation polymer cross-linked with resorcinol, and into a cross-linked, oporous polystyrene by diazo coupling.

Optimal pH conditions for the formation of many metal–PAR complexes in spectrophotometric determinations and when PAR is used as a complexic indicator have been reported in the literature[4]; these pH values would xpected to be the values at which a PAR resin would show maximal city for the corresponding metal ion. Resins containing PAR functional ps should show selectivity for copper(II) over nickel(II), and for uranyl zinc ions, for the reported stability constants[2,3], for the copper and uranyl plexes with PAR are greater than the values for nickel and zinc com-es by *ca.* 10^3.

The validity of this simple approach was tested by examining the behaviour he PAR resins produced with nine ionic species known to form PAR ıtes.

RIMENTAL

aration of PAR

PAR was synthesized by the reaction of 2-aminopyridine with sodium

ethoxide and isoamyl nitrite, the resulting diazo compound being allowe react with resorcinol in alcohol[6].

Preparation of condensation polymer

PAR (0.03 mole), resorcinol (0.03 mole) and sodium hydroxide ((mole) were dissolved in 30 ml of water and 0.016 mole of formaldehyde a 40% solution) was added. The solution was placed on a water-bath fo min, and then allowed to stand at room temperature until gelation occurred. gel was cured at 115° for 48 h, the resulting resin being crushed and si and the 30–60 mesh fraction retained.

The resin was washed repeatedly with sodium hydroxide solution with water, and was then shaken for 16 h with *M* hydrochloric acid. A water washing, until a pH of 4.5 was achieved, was followed by air-dryin the material.

Preparation of polystyrene–PAR

The starting material was a lightly cross-linked, macroporous polysty divinylbenzene copolymer (Amberlite XAD-2, Rohm and Haas Co., 20–50 m The nitration, reduction and diazotization steps were carried out as desc by Davies *et al.*[7]. Coupling of the diazotate to PAR was carried out i alkaline solution maintained at 0–5°. The product was thoroughly wa with water, Soxhlet-extracted with ethanol for 16 h and then washed witl *M* hydrochloric acid and finally with water. The product was air-dried.

Resin characterization

Water regain. Samples of air-dried resin were allowed to stand in ionized water for 48 h. The resins were then filtered by suction and li pressed between filter papers to remove surface moisture. The moisture tents were determined by drying at 100° for 48 h.

Microanalysis. Oven-dried resin samples were crushed to a fine po and stored *in vacuo* over phosphorus pentoxide. Carbon, hydrogen and nitr contents were obtained with a Perkin-Elmer 240 Elemental Analyzer. S samples from each stage of the preparation were also retained for analysis.

Non-aqueous titrimetry. The polystyrene exchanger underwent a redu step to the amine during its preparation. The amine content was deter by titration with perchloric acid in acetic acid as described earlier[5].

Resin capacity determinations

The nine elements used in capacity determinations were aluminium, cc copper, iron(III), nickel, uranium (as uranyl ion), vanadium(V), zinc zirconium. Capacity measurements were obtained for sodium acetate–acetic buffers which were 0.1 *M* in the metal ion concerned. The resin and buf solution were equilibrated for 48 h, after which time the resin was fil and washed with buffer of the appropriate pH, and the metal was e from the resin with 4 *M* hydrochloric acid before its spectrophoto determination.

The spectrophotometric methods used were diethyldithiocarbamate

per[8], thiocyanate–acetone for cobalt[9], dimethylglyoxime for nickel[9], zincon zinc[10], 8-hydroxyquinoline for aluminium[11] and uranium[8], thioglycollic acid iron[8], N-benzoylphenylhydroxylamine for vanadium[12], and alizarin for onium[13].

ilibration rate

From the capacity studies, the total capacity of the resin for copper known. Twice this theoretical quantity of copper ions was diluted with er to give a 0.05 *M* solution, and this mixture was equilibrated at the imal pH with 1 g of air-dried resin. Using eight equilibrations with the n, the resin was removed from the solutions at various times over a period 48 h, and the copper content of the resin was determined. Graphs of per capacity against time were then constructed.

ULTS AND DISCUSSION

R–*resorcinol–formaldehyde resin*

It was found that the PAR–resorcinol–formaldehyde resin, even after ated washing procedures, was readily leached by alcohol with subsequent of ion-exchange properties. Furthermore, on attempting to remove ions n the resin by washing with 4 *M* hydrochloric acid, yellow material was hed from the resin and was precipitated when the acid was diluted. It was cluded that it was impossible to prepare a cross-linked, PAR–formaldehyde densate with satisfactory properties for ion exchange. Consequently, the only acity determinations on this resin were made after the work on poly-ene–azo–PAR had been completed, and were restricted to capacities for three c species at a pH corresponding to the optimal pH found for the poly-ene exchanger. These capacities of the polycondensate were very low, the iest being 0.13 mmole g^{-1} for iron(III); the resin was quite unsuitable as ielating ion-exchanger (Table I).

ystyrene–azo–PAR resin

Curves of total capacity against pH for the polystyrene–azo–PAR resin

LE I

AL CAPACITY OF PAR RESINS AT OPTIMAL pH

n	*Capacity (mmole g^{-1}) at optimal pH*				
styrene–azo–PAR	*Cu(II)*	*Fe(III)*	*Zr(IV)*	*V(V)*	
	0.72	1.50	0.09	1.35	
	(>5.4)	(6.1)	(6.1)	(2.0)	
–resorcinol–aldehyde	0.03	0.13	—	0.01	
styrene–azo–PAR	*Co(II)*	*Ni(II)*	*UO_2(II)*	*Zn(II)*	*Al(III)*
	0.29	0.23	0.13	0.33	0.27
	(5.8)	(6.1)	(2.3)	(6.1)	(4.6)

are shown in Fig. 1; the capacities at the optimal pH for each metal are given in Table I. This resin had a water regain of 0.7 g g^{-1} correspon to 43% moisture. From equilibration rate measurements, the time to 50% r saturation was found to be 45 min, which is a sufficiently short time for resin to be operated efficiently in column form as has been shown in earlier wo

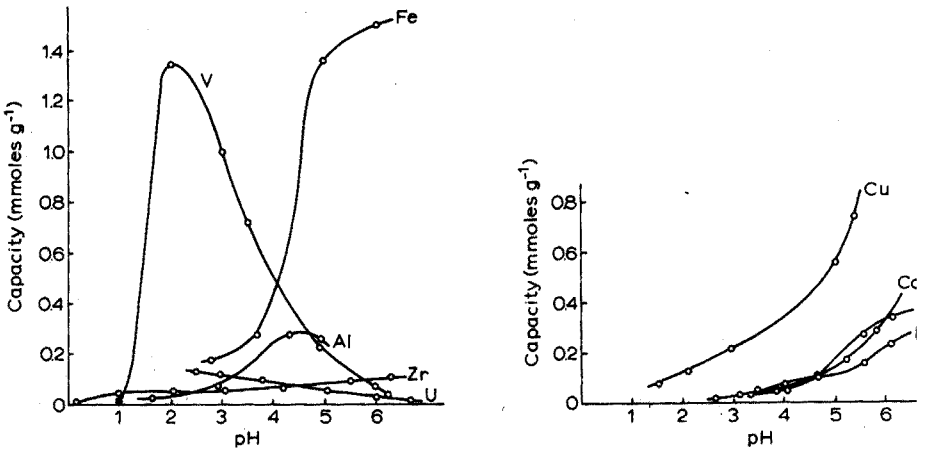
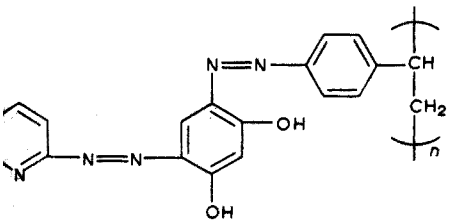


Fig. 1. Capacity versus pH curves for cations on polystyrene–azo–PAR resin.

The high capacities found for iron and vanadium show that these ions can be separated from other metal ions and from each other. As iron interferes in the spectrophotometric determination of vanadium with N-benz phenylhydroxylamine, the resin could find application in the analysis of vanad steels. Separation of copper from nickel, as predicted from the stability const of the metal–PAR complexes, is shown by the capacity curves to be feasibl the pH range 4–5. The behaviour of uranyl and zinc ions also accords stability constant measurements. Uranium can be separated from zinc at 2–2.5, and although the capacity for the uranyl ion has the low value of mmole g^{-1}, this corresponds to a resin uptake of 30 mg of uranium p of resin.

Elemental analysis of the dried resin showed a nitrogen content of 7 From the nitrogen contents of the nitro- and amino-polystyrene stages titration values on the poly(aminostyrene), it was found that this material tained 2.65 mmole of nitro groups and 3.9 mmole of amino groups per g. 7.7% nitrogen, after coupling to PAR, can therefore be accounted for, if resin contains 2.65 mmole of nitro, 0.71 mmole of amino and 0.43 mmol chelating groups per g; this would correspond to a 75% conversion of am to azo-PAR units. This value of 0.43 mmole g^{-1} should be the maxir total capacity of the resin if 1:1 complexes are formed. The value is cl exceeded by copper, iron and vanadium; as azo coupling to PAR prob proceeds *via* the 6 position, the resin will have structure I.

This structure has two chelating sites, the PAR and the azoph groupings. If both are used, the maximum capacity should therefore be



I

mole g $^{-1}$. The maximal observed capacity for iron(III), 1.50 mmole g^{-1}, can nly be achieved if the diazo-coupling step proceeds to 100% and both chelating ites are used. Unfortunately, it was not possible to verify the amino content f the product by non-aqueous titration; if amino units are present, however, hey would be expected to function as anion-exchangers in an acid medium. The apacity of the resin for iron in 7.5 *M* hydrochloric acid was therefore deter- ained and values of 0.30 mmole g^{-1} were obtained, the absorbed species being he chloroferrate anion.

'apacities in the presence of a competing ligand

The system studied was resin–iron(III) at pH 6.1; acetate buffers which ere 0.1 *M* in iron(III) and 0.1 *M* in competing ligand(s) were used. In the resence of acetate buffer only, the capacity was 1.50 mmole g^{-1}. Citrate educed the capacity to 0.34 mmole g^{-1}, citrate and cyanide to 0.30, citrate nd thiocyanate to 0.31, and citrate and EDTA to 0.03 mmole g^{-1}.

ffect of initial concentration of metal ion

The resin–uranyl system was studied; the uranyl concentration was varied etween 0.01 and 0.1 *M* with a constant ionic strength of 0.50 maintained y addition of sodium nitrate. In this system, the capacities were higher than ose shown in Table I, owing to the presence of the backing electrolyte. The apacity showed a strong dependence on uranyl concentration in the region 0.01– .05 *M*, becoming constant as the concentration increased above this range. 'apacity values for 0.01, 0.05 and 0.1 *M* uranyl solutions were 0.19, 0.24 and .24 mmole g^{-1}, respectively.

ffect of co-ion on capacity

The resin–uranyl system was studied in the absence of backing electrolyte; .05 *M* uranyl solutions were used and a pronounced effect on capacity was bserved. The three systems examined were nitrate, chloride and acetate, which ielded uranyl capacities of 0.12 and 0.24 and 0.41 mmole g^{-1}, respectively.

ONCLUSIONS

The preparation of a polymerized PAR moiety by reaction of PAR with ormaldehyde is feasible in theory, but cannot be realised in practice.

The polystyrene–azo–PAR chelating resin exhibited interesting chelating roperties by comparison with PAR itself. The high capacities for copper, iron nd vanadium suggest a method of separating these metals from other elements

by use of the exchanger in column form. However, the exchange mechani is complex and would appear to involve the nitroso-phenol structure in addit to the PAR grouping in the resin.

The marked reduction in resin capacity in the presence of citrate a competing ligand indicates that the stability of the iron(III)–resin complex not very high. This is in agreement with the capacity curve for iron(III) wh shows that appreciable uptake by the resin occurs only above pH 4. For ura ion (and possibly other species) the resin capacity is highly dependent on uranium concentration below 0.01 *M* where film diffusion becomes the r controlling factor, and on the nature of the co-ion.

SUMMARY

The synthesis of a cross-linked polystyrene–azo–PAR resin, and its chelat ion-exchange properties with nine ionic species, are described. A resin structu containing both PAR and azophenol chelating groups is proposed. The eff on capacity of varying ionic concentration and the nature of the co-ion w studied.

RÉSUMÉ

La synthèse d'une résine polystyrène–azo–PAR est décrite. On examine propriétés chélatantes d'échange ionique avec neuf composés ioniques. On prop une structure de résine contenant à la fois PAR et azophénol. L'influence concentrations ioniques variables et de la nature des ions est étudiée.

ZUSAMMENFASSUNG

Die Synthese eines quervernetzten Polystyrol–Azo–PAR-Harzes und des chelatisierende Ionenaustausch-Eigenschaften bei neun ionischen Spezies wer beschrieben. Es wird eine Harzstruktur vorgeschlagen, die sowohl PAR als a Azophenol als chelatisierende Gruppen enthält. Der Einfluss auf die Kapaz bei Variation der Ionenkonzentration und der Art des Co-Ions wurde un sucht.

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SELECTIVE GAS CHROMATOGRAPHIC DETECTOR FOR OLYNUCLEAR AROMATICS BASED ON ULTRAVIOLET LUORESCENCE

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eceived 6th February 1973)

Many aromatic ring systems ranging from benzene to the more complicated lynuclear arenes are frequently encountered as air pollutants. These substances cur in motor fuels, and enter the open atmosphere via automobile exhausts; they so occur at construction sites, refineries, and even in household items. Polynuclear omatic compounds have been definitely shown to be toxic and in some cases rcinogenic to people.

The combination of gas chromatography with a vapor-phase fluorescence tector offers a selective and sensitive method of analysis for polynuclear aromatic ıg systems. In the detector described, only a simple change of excitation and ission filters is needed to observe the fluorescence of different types of aromatic ıg systems. The electron-capture detector has been used previously for the analysis the polynuclear ring systems but it lacks selectivity, requires special handling, and expensive.

There are at least three previously published papers involving the adapta-)n of a fluorescence detector to a gas chromatograph. Bowman and Benzoa[1] vised a system in which the gas effluent was dissolved in a stream of ethanol 5%). The alcohol stream was then monitored in a flow cell at the desired excitation id emission wavelengths. Burchfield *et al.*[2] developed a system by interfacing an minco-Bowman spectrofluorimeter with a gas chromatograph, thus measuring ıe vapor-phase fluorescence. Freed and Faulkner[3] improved both the qualitative id quantitative aspects of Burchfield's instrument by the direct coupling of a fast-anning fluorescence spectrometer to a gas chromatograph. Their instrument nerated both excitation and emission spectra. All these publications gathered ıportant data and demonstrated the feasibility of a fluorescence detector. But the ıorescence detectors described did not lend themselves easily to commercial oduction owing to large size, high cost and a high degree of complexity.

The vapor-phase effluent detector described herein is compact, inexpensive, latively simple. It provides reliable quantitative data. The sensitivity limit of the tector, was shown to be of the order of nanograms for the compounds examined.

The principle of the detector is that the compounds are exposed to wide band v. excitation radiation (range 200–350 nm). Any generated fluorescence is measured so over a wide band range (360–460 nm). Filters are used to select the band-sses. The excitation and fluorescence ranges selected can be altered at will. They e non-selective, also they do not overlap each other, thus avoiding light scattering

problems. It was felt that the wide bands increased analytical sensitivity, and wc be very simple to construct on a commercial basis.

EXPERIMENTAL

Excitation sources

A Xe–Hg lamp (Hanovia Lamp Division) was housed in Schoffel Instrun lamp housing. The maximum luminous flux was 30,000 lumens with an aver brightness of 360 cds mm^{-2}.

A Honeywell temperature controller Model R7350, a Techtron photon tiplier power supply, and a Sargent-Welch Model SRLG recorder with a maxim full-scale sensitivity of 0.4 mV were used.

The benzene solvent was Mallinckrodt analytical-grade reagent. Arom hydrocarbons were obtained from Matheson, Coleman and Bell and Ald Chemical Company.

The carrier gases were obtained from Airco of New York.

RESULTS AND DISCUSSION

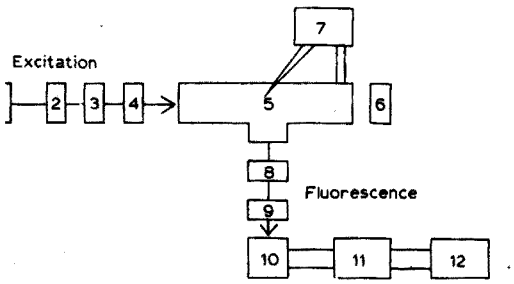
In the normal fluorescence process a molecule in the ground singlet st absorbs a photon of radiation. It is promoted to an excited singlet state, unc going internal conversion to the lowest excited singlet state (S_1). It then er radiation (fluorescence) and simultaneously returns to the ground singlet st (S_0). There are two other pathways for an excited molecule to return to the grou state: internal conversion and intersystem crossing followed by phosphorescer Vapor-phase luminescence of polynuclear aromatic ring systems at high temperat is almost totally restricted to fluorescence, thus phosphorescence will be igno Internal conversion, however, cannot be neglected, because a large portion of excited molecular species can return to the ground singlet state by this mechani It has been assumed that this quenching mechanism is due to energy tran during collision between the excited molecular species and the "carrier gas" t the molecular species and the solvent, benzene. This is particularly true at the eleva temperatures necessary to separate high-molecular-weight polynuclear aromatics gas chromatography.

In the construction of the instrument the design of the cell was critical si it was desirable to keep the background radiation from reflection low. Several designs were attempted before the cylindrical cell was adopted. One problem v the cylindrical cell was that only a fraction of the total fluorescence proceeded dc the light-path. In the final cell, the fluorescence window viewed only 3.7 cm the total cell volume which was 116 cm^3. But this cell was designed to measure fluorescence of a molecular species in a moving carrier gas stream thereby simula the fluorescence of a molecular species in a gas chromatograph. The advent of the v bandpass excitation and emission filters with a small "dead zone" between radiation zones reduced problems caused by scattering of the excitation light that cell design is less critical.

An excitation filter (250–380 nm) and a fluorescence filter (400–500 were incorporated into the fluorescence detector for wavelength isolation inst

using monochromators as has been done previously. There was a 20-nm "dead ıe" (380–400 nm) where neither filter transmits radiation, thus the photomulti- er tube detector was isolated from any scattered radiation from the source, and ected only the fluorescence radiation. These wide bandpass filters increased ısitivity by several orders of magnitude over the interference filters with a band- ss of 10 nm. The monochromators used by Burchfield *et al.*[2] and Freed and ulkner[3] generated a bandpass of 3–5 nm, thus the sensitivity of their systems s reduced. But their fluorescence spectra permitted qualitative information for identification of molecular species. The vapor-phase fluorescence detector scribed herein is most useful for quantitative work and yields little structural ormation.

A complete schematic diagram of the instrument is illustrated in Fig. 1. ere were two proposed analytical procedures.



1. Schematic diagram of equipment. (1) Xe–Hg lamp; (2) H_2O filter; (3) activation filter 250–380 (4) lens; (5) cell; (6) mirror; (7) temperature control unit; (8) lens; (9) fluorescence filter 400–500 (10) P.M. tube; (11) P.M. tube power supply and amplifier; (12) X-Y recorder.

cedures used to measure fluorescence

The two procedures used were (1) measurement of fluorescence intensity ler static conditions, and (2) measurement of fluorescence intensity under flowing ıditions. In the first process, the cell was flushed with the carrier gas, then the flow was stopped, the sample was injected and the fluorescence intensity asured. This static method was used for the preparation of the calibration curves l other data presented in this publication. When the second dynamic system s used, the fluorescence intensity was reduced because of differential vaporization. ıen the sample and solvent were injected into the front of the cell, the sample orized over a period of time. Thus the carrier gas swept varied concentrations nolecular species past the fluorescence window. This resulted in a small irregular ık with a broad base. There was an obvious reduction in sensitivity when peak ght was used as a measure of concentration. Peak area was difficult to measure he lower concentrations but appeared to yield approximately the same sensitivities peak height for the flowing system. If the detector is coupled to a gas omatograph, the problem of vaporizing the sample will be eliminated and each nponent of the sample should enter the detector over a short period of time, ıs eliminating the time *versus* concentration problem.

ısitivity

Under static conditions, peak height was used as a measure of fluorescence

intensity and was correlated with sample concentration. It was shown that peak height remained relatively stable over a period of time.

Sensitivities obtained were as follows.

Compound	*Concentration (M)*	*Signal (div.)*	*Sensitivity (ng*
Anthracene	10^{-5}	2.0	1.07
9-Phenylanthracene	10^{-5}	6.5	2.54
9-Methylanthracene	10^{-4}	30.0	19.0

Quenching studies

The first study carried out was quenching due to both the carrier gas and benzene solvent. Figure 2 demonstrates clearly the effect of differing volumes benzene on the same sample size (254 ng) at the same pressure (1 atm). As can seen from the curve, benzene was shown to reduce the fluorescence intensity. T problem would be eliminated by interfacing the detector with a gas chromatogra because the solvent and sample would be separated on the column. Quenching the carrier gas increased in the following order, $Ar < N_2 < CO_2 < He$.

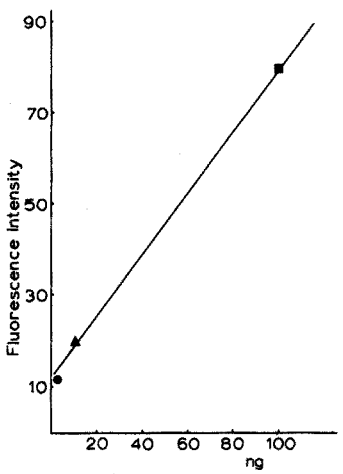


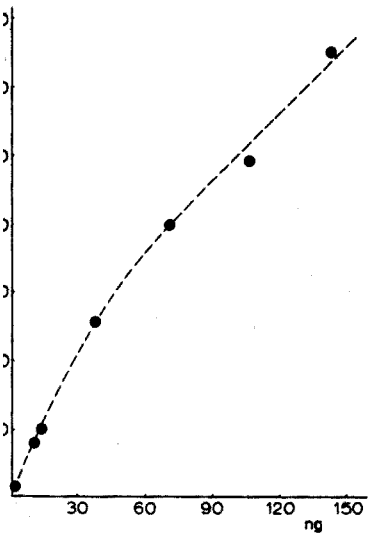
Fig. 2. Quenching effect of benzene. A constant quantity of 9-phenylanthracene (10^{-9} mole; 254 ı was introduced into the constant volume cell maintained at 1 atmosphere with mixtures of benzene a argon. The concentration of benzene was varied between samples: (■) 1 μl benzene (10^{-3} *M*); (▲) μl benzene (10^{-4} *M*); (●) 100 μl benzene (10^{-5} *M*).

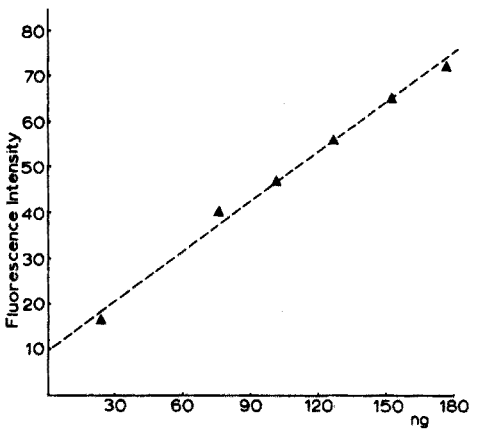
Burchfield *et al.*[2] demonstrated that fluorescence intensity changed with tei perature. The results obtained here for *ca.* 2 μg of anthracene indicated negligit reduction in intensity over a temperature range of 288–412°. It cannot be conclud that the fluorescence detector was independent of temperature, but it was shown be relatively constant over a useful range of temperatures. It was found that f 9,10-dichloroanthracene and other compounds, decomposition occurred the higher end of this range. To avoid decomposition problems, the fluorescen cell was kept at *ca.* 350° by a proportional temperature controller (Honeywell).

A calibration curve relating fluorescence intensity, as measured by pe height, to concentration of anthracene is shown in Fig. 3; it can be seen that

approximately linear above 50 ng; below this, there is a downward bending, ich may be attributed to benzene quenching.

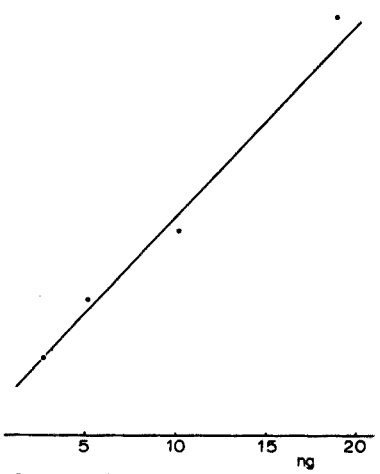
The plot of fluorescence intensity *versus* concentration for 9-phenylanthracene s linear from 25 to 180 ng (Fig. 4). An extended plot of the lower end of the range m 2.5 ng to 21 ng is given in Fig. 5. The curves showed deviation from linearity

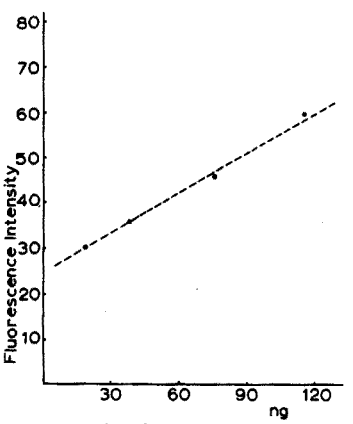




3. Fluorescence intensity *vs.* sample size (ng) for anthracene. 1-μl sample volumes.

4. Fluorescence intensity *vs.* sample size (ng) for 9-phenylanthracene. 1-μl sample volumes.





. Lower end of curve. Fluorescence intensity *vs.* concentration for 9-phenylanthracene. 1-μl sample ies.

Fluorescence intensity *vs.* sample size (ng) for 9-methylanthracene. 1-μl sample volumes.

when large changes in benzene/sample concentrations were encountered but small benzene/sample changes there was no deviation from linearity. It was felt th relatively high concentrations, quenching by the benzene became more appare

The calibration curve for 9-methylanthracene is given in Fig. 6. In concentration range 19–120 ng, the plot was linear.

Conclusion

The system described utilizes broad excitation radiation. This ensur highly efficient means of exciting the sample molecules. After excitation, the m cules fluoresce at a longer wavelength than the excitation wavelength. The fluc cence is observed after passing through a broad band wavelength filter. This ens that a large portion of the fluorescence proceeded down the light-path and measured.

The wavelength ranges of the excitation and fluorescence filter did not c lap; this avoided interference caused by scattering.

A number of polynuclear aromatics were examined. The sensitivities tained were about 10^{-9} g at temperatures up to 350°. The system can be use a g.c. detector.

SUMMARY

A vapor-phase fluorescence detector for the analysis of mixtures of p nuclear aromatic ring systems has been developed. This system utilizes wide b pass excitation and wide band emission filters, thus increasing sensitivity decreasing the complexity of previously designed instruments. The sensitivity o detector has been demonstrated to be at the nanogram level with reasonable p sion.

RÉSUMÉ

On propose un détecteur de fluorescence, en phase vapeur, pour l'analys mélanges aromatiques polynucléaires. On utilise un système d'excitation et d'émis à bande large, permettant d'augmenter la sensibilité tout en diminuant la c plexité des instruments préalablement décrits. La sensibilité du détecteur es l'ordre du nanogramme, offrant une précision satisfaisante.

ZUSAMMENFASSUNG

Ein Dampfphasen-Fluoreszenzdetektor für die Analyse von Gemischen m kerniger aromatischer Ringsysteme wurde entwickelt. Bei dem System we Anregungsfilter mit breitem Bandpass und Breitband-Emissionsfilter verwer wodurch die Empfindlichkeit vergrössert und die früher vorgeschlagenen Instrum vereinfacht werden. Die Empfindlichkeit des Detektors liegt im Nanogrammbe bei hinreichender Reproduzierbarkeit.

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LUBLE ALUMINUM IN MARINE AND FRESH WATER BY S–LIQUID CHROMATOGRAPHY*

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eived 18th December 1972)

Considerable quantities of alumino-silicate particulate material—the products rrestrial weathering—are transported to the oceans, and the distribution patterns his suspended sediment have been studied as a potential fresh–marine water ing tracer[1–3]. Examples of average particulate aluminum values obtained are $\mu g\ l^{-1}$ for Californian coastal waters[1] and 2.0 $\mu g\ l^{-1}$ in the Gulf of Mexico. At pH of sea water, aluminum would be expected to be substantially precipitated he hydroxide, and little is known of the distribution patterns or character of the olved species although polyhydroxy, polynuclear complexes might be predicted ı $Al(OH_4)^-$ as the dominant species. Partial stabilization as organic complexes also been suggested[3]. Mean dissolved values of 2.5 and 1.0 $\mu g\ l^{-1}$ have been cited restricted Atlantic[4] and Pacific[1] Ocean areas, respectively. The soluble–particulate ndary is generally defined, as in most oceanographic work, by retention of the er on a 0.45-μm filter membrane. Of all the trace metal constituents of the ans, aluminum appears to have the highest uptake concentration factor onto lower trophic level organisms[5].

Aluminum in sea water has most usually been determined fluorimetrically ı the pontachrome blue–black R reagent[1,3,4] with due regard[6] for iron internce. This procedure has been noted[2] to be considerably more sensitive than commonest absorption spectrophotometric method employing ferron[7]. Atomic trometric analysis is insufficiently sensitive to provide for a direct determination he dissolved aluminum present in natural waters. Atomic absorption preceded various extraction and concentration steps has been advocated[8], but routine lication demands extreme care to avoid the errors commonly introduced during ı pre-analysis manipulations. Ottaway *et al.*[9] have recently introduced a conrably more sensitive indirect atomic absorption procedure based upon the ancement of iron absorption by coexisting aluminum. The detection limit (10 b.) claimed for this procedure may theoretically suffice for many natural waters is inapplicable to sea water without prior treatment to separate the metal from concomitants and to increase the soluble iron content.

Gas–liquid partition chromatography (g.l.c.) is an exceedingly sensitive).b. range) technique for the determination of certain metals present in the form rgano-complexes[10–12]. The organic ligand–solvent system is conveniently chosen

* Contribution No. 187 from the Institute of Marine Science. Part of this work was presented at A.G.U. National Fall Meeting, San Francisco, December, 1971.

to be compatible with the requirements of electron-capture detection, and we h previously[13] reported on the application of trifluoroacetylacetone in toluene determinations of Co, Fe, In and Zn in a sea water matrix. It has been further note that this system is particularly well suited to the frequently difficultly determin trivalent elements, and no other completely satisfactory analytical method e for aluminum at the trace level as noted above. G.l.c. analyses for aluminum pre in several materials have been reported[14,15], but these methods have not previo been applied to the extractable contents of natural waters. This contribution de the procedures necessary for obtaining optimal instrumental conditions for the de mination of aluminum trifluoroacetylacetonate, and demonstrates the detec of aluminum extracted from both marine and fresh water samples. The extrac efficiency of the trifluoroacetylacetone–toluene system for aluminum from water has not been determined, although no problems are envisaged in this a It has been reported[12,14] that aluminum may be totally extracted from fresh w by trifluoroacetylacetone into benzene at pH 4 or greater, and it has been show that the trifluoroacetylacetone–toluene system in general yields superior extrac characteristics from sea water compared with fresh waters of lower ionic stren

EXPERIMENTAL

Preparation of aluminum–trifluoroacetylacetonate

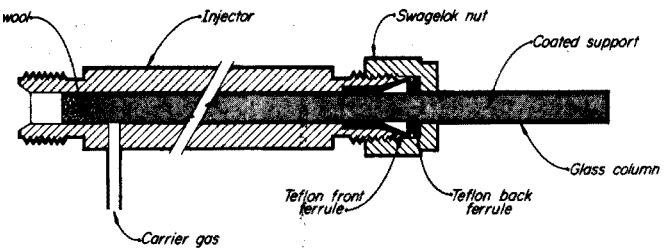
Aluminum nitrate (25 g) and sodium acetate (15 g) were dissolved in 250 of double-distilled water. This solution was mixed with 250 ml of trifluoroace acetone (0.1 *M*) in ethanol and mechanically shaken. The impure, colored precipi which formed within 20 min consisted predominantly of copper and iron c plexes. This was discharged and the supernate was shaken until the reaction completed. The final precipitate was recrystallized from Baker G.C.-grade benz and dried under slight vacuum at room temperature to obtain the pure alumin chelate (m.p. 122°).

Apparatus

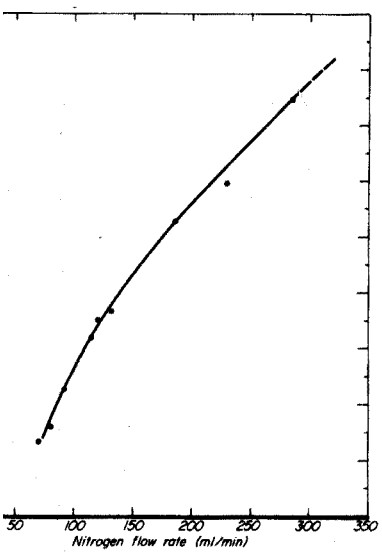
A Varian Model 1520B gas chromatograph equipped with a tritium electr capture detector and an ancillary cell voltage regulator was employed. The inject port of the instrument was modified for on-column injection. The injector insert removed and a 6-mm o.d. glass column was inserted to within about 7 mm of septum as shown in Fig. 1. A 10-μl syringe was used for injecting 2-μl sam volumes into the column. Two 150 × 6 mm o.d. pyrex glass columns were pac with mixed liquid phases, 5.08% silicone SE 30–0.34% carbowax 20 M, and 4 DC 710–0.2% carbowax 20 M, respectively, on 60–80 mesh Gas Chromo Z. support was coated following the method advocated by Parcher and Vrone[16] both columns were preconditioned for 24 h at 25° below the lowest recommen maximal temperature of the liquid phases.

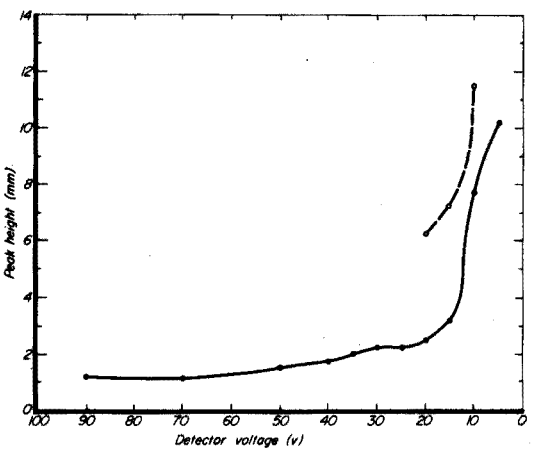
Operating conditions

Optimal nitrogen flow rate and cell voltage parameters were establishe illustrated in Figs. 2 and 3. The chromatograph operating conditions determi for this work were as follows: injection port, on-column injection at 123°; colu



1. Modification of injection port used for on-column injection.





2. Detector response to $1.1 \cdot 10^{-9}$ g of aluminum trifluoroacetylacetonate as a function of nitrogen r gas flow rate at an applied potential of 20 V. Broken line indicates region of unstable background.

3. Detector response to $1.1 \cdot 10^{-9}$ g of aluminum trifluoroacetylacetonate as a function of applied tor voltage. Nitrogen flow rate: (——) 114 ml min^{-1}; (----) 285 ml min^{-1}.

perature, 118°; cell voltage, 5 V; detector temperature, 203°; carrier gas, pre-fied nitrogen; flow rate, 285 ml min^{-1}. The preferred column was 4.6% DC 710–; carbowax 20 M on 60–80 mesh Gas Chromo Z.

ple preparation for chromatography

The sea water sample (30 ml) was mechanically shaken in a separatory funnel l h with 15 ml of trifluoroacetylacetone (0.1 *M*) in toluene solution. Trifluoro-ylacetone is a high electron-affinity compound which causes a strong detector onse. Since this ligand was added in excess, it was necessary to remove the acted fraction, and this was accomplished following the initial separation with mmonia solution (0.01 *M*) wash as suggested by Gentry *et al.*[14]. One additional water sample was spiked with 10^{-6} g of aluminum as the nitrate and treated as ribed.

Fresh water samples may be prepared for chromatographic analysis in a

similar fashion. The sample utilized for this present study (from Smith Lake shallow interior Alaskan pond) had a high dissolved organic content which cau the electron-capture detector to function abnormally. In this case the water v oxidized by a standard ultraviolet irradiation technique before the chelation a extraction steps.

RESULTS AND DISCUSSION

On-column injection

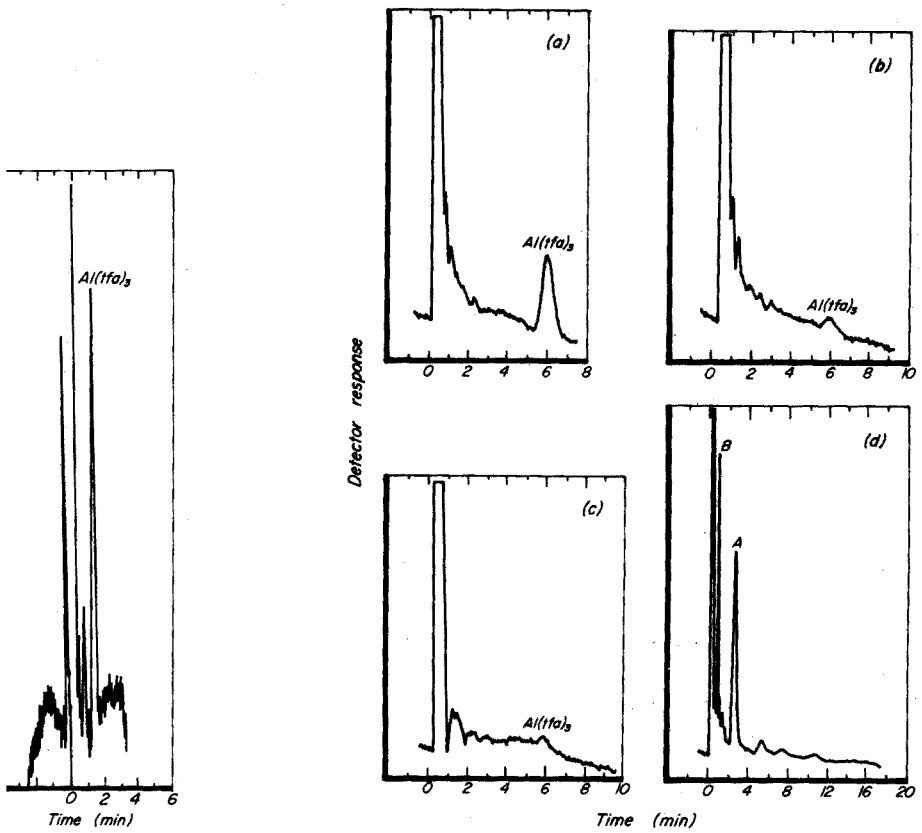
To obtain sharp chromatographic peaks, the flash-vaporization injecti temperature is usually maintained at least 20–30° in excess of the column temperatu Many trifluoroacetylacetone chelates are eluted at column temperatures betwe 100–150°, and an injection temperature of around 135° is commonly employed order to produce optimal chromatograms[10–12,14,15]. Unfortunately, at this te perature, it has been noted[10] that the trifluoroacetylacetone complexes with Hf, Mn, Zn and Zr tend to decompose, whilst any significant reduction in inject temperature yields flattened peaks. Although no definitive data in this resp are available for the aluminum chelate, it was decided to employ direct on-colu injection at the temperature cited above. Excellent chromatograms were obtai in this fashion as shown in Figs. 4 and 5, and no thermal decomposition of the m chelates was observed.

Performance of electron-capture detector

Many factors affect the response of the electron-capture detector to alumin trifluoroacetylacetonate. The sensitivity improved with increasing nitrogen flow r up to 285 ml min^{-1} (Fig. 2); beyond this, the background signal interfered a became highly unstable. Decreasing the cell voltage increased the response of detector (Fig. 3), since free electrons have comparatively smaller energies at l voltages and are more easily captured to form negative ions. The operation of electron-capture detector depends on a reduction in current in the presence of electron-absorbing vapor, but the operation of other mechanisms may prod spurious signals. For example, the detector may act as a cross-section detecto the absence of electron capture. This effect produces an increase in current opposition to the electron-capture effect. Since a high concentration of a co pound with no or low electron affinity may yield such false responses[17], it imperative to employ a column capable of separating the solvent and any impuri from the analyte chelate. As shown in Figs. 4 and 5, the column used in this st gave completely satisfactory results in this respect.

The chromatograms

Figure 4 illustrates a chromatogram for a 2-μl solution of aluminum fluoroacetylacetonate in toluene containing $6 \cdot 10^{-12}$ g aluminum. The solu aluminum contents of both a sea water and the lake samples chelated and extrac as described yielded the g.l.c. peaks shown in Figs. 5b and 5d. It may be seen that aluminum trifluoroacetylacetonate peaks are well separated from the concomitan In these particular examples, different columns and instrumental parameters w utilized, as detailed in the captions, and since the conditions were unoptimi



4. Chromatogram of 2-μl sample of aluminum trifluoroacetylacetonate ($6.1 \cdot 10^{-12}$ g Al) in toluene ɛr the optimal operating conditions.

5. Chromatograms of aluminum chelated with trifluoroacetylacetonate and extracted into toluene. ɛa water sample spiked with 1 p.p.m. Al; (b) unmodified sea water sample; (c) reagent blank; (d) lake ɛr sample from Smith Lake, central Alaska: (A) aluminum trifluoroacetylacetonate peak, (B) untified. (a), (b) and (c) Operating conditions: nitrogen flow rate, 55 ml min^{-1}; glass column, 5.08% ɔne 30–0.34% carbowax 20 M on 60–80 mesh Gas Chromo Z; column temperature, 119°; detector ɔerature, 205°; applied voltage, 20 V. (d) Operating conditions, optimal as given in text.

potential of these procedures for marine samples is even greater than strated. The chromatogram given as Fig. 5a is for sea water spiked with 1 mg Al , and Fig. 5c is a blank reagent run. It may be concluded that these procedures ɛr considerable potential for the determination of aluminum in all natural waters, particularly so for sea water where a sensitive and rapid technique is at a premium.

This work was principally supported by U.S. Atomic Energy Commission ɲtract No. AT(45-1)-2229. We are grateful to our colleagues for continuing ice and particularly to W. S. Reeburgh for critically reviewing the manuscript.

SUMMARY

The feasibility of determining the extractable aluminum contents of nat waters, with particular emphasis on sea water, by gas–liquid partition chroma graphy has been demonstrated. The metal is chelated with trifluoroacetylacet extracted into toluene and injected into the chromatograph using direct on-colu injection. Under optimized instrumental conditions, better than picogram qu tities of aluminum as the trifluoroacetylacetone complex may be detected.

RÉSUMÉ

L'aluminium contenu dans des eaux naturelles, en particulier l'eau de n peut être dosé par chromatographie de partage gaz–liquide. Le métal est ché au moyen de trifluoroacétylacétone, extrait dans le toluène et injecté directem sur la colonne du chromatographe. Dans des conditions instrumentales optima il est ainsi possible de déceler des quantités d'aluminium même inférieures au p gramme.

ZUSAMMENFASSUNG

Es wird gezeigt, dass der extrahierbare Aluminiumgehalt von in der Na vorkommendem Wasser, insbesondere Meerwasser, durch Gas–Flüssig-Verteilu chromatographie bestimmt werden kann. Das Metall wird mit Trifluoracetylace chelatisiert, mit Toluol extrahiert und direkt in die Säule des Chromatograp injiziert. Unter optimalen instrumentellen Bedingungen können Picogramm-Men Aluminium als Trifluoracetylaceton-Komplex nachgewiesen werden.

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ETERMINATION OF TRACES OF ANTIMONY AND TIN IN COPPER Y ANODIC STRIPPING VOLTAMMETRY

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eceived 14th February 1973)

This paper deals with the determination of traces of antimony and tin in ›pper and copper compounds by means of anodic stripping voltammetry on a ıanging mercury drop electrode. The determination of bismuth[1] and of lead, ıdmium, zinc and manganese in copper[2] has already been described.

In the literature, various methods have been reported for the polarographic, ›lorimetric and spectrographic determination of antimony and tin in copper and ›pper alloys[3–6]. The procedures described generally allow the determination of as ttle as about $10^{-4}\%$–$10^{-5}\%$ of antimony and tin. In all cases except for emission ›ectrography, separations are necessary. This investigation showed that the ɛtermination of much lower concentrations of antimony and of tin in copper is ɔssible.

Anodic stripping voltammetry has already been used for the determination of aces of antimony and (or) tin in aqueous solution and in high-purity materials[7,8].

olarographic data

Direct polarographic determination of traces of antimony and tin in copper impossible because of the large excess of copper in the case of tin and the nall difference in the half-wave potentials of the copper(II) and antimony(III) ıetal ions in various supporting electrolytes[9].

Preliminary separation from the copper matrix is necessary. A high sensitivity ır antimony(III) was obtained from the reversible three-electron reduction or xidation reaction in 1 *M* hydrochloric acid. In this supporting electrolyte the alf-wave potentials of antimony(III) and bismuth(III) only differ by 60 mV, and ismuth can interfere, especially if the bismuth/antimony concentration ratio is nfavourable. In complexing media antimony does not interfere with bismuth but ıe anodic stripping sensitivity is seriously lower.

For tin(IV) well defined anodic stripping curves were recorded in 2 *M* ydrochloric or hydrobromic acid. In these media tin(IV) coincides with lead(II) hich is normally present in excess with respect to tin. A classical method to ɛtermine tin and lead involves measuring the total diffusion current from ıad(II) and tin(IV) in hydrochloric solution and after addition of sodium ydroxide, determining the concentration of tin by difference.

Because the tin content is generally much lower than that of lead, this ıethod cannot be applied to copper. Even with comparable lead and tin oncentrations a direct method is more suitable. For the voltammetric determination

of tin(IV) not only separation from the copper matrix is necessary but also fro lead, present as a major impurity[2].

With a mercury drop of 0.0233 cm^2, a pre-electrolysis time of 15 mi a scanning rate of 0.167 V min^{-1} and a volume of 10 ml, the determinati limit according to Currie[10] is about $1.4 \cdot 10^{-9}$ M for antimony(III) in 1 hydrochloric acid; this gives a peak height of 10 mm at an instrumen sensitivity of $2 \cdot 10^{-10}$ A mm^{-1}. The determination limit for tin in 2 M hydrobron acid is about $7 \cdot 10^{-10}$ M with a pre-electrolysis time of 25 min at an instrumen sensitivity of 10^{-10} A mm^{-1}.

To verify the precision of the voltammetric determination, calibration curv for antimony and tin were established respectively in 1 M hydrochloric acid a in 2 M hydrobromic acid, in the concentration range 10^{-7}–$9 \cdot 10^{-7}$ M (Table No blank values were obtained for antimony, tin or lead ($< 10^{-9}$ M).

The standard deviation for concentrations at the 10^{-7} M level was 1% f antimony and 1.5% for tin (10 determinations).

TABLE I

CALIBRATION CURVE VALUES FOR ANTIMONY AND TIN

(Scanning rate, 0.167 V min^{-1}; sensitivity, 10^{-9} A mm^{-1}; temperature, 25°. Pre-electrolysis tim for antimony(III) in 1 M HCl, 3 min at −0.5 V *vs.* Ag/AgCl electrode; for tin(IV) in 2 M H 4 min at −0.8 V)

Concn. ($\cdot 10^{-7}$ M)	1	2	3	4	5	6	7	8	9
Peak ht. (mm)									
for Sb	25.5	51	75	101	127	153	177	201	226
for Sn	25	49	76	102	125	148	174	201	222

Separation techniques

Separation of antimony. Electrolysis[11,12], precipitation[13], coprecipit tion[5,14–16], extraction[17–19] and distillation can be used for the separation antimony from a large amount of copper.

To allow the determination of antimony in copper at any concentration bismuth, the antimony has not only to be separated from copper but also fro bismuth. Coprecipitation of antimony with the hydroxides of iron(III), manganes (IV) or aluminium(III) is unsatisfactory because too much copper coprecipitat rendering inverse voltammetric determination impossible.

Antimony(III) can be distilled from a sulphuric acid–hydrochloric ac solution in a Sherrer micro-distillation apparatus at a temperature of 155–16 with a stream of carbon dioxide (or nitrogen) and with dropwise addition hydrochloric acid (1 + 1). To prevent the copper from being carried over with t antimony, the classical Sherrer micro-distillation apparatus was supplied with extra bulb. The distillate was collected in a beaker with 20 ml of ice-cooled, twi distilled water.

After distillation a relatively large volume was obtained. To reduce the volur antimony was coprecipitated with iron(III) hydroxide. About 50 mg of iron(I

)ride was added to the solution which was neutralized with ammonia till the :ipitate nearly began to form. Then urea was added and the solution was med till the pH reached the desired value (pH 3) by the hydrolysis of the ı. Directly, the precipitate was filtered on a glass-filter (Jena type G4), washed :e times and dissolved in 2 *M* hydrochloric acid. Because iron(III) interfered he anodic stripping voltammetry it was necessary to reduce it to iron(II), ch was done with ascorbic acid. The coprecipitation with iron(III) hydroxide quantitative.

Known quantities of antimony added before distillation were never quantitaly recovered, though the coprecipitation with iron(III) hydroxide was quantita. Maybe this is due to oxidation of some antimony(III) to antimony(V) in warm)huric acid medium; antimony(V) is not volatile as its chloride.

Because antimony(III) and antimony(V) are volatile as their bromides, ıixture of hydrobromic acid (47–48%) and 12 *M* hydrochloric acid was added pwise during the distillation. After distillation at 165° and after coprecipitation ı iron(III) hydroxide always more than 98% of the previously added antimony recovered.

Separation of tin. Electrolysis[12], coprecipitation[14,16] and ion exchange[20,21] e been described for the separation of tin from a large amount of copper.

In this investigation tin was separated by distillation because in this manner ıration was obtained not only from copper(II) but also from lead(II) which rferes with the anodic stripping determination of tin(IV). Because tin(IV) is ıtile as its bromide, the distillation was carried out at 155° in perchloric acid lium under dropwise addition of hydrobromic acid (47–48%) while carbon ıide was bubbled through the solution. The distillate was caught in a beaker with cooled water. No blank value of lead could be determined.

After distillation the solution had to be diluted because the acid concentration too high. This dilution considerably decreased the sensitivity. By evaporating distillate to a small volume, enrichment was achieved, but evaporation must controlled so that no loss of tin occurs. According to Kodama[22] there is no when tin solutions are evaporated to dryness in presence of sulphuric acid. wever, when sulphuric acid must be added, there is a great danger of lead tamination. Temmerman and Verbeek[23] did not experience tin losses when tin ıtions were evaporated in the absence of sulphuric acid, paying attention to the essary precautions; the tin solution was evaporated by surface warming under an bulb, mounted 20 cm above the surface. After distillation and evaporation, separation was quantitative.

'ERIMENTAL

aratus and reagents

Polarograph, Metrohm E 261 R. The working conditions were described viously[1].

Water, mercury, nitrogen and sulphuric, hydrochloric and nitric acids were ified as previously described[1,2].

Hydrobromic acid, analytical grade, was distilled in a Sherrer micro-illation apparatus.

All other reagents (analytical grade) were used without further purificat

Antimony(III) and tin(IV) stock solutions were prepared from the analy grade metals and standardized.

Procedures

Determination of antimony. Dissolve about 2 g of the copper sample in 1(of nitric acid (1+1) and evaporate to dryness. Dissolve the residue in 30 m hydrochloric acid (1+1). Pour the solution into a Sherrer micro-distillat apparatus containing 50 ml of sulphuric acid (1+1). Distil at 165° with dr wise addition of (1+2) 47–48% hydrobromic acid–12 *M* hydrochloric acid carry out a precipitation with iron(III) hydroxide as described above. Dissolve residue in 2 *M* hydrochloric acid. Reduce the iron(III) to iron(II) with asco acid and dilute with 2 *M* hydrochloric acid to 25 ml (or 10 ml).

Transfer 20 ml (or less) of the solution to the polarographic cell ther stated at 25.0±0.1° and deaerate for 10 min. Perform a pre-electrolysis a potential of −0.5 V *vs.* the silver–silver chloride reference electrode for 3–15 while stirring. Stop stirring at the end of the timed electrolysis and allow solution to settle during 30 s. Record the anodic stripping curve using a line varying potential of 0.167 V min^{-1}. Determine the concentration of the antim by the standard addition method. Prepare a blank solution and record a curr voltage curve under the same conditions.

Determination of tin. Dissolve the copper metal in nitric acid (1+1) evaporate with care to dryness. Dissolve in 50 ml of perchloric acid (1+1) pour the solution into the Sherrer micro-distillation apparatus. Distil at 155° dropwise addition of 47–48% hydrobromic acid, and reduce the volume to at 5 ml by heating under an i.r. bulb as described above. Dilute to 25 ml 10 ml) with twice distilled water. Transfer 20 ml (or less) of the solution to polarographic cell. Determine the tin concentration after pre-electrolysis for 3 min at −0.8 V *vs.* the silver–silver chloride reference electrode. Record a bl solution under the same conditions.

TABLE II

DETERMINATION OF ANTIMONY AND TIN IN SYNTHETIC SAMPLES

(2 g of copper)

Element	*Weight added (μg)*	*Weight found (μg)*	*Weight recovered (%)*
Sb	0.304	0.289	95.1
	0.609	0.592	97.3
	1.217	1.172	96.3
	3.044	3.105	102.0
Sn	0.030	0.031	103.9
	0.297	0.293	98.9
	0.593	0.601	101.3
	1.186	1.162	98.0
	2.966	3.113	104.9

ESULTS

Several analyses were performed on synthetic samples by the described rocedures.

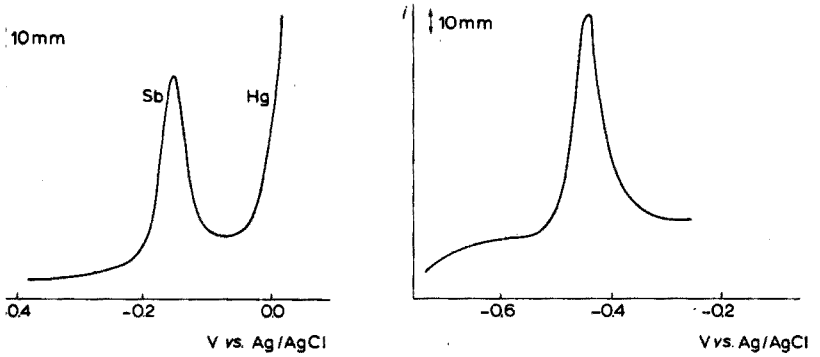
Known quantities of antimony and tin were added to copper(II) chloride olutions, previously freed from antimony and tin by distillation. The results are

ABLE III

ETERMINATION OF ANTIMONY AND TIN IN ANALYTICAL-GRADE COPPER AND OPPER COMPOUNDS

g of sample)

roduct	*Antimony (p.p.m.)*	*Tin (p.p.m.)*
opper	0.623	0.186
	0.653	0.178
	0.665	0.188
opper	0.320	0.033
	0.309	0.035
	0.312	0.032
$uCl_2 \cdot 2H_2O$	0.347	0.122
	0.359	0.119
	0.368	0.117
	0.368	0.124
$uSO_4 \cdot 5H_2O$	0.153	0.098
	0.160	0.102
	0.161	0.096



. 1. Anodic stripping voltammogram of $2.03 \cdot 10^{-7}$ *M* antimony in 2 *M* hydrochloric acid responding to 0.309 p.p.m. of antimony in analytical-grade copper. Pre-electrolysis for 5 min at .5 V; scanning rate, 0.167 V min^{-1} at 10^{-9} A mm^{-1}; temperature $25.0 \pm 0.1°$.

. 2. Anodic stripping voltammogram of $1.20 \cdot 10^{-7}$ *M* tin in 1.8 *M* hydrobromic acid corresponding 0.178 p.p.m. of tin in analytical-grade copper. Pre-electrolysis for 10 min at -0.8 V; scanning e 0.167 V min^{-1} at 10^{-9} A mm^{-1}; temperature $25.0 \pm 0.1°$

summarized in Table II. Typical anodic stripping curves of antimony in 2 hydrochloric acid and of tin in 1.8 M hydrobromic acid are shown in Figs. and 2. In the blank solutions no antimony, tin or lead could be detected ($\ll 10^{-9}$ M Finally, the described procedures were applied to the analysis of commercia available copper samples. Reproducible results are obtained, as can be seen fr Table III. Anodic stripping voltammetry allows the determination of about $1.4 \cdot 10$ M antimony and $7 \cdot 10^{-10}$ M tin in solution for pre-electrolysis times of respectiv 15 and 25 min. This corresponds to 0.8 p.p.b. of antimony and 0.3 p.p.b. of for a 2-g sample and a final volume of 10 ml after separation. In both cases blank values could be detected ($\ll 10^{-9}$ M). Because of the separation used in t investigation, it is possible to determine antimony and tin in copper regardless the bismuth or lead content.

Thanks are due to the I.W.O.N.L. for financial support to one of us (G.V.D.

SUMMARY

The determination of antimony and tin impurities in copper by anod stripping voltammetry on a hanging mercury drop electrode is described. Antimon and tin were previously separated from copper by distillation with hydrobrom acid or a mixture of hydrobromic acid and hydrochloric acid. The method w applied to the analysis of various high-purity copper samples, commercial available, showing satisfactory sensitivity and precision. The determination lim was about $1.4 \cdot 10^{-9}$ M for antimony and $7 \cdot 10^{-10}$ M for tin in solution, f pre-electrolysis times of respectively 15 and 25 min; this corresponds to 0.8 p.p. of antimony and 0.3 p.p.b. of tin for a 2-g sample and a final volume of 10 m after separation.

RÉSUMÉ

On décrit une méthode de dosage d'antimoine et d'étain, comme contamin tion de cuivre, par voltammétrie anodique strippante sur électrode à gout pendante de mercure. L'antimoine et l'étain sont séparés au préalable du cuiv par distillation au moyen d'acide bromhydrique ou d'un mélange acide bro hydrique–acide chlorhydrique. Cette méthode a été utilisée pour l'analyse de div échantillons de cuivre très pur. La limite de dosage est d'environ $1.4 \cdot 10^{-9}$ M po l'antimoine, et $7 \cdot 10^{-10}$ M pour l'étain en solution pour des temps de pr électrolyse de 15 et 25 min respectivement, ce qui correspond à 0.8 p.p. d'antimoine et 0.3 p.p.b. d'étain pour des échantillons de 2 g et un volume fi de 10 ml après séparation.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Antimon- und Zinnverunreinigungen in Kupf durch anodische Stripping-Voltammetrie an einer hängenden Quecksilbertropfe elektrode beschrieben. Antimon und Zinn wurden vorher vom Kupfer dur Destillation mit Bromwasserstoffsäure oder einem Gemisch von Bromwasserstof

ire und Salzsäure abgetrennt. Die Methode wurde auf die Analyse von ver-
iedenen Proben handelsüblichen Reinstkupfers angewendet und zeigte zufrieden-
llende Empfindlichkeit und Reproduzierbarkeit. Die Bestimmungsgrenze war etwa
$\cdot 10^{-9}$ *M* für Antimon und $7 \cdot 10^{-10}$ *M* für Zinn in Lösung bei Vor-Elek-
lysezeiten von 15 bzw. 25 min; dies entspricht 0.8 p.p.b. Antimon und 0.3 p.p.b.
in bei einer Probe von 2 g und einem Endvolumen von 10 ml nach der
trennung.

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IZYME ELECTRODE SYSTEM FOR ASSAY OF SERUM IOLINESTERASE

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Electrode systems have been developed which are capable of determination enzymes and substrates[1–4]. An ammonium ion-specific electrode which can rate at or near physiological pH values has also been reported[5]. The fundamental nciple behind all of this work has been to develop electrode systems by com- ing ion-sensing electrodes with thin polymer film(s). For example, a simple and id responding urease enzyme sensor was made by coupling the substrate urea he active surface of a cationic electrode responsive to ammonium ion, a product he urea–urease reaction. The electrode was covered with a layer of cellophane pping a thin layer of urea solution between the glass sensing bulb and the mbrane. When the electrode was dipped into a solution containing urease, the a which diffused out of the cellophane membrane reacted with urease (which not diffuse through the membrane) to produce ammonium ion at the membrane face. The build-up of an ammonium ion activity gradient caused diffusion of ion back to the electrode, where it was sensed. As another example, a totally cific ammonium ion electrode which can operate at or near a neutral pH was eloped by wrapping a monovalent glass cationic electrode with a hydrophobic -permeable membrane[5].

It seems that there are obvious advantages in utilizing thin polymer mem- nes to develop enzyme- and substrate-sensing electrode systems and suitable trochemical transducers to utilize in electrode systems.

Work has been directed in these laboratories to develop a useful electrode em for assay of serum cholinesterase via potentiometric detection of the acid duced. There are, of course, several procedures published for potentiometric ction of the acetic acid produced[6,7]. However, homogeneous enzymatic catalysis tilized. In such cases the spontaneous or non-enzymatic decomposition of the strate is quite noticeable and a correction must be applied to the data.

In the present paper, a simple and fast responding electrode system is sented for assay of serum cholinesterase via pseudo-homogeneous catalysis in a -layered electrochemical cell. The technique is based on coupling a pH electrode n appropriate thin polymer membrane. At the electrode surface, serum cholineste- reacts with acetylcholine (the preferred substrate for serum cholinesterase) to duce acetic acid, which is detected by the pH electrode. The excellent sensitivity ieved is due to:

(*a*) the use of a micro-layer of enzyme solution,

(*b*) extremely low buffer strength of enzyme solution, and

(*c*) virtually zero suppression of the effects of spontaneous hydrolysis substrate.

EXPERIMENTAL

Reagents

All chemicals were of reagent grade unless stated otherwise. Acetylchol bromide and horse serum cholinesterase were obtained from Sigma Chemical Co pany, St. Louis. The enzyme was assayed spectrophotometrically[8] with ace choline bromide and the activity was found to be 120 Rappaport Units per mg solid. One Rappaport Unit of cholinesterase will hydrolyze 1 μmole of ace choline in 30 min at 25°.

Stock phosphate buffer. To 500 ml of 0.1 *M* K_2HPO_4 was added 0.1 KH_2PO_4 until the pH was exactly 8.00.

Stock PEI solution. A 10% (w/v) solution of Dow PEI 1000 (polyethylenimi molecular weight 100,000) was prepared in 100-ml quantities with saline soluti

Saline solution. A 0.9% (w/v) solution of sodium chloride was prepared w distilled water.

Substrate solution. A 0.1 *M* solution of acetylcholine bromide was prepared dissolving 0.2261 g of the substrate in a solution containing 9 ml of saline solut and 1 ml of PEI solution. The pH was adjusted to 7.95.

Blank enzyme solution. This solution was made with saline solution buffe with phosphate (1.3 ml of stock phosphate buffer was diluted to 100 ml with sal solution).

Stock cholinesterase solution. Cholinesterase (10 mg) was dissolved in 100 of the blank enzyme solution.

Monitrol-I and monitrol-IX solutions. Each vial was reconstituted with 5 water and diluted to 50 ml with saline solution.

Human serums. Each serum was diluted (1+9) with saline solution and pH was adjusted to 7.7–7.8.

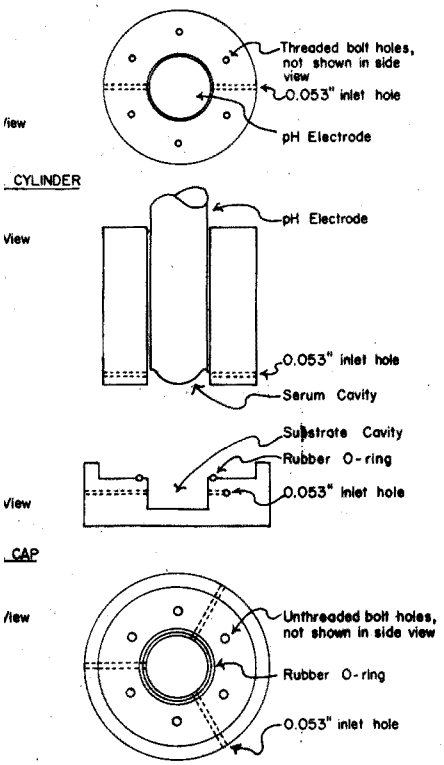
Distilled water. All water used was purified by distillation in a glass still.

Instrumentation and electrodes

A Corning research pH meter was used for potential measurements. A Corn Super Rugged pH Electrode (with slightly convex sensing tip) was used as indicating electrode to measure the acetic acid produced. An S.C.E. was used reference. The indicating and reference electrodes were connected to the appropri terminals on the pH meter. The pH meter was operated in the mV mode. The recor terminals of the pH meter were connected to a Sargent mV recorder. The sensiti of the recorder was adjusted so that 1 mm = 0.125 mV.

Micro electrochemical cell

Figure 1 shows a schematic of the micro (thin-layered) electrochemical used. Both the cell cylinder and cell cap were made of Plexiglass. The ins diameter of the cylinder was 1.0 cm; the outside diameter, 3.0 cm. The pH electr was inserted through the Plexiglass cell cylinder so that the glass sensing tip



1. Thin-layered enzyme electrode.

acent to the 0.053-in diameter holes (drilled into opposite sides of the cell nder). The electrode tip was aligned in the cylinder as follows. A 10-μm spacer meter about 0.5 cm) was placed on a flat surface. The electrode and cell cylinder e positioned over the 10-μm spacer so that only the electrode tip was touching spacer. The distance between the electrode and end of the cell cylinder was s calibrated at 10.0 μm. The volume of the resultant thin-layered cavity was 7.1 Dow-Corning silicone adhesive was applied around the electrode stem on top he cell cylinder. After the adhesive had hardened, the electrode was mounted ide down and a very thin ring of the sealant was applied to the electrode-nder wall. Into one of the 0.053-in diameter holes was inserted one end of a m length of 0.05-in o.d. polyethylene intramedic tubing. A 70-cm long piece he tubing was similarly inserted into the other 0.053-in hole. The tubings were led in place with the silicone adhesive.

The hollow cylindrical portion of the cell cap was 1 cm in diameter by 3 mm volume of this cavity was 300 μl). A groove was drilled for a rubber "O" ring ch surrounded this cavity. Three 0.053-in diameter holes were drilled into the s of the cell cap. The holes were placed at 120° to each other. A 10-cm length of 5-in o.d. tubing was sealed into two of the holes. A 70-cm length of the tubing was led into the third hole.

A wet cellophane membrane, 16 μm thick and 1.5 in diameter, was placed over

the electrode. The membrane was stretched over the electrode cavity by virtue its ability to cling to the Plexiglass. The cell cap was joined to the cell cylinder w 6 brass screws (1/8 × 3/4 in).

The exposed tip of each of the tubings from the cell cylinder portion of micro electrochemical cell was connected to the plastic barrel of a 10-ml syringe. T syringe barrel affixed to the 19-cm length of tubing received a S.C.E. which ser as the reference electrode for the system. The other syringe barrel served as a deliv reservoir for enzyme solutions.

The exposed tip of the 70-cm length of the tubing from the cell cap port of the cell was also connected to a 10-ml syringe barrel. The exposed tips of t other two tubings were connected to a drain tube.

The assembled cell was placed in a water bath equilibrated at 25°. A me stick was mounted in a vertical position alongside the electrochemical cell.

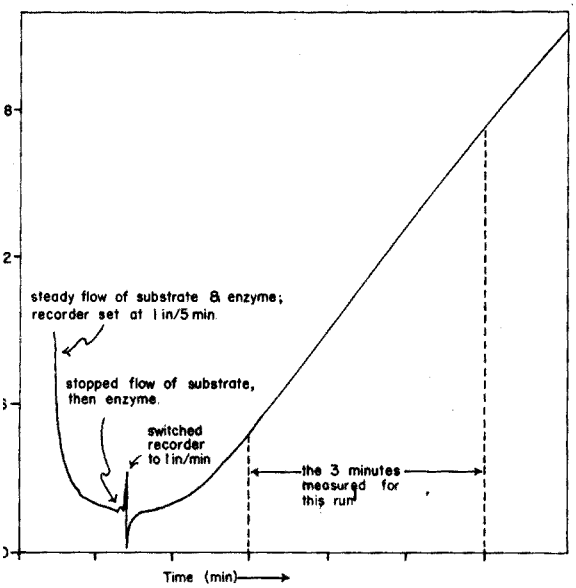
Procedures

An S.C.E. was placed in one of the syringes connected to the cell cylin via the intermediate tubing. Each of the other two syringes were fitted with a test tu clamp which, in turn, was connected to a vertical rod mounted alongside the me stick. Enzyme and substrate solutions were fed to the electrode assembly unde gravity-induced hydrostatic head of about 60 cm; both syringes (liquid reservoi were raised to the 60-cm mark. Enzyme solution (human serum, monitrol, or ho serum cholinesterase) was added to the syringe connected to the cell cylind substrate solution was added to the syringe connected to the cell cap. A screw-ty pinch clamp connected to each of the tubings leading to the syringes regulated interrupted flow of liquid. (In some instances, a micro roller pump (Holter Compa was used in place of the pinch clamps.) Enzyme and substrate flow was allowed continue until the micro cell was thoroughly flushed and the level of both solutio in the syringes had depleted to a predetermined mark. Both reservoirs were th lowered to reduce the hydrostatic load to zero. Flow of substrate was termina 8–10 s before enzyme flow, which compensated for any flexing of the membrane the electrochemical cell.

After recording the resultant potential for a few minutes, both reservo were again raised to the 60-cm mark. Buffered saline solution was added to the ser reservoir and more substrate added to the substrate reservoir. The thin-layered c was thoroughly flushed before the next serum sample was added to the electro system.

RESULTS AND DISCUSSIONS

Figure 2 shows a typical response curve obtained with 19.8 Rappap Units of cholinesterase per ml of serum and 1.0% PEI added to the substrate. Wi a steady flow of substrate and enzyme through the electrode system the respor drops to a low steady-state value. Immediately after termination of flow throu the system, the potential rises with time, because acetic acid is produced via t enzyme–substrate reaction. After an incubation period of only about 1 min, t response is linear with time. It was, therefore, possible to assay for cholinester by a kinetic technique. At low enzyme levels, the slope of the linear portion of t



2. Complete response curve obtained for serum cholinesterase. 1.0% PEI; 19.8 Rappaport Units ml.

ve was found to be directly proportional to the enzyme activity. Although all a presented here were calculated over a 3-min run, a 0.5–1.0 min run would ve sufficed. Therefore, it is possible to perform an assay in only 1.5 min.

The high sensitivity of this electrode system is due to the low buffer capacity erent in the diluted sera. Previously, cholinesterase assays with weakly buffered yme solutions could not be done because the rate of spontaneous decomposition he substrate was such that it could not be ignored when compared with curves ained from human sera.

Figure 3 illustrates the chemistry involved in this electrode system for serum linesterase. The thin polymer membrane (molecular weight cut-off of 5000) arates the thin-layered cholinesterase (enzyme) and acetylcholine (substrate) solu-ıs. During flow of substrate and enzyme through the system, as denoted by ɔws pointing up, diffusion processes across the membrane are minimized. When flow is stopped, only the diffusion of the low molecular weight acetylcholine is ɔortant. The diffusion of acetic acid, produced by spontaneous decay of acetyl-line, from the substrate layer to the cholinesterase layer would result in an reciable non-enzymatic response curve. However, the effect of the spontaneous ɔmposition of the substrate was repressed to zero by adding a high-molecular-ght PEI buffer to the substrate layer. The PEI buffer converts the acetic acid to ounter ion. Hence there is no build-up of an acetic acid activity gradient in the ɜtrate layer. The high molecular weights of both the acidic and basic forms ıe PEI buffer prevent diffusion of the buffer into the enzyme layer which would ıce the sensitivity of the electrode system.

The acetylcholine which diffuses into the cholinesterase layer reacts with the yme to produce acetic acid, which is detected by the pH-sensing electrode.

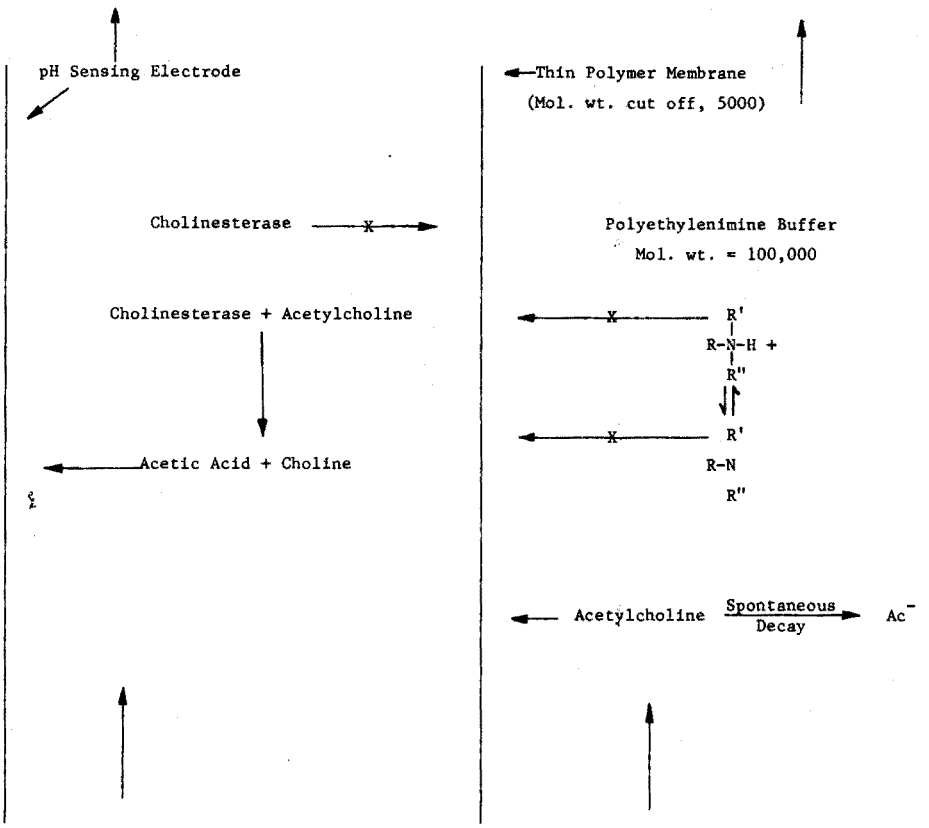
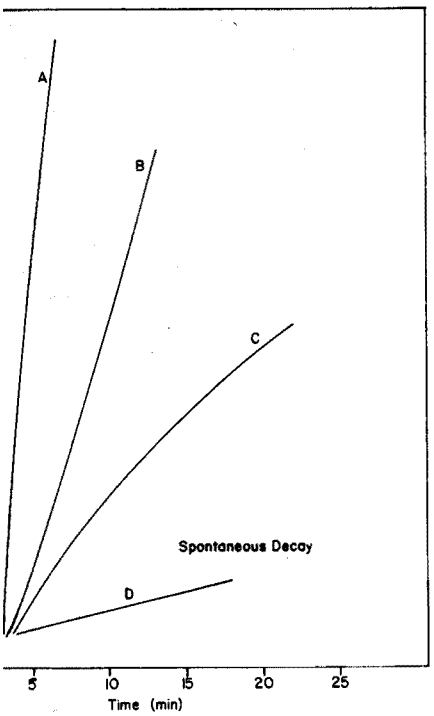


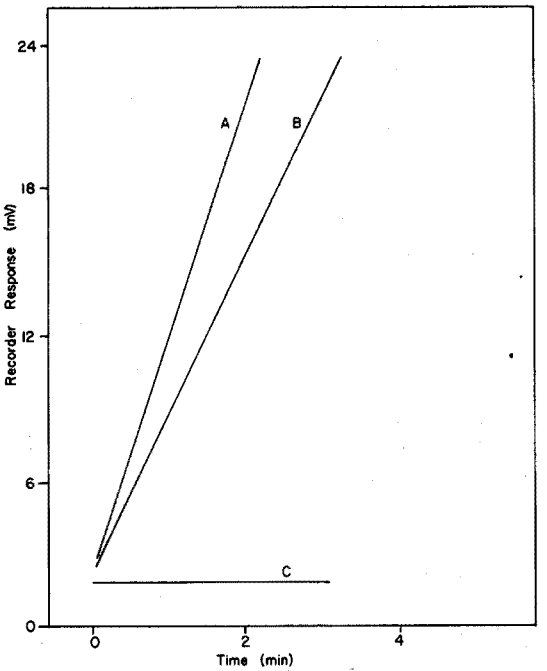
Fig. 3. Chemistry of cholinesterase-sensing electrode.

Because of static (non-stirred) conditions in the enzyme reaction layer, diffusi processes could become rate-limiting. Therefore, an average reaction layer thic ness of only 10 μm was utilized.

The normal value for cholinesterase in human sera is 40–80 Rappapc Units per ml of serum[8].

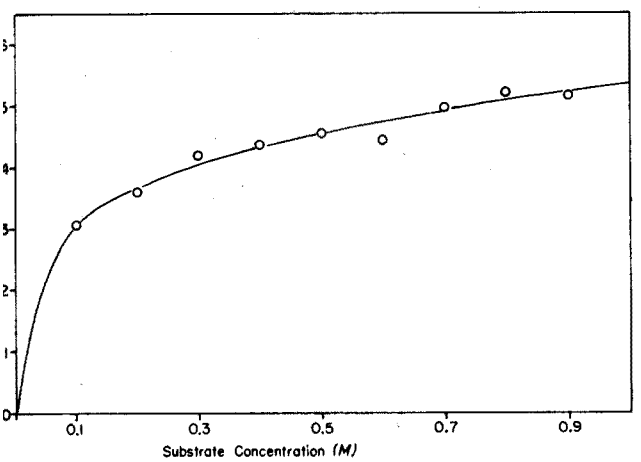
Figures 4 and 5 show the response curves obtained as a function of enzyr activity and % PEI added to 0.1 *M* acetylcholine substrate. As shown in Fig. with an enzyme activity of about a hundredth of that found in human serum, t spontaneous decay of acetylcholine is still noticeable when the PEI concentrati is 0.06%. Even if the substrate had been freshly prepared, stored at 0°, and us within 4–8 h, the electrode system would not have been able to tolerate the drift the spontaneous decomposition of acetylcholine to acetic acid. This is becau as the buffer capacity of the PEI is reduced in the neutralization of the acetic ac the change in potential becomes exponential with time (the spontaneous decompo tion can be considered pseudofirst order in substrate at 0.1 *M* level). The variati of the slope of curves A, B, and C with PEI concentration is due to a build-up an acetic acid activity gradient in the cholinesterase reaction layer. Some of t gradient is dissipated by diffusion into the static PEI layer. The rate at which t boundary layer of PEI is neutralized depends on the PEI buffer capacity.





. 4. Variation of response with PEI concentration at low enzyme levels. 0.4 Rappaport Units per % PEI: (A) 0.06; (B) 0.12; (C) 0.20; (D) 0.06.

. 5. Variation of response with PEI concentration at enzyme levels found in human serum. 32 Rappaport its per ml. % PEI: (A) 0.5%; (B) 3.0%; (C) 1.0% with no added enzyme.



. 6. Dependence of electrode response on substrate concentration. 1.0% PEI. 12.5 Rappaport Units r ml.

It is important to note that the sensitivity of this system is greater t that obtained by homogeneous catalysis with an equivalent amount of phosph buffer added to the system. This is due solely to the localization of the acetic a produced in the very weakly buffered and static cholinesterase reaction layer.

Figure 5 shows the response curves obtained with an enzyme activity of Rappaport Units per ml and a higher PEI concentration. With 1.0% PEI, the eff of the spontaneous hydrolysis of the substrate has been reduced to zero.

The variation of the reaction rate slope with substrate concentration shown in Fig. 6. The electrode system showed a first-order response to acetylchol in the range 0–0.05 *M*. Above 0.05 *M*, the response approached a zero-or dependence.

Figure 7 shows the linear portion of curves obtained with varying enzy activity. Figure 8 shows the resultant calibration curve obtained. The curve v obtained by heat deactivation of pooled monitrol-I and IX at 60° for 12 min, a subsequent addition of horse serum cholinesterase to the inactivated serum mat Figure 9 demonstrates the validity of the calibration curve for human sera. A port of a monitrol-I sample was assayed for cholinesterase by the spectrophotome technique[8]. Another portion of the same sample was heat-deactivated, and then equivalent amount of horse serum cholinesterase was added to the sample. shown in Fig. 9, the two response curves are identical.

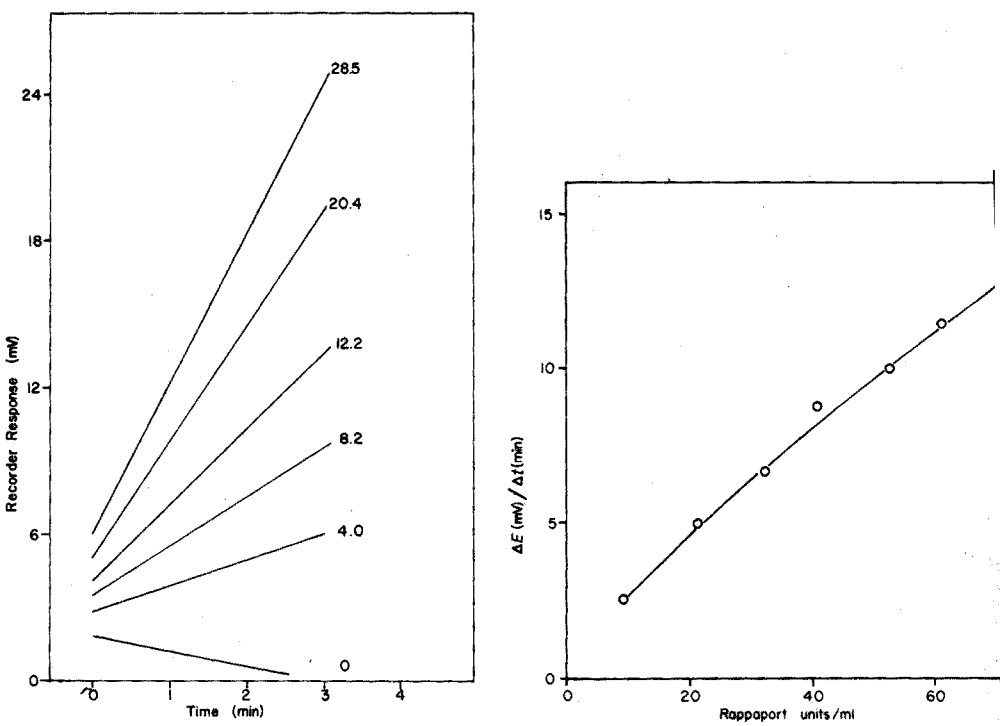
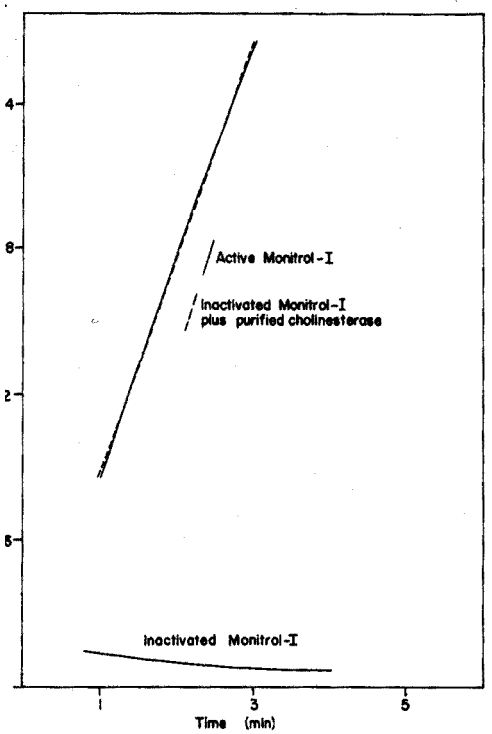


Fig. 7. Linear portion of response curves as a function of enzyme activity. 1.0% PEI. The numbers o the lines are Rappaport Units per ml.

Fig. 8. Calibration curve for cholinesterase in human sera.



. 9. Responses obtained with monitrol-I. 1.0% PEI. 49 Rappaport Units per ml.

BLE I

ECISION OF CHOLINESTERASE ASSAYS

um no.	*ΔE (mV)/Δt (min)*		*Activity (Rappaport Units per ml serum)*	*s*	s_r *(%)*
	Each run	*Average*			
	9.48	9.86	50.7	0.35	3.5
	10.32				
	9.78				
	9.12	9.24	46.0	0.13	1.4
	9.18				
	9.42				
	8.76	8.58	41.5	0.22	2.5
	8.58				
	8.76				
	8.22				
	9.18	9.34	46.5	0.12	1.3
	9.48				
	9.36				

TABLE II

COMPARISON OF RESULTS FOR SERUM CHOLINESTERASE WITH THOSE OBTAINE BY COLORIMETRIC ASSAYS

Serum no.	*Activity, avg. (Rappaport Units per ml)*		*Accuracy*[a]
	This method (A)	*Colorimetric (B)*	
1	50.7	49.2	3.1
2	46.0	44.8	2.7
3	41.5	43.0	3.5
4	46.5	45.6	2.0

[a] Accuracy (%) = (B − A)/B · 100.

Tables I and II show the precision and accuracy data obtainable with th system. The relative standard deviation (s_r) of 1.3–3.5% indicates the precisio attainable. The results obtained with the electrode system agreed well with tho obtained by the spectrophotometric technique (Table II).

The low incubation time (1.5 min) required in this electrode system sugges that the technique could be easily automated by incorporating the system into a Autoanalyzer. Experiments of this type are being initiated.

This research was supported by National Institutes of Health grant GM 17929.

SUMMARY

An enzyme-sensing electrode system for serum cholinesterase was prepare by coupling a pH-sensing electrode to a thin polymer membrane with a lo molecular-weight cutoff. The electrode system utilized two thin-layered solutio to form a micro electrochemical cell. One layer contained the serum; the oth contained acetylcholine substrate which had been stabilized to annul the no enzymatic decay of the substrate by using a high-molecular-weight buffer. An assa can be performed in 1.5–4.5 min. The precision and accuracy of the techniq is comparable with those obtained by spectrophotometric techniques.

RÉSUMÉ

Un système d'électrode à enzyme est proposé pour la cholinestérase d sérum. Il consiste à utiliser deux solutions en couches minces, formant une micropil électrochimique. Une des couches contient le sérum; l'autre contient le substr acétylcholine, stabilisé au moyen d'un tampon à poids moléculaire élevé. Un ess peut être effectué en 1.5 à 4.5 min. La précision et l'exactitude sont comparables celles obtenues par des techniques spectrophotométriques.

ZUSAMMENFASSUNG

Es wurde ein enzymempfindliches Elektrodensystem für Serum-Cholinesteras

rgestellt, indem eine pH-empfindliche Elektrode mit einer dünnen Polymermem-
ın verbunden wurde. Bei dem verwendeten Elektrodensystem bilden zwei Lö-
ıgen in dünner Schicht eine elektrochemische Mikrozelle. Die eine Schicht ent-
lt das Serum, die andere Acetylcholin-Substrat, das durch Verwendung eines
ffers hohen Molekulargewichtes zur Unterdrückung des nichtenzymatischen Zer-
ls des Substrates stabilisiert worden ist. Eine Bestimmung kann in 1.5–4.5 min
sgeführt werden. Die Reproduzierbarkeit und die Genauigkeit des Verfahrens
ıd mit jenen vergleichbar, die bei spektrophotometrischen Methoden erzielt
rden.

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IE STABILITY OF ETHANOL IN STORED BLOOD

ART I. IMPORTANT VARIABLES AND INTERPRETATION OF ESULTS

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ceived 3rd February 1973)

The stability of ethanol in stored blood has achieved a new importance in e United Kingdom since the Road Safety Act 1967, now consolidated by the Road affic Act 1972, which makes it an offence for the drinking driver to exceed a blood ohol level of 80 mg per 100 ml (80 mg%).

Krauland *et al.*[1,2] placed blood samples, some of which had been preserved th fluoride, in a refrigerator and analysed them after storage periods up to 686 ys. They concluded that if an allowance were made for the specific gravity of the um, the results of an original analysis could be checked reliably by their procedures any time up to almost three years.

Sachs[3] refrigerated samples in rubber-stoppered bottles having a volume five seven times that of the blood. He was unable to demonstrate any fall in blood ohol concentration over a period of 23 days. As would be expected theoretically, e fraction of the alcohol residing even in these relatively large air spaces proved gligible.

Other studies have been reported by Bonnichsen and Lundgren[4], Karger d Sachs[5] and Glendening and Waugh[6]. Since these results were reported, analytical curacy has been considerably improved by use of gas-chromatographic methods d therefore a reappraisal of the stability of blood alcohol is necessary.

In a small proportion of prosecutions under the Road Safety Act 1967, nsiderable discrepancies have been observed between forensic science laboratory sults and those of the defence analyst. A common feature in such cases has been relatively long time of storage of the defence sample at room temperature before alysis. At the present time, the published data are inadequate to interpret such screpancies when they occur. Some of the scientific problems associated with the oad Safety Act have been discussed by Robinson and Camps[7].

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PRELIMINARY INVESTIGATION OF VARIABLES

The five factors time, fluoride concentration, alcohol concentration, tempe ture and type of container were studied by means of a factorial experiment. The fact which were found to be significant were then studied in detail.

Experimental

Alcohol solutions were prepared by diluting aqueous 5% (w/v) etha with blood or distilled water. Unless otherwise stated, blood alcohol solutions w prepared from one month old transfusion blood containing acid citrate dextr as anticoagulant to which 1% (w/v) sodium fluoride was added as preservative.

The samples in this study were stored either in standard Road Safety A (RSA) containers or sealed glass ampoules. RSA containers are round-bottom polypropylene cups of 0.3 ml capacity with snap-on polypropylene caps. The lid each container was secured as soon as the sample had been introduced. At the e of the storage period, each sample was shaken, opened, analysed and then discard

Alcohol concentrations were determined by gas chromatography with adap tions of the method described by Curry *et al.*[8]. Aqueous *n*-propanol was used internal standard at a concentration of *ca.* 15 mg%. Samples were diluted w the *n*-propanol solution by means of modified Griffin and George haemoglobin t 221 diluspences. Peak areas were measured electronically and ethanol/propanol p area ratios were calibrated by reference to alcohol standards of known concent tion.

The gas chromatographs used were a Perkin Elmer F11 and a Perkin Elr Multifract F40 Headspace Autoanalyser. The instrumental conditions were follows:

Perkin Elmer F11

Column:	4 ft Porapak Q
Oven temperature:	170°
Injection volume:	1.5 μl
Carrier gas:	Nitrogen
Detector:	Flame ionization

Perkin Elmer F40 Autoanalyser

Column:	5 ft Porapak Q
Oven temperature:	140°
Water bath temperature:	62°
Injection time:	5 s
Carrier gas:	Nitrogen
Detector:	Flame ionization

Note. Propanol solutions used with the F40 Autoanalyser also contain 0.5% (w/v) sodium hydrogen sulphite.

Design of factorial experiment

Two levels for each of five factors were considered in a 2^5 factorial experi ment. There were thus 32 possible combinations of the five factors. The two level

ɜre as follows:

ɪme of storage:	4 weeks and 8 weeks
ɯoride concentration:	Nil and 1% (w/v) NaF
lcohol level:	110 mg% and 220 mg%
ɜmperature of storage:	4° and 17°
ɔntainer:	Polypropylene cups and sealed, ring-snap, glass ampoules.

Six samples were prepared for each of these 32 treatment combinations and e alcohol concentrations of the 192 resultant samples were measured in duplicate. ɪe range of alcohol losses and the mean alcohol loss for each treatment combination e shown in Table I.

NGE OF ETHANOL LOSSES AND THE MEAN ETHANOL LOSS IN mg% FOR THE 32 TREAT-OMBINATIONS

	4 Weeks				*8 Weeks*			
	110 mg%		*220 mg%*		*110 mg%*		*220 mg%*	
	Ampoules	*RSA cups*	*Ampoules*	*RSA cups*	*Ampoules*	*RSA cups*	*Ampoules*	*RSA cups*
17°	13.0–10.4	23.1–11.6	17.1–10.4	23.1–15.9	18.0–14.7	27.9–19.4	30.3–19.6	24.4–16.1
Mean	11.53	15.44	14.35	20.15	16.03	21.88	24.50	19.37
4°	11.3–5.3	6.2–4.1	9.2–2.7	10.7–7.9	5.1–2.3	18.8–5.2	12.0–6.1	13.3–3.9
Mean	7.95	5.42	5.68	9.14	4.16	9.35	8.05	5.63
17°	110.0–7.8	24.7–18.7	30.9–10.8	83.7–14.2	110.0–15.4	102.4–21.7	206.8–19.1	163.3–30.5
Mean	72.64	20.07	17.38	30.77	83.33	66.87	68.85	109.24
4°	48.6–3.6	4.8–1.1	9.9–1.4	15.8–3.5	7.7–3.1	19.4–5.8	12.4–8.5	16.9–3.3
Mean	12.92	3.81	4.69	11.97	5.39	9.21	10.23	9.58

The factors were identified as follows:

A = time (8 weeks = a; 4 weeks = 1)
B = fluoride concentration (1% NaF = b; Nil = 1)
C = alcohol concentration (220 mg% = c; 110 mg% = 1)
D = temperature (17° = d; 4° = 1)
E = container (RSA cups = e; glass ampoules = 1)

The treatment combinations are thus identified as shown in Table II.

ɪtistical analysis of results

From the total alcohol losses for each treatment combination, the magnitude the effects and interactions were calculated by a method due to Yates[9], as ɜcribed by Davies[10]. The results, together with their significance levels, are shown Table III. It is apparent that the highly significant factors are temperature (D), ɜsence of fluoride (B) and time of storage (A). The factors alcohol concentration) and type of container (E) are of no significance.

TABLE II. AN IDENTIFICATION TABLE FOR THE 32 TREATMENT COMBINATIONS

		4 Weeks				*8 Weeks*			
		110 mg%		*220 mg%*		*110 mg%*		*220 mg%*	
		Ampoules	*RSA cups*	*Ampoules*	*RSA cups*	*Ampoules*	*RSA cups*	*Ampoules*	*R ct*
1% NaF added	17°	bd	bde	bcd	bcde	abd	abde	abcd	al
	4°	b	be	bc	bce	ab	abe	abc	al
No fluoride	17°	d	de	cd	cde	ad	ade	acd	a(
	4°	(1)	e	c	ce	a	ae	ac	a(

TABLE III. YATES' METHOD APPLIED TO THE 32 TREATMENT COMBINATIONS

Treatment combination	*Total alcohol loss in mg% × 10*	*Effect in mg% × 10*	*Mean square of effect*	*Significance level*[a]	**** effects arranged in order of significance*
(1)	1550				
a	647	134	1,713,607	***	D
b	954	−214	4,394,276	***	B
ab	499	−109	1,150,407	***	BD
c	563	−2	219		A
ac	1228	44	188,417	*	AD
bc	681	20	39,935		AB
abc	966	48	219,842	*	ABD
d	8717	310	9,197,102	***	BCE
ad	10600	132	1,680,633	***	CE
bd	1384	−200	3,827,610	***	BCDE
abd	1923	−106	1,072,517	***	
cd	2086	−9	7,298		
acd	8262	38	139,004		
bcd	1722	24	53,204		
abcd	2940	−38	141,681		
e	457	−4	1,262		
ae	1105	36	121,695		
be	650	21	43,563		
abe	1122	−45	190,371	*	
ce	1316	80	614,560	***	
ace	1149	−32	95,445		
bce	1097	−93	837,387	***	
abce	696	−2	241		
de	2408	−9	7,211		
ade	8024	30	63,963		
bde	1853	17	27,983		
abde	2626	−39	148,601		
cde	3692	68	448,950	**	
acde	13109	10	10,189		
bcde	2418	−78	580,326	***	
abcde	2324	−9	8,475		

[a] *** = 99.9%, ** = 99%, * = 95%.

Inspection of individual alcohol losses at the higher temperature in the sence of fluoride shows large and apparently random fluctuations about the mean lues. The largest losses appear from the 110 mg% samples in ampoules, over half these losing all their alcohol. This was interpreted as being due to contamination this batch of samples with micro-organisms.

It could be argued that this abnormal batch produced spuriously low values r the effects C and E. To test this hypothesis, the data for RSA cups alone were alysed by the method of Yates. From the results (Table IV) it is apparent that e alcohol concentration independence shown in Table III is a genuine effect and ot caused by the abnormal batch. Likewise, the data for 220 mg% samples alone ere analysed (Table V). The container independence from Table III is also shown be a genuine effect.

The highly significant interactions readily fall into two groups, namely, those volving the highly significant factors and those involving the insignificant factors.

The important interactions between D, B and A can be interpreted in ysical terms by reference to the mean alcohol losses in Table I. For example, the st important interaction, BD, is due to the fact that the presence or absence of oride at low temperatures makes little difference to the mean alcohol loss, ereas at higher temperatures the presence of fluoride has a marked effect. The parent significance in Table III of the interactions involving the unimportant tors C and E is caused by the results from the contaminated batch. It is interesting note that Tables III–V produce a similar order of significance for the important tors and interactions.

BLE IV

TES' METHOD APPLIED TO THE 16 TREATMENT COMBINATIONS INVOLVING RSA PS

atment bination	*Total alcohol loss in mg% × 10*	*effect in mg% × 10*	*Mean square of effect*	*Significance level*[a]	**** effects arranged in order of significance*
	457				
	1105	169	1,374,310	***	D
	650	−193	1,781,396	***	B
	1122	−154	1,138,368	***	BD
	1316	78	295,788		A
	1149	13	7,829		AD
	1097	73	255,792		AB
	676	−49	117,315		ABD
	2408	301	4,344,635	***	
	8024	158	1,200,169	***	
	1853	−183	1,600,526	***	
	2626	−145	1,009,780	***	
	3692	60	170,885		
	13109	48	112,230		
	2418	−54	141,050		
e	2324	−48	109,730		

=99.9%.

TABLE V

YATES' METHOD APPLIED TO THE 16 TREATMENT COMBINATIONS INVOLVING ALCOHOL CONCENTRATION OF 220 mg%

Treatment combination	*Total alcohol loss in mg% ×10*	*Effect in mg% ×10*	*Mean square of effect*	*Significance level*[a]	**** effects arranged in order of significance*
c	563				
ac	1228	180	1,519,230	***	D
bc	681	−194	1,798,196	***	B
abc	966	−157	1,188,024	**	A
cd	2086	301	4,343,131	***	BD
acd	8262	170	1,393,156	***	AD
bcd	1722	−176	1,489,137	***	
abcd	2940	−144	996,913	**	
ce	1316	76	280,067		
ace	1149	4	796		
bce	1097	−72	249,480		
abce	676	−46	102,075		
cde	3692	60	171,184		
acde	13109	36	62,605		
bcde	2418	−61	176,722		
abcde	2324	−49	114,026		

[a] *** = 99.9%, ** = 99%.

INVESTIGATION OF IMPORTANT VARIABLES

Factorial experiments at two levels of each variable show general tre and reveal those factors which require further investigation. The variables t perature, fluoride concentration and time have therefore been studied in detail this instance.

Temperature dependence

Alcohol loss *versus* time curves were constructed at five different temperatu for blood containing 1% (w/v) sodium fluoride in sealed containers. The sa blood sample was used for all these experiments. The temperatures were − in a deep freeze, 4° in a domestic refrigerator, 22° at room temperature, 37° an air oven and 62° in the Multifract F40 Headspace Autoanalyser. Owing to very long storage period involved, the temperatures −20°, 4° and 22° could be controlled accurately. The temperatures 37° and 62° were thermostatically c trolled to better than ±1°.

The initial rate of alcohol loss was determined graphically from the alco loss *versus* time curve at each temperature. The results are shown in Table VI. ' initial rate of alcohol loss rises very rapidly with temperature. For example increases by a factor of 22 between 22° and 37°, a result of particular significa for countries with high ambient temperatures. These results are in agreement v the conclusion from the factorial experiment that temperature is the most impor factor controlling alcohol losses.

At 62° a second peak was observed in the chromatogram which rapidly ncreased in size as the ethanol peak decreased. This substance possessed similar etention times on Porapak Q and polyethylene glycol 400 columns to acetal- ehyde and was removed by the addition of sodium hydrogensulphite solution, ith which aldehydes form non-volatile addition complexes. The initial chroma- ogram of whole blood and that produced after 3 h are shown in Fig. 1. Acetaldehyde as not observed as a product at the other temperatures studied. Thus it appears hat ethanol is oxidized to acetaldehyde in blood, at least at 62°. Plots of alcohol xidized and acetaldehyde produced *versus* time at 62° are shown in Fig. 2. It can e seen that initially 1 mole of ethanol being oxidized produced 1 mole of acetal- ehyde, which clearly demonstrates that acetaldehyde is produced by ethanol oxida- ion.

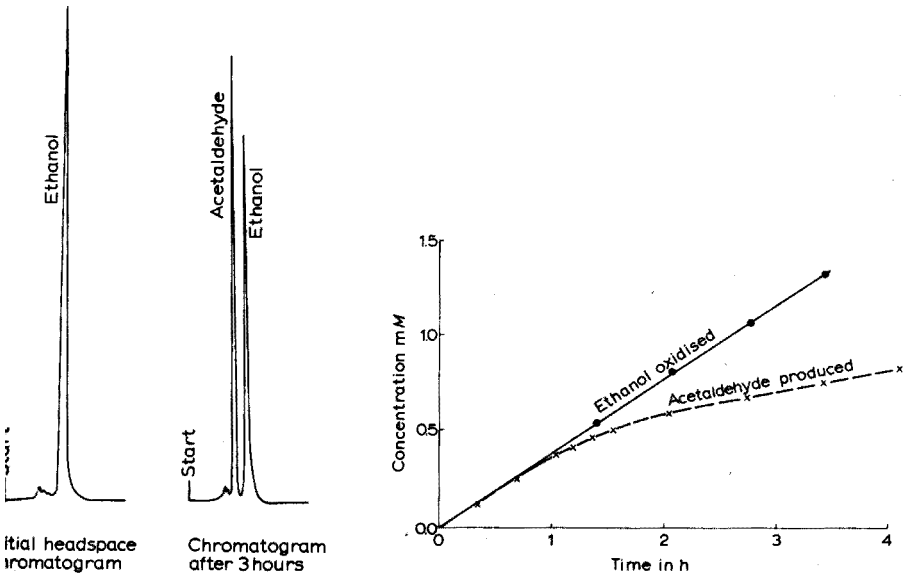
The rate of alcohol loss was found to be independent of alcohol concen- ation over the range 50–250 mg% at all temperatures studied. This confirms nother of the conclusions from the factorial experiment. The alcohol oxidation

ABLE VI

HE TEMPERATURE DEPENDENCE OF THE RATE OF ALCOHOL LOSS FOR ONE LOOD SAMPLE

he initial rate of alcohol loss is given in mg% per day)

emperature (°)	−20	4	22	37	62
ate of loss	<0.007	0.02	0.29	6.0	43.1



g. 1. Acetaldehyde production by whole blood at 62°.

g. 2. Ethanol oxidized and acetaldehyde produced in whole blood at 62°.

observed in the investigation of the temperature variable exhibits several interesti features.

Fluoride concentration

Blood alcohol losses were determined from a single blood sample contain 110 mg% alcohol after a storage period of 5 days at 37° in sealed Multifract bott The sodium fluoride concentrations used were 0.0, 0.5, 1, 2 and 4% (w/v). The resu are shown in Table VII. Alcohol losses with aqueous samples containing phen mercury(II) nitrate stored under similar conditions proved negligible. Table V shows that the presence of sodium fluoride is indeed important but that the co centration is of little significance in the range 0.5–4% (w/v). This result is entir consistent with the hypothesis that the large random alcohol losses in the abse of fluoride are due to the growth of micro-organisms. This growth is inhibited sodium fluoride levels of 0.5% (w/v) and also, as can be seen in Table I, un refrigerated conditions. It is also apparent from Table VII that blood alcol oxidation losses, which amount to about 13 mg% after 5 days, are not inhibi to any extent by sodium fluoride.

TABLE VII

ALCOHOL LOSSES AT VARIOUS CONCENTRATIONS OF SODIUM FLUORIDE DURI 5 DAYS AT 37°

NaF concn. (% w/v)	0	0.5	1.0	2.0	4.0
Alcohol loss (mg%)[a]	68.0	14.6	14.9	11.7	12.1

[a] Mean of duplicate analyses.

It is worthy of note that not a single sample examined showed an increasi alcohol level either in the presence or absence of sodium fluoride.

Time dependence

Alcohol losses were determined for 50 samples of blood in RSA cups af storage at a room temperature of *ca.* 22°. The samples were analysed in batches 10 at intervals up to 83 days. The mean alcohol loss was calculated for each bat of samples. Individual results which were 4 mg% or more from the original me were excluded and the adjusted mean and standard deviation (s) were calculat The results are recorded in Table VIII. The majority of samples showed a stead increasing alcohol loss with time, consistent with the alcohol oxidation mechani already discussed. However, in a small number of containers, significantly grea losses were detected as shown in Table VIII.

If the results summarized in Table I are examined, it can be seen that so samples in RSA cups containing 1% sodium fluoride did indeed show abnorn losses whereas no equivalent sample in glass ampoules did so. This did not app in the overall statistical analysis as a container-dependence, because of the sm incidence of abnormal losses observed in the RSA cups. These results can be int preted as being due to poor closure of some of the polypropylene containers whi resulted in loss of alcohol by diffusion.

TABLE VIII

THE TIME DEPENDENCE OF ALCOHOL LOSSES FROM BLOOD AND AQUEOUS SOLUTIONS IN RSA CUPS AT ROOM TEMPERATURE

Type of sample	*Blood*					*Aqueous*				
Storage time (days)	0	13	35	48	83	0	21	36	55	84
Mean alcohol loss $\pm s$ (mg%)	0.0 ± 0.7	2.5 ± 0.8	8.1 ± 1.4	10.4 ± 1.4	13.2 ± 1.5	0.0 ± 0.9	0.8 ± 0.6	0.9 ± 1.4	-0.3 ± 1.2	-0.1 ± 1.4
No. of results used	10	10	10	9	9	10	9	8	9	8
Results excluded	—	—	—	18.6	17.6	—	6.2	41.6 17.5	14.2	10.4 12.9

To test this hypothesis, alcohol losses were determined for 50 aque samples in RSA cups after storage at room temperature. The aqueous alco solution contained the inhibitor phenylmercury(II) nitrate. The samples w analysed in batches of 10 at intervals up to 84 days. The results were analysed described previously and are shown in Table VIII. It can be seen that the majo of the aqueous samples are essentially stable with time. In a number of contain however, significant losses were again detected. These results are entirely consist with the suggestion that alcohol losses occur from a small percentage of RSA c because of closure failure. Clearly a process of this kind would be unpredicta since the areas available for diffusion must vary considerably from one contai to another.

Experiments of the above type were repeated in our laboratories in or to determine the closure failure rate. A total of 553 samples were analysed i separate experiments during periods of storage up to 106 days at room temp ture and 31 results were found which could be attributed to closure failure (Ta IX). This represents an overall failure rate of 5.6% for RSA cups.

TABLE IX

DETERMINATION OF CLOSURE FAILURE RATE FOR RSA CUPS

Experiment	1	2	3	4	5
No. of cups examined	200	60	195	48	50
No. of failures	8	2	11	4	6

The closure failure rate for each experiment was compared to the combin rate using the χ^2 test. The value of χ^2 obtained was 5.8 (4 degrees of freedom) whi is less than the value at the 10% level of significance from Tables. The χ^2 t cannot be strictly applied when the expected frequency in any experiment is l than 5. If, to overcome this difficulty, the results for experiment 1 are amalgamat with 2, and 4 with 5, then the value of χ^2 obtained is 5.1 (2 degrees of freedom) whi is greater than the value at the 10% level of significance but less than the value the 5% level from Tables.

DISCUSSION

This investigation of the important variables, temperature, fluoride co centration and time, has resulted in three mechanisms of alcohol loss bei identified. From the investigation of the temperature dependence of alcohol losse a previously unknown oxidation reaction was discovered; from the investigation fluoride concentration the effect of micro-organisms was determined; and from t time of storage random alcohol losses by diffusion from some RSA containe were found.

The important factors and interactions in order of significance can now explained in terms of the three mechanisms of alcohol loss. Temperature (D) the most important factor because the growth of micro-organisms and the alcoh

idation reaction are strongly temperature-dependent. The fluoride concentration important because it inhibits the catastrophic losses due to the growth of icro-organisms. The fluoride concentration–temperature interaction (BD) arises cause the presence of fluoride is more important at room temperature than der refrigerated conditions, where micro-organism growth is unlikely even contamination has occurred. The time of storage (A) is obviously important for l three mechanisms. The time–temperature interaction (AD) is significant because e time of storage is more important at high temperatures than at low temperatures, ce again, for all three mechanisms. The time–fluoride interaction (AB) is significant cause the time of storage is more important without fluoride than with fluoride, hich eliminates the growth of micro-organisms. Thus all the significant effects and teractions can be explained in terms of the proposed mechanisms.

The factorial experiment did not show a significant container dependence cause such experiments give only overall trends and the failure rate of the RSA ps was insufficient to produce a statistically significant container dependence.

The results reported here are more comprehensive but broadly similar to ose of previous authors[2,6]. However, the interpretation given here differs conderably from other authors. For example, Krauland *et al.*[2] stored samples at and performed serum alcohol analyses. They proposed that the alcohol losses ey observed were in fact due to an increase in the specific gravity of the serum ring storage. The results reported here rule out this theory since similar alcohol sses were observed from the analysis of whole blood. They also dismissed an cohol oxidation mechanism with the assertion that there was insufficient oxygen the container. It would appear that only oxygen in the air space was nsidered in this respect and that combined oxygen as oxyhaemoglobin was nored. In the work reported here sufficient oxygen would certainly have been resent in free and combined forms to explain the alcohol losses produced by the idation reaction.

The results described here are thus interpreted in terms of three principal echanisms of alcohol loss.

1. Alcohol loss occurring by oxidation to acetaldehyde. This mechanism hibits three main features:

(*a*) marked temperature dependence, the initial rate of alcohol oxidation creasing 22 times between 22° and 37°;

(*b*) the rate of oxidation is independent of ethanol concentration over a ide range;

(*c*) acetaldehyde is observed as the oxidation product at 62° but not at the wer temperatures studied.

2. Alcohol loss occurring in blood containing no preservative, owing to the owth and metabolism of micro-organisms. These losses are randomly distributed d often very large, amounting to complete alcohol loss, but are inhibited by ncentrations of sodium fluoride at or above 0.5% (w/v). It is normally accepted at sodium fluoride inhibits the growth of organisms which would produce a rise blood alcohol. In this paper no net increase in the alcohol concentration of y sample was found which shows clearly that the significant effect of sodium oride is to inhibit ethanol-metabolizing organisms.

3. Alcohol loss occurring by diffusion from RSA cups owing to closure failure.

RSA cups are mass-produced and some, by the laws of normal distribution, h small closure defects. In this study 553 cups were stored at room tempera and 5.6% closure failures were detected.

The mechanism of ethanol oxidation in stored blood has been investig further and the results are reported by Smalldon and Brown[11].

The authors gratefully acknowledge the advice and encouragement of P. G. W. Cobb, the Director of the Home Counties Forensic Science Laborat and Dr. R. L. Williams, the Director of the Metropolitan Police Laborat during the preparation of this paper.

SUMMARY

The effects of the factors time, sodium fluoride concentration, ethanol c centration, temperature of storage and type of container on the ethanol losses fr stored human blood have been investigated by means of a 2^5 factorial experim The important factors were found to be temperature, fluoride concentration a time of storage. A detailed study of the important factors enabled three disti mechanisms of ethanol loss to be identified. These were a highly temperatu dependent ethanol oxidation reaction which was independent of the etha concentration over a wide range; destruction of ethanol by the action of mic organisms in the absence of a preservative, which could be inhibited by 0. (w/v) sodium fluoride, and diffusion which was found to occur from 5.6% of polypropylene containers used in Britain for the purposes of the Road Tra Act 1972.

RÉSUMÉ

On examine l'influence de divers facteurs: temps, concentration en fluorure sodium, concentration en éthanol, température de stockage et type du récipie sur les pertes en éthanol de sang humain stocké. Les plus importants sont température, la concentration en fluorure et la durée du stockage. Une étu détaillée de ces facteurs a permis d'établir trois mécanismes distincts de pe d'éthanol: réaction d'oxydation de l'éthanol très dépendante de températu destruction de l'éthanol par action de micro-organismes, en l'absence de préserv et diffusion dans des récipients de polypropylène.

ZUSAMMENFASSUNG

Der Einfluss der Faktoren Zeit, Natriumfluoridkonzentration, Äthan konzentration, Lagertemperatur und Gefässart auf die Äthanolverluste in a bewahrtem menschlichem Blut wurde mit Hilfe eines 2^5-Faktoriellen-Experimen untersucht. Als wichtige Faktoren wurden die Temperatur, Fluoridkonzentrati und Lagerzeit ermittelt. Durch genaue Untersuchung der wichtigen Faktoı wurden drei verschiedene Mechanismen des Äthanolverlustes festgestellt. Di waren eine stark temperaturabhängige Äthanoloxidationsreaktion, die in ein weiten Bereich von der Äthanolkonzentration unabhängig war, Äthanolverl

urch die Wirkung von Mikroorganismen in Abwesenheit eines Schutzmittels, der urch 0.5% (G/V) Natriumfluorid verhindert werden konnte, und Diffusion, die bei .6% der verwendeten Polypropylengefässe auftrat.

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E STABILITY OF ETHANOL IN STORED BLOOD

RT II. THE MECHANISM OF ETHANOL OXIDATION*

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Many countries have legislation designed to control the drinking driver by osing a limit on the permitted concentration of ethanol in the blood. In this ntry the appropriate legislation is the Road Traffic Act (RTA) 1972. The ration of statutory limits of this type, where the defendant is given a sample lood for his own analysis, requires that stable blood ethanol samples are lable, which will not be the case unless special precautions are taken.

In a previous paper[1] the variables which affect the stability of ethanol in ed blood were identified. In no instance was an increasing ethanol concentration id but three mechanisms of ethanol loss were identified. One of these mechanisms diffusion from imperfectly sealed containers, which obviously has a simple edy in improved container design. Another mechanism involved ethanol abolism by the growth of micro-organisms in the absence of a preservative; this wth was inhibited by 0.5% (w/v) sodium fluoride. The preservative currently l for samples collected in this country is 1% (w/v) sodium fluoride. The third hanism was a strongly temperature-dependent ethanol oxidation reaction which not inhibited by sodium fluoride and had not previously been reported. This hanism had not been recognised by other workers because the product of the lation, acetaldehyde, could only be detected at elevated temperatures. The initial of oxidation in whole blood was found to be independent of the ethanol centration over the significant part of the physiological range and varied from ually zero under frozen conditions, through 0.29 mg% per day at room perature (22°), to 43 mg% per day at 62°. The storage of samples in a deep ze is clearly one solution to the problem of producing stable blood ethanol itions. However, it is of limited practical value as samples will inevitably be ed under less favourable conditions in many instances.

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It is the aim of this paper to investigate the mechanism of ethanol oxi in stored blood and to determine how it can be prevented.

EXPERIMENTAL

The containers used were airtight glass bottles. Unless otherwise state blood used was one month old transfusion blood containing acid citrate de as anticoagulant.

Blood samples were analysed by gas chromatography using a Perkin I Multifract F40 Headspace Autoanalyser. The procedures and instrun conditions used were as described previously[1].

RESULTS AND DISCUSSION

Individual variation

Fresh samples of blood were obtained from 10 different individuals had consumed alcohol. Potassium oxalate (0.1% w/v) was used as anticoag and sodium fluoride (1% w/v) as preservative, which is the normal practic samples obtained under the RTA 1972. Samples were stored at 37° and the i rate of ethanol loss was estimated graphically for each sample. The mean i rate was 5.5 ± 1.5 mg% per day. This result is not significantly different from obtained previously with a sample of transfusion blood of 6.0 mg% per These results show that ethanol-oxidizing activity is present to a similar exte all the individuals examined and that the results for transfusion blood are dir applicable to samples collected for the purposes of the RTA 1972.

Location of oxidizing activity

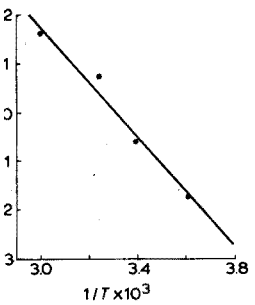
A fluoride-free sample of transfusion blood was centrifuged. The sepa cells and serum were analysed for ethanol-oxidizing activity after incubation i water bath of the Multifract F40. The activity was found to reside in the and when these were diluted with serum, the activity was diluted in approxim the same ratio.

Washed and packed corpuscles were diluted with one volume of dis water. The centrifuged solution was concentrated by dialysis in Visking sa casing against saturated ammonium sulphate in a refrigerator. Crude granul oxyhaemoglobin were then prepared as described by Drabkin[2]. Aqueous solu of these granules possessed marked ethanol-oxidizing activity at 62°.

Kinetics

It has already been shown that the initial rate of ethanol oxidation is order with respect to ethanol concentration[1]. Thus ethanol does not take pa the rate-determining step.

The order with respect to oxyhaemoglobin was determined at 62 measuring the initial rate of acetaldehyde production by different concentra of oxyhaemoglobin prepared by diluting whole blood with up to five time volume of distilled water. The plot of initial rate *versus* oxyhaemoglobin concentr was linear, indicating that the reaction is first order with respect to oxyhaemogl



. 1. Arrhenius plot of $\log_{10}k$ against $1/T$.

The variation of the initial reaction rate (k) with temperature (T) has ady been determined[1]. A plot of $\log_{10}k$ against $1/T$ is shown in Fig. 1. The e was calculated by least-squares analysis, the result at $-20°$ being ignored, t this temperature a change of state has occurred. The Arrhenius equation ds from the slope an activation energy of 25 kcal mole^{-1} for the process in id blood. This activation energy suggests a chemical reaction mechanism. A y much smaller activation energy would be expected for a diffusion-controlled cess. A variation of activation energy and therefore a non-linear Arrhenius plot ld be expected for micro-organisms. Typical activation energies for enzyme-lysed reactions[3] are in the range 5–13 kcal mole^{-1}. Deactivation would also be ected to occur in mammalian enzyme systems before 62°.

nzyme dependence

The rate of alcohol oxidation was studied at 37° and 62° with whole od to which only nicotinamide adenine dinucleotide (NAD), adenine dinucleotide sphate (NADP) or their reduced forms (NADH, NADPH) had been added at a centration of 0.5 mg ml^{-1}. This represents at least a tenfold increase over the ural levels of these coenzymes observed in human erythrocytes.

Marginal increases in the rate of alcohol oxidation were caused by the uced coenzymes NADH and NADPH. It was therefore concluded that the hol oxidation mechanism was not significantly coenzyme-dependent.

ent of ethanol oxidation

The ethanol concentrations of the blood samples in sealed containers with ited air spaces which were examined at various temperatures, fell approximately onentially to a value about 20 mg% below the starting concentration. In the of sealed containers two-thirds filled with blood, the mean alcohol loss over a iod of eighteen months at room temperature was 35 mg%.

Scaplehorn[4] has shown that the extent of alcohol losses does depend on the ume of the air space in the container.

mical inhibitors

The effect of various compounds on the rate of alcohol oxidation in sfusion blood was studied at 37° and 62°. The substances studied included ium fluoride, potassium cyanide, sodium azide, sodium hydrogensulphite,

iodoacetic acid, 8-hydroxyquinoline, ethylenediaminetetracetic acid, sodium dit nite, and sodium nitrite. Sodium azide, hydrogensulphite, dithionite and ni were found to inhibit alcohol oxidation significantly.

Proposed mechanism of ethanol oxidation

The mechanism proposed to explain the above experimental results is sh in Fig. 2. The ethanol-oxidizing activity is associated with an unknown in mediate oxidizing agent or catalyst in the breakdown of oxyhaemoglobin. As rate of ethanol oxidation is zero order with respect to ethanol, and first order v respect to oxyhaemoglobin, it is postulated that this intermediate (X) is produ slowly and reacts rapidly with ethanol to produce acetaldehyde. Thus the activat energy of 25 kcal mole^{-1} applies to the production of the intermediate. methods used do not enable the nature of this intermediate to be determi However, Rostofer and Cormier[5] have shown that hydrogen peroxide or radicals are produced in the reaction of oxyhaemoglobin with methaemoglol forming agents. Itano and Robinson[6] also separated electrophoretically intermed compounds during partial oxidation of carbonmonoxyhaemoglobin. A cou oxidation of haemoglobin and ascorbic acid in the presence of oxygen has b reported by Lemberg *et al.*[7].

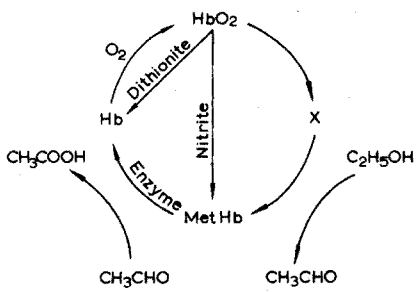


Fig. 2. Proposed mechanism for ethanol oxidation in erythrocytes.

The minor coenzyme dependence on NADH and NADPH may be interpret in terms of stimulation of the NADH-dependent "diaphorase" and NADP dependent methaemoglobin reductase systems[8].

Methaemoglobin (MetHb) is produced from blood samples on storage and known to be reduced to haemoglobin (Hb) by mammalian erythrocytes in t presence of aliphatic aldehydes. Matties[9] has shown that this reaction is enzyma in nature and depends on the structural integrity of the erythrocytes. The reacti he proposes is of the form:

$$CH_3CHO + H_2O + 2\,MetHb \xrightarrow{\text{enzyme}} CH_3COOH + 2Hb + 2H^{\cdot}$$

Thus the appearance of acetaldehyde as a product at high temperatures simp indicates that the structural integrity of the cell is breaking down. Once haem globin is produced by the methaemoglobin reduction, oxyhaemoglobin could formed by oxygen from the air in the container. This could be the explanation f the air space-dependence of alcohol losses observed by Scaplehorn.

Saturated blood normally contains 20 ml of oxygen per 100 ml of blood. e reaction to produce acetaldehyde involved one molecule of oxyhaemoglobin quivalent and one molecule of ethanol, then the maximum fall in blood alcohol centration would be *ca.* 20 mg%. If there were an air space above the blood, alcohol loss could increase further. The alcohol losses observed in practice amples with air spaces are 20–40 mg% after long periods of storage.

The action of sodium nitrite on oxyhaemoglobin is to convert it to methaemoin, and sodium dithionite reduces oxyhaemoglobin to haemoglobin. Thus the bition of ethanol loss by nitrite and dithionite can be interpreted from the posed mechanism, because the production of the intermediate (X) is bypassed n these inhibitors are added. The addition of sodium hydrogensulphite and um azide to blood samples causes a distinctive change in colour. This suggests these inhibitors are also effective because they destroy oxyhaemoglobin.

The present study shows that ethanol oxidation in stored human blood is ed by an oxyhaemoglobin intermediate and can therefore be prevented by pounds which destroy oxyhaemoglobin. It is interesting to speculate whether oxidation could occur, at least to some extent, *in vivo*.

For practical purposes the ideal inhibitor of blood ethanol oxidation should table, effective at low concentrations and preferably inexpensive. It is also ortant that any inhibitor should not interfere with existing methods of ethanol ysis, including those based on alcohol dehydrogenase. If the inhibitor would act as a preservative and prevent the growth of micro-organisms this would be dded advantage. Sodium azide would appear to show considerable promise in respect. Further work is clearly necessary to select the inhibitor and its centration which best fulfils the above criteria and provides stable blood ethanol tions.

MARY

The oxidation of ethanol in stored human blood has been investigated. The izing activity is shown to arise from an oxyhaemoglobin intermediate and to be bited by compounds which destroy oxyhaemoglobin. The reaction is first order respect to oxyhaemoglobin concentration and zero order with respect to nol concentration. The activation energy for the production of the intermediate lculated from an Arrhenius plot as 25 kcal mole^{-1}. An overall mechanism oposed for blood ethanol oxidation and the stabilization of blood ethanol tions is discussed.

JMÉ

Une étude est effectuée sur l'oxydation de l'éthanol dans un sang humain cé. On constate que l'activité oxydante est due à la formation d'un interiaire d'oxyhémoglobine; elle est empêchée par addition de composés détruisant hémoglobine. La réaction est de premier ordre en fonction de la concentration oxyhémoglobine et d'ordre zéro en fonction de la concentration en alcool. ergie d'activation pour la formation de l'intermédiaire est de 25 kcal mole^{-1}, Arrhenius. Un mécanisme est proposé pour l'oxydation de l'éthanol du sang; xamine les possibilités de stabilisation de l'éthanol dans le sang.

ZUSAMMENFASSUNG

Die Oxidation von Äthanol in aufbewahrtem menschlichem Blut wi untersucht. Die oxidierende Wirkung rührt von einer Oxyhämoglobin-Zwisch stufe her und kann durch Verbindungen gehemmt werden, die Oxyhämoglo zerstören. Die Reaktion ist erster Ordnung in Bezug auf die Oxyhämoglo konzentration und nullter Ordnung in Bezug auf die Äthanolkonzentration. Aktivierungsenergie für die Bildung der Zwischenstufe wird aus einer Arrhen Auftragung zu 25 kcal mol^{-1} ermittelt. Es wird ein Gesamtmechanismus für Blut–Äthanoloxidation vorgeschlagen und die Stabilisierung von Blut–Ätha lösungen diskutiert.

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REACTION OF METHYL ORANGE WITH BROMINE

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:d 22nd February 1973)

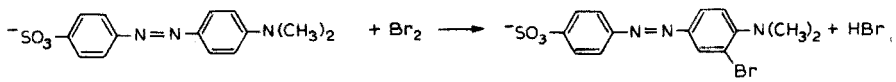
Since its introduction by Györy[1] in 1893, methyl orange has remained a ar indicator for many titrations involving potassium bromate as oxidant. The ons of arsenic(III)[2–5], antimony(III)[2,3] and hydrazine[6] have been accomplished nethyl orange indicator; and although apparently superior indicators have roposed[7,8], its application still appears in many standard textbooks[8,9]. Methyl e as a redox and acid–base indicator has recently been reviewed[10].

There are considerable variations in the recommended conditions particularly respect to the most appropriate acid concentration. The red colour (λ_{max} m) of methyl orange in acid solution is bleached by the free bromine ced at the end-point of a titration with potassium bromate in hydrochloric nedium. The lower limit for the acidity in the above titrations is due to the release of the active oxidants, chlorine and bromine, from the bromate[11]. arsenic(III) or antimony(III) cannot be determined below *ca.* 0.3 *M* hydro- c acid in the presence of 0.1 *M* added bromide or below *ca.* 0.5 *M* chloric acid in the absence of added bromide. It is possible to determine c(III) with bromate at lower acid concentrations than this if osmium ide is used as catalyst but indicators cannot then be used[12]. Most authors nowever, specified an upper acid limit as well as the lower limit[2–5]. The upper nust be a consequence of the indicator reaction, for potentiometric titrations ecise at much higher acid concentrations[11] but no information is available lain this effect. Kew *et al.*[5] stated that the indicator reaction becomes sluggish e the range 1.2–3.5 *M* hydrochloric acid, a statement with which most rs seem to agree. This explains the frequent use of elevated temperatures in titrations, although this has been shown to be unnecessary[3].

The methyl orange–bromine reaction is irreversible, and its indicator action se titrations is based on the rate of the bromine–reductant reaction being faster than that of bromine with the indicator. It therefore depends on the es and mechanism of both these reactions. Kinetic methods for the nination of phenols[13], and arsenic(III), antimony(III) and ascorbic acid[14] been developed, based on homogeneous generation of bromine with methyl e to indicate the completion of the oxidation of the reductant concerned, also depend on the favourable kinetics of these systems. Catalytic methods e determination of chloride and bromide have also been based on this ple[15].

In addition to its use as bromometric indicator, methyl orange has also been n colorimetric determinations of chlorine and bromine[16–18]. Laitinen and

Boyer[18] have shown that both chlorine and bromine can be determined simu eously and have also demonstrated that the reaction of methyl orange bromine proceeds at greater than 95% by the reaction



provided that the methyl orange is in excess.

The products of the reaction of methyl orange with bromine have ther been established, but all the above applications depend on the rate at which reaction proceeds. During a recent study of the reaction of methyl orange potassium bromate in initially halide-free media, it was found that under ce conditions the reaction rate was controlled by the rate of the bromine–m orange reaction. This prompted a detailed kinetic study of the reaction, whic reported here and allows definitive comment on the use of methyl orange bromometric indicator.

EXPERIMENTAL

Reagents

Potassium bromate, 0.1 M. Analytical-reagent potassium bromate was crystallized twice from distilled water and air-dried. The required amoun recrystallized potassium bromate was dissolved in distilled water and the solu was standardized by titration with primary-standard arsenic(III) solution methyl orange indicator.

Methyl orange, 0.001 M. Laboratory-reagent methyl orange (sodium salt) recrystallized twice from distilled water. After drying at 110° for 3–4 h, required amount of methyl orange was dissolved in distilled water. The solu was standardized by spectrophotometric titration with 10^{-4} *M* potassium brom in a Spectrotitrator (Evans Electroselenium Ltd., filter no. 605 with transmiss maximum at 550 nm). Methyl orange (2 ml of $6.12 \cdot 10^{-4}$ *M*) solution was dilu to 20 ml for titration, the final solution being 2 *M* in sulphuric acid and 0.1 *M* potassium bromide; the methyl orange solution was found to be $6.21 \cdot 10^{-4}$ based on a 1:1 stoichiometry between methyl orange and the bromine genera from the bromate–bromide reaction or a 3:1 stoichiometry for the methyl oran bromate reaction. This was considered reasonable agreement. However, it was no that at the beginning of the titration a small amount of bromate had to be ad before the absorbance of methyl orange started to fall. This was thought to be to impurities in the methyl orange absorbing bromine, but on recrystallization, consumption of bromate in this side reaction remained constant and reproduci Subtraction of the volume of bromate consumed in this way gave a result for assay of the methyl orange in precise agreement with the theoretical value.

Perchloric acid, 5 M. Perchloric acid (60% w/w) was diluted with water standardized by titration with sodium carbonate, with methyl orange as indica

Sodium perchlorate, 2 M. Analytical-reagent sodium perchlorate was dissol in distilled water and then standardized by evaporating a known volume of solution to constant weight.

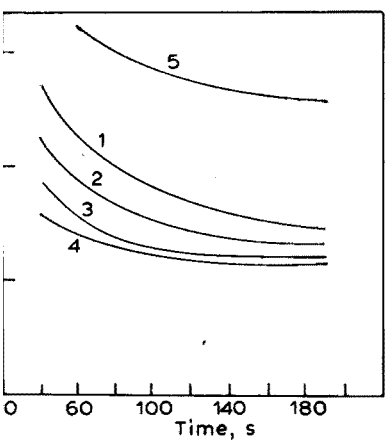
Sodium bromide, M. The required amount of analytical reagent-grade sodium ıide was dissolved in distilled water.

High-purity glass-distilled water was used throughout.

tic studies

The reaction was followed spectrophotometrically by measuring the rate of ge in absorbance of methyl orange at 510 nm (Hitachi-Perkin Elmer 139 rophotometer). A Honeywell Electronik 15 recorder was attached to provide ıtinuous record. A two-limbed reaction vessel was used to contain the reactant ions during a preliminary 30-min thermostatting period. Potassium bromate, ıloric acid, sodium bromide and sodium perchlorate were added to the main of the reaction vessel, and methyl orange was placed in the smaller side-arm. ɛr these conditions the bromate was entirely converted to bromine during the ıostatting period. The vessel was not deaerated, but it was effectively sealed event loss of bromine. The reaction was started by mixing and shaking the ions thoroughly and at the same time the recorder chart drive was switched . sample of the reaction mixture was then transferred rapidly to a thermostatted m spectrophotometer cell, and the cell was replaced in the spectrophotometer. total volume of reaction solutions was, in all cases, 100 ml and an ionic gth of 1.00 *M* was maintained constant with sodium perchlorate solution.

Initial tests showed that the reaction was too fast to allow study under ılo first-order conditions. The reaction was therefore investigated under second- : conditions, *i.e.* with methyl orange and bromine present at approximately /alent concentration, and was slowed down further by taking fairly high ɔgen ion concentrations. Some typical absorbance–time plots are shown in 1. The reaction was observed at a wide range of reactant concentrations ɔllows: bromine, $6.00–15.00 \cdot 10^{-6}$ *M*; hydrogen ion, 0.3–0.9 *M*; bromide, 0.20 *M*; and methyl orange, $0.909–1.818 \cdot 10^{-5}$ *M*. The temperature and ionic gth were kept constant at $25.0 \pm 0.1°$ and 1.00 *M*, respectively.

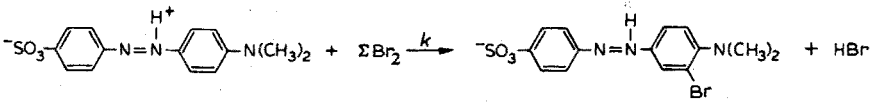


. Reaction curves for the reaction of methyl orange with bromine at various hydrogen ion ıtrations. (1) 0.8 *M* $HClO_4$; (2) 0.6 *M* $HClO_4$; (3) 0.4 *M* $HClO_4$; (4) 0.3 *M* $HClO_4$, all in Br^-, $1.2 \cdot 10^{-5}$ *M* methyl orange and $12 \cdot 10^{-6}$ *M* bromine. Curve (5) was the same, except ı *M* $HClO_4$ and $9 \cdot 10^{-6}$ *M* bromine.

RESULTS AND DISCUSSION

It is clear from the present work and the results of Laitinen and Boy that the decolorization of methyl orange with bromine proceeds with 1:1 stoic metry and according to reaction (1). The methyl orange molecule may subsequ be di- or even tribrominated or the azo linkage may be broken, but decolorizati complete at the monobromination stage, which proceeds exclusively as long as m orange is in reasonable excess over bromine. Within certain limitations, which be mentioned shortly, reaction (1) is the one which is being followed.

At hydrogen ion concentrations between 0.1 M and 1 M, methyl or is more or less completely in the protonated form, for the pK value[10] is The red acid form exists in a number of resonance structures but the rea with bromine can be formulated:



where ΣBr_2 represents all possible bromine species present. Under the condi used (0.02–0.20 M bromide), the only species of bromine present are Br_2 Br_3^-. Hence

$$\Sigma[Br_2] = [Br_2] + [Br_3^-]$$

Since under all conditions used, the concentrations of bromide and hydroger were in large excess of the bromine and methyl orange, their concentrations remain essentially constant during the reaction. Under the second-order ki conditions used therefore, the rate of reaction (2) is given by

$$-d[M]/dt = k[M][\Sigma Br_2]$$

where M stands for methyl orange and k is the overall rate constant for all bromine species. Integrating this equation between $t=0$ when $[M]=[M]_0$ $[\Sigma Br_2]=[\Sigma Br_2]_0$ and $t=t$ when $[M]=[M]_0-x$ and $[\Sigma Br_2]=[\Sigma Br_2]_0-x$, where the concentration of methyl orange reacted at the time t and $[M]_0$ and $[\Sigma$ are the initial concentrations of methyl orange and bromine respectively, we ob the usual second-order integrated form

$$\frac{2.303}{[\Sigma Br_2]_0-[M]_0} \cdot \log \frac{[M]_0([\Sigma Br_2]_0-x)}{[\Sigma Br_2]_0([M]_0-x)} = kt$$

which may be used to interpret the data and evaluate k.

A problem was encountered in the interpretation of the results: if $12 \cdot 10^-$ methyl orange was taken with $12 \cdot 10^{-6}$ M bromine, then only *ca.* $9.3 \cdot 10^-$ methyl orange was consumed, as determined by the absorbance at infinite t When this work was carried out, the explanation for this was not clear. How Laitinen and Boyer[18] have recently shown that the stoichiometry of the reac depends critically on the relative concentrations and mixing of the reagents. if methyl orange is not kept in both overall and local excess, some bromi consumed in bromination of the reaction product. In the present system, l

sses of bromine occur during the mixing of reagents, which explains the epancy. After mixing, the solution is homogeneous, and the reaction proceeds nally but at a lower apparent concentration of bromine. This difficulty was mvented by assuming that the amount of methyl orange consumed at infinite was equal to the initial concentration of bromine taking part in the mono-nination reaction; this led to entirely consistent results.

The initial concentration of bromine $[\Sigma Br_2]_0$ was therefore set equal to $)-[M]_\infty$. Values of k in eqn. (5) were then calculated for 8–10 points in each tion; some typical results are shown in Table I. Mean values of k for each set action conditions were then calculated (Table II). The constancy of the values of thin each experiment, as well as at different initial concentrations of methyl ıge and bromine (first 7 results of Table II) confirm that the reaction is second

.E I

ERMINATION OF VALUES OF k FROM EXPERIMENTAL DATA

Conditions	*Time (s)*	*[M] reacted* ($\cdot 10^{-5}$ *M*)	$\cdot 10^5$ *L.H.S. eqn. 5*	$k \cdot 10^3$ ($l\ mole^{-1}\ s^{-1}$)
$[M]_0$ $1.212 \cdot 10^{-5}$ *M*	50	0.792	2.75	5.89
$[\Sigma Br_2]$ $9.56 \cdot 10^{-6}$ *M*	60	0.827	3.34	5.57
$[HClO_4]$ 0.6 *M*	70	0.855	4.01	5.72
$[Br^-]$ 0.1 *M*	80	0.875	4.60	5.75
	90	0.888	5.17	5.74
	100	0.896	5.56	5.56
	110	0.908	6.28	5.71
	120	0.915	6.81	5.67
$[M]_0$ $1.212 \cdot 10^{-5}$ *M*	50	0.509	1.49	2.98
$[\Sigma Br_2]$ $6.96 \cdot 10^{-6}$ *M*	60	0.554	1.90	3.16
$[HClO_4]$ 0.90 *M*	70	0.580	2.21	3.15
$[Br^-]$ 0.1 *M*	80	0.600	2.51	3.14
	90	0.615	2.80	3.11
	100	0.627	3.07	3.06
	110	0.636	3.31	3.07
	120	0.644	3.56	2.96
$[M]_0$ $1.212 \cdot 10^{-5}$ *M*	50	0.717	2.04	4.08
$[\Sigma Br_2]$ $9.36 \cdot 10^{-6}$ *M*	60	0.775	2.72	4.58
$[HClO_4]$ 0.90 *M*	70	0.797	3.07	4.18
$[Br^-]$ 0.08 *M*	80	0.818	3.49	4.36
	90	0.838	3.99	4.43
	100	0.849	4.33	4.33
	110	0.860	4.73	4.29
	120	0.869	5.11	4.26
$[M]_0$ $0.909 \cdot 10^{-5}$ *M*	50	0.548	1.59	3.17
$[\Sigma Br_2]$ $9.36 \cdot 10^{-6}$ *M*	60	0.587	1.90	3.16
$[HClO_4]$ 0.90 *M*	70	0.615	2.17	3.10
$[B^-]$ 0.1 *M*	80	0.640	2.46	3.07
	90	0.670	2.88	3.20
	100	0.689	3.03	3.03
	110	0.695	3.32	3.01
	120	0.712	3.67	3.07

TABLE II

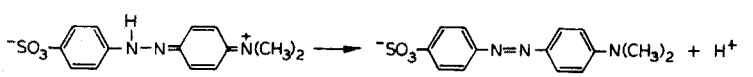
RATE CONSTANTS FOR THE BROMINE–METHYL ORANGE REACTION

($K = 4 \cdot 10^{-4}$, $K_1 = 16$)

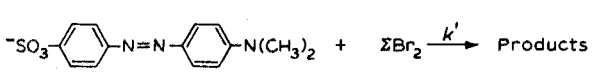
$[\Sigma Br_2]$ taken ($\cdot 10^{-6}$ M)	$[\Sigma Br_2]$ consumed in reaction ($\cdot 10^{-6}$ M)	$[M]_0$ ($\cdot 10^{-5}$ M)	$[H^+]$ (M)	$[Br^-]$ (M)	$k \cdot 10^3$ (l mole^{-1} s^{-1})	$k_1 \cdot 10^7 = \frac{k[H^+](1+K_1[B}{K}$ (l mole^{-1} s^{-1})
6	4.18	1.212	0.90	0.10	3.15	1.85
9	6.96	1.212	0.90	0.10	3.16	1.86
12	9.26	1.212	0.90	0.10	3.35	1.95
15	11.10	1.212	0.90	0.10	3.75	2.14
12	9.36	1.818	0.90	0.10	3.75	2.18
12	9.36	1.515	0.90	0.10	3.30	1.93
12	9.36	0.909	0.90	0.10	3.15	1.84
12	9.38	1.212	0.80	0.10	4.35	2.26
12	9.56	1.212	0.70	0.10	4.70	2.13
12	9.56	1.212	0.60	0.10	5.65	2.20
12	9.58	1.212	0.50	0.10	7.25	2.30
12	9.67	1.212	0.40	0.10	9.26	2.40
12	9.73	1.212	0.30	0.10	11.59	2.23
12	9.36	1.212	0.80	0.20	1.89	1.57
12	9.36	1.212	0.80	0.15	2.52	1.66
12	9.36	1.212	0.90	0.10	3.35	1.98
12	9.36	1.212	0.90	0.08	4.30	2.20
12	9.36	1.212	0.90	0.06	6.12	2.70
12	9.36	1.212	0.90	0.06	5.15	2.08
12	9.36	1.212	0.90	0.04	7.70	2.77

order and satisfies eqns. (4) and (5). They also suggest that the assumption mac above is reasonable.

The values of k were, however, found to depend on the concentrations hydrogen and bromide ions. Values of k in Table II are inversely proportional [H^+]. This can be explained by deprotonation of the predominant acid form methyl orange before reaction with bromine:



followed by



If the ionization of methyl orange is represented by

$$MH \rightleftharpoons M^- + H^+$$

then

$$K = [M^-][H^+]/[MH]$$

where K is the ionization constant of methyl orange ($4 \cdot 10^{-4}$ mole l^{-1}).

drogen ion concentrations of 0.3–0.9 M, [MH] is essentially equal to the total ıcentration of methyl orange, $[M]_T$

$$[M]_T = [MH] + [M^-] \simeq [MH]$$

us $$[M^-] = K[M]_T/[H^+] \tag{9}$$

e rate of reaction (7) is therefore,

$$\frac{-d[M]}{dt} = k'[M^-][\Sigma Br_2] = \frac{k'K[M]_T[\Sigma Br_2]}{[H^+]} \tag{10}$$

ıere $k = k'K/[H^+]$.

Values of k increase with decreasing concentration of bromide (Table II). This ı be explained by the increasing formation of Br_2 instead of Br_3^- and the umption that the rate of reaction of methyl orange with Br_3^- is either negligible lower than that of Br_2. The results can be interpreted as follows.

If we assume that the two reactions proceed simultaneously, then we have,

$$M^- + Br_2 \xrightarrow{k_1} \text{Products} \tag{11}$$

$$M^- + Br_3^- \xrightarrow{k_2} \text{Products} \tag{12}$$

e total rate of reaction will be

$$\frac{-d[M]}{dt} = k_1[M^-][Br_2] + k_2[M^-][Br_3^-]$$

$$= \frac{k_1[M]_T K}{[H^+]}\left([Br_2] + \frac{k_2}{k_1}[Br_3^-]\right) \tag{13}$$

e reaction

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

s an equilibrium constant K_1 of 16 at 25°[19].
bstituting for Br_3^- in eqn. (13), gives

$$\frac{-d[M]}{dt} = k_1K[M]_T[Br_2]\left(1 + \frac{k_2}{k_1}K_1[Br^-]\right) \tag{14}$$

eqn. (4) we have $[\Sigma Br_2]$, and

$$[\Sigma Br_2] = [Br_2] + [Br_3^-] = [Br_2](1 + K_1[Br^-])$$

bstituting for $[Br_2]$ in eqn. (14) gives

$$\frac{-d[M]}{dt} = \frac{k_1K[M]_T[\Sigma Br_2](1 + k_2K_1[Br^-]/k_1)}{[H^+](1 + k_1[Br^-])} \tag{15}$$

is is the full rate equation, if the hydrogen ion and bromide ion concentrations nain constant during the reaction.

Comparison of eqns. (15) and (4) shows that

$$k = \frac{k_1K(1 + k_2K_1[Br^-]/k_1)}{[H^+](1 + k_1[Br^-])} \tag{16}$$

Rearrangement gives

$$k[H^+](1+K_1[Br^-])/K = k_1 + k_2 K_1[Br^-]$$

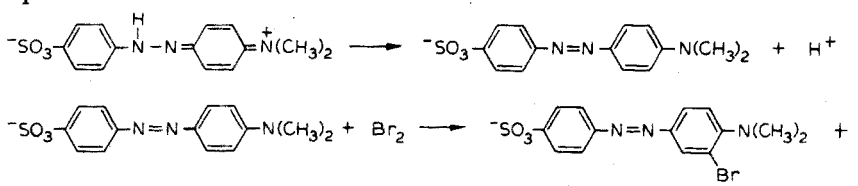
Values of $k[H^+](1+K_1[Br^-])/K$ are constant with varying bromide concentrat (Table II) and the value of $k_2K_1[Br^-]$ is therefore much smaller than k_1 for bromide concentrations considered. The reaction of Br_3^- with methyl orang therefore insignificant under these conditions and the rate equation simplifie

$$\frac{-d[M]}{dt} = \frac{k_1 K[M]_T[\Sigma Br_2]}{[H^+](1+K_1[Br^-])}$$

Values of k_1 are given in Table II and are constant within experimental e for all the reaction conditions considered. An average k_1 value of $2.11 \cdot 10^7$ l mol s^{-1} was obtained. The higher scatter of values of k_1 at low bromide concentrati is due to the much faster reactions under these conditions.

Conclusions

The monobromination reaction of methyl orange with bromine proceeds two steps:



in which the second step is rate-determining. The rate equation is

$$\frac{-d[M]}{dt} = \frac{k_1 K[M]_T[\Sigma Br_2]}{[H^+](1+K[Br^-])}$$

under conditions of 0.3–0.9 M $[H^+]$ and 0.2–0.04 M $[Br^-]$. The value of k_1 $2.11 \cdot 10^7$ l mole^{-1} s^{-1}.

With regard to methyl orange as a bromometric indicator, the results obtain demonstrate conclusively that at high acidities the bleaching reaction of the indicat will become sluggish because the concentration of deprotonated indicator—t form which reacts with bromine—is much smaller. The variation of "suitabl conditions reported by various workers is to be expected, because the rate depen on the concentrations of both bromide and hydrogen ion present. Variation of t rate of titration between various operators will also be an important factor. If meth orange is to be used as an indicator in bromate titrations, then the acid concentratic must be controlled between the 0.4 M hydrochloric acid required for effici generation of bromine and the 2–3 M hydrochloric acid at which the indicat reaction becomes sluggish. It is quite clear that as low a concentration of bromi as possible is advantageous; this explains the original contention of György[1] th better end-points are obtained in the absence of added bromide.

The application of methyl orange in kinetic methods of analysis[13,14], as we as in titrations, also depends on the relative rates of reaction of the reductant ar methyl orange with bromine[13]. Since the indicator reaction is irreversible, its ra

ıst be substantially slower than that of the bromine–reductant reaction. Increasing
: hydrogen ion and bromide concentrations will obviously slow down the methyl
ınge–bromine reaction, but the optimal conditions for any particular reductant
ll also depend on the kinetics of the reductant–bromine reaction and the rate
nstants. At 1 *M* hydrogen ion concentration and at bromide concentrations
low 10^{-3} *M*, the effective second-order rate constant for the methyl orange
ɔmine reaction will be $8 \cdot 10^3$ l mole^{-1} s^{-1}. The corresponding rate constant for
: reductant–bromine reaction must be at least two or three orders greater than
s. Arsenic(III) and the other reductants studied to date obviously satisfy these
nditions, the arsenic(III)–bromine reaction having an effective second-order rate
nstant of the order 10^{10} l mole^{-1} s^{-1}.

MMARY

The kinetics of the reaction between bromine and methyl orange have been
ıdied in bromide medium and at perchloric acid concentrations of 0.3–0.9 *M*. A
:e equation has been derived and a mechanism is proposed which is in agreement
th the experimental results. The application of methyl orange as an indicator
· bromine in potassium bromate titrations and in kinetic methods of analysis is
ɔlained on the basis of the kinetic results.

SUMÉ

Une étude est effectuée sur la cinétique de réaction entre brome et méthyl-
ınge, en milieu bromure, avec des concentrations en acide perchlorique 0.3 et 0.9 *M*.
mécanisme proposé correspond aux résultats expérimentaux. On examine le
:e du méthylorange comme indicateur du brome lors des titrages au bromate
potassium, ainsi que dans les méthodes cinétiques d'analyse.

SAMMENFASSUNG

Die Kinetik der Reaktion zwischen Brom und Methylorange wurde in
ɔmidmedium und bei Perchlorsäurekonzentrationen von 0.3–0.9 *M* untersucht.
ıe Geschwindigkeitsgleichung wurde abgeleitet, und es wird ein Mechanismus
rgeschlagen, der mit den experimentellen Ergebnissen übereinstimmt. Die An-
ndung von Methylorange als Indikator für Brom bei Titrationen mit Kalium-
ɔmat und bei kinetischen Analysenmethoden wird auf der Grundlage der
ıetischen Ergebnisse erklärt.

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ORT COMMUNICATION

mic absorption and fluorescence spectrometry with a carbon filament atom reservoir

t XIV. The determination of vanadium in fuel oils

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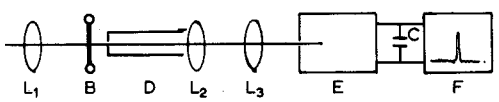
eived 2nd February 1973)

The use of the carbon filament atom reservoir in the determination of vana-
m in aqueous media[1] and copper, silver[2] and nickel[3] in lubricating oils has been
cribed previously. The extension of the technique to include vanadium in
roleum products is described here. The normal range of the technique is 0.5–20
m., but a solvent extraction procedure has been developed to include the range
l–0.5 p.p.m. vanadium.

ɔerimental

The carbon filament atom reservoir. An enclosed cell similar to that used by
kson and West[1] was employed. A recess 2 mm long by 1 mm deep was made in
middle of a 10 × 2 mm carbon rod to locate the sample. A shallow longitudinal
ove.was made in the centre of the recess to prevent the samples creeping over
edges of the filament.



1. (A) Hollow-cathode lamp; (B) CFAR; (C) 0.068 μF condenser; (D) collimator tube; (E) mono-
ımator and photomultiplier of the SP900A; (F) "Telequipment" amplifier and oscilloscope; (L_1, L_3) lenses.

Instrumental arrangement. This is described in Fig. 1. The light from a vana-
m hollow-cathode lamp (Hilger and Watts Ltd., London) was focussed on to a
hole (0.6 mm diameter) in a thin copper sheet mounted on a collimator tube.
is tube was placed so that the pinhole received radiation that just grazed the
ment but not an excessive amount of the intense continuum radiation emitted
the glowing filament. By measuring the absorption in this way, maximal atomic
ɔulation in the light path was ensured and interferences and matrix effects were
ıimized.

The divergent light beam was then focussed on the entrance slit of a Unic SP900A monochromator and the signal was detected by an EMI 9601B pho multiplier tube mounted in the instrument. The signal from the photomultip was then fed to the y-axis input of a "Type K" amplifier mounted in a "Telequipme storage oscilloscope. A 0.068-μF condenser was placed across the input terminals the oscilloscope to damp short-term noise. The rise time to full-scale deflection this arrangement was 300 ms.

The operating conditions were as follows: monochromator slitwidth, 0 mm; lamp current, 15 mA; nitrogen flow rate, 1.75 l min^{-1}; E.H.T., -1100 V. T vanadium atomic line at 318.4 nm was used.

Calibration solutions. Vanadium naphthenate was dissolved in redistil 100–120° boiling range petroleum ether to give a stock solution of 1263 p.p.m. All solutions were made up by dilution of this stock, those of 10 p.p.m. or l being made up daily. The petroleum ether used as solvent gave no blank readi

Sampling. Sample sizes used were 1 μl for the standards and 10 μl for solvent extracts. Disposable Drummond glass micropipettes (Shandon Scient Ltd.) were used to place the sample on the filament.

The preheating and atomizing procedure for all solutions was as follows

$t=0$. The sample was extruded on to the filament which was still warm fr the previous "flash".

$t=15$. The sample was ashed at 3.6 V for 15 s. The oscilloscope scan v triggered, 100% absorption set and at $t=45$ s the filament was "flash-heated" 11.4 V for 1 s and the absorption peak was recorded.

This procedure was repeated every 90 s. When this procedure was used, filament was good for about 120 "flashes" before reproducibility began to fall ow to the increased porosity of the filament.

Solvent extraction of vanadium. Vanadium was stripped from petroleum et solutions with 2 *M* hydrochloric acid and then extracted with 0.1% 1-(2-pyridyl-a 2-naphthol) (PAN) into chloroform.

The procedure was as follows: 10 ml of sample solution (*ca.* 5 g/25 ml) v shaken with 2 *M* hydrochloric acid (10 ml) for 5 min and separated. To the a layer was added 0.1% PAN in ethanol (5 ml) and the pH was adjusted to 4.0 v concentrated ammonia. The vanadium–PAN complex was then extracted with 1 of chloroform, 10 μl of which was taken for analysis.

The efficiency of the acid stripping is greater than 95% and that of the P extraction is 100%, giving an overall extraction of greater than 95%. By this meth the detection limit of vanadium in the original sample is 0.007 p.p.m. (w/w).

Results and discussion

The sensitivity of the method (1% abs.) was $1.3 \cdot 10^{-10}$ g and the detect limit (S:N=2) was $3.0 \cdot 10^{-10}$ g; the reproducibility for 15 replicates at the 10 level was $\pm 4.0\%$. It was found that when a damping condenser was not us although there was an increase in sensitivity of 20%, the detection limit was doub and the reproducibility of peak heights was worse because of increased noise.

The calibration curve was linear from 0–10 p.p.m., the absorbance at upper level being *ca.* 0.3, but curvature was such that it was useable up to 20 p.p. for 1-μl samples.

After dilution, seven fuel oils were analysed by reference to the calibration ph and by the method of standard additions. Two gas turbine fuel oils were ılysed by the solvent extraction procedure. These results are given in Table I.

BLE I

ALYSIS OF SAMPLES BY ATOMIC ABSORPTION

ıple oils	*Vanadium found (p.p.m.)*		*Spark emission*[a]
	Direct calibration	*Standard addition*	
'37	241 ±3.0	266 ±19	258
'38	13.3±1.0	15.4±0.6	18
'39	18.4±1.0	40.8±4.2	42
'40	187 ±3.0	197 ±16	193
'50	174 ±10	170 ±10	194
'30	13.7±1.0	26.2±1.0	24
'31	14.8±0.5	26.4±2.5	26
	By solvent extraction	*Neutron activation*	
gil	0.012±0.002	0.021[a]	
	0.012±0.001		
yan	0.016±0.001	—	
	0.016±0.001		

ata supplied by B.P. (Research) Ltd.

Vanadium may be readily determined in fuel oils in the range 1 p.p.m. upwards hout any sample pretreatment except dilution where necessary. There are, how-r, matrix effects and when the ash content of the oil is high, the method of standard litions must be used to obtain accurate results.

Oils containing vanadium in the range 0.01–1 p.p.m. may also be readily ılysed by use of solvent extraction.

The sensitivity, reproducibility and repeatability of the method are good.

We are grateful to the S.R.C. for the award of a CAPS studentship to G.L.E. l to The British Petroleum Co., Sunbury, for the provision of the naphthenate ndards and samples for analysis.

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Analytica Chimica Acta, 62 (1973) 304

SHORT COMMUNICATION

Spectrophotometric determination of plutonium in curium oxide

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The ingrowth of plutonium-240 into a sample of curium-244 (half-life 18.1 at a rate of about 0.3% per month precludes storage of high-purity curium- compounds. Thus, work with such compounds necessarily involves frequent pu fication. A check of the plutonium-240 content in the freshly purified produc not feasible by radiometric methods because of the low specific activity (half- 6580 y) of this nuclide. In the literature only results of α-spectroscopy on "o samples have been reported[1]. The analysis may be done by mass spectromet with an isotope dilution technique. Analysis for plutonium by absorption spect photometry, however, is simple and specific[3]. An argument in favour of absorpt spectrophotometry would also be the possible determination of curium(III) a americium(III)[4] together with plutonium(VI). In the wavelength region of the m absorption band of plutonium(VI) at about 830 nm, no absorption bands due curium have been detected[5], so that curium would not interfere with the plutoniu (VI) absorption. It remained to be seen, however, if the α-radiation from considera amounts of curium-244 would affect the oxidation–reduction properties of plutoni solutions.

Apparatus and reagents

The spectra were recorded with a Beckman DK-2A spectrophotomet attached to a glove-box[3]. Scale expansion was used for low absorbances. T measurements were carried out with a constant slitwidth. Curium oxide was high purified[6] and calcined at 700° for 6 h in air in order to assure the stoichiomet of the compound CmO_2, which was verified by the weight differences found several oxidation–reduction cycles.

Selection of conditions

The spectrophotometric determination of plutonium(VI)[3] is normally do in nitric acid medium; oxidation methods involving silver ions are obviously i compatible with chloride media.

By gentle heating, curium dioxide dissolves readily in 2 *M* nitric acid. F

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analyses, dissolution in 5 *M* nitric acid was chosen. After dissolution of a onium-containing sample of curium dioxide in less than 7 *M* nitric acid, an reciable quantity of plutonium(VI) was found. However, the α-radiation of mg unts of curium generated radiolysis products, which reduced plutonium(VI). s, in the presence of curium, the stability of plutonium(VI) must be assured he addition of excess of oxidizing agent. For a determination of plutonium oxidation with silver(II) oxide[3], however, the excess of oxidant must be royed in order to obtain a clear solution. Oxidation of plutonium by excess of nonium persulphate with a trace of silver as a catalyst produced a solution ch was stable with regard to autoreduction. The oxidation was complete if the ity was less than 5 *M*. The amount of ammonium persulphate added should vary more than about 20% between different analyses, because on decomposition creases the acidity and forms sulphate ions, which reduce the absorbance of onium(VI). Under the established conditions the solutions were stable for at t 2 h; after longer periods of time, the α-radiation of curium reduced onium(VI).

The measurements were carried out in 0.5 *M* nitric acid, because at this ity the reduction of plutonium(VI) in the presence of excess of persulphate inimal. The maximum of the plutonium(VI) absorption peak is at 835 nm, ntly shifted from its position in 4 *M* nitric acid by the influence of the sulphate

Americium(III) could be determined together with plutonium(VI) by suring its absorption peak at 504 nm. Americium stayed in the trivalent state, ong as the acidity was higher than 1.5 *M* during the oxidation of plutonium ı ammonium persulphate.

The gamma and neutron radiation properties of curium-244 necessitates a imum of handling. Weighing the sample can be avoided by determining the ium in solution by measurement of its absorption peak at 396 nm.

rferences

The plutonium method is insensitive to the presence of most other impurities urium dioxide. It should be noted that chloride, complexing or reducing anions fluoride, oxalate), and manganese may interfere if the procedure is used for the lysis of curium solutions.

ommended procedure

Dissolve up to 10 mg of curium dioxide in 5 ml of 5 *M* nitric acid le heating to about 60°. Add 5 ml of water, 400 mg of ammonium persulphate 3 drops of a 0.02% silver nitrate solution. Boil the solution for 1 min and let l. Transfer the solution to a 50-ml volumetric flask and make up to volume with illed water. Prepare a blank solution by the same procedure. Record the orption spectrum of the sample solution against the blank in 10-cm cells. Take that the slitwidth of the instrument when scanning the plutonium(VI) peak entical to the one used during calibration. The wavelength ranges to be measured 750–900 nm for plutonium(VI), 450–550 nm for americium(III) and 375–425 nm curium. Measure the peak heights with respect to the interpolated base lines, determine the concentrations with the aid of calibration equations or graphs.

Calibration

A calibration graph was constructed for plutonium(VI) by the recommend procedure with concentrations varying between 0.033 and 0.330 mg per 50 m The slitwidth of the instrument was 0.045 mm when the 835-nm peak w recorded. The calibration line was slightly curved owing to the sharpness of t absorption peak[3]. A least-squares calculation gave $E=0.205\ C-0.047\ C^2$, whe E is the absorbance measured in a 10-cm cell, and C the concentration plutonium-240 in mg per 50 ml. For americium-243 in the range 0.03–0.09 m per 50 ml, a straight line was found: $E=0.318\ C$. Curium-244, in the range 0.8–3 mg per 50 ml gave a straight line with the equation: $E=0.0351\ C$.

Discussion

The method was applied to several samples of curium-244 containing vary amounts of plutonium-240, which were calculated from the time elapsed sin purification. The results are shown in Table I.

TABLE I

COMPARISON BETWEEN MEASURED AND CALCULATED AMOUNTS OF PLUTONIUM-240 IN SAMPLES OF CURIUM-244

Cm weighed out (mg/50 ml)	*Pu found (mg/50 ml)*	*Pu calculated (mg/50 ml)*
2.79	0.150	0.152
1.54	0.078	0.078
2.83	0.152	0.150
1.92	0.020	0.017

The results are in perfect agreement also with earlier measurements plutonium[3] and americium[4]. These previous results were based on a considerab greater number of measurements and should therefore give reliable indicatio about precision and limits of detection. For plutonium and americium the standa deviations were 0.007 and 0.002 mg per 50 ml, respectively. The limits of detecti were 0.02 mg of plutonium and 0.007 mg of americium per 50 ml, which for 10-mg sample of curium would amount to 0.2% and 0.07%.

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ORT COMMUNICATION

ent extraction and spectrophotometric determination of indium(III) with thiothe-trifluoroacetone

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ived 23rd January 1973)

The thioderivative of thenoyltrifluoroacetone (*i.e.* 1,1,1-trifluoro-4-(2-thienyl)-ercaptobut-3-en-2-one; HSTTA) was first synthesized by Chaston *et al.*[1]. Berg Reed[2] isolated some of its metal complexes, and its application as an extracting it has been explored[3]. In recent work on this reagent, it was observed that ium(III) can be quantitatively extracted at pH 4.5–5 with 10^{-3} *M* reagent in on tetrachloride as a yellow-orange complex. The complex can be measured trophotometrically at 480 nm.

Amongst β-diketones, acetylacetone has been used for the extraction of um[4,5]; the extracted complex can be determined polarographically[6]. Benzoyl-one has been used for the extractive separation of indium from cadmium[7,8]. enzoylmethane has also been used[9], but 2-thenoyltrifluoroacetone has been most nsively studied[10,11]. However, such extractions are only feasible in the presence arrier and with high reagent concentrations. The synergic effect of tributyl-sphate or dibutyl sulphoxide has been studied[12]. Other methods for the solvent action of indium have been recently summarized[3].

The method proposed here is simple and rapid. With a low reagent con-ration, it is possible to extract and determine indium at tracer concentrations. um can be separated from moderate amounts of lead, iron, silver, zinc, etc., ch are associated with it in minerals and fission products.

erimental

Apparatus and reagents. A Type SF-4 quartz spectrophotometer with 10-mm rtz cells, a Cambridge pH meter with glass electrode, and a wrist-action flask ker were used.

Thiothenoyltrifluoroacetone (STTA) was prepared from 2-thenoyltrifluoro-one (B.D.H) by the usual procedure[2]. About 10^{-3} *M* reagent was used in carbon achloride solution. The reagent was always stored in a refrigerator.

A stock solution of indium chloride was prepared by dissolving *ca.* 1.30 g ndium chloride trihydrate (B.D.H.) in 100 ml of distilled water, 1 ml of con-rated hydrochloric acid was also added. The solution (4.91 mg In ml^{-1}) was dardized complexiметrically[13]. Solutions of lower concentration were prepared ppropriate dilution.

General procedure. Adjust an aliquot of indium chloride solution containi about 40 μg of indium to pH 4.5–5.00 with 0.01 *M* ammonia solution hydrochloric acid, the final volume being 25 ml. Transfer the solution to a separati funnel, and shake with 10 ml of 10^{-3} *M* STTA in carbon tetrachloride f 10 min. Allow the layers to separate, and remove the organic phase into a 10-r volumetric flask. Measure the absorbance of the indium complex at 480 nm agai a reagent blank prepared similarly. Compute the amount of indium from a calibrati curve.

Results and discussions

Absorption spectra. The absorption spectra of solutions of the indium(III STTA complex (40 μg In) against a reagent blank (curve B) and against carb tetrachloride (curve C) are shown in Fig. 1. The spectrum of the reagent bla against carbon tetrachloride (curve A) is also given. Measured against the reage blank, the absorbance of the complex shows a maximum at 480 nm. The mol absorptivity of the complex was $6.7 \cdot 10^3$.

Effect of pH. The extraction of indium (40 μg) was studied in the pH regic 0.5–8. Extraction was quantitative (100%) in the pH range 4.5–5. Below and abo this pH, extraction was incomplete, and there was no extraction below pH 2.5 above pH 8.

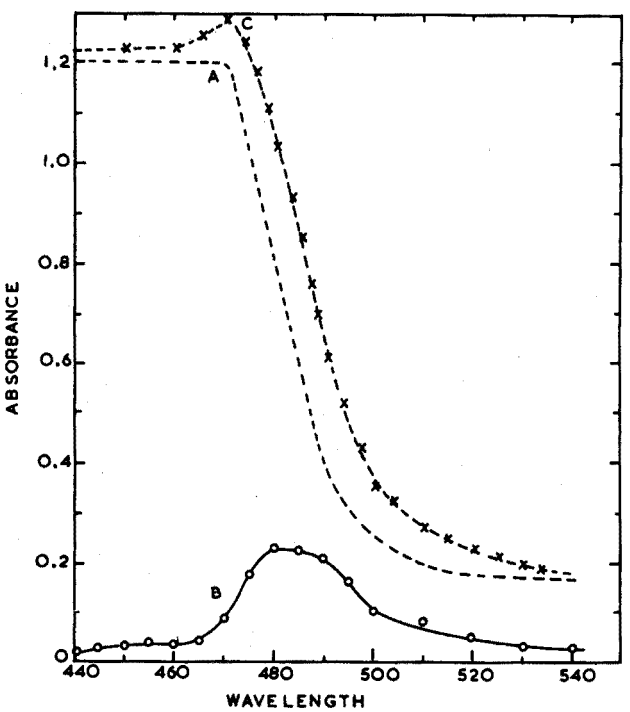

Fig. 1. Absorption spectra. (A) Reagent against CCl_4 as blank; (B) In(III)–STTA complex agai STTA as blank; (C) In(III)–STTA complex against CCl_4 as blank. In = $3.478 \cdot 10^{-6}$ *M*; STTA = $1 \cdot 10$ *M*; pH 4.5.

Beer's law. Different amounts of indium(III) (10–200 μg per ml) were tracted at pH 4.5. The absorbance of the complex was measured at 470, 480 d 490 nm. Beer's law was obeyed over the range of 1–20 μg In ml^{-1} only at 0 nm. All absorbance measurements were therefore carried out at this wavelength.

Stability of the complex. The absorbance of the indium(III)–STTA complex prepared by the general procedure, was measured at elapsed intervals of 0, 0.5, 8, 16, 24, 48, 72, 96 and 120 h. The complex was stable upto 72 h.

Effect of reagent concentration. Indium was extracted with different volumes d concentrations of reagent, varying from 10 ml of $2.5 \cdot 10^{-4}$ *M* reagent to 10 ml $1.5 \cdot 10^{-3}$ *M* reagent. In all cases, the volume of the solution was made up to ml and an appropriate reagent blank was used. The results showed that a single traction with 10 ml of 10^{-3} *M* reagent sufficed for quantitative extraction of dium. The extraction was incomplete with lesser volumes of reagent at this ncentration. There was no significant enhancement in the extraction of indium

BLE I

FECT OF DIVERSE IONS

III)=40 μg, pH 4.5, 10^{-3} *M* STTA in carbon tetrachloride)

eign	*Added as*[a]	*Tolerance limit (μg)*	*Foreign ion*	*Added as*[a]	*Tolerance limit (μg)*
+	$AgNO_3$	250	Sr^{2+}	$SrCl_2$	2,000
2+	$Pb(NO_3)_2$	250	Ba^{2+}	$BaCl_2$	2,000
2+	$HgCl_2$	200	Ge^{4+}	$GeCl_4$	600
	$TlNO_3$	2,000	Li^+	LiCl	5,000
2+	$CuSO_4$	None	Rb^+	RbCl	2,000
2+	$CdCl_2$	None	Cs^+	CsCl	2,000
+	$SbCl_3$	500	$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}$	100
3+	$HAuCl_4$	400	WO_4^{2-}	Na_2WO_4	500
+	$Bi(NO_3)_3$	100	SeO_3^{2-}	Na_2SeO_3	300
+	H_2PtCl_6	None	TeO_3^{2-}	Na_2TeO_3	None
3+	$RhCl_3$	200	NO_2^-	$NaNO_2$	1,000
3+	H_3OsO_3	500	F^-	NaF	2,000
	$VOSO_4$	500	Br^-	KBr	2,000
+	$Fe(NO_3)_3$	200	I^-	KI	1,000
+	$Cr(NO_3)_3$	200	CN^-	KCN	2,000
+	$Al(NO_3)_3$	1,000	SCN^-	KSCN	2,000
2+	$ZnSO_4$	200	$S_2O_3^{2-}$	$Na_2S_2O_3$	2,000
2+	$MnCl_2$	800	SO_3^{2-}	Na_2SO_3	1,000
2+	$CoCl_2$	None	PO_4^{3-}	Na_2HPO_4	None
+	$NiSO_4$	None	$C_2O_4^{2-}$	$H_2C_2O_4$	None
+	$UO_2(NO_3)_2$	200	$Ascorb^-$	Ascorbic acid	2,000
4+	$Th(NO_3)_4$	250	CH_3COO^-	CH_3COOH	2,000
+	$Zr(NO_3)_4$	500	Mal^{2-}	Malonic acid	2,000
+	$Ce(SO_4)_2$	500	Cit^{3-}	Citric acid	2,000
+	$BeSO_4$	1,000	$Tart^{3-}$	Tartaric acid	2,000
+	$CaCl_2$	5,000	$EDTA^{4-}$	EDTA (disodium salt)	None

ater of hydration is omitted for brevity.

with larger volumes or higher reagent concentrations.

Effect of salting-out agents. The chlorides of alkali and alkaline earth metals were used as salting-out agents to study the effect on extraction of indium with 10^{-3} *M* STTA at pH 4.5. Chlorides of lithium, sodium and ammonium (1–6 *M*) and chlorides of magnesium, calcium and potassium (1–3 *M*) had an insignificant effect on the extraction.

Period of equilibration. The indium(III)–STTA complex was equilibrated for times varying from 3 to 20 min. Extraction was quantitative in 8–10 min; a time of 10 min is therefore recommended.

Effect of diverse ions. Various ions were tested for possible interference (Table I). The tolerence limit was taken as the amount of foreign ion required to cause a $\pm 2\%$ error in the recovery of indium. Ions such as thallium, aluminium, and alkali and alkaline earth metals, common complexing anions, and various organic anions were tolerated in quite high ratios (1:50). Ions such as silver, antimony, thorium, uranium, platinum metals, and molybdate were tolerated in moderate amounts. Ions showing strong interference were copper, cadmium, cobalt, nickel, tellurite, phosphate, EDTA and oxalate. The interference of some of these ions may be eliminated by masking[14]. For example, aluminium and zirconium can be masked with sodium fluoride; manganese with citric acid; bismuth, iron and tungstate with tartaric acid; lead and vanadium with malonic acid; gold, mercury and zinc with potassium cyanide.

From ten determinations with 40 μg of indium the absorbance was found to be 0.230 ± 0.010. The relative standard deviation was about $\pm 1.06\%$. The total operation requires about 30 min. The sensitivity by Sandell's definition is 0.0174 $\mu g\ cm^{-2}$.

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HORT COMMUNICATION

he removal of trace elements from potassium thiocyanate for stripping voltammetry y zone refining

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eceived 1st January 1973)

Interest in the ultrapurification of potassium thiocyanate derives from the ct that the reagent is frequently used in many analytical techniques. Furthermore, s use as a supporting electrolyte has been extended recently in stripping voltam- etric analysis for the determination of some transition elements (Fe, Co, Ni)[1,2] : concentrations of 10^{-6} wt.%. Ultrapurification is then very necessary because me naturally occurring impurities in potassium thiocyanate make it impossible identify the transition elements; intermetallic compounds may be formed (*e.g.* u and Pb for Co)[1] or almost identical electrodissolution potentials may be found .g. Cd for Fe and Co).

In this communication, a method for the purification of potassium thiocyanate y zone refining at *ca.* 0.01 p.p.m. concentration levels is reported. The method nsists of using a strong cooling technique by placing in direct contact with quid air that part of the charge which is located in the direction of zone travel. tripping voltammetry of commonly occurring cations in potassium thiocyanate, ch as Cu, Pb, Cd, and Zn, was then used to verify the degree of purification btained.

ethod of purification

The potassium thiocyanate salt is placed in a quartz test-tube that has been eviously outgassed at 600°. It is then kept under dynamic vacuum (10^{-6} mm Hg) 150° for 24 h for dehydrating and outgassing. The test-tube is then flame-sealed der vacuum. The salt is brought to its melting point and then rapidly cooled order to achieve a homogeneous distribution of the traces throughout the bstance. The charge is submitted to zone refining in a vertical direction with ovement from the bottom to the top. The apparatus used[3] features automatic version of motion and a fast return to the initial position for a new cycle. The tal charge length (L) is 10 cm, the length of the molten zone (l) is 1 cm and e section is 1.3 cm. Average zone travel speed is 2 cm h^{-1}. These parameters re held constant in all experiments.

nalytical method

The cations examined, which are usually present in the starting salts (Pb,

Cu, Cd, Zn), were determined by stripping voltammetry. The polarograph u has been described[4]. In order to obtain a 1 *M* solution for transference to polarographic cell, an appropriate quantity of the thiocyanate was taken fro specific portion of the charge. The polarograms were recorded at 20°, wit scanning velocity of 0.4 $V \cdot min^{-1}$, and a pre-electrolysis potential of −1.4 V S.C.E. For the cations mentioned, the direct proportionality of peak heigh concentration in purified 1 *M* KSCN medium was verified previously for concen tions ranging from 0.025 to 0.25 $\mu g\ ml^{-1}$. The simultaneous determination several cations was possible. However, when both copper and lead were pres in different concentrations, identification was difficult, owing to neighboring elec dissolution potential values (Table I). The thiocyanate medium presents the c known case where the electrodissolution potential for lead is more positive t that for copper.

TABLE I

ELECTRODISSOLUTION POTENTIAL *vs.* S.C.E. OF Pb, Cu, Cd AND Zn IN 1 *M* KS MEDIUM

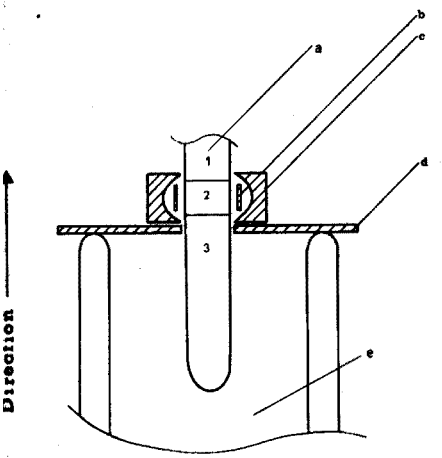
Cation	Pb	Cu	Cd	Zn
Potential (V)	−0.50	−0.60	−0.72	−1.12

Results and discussion

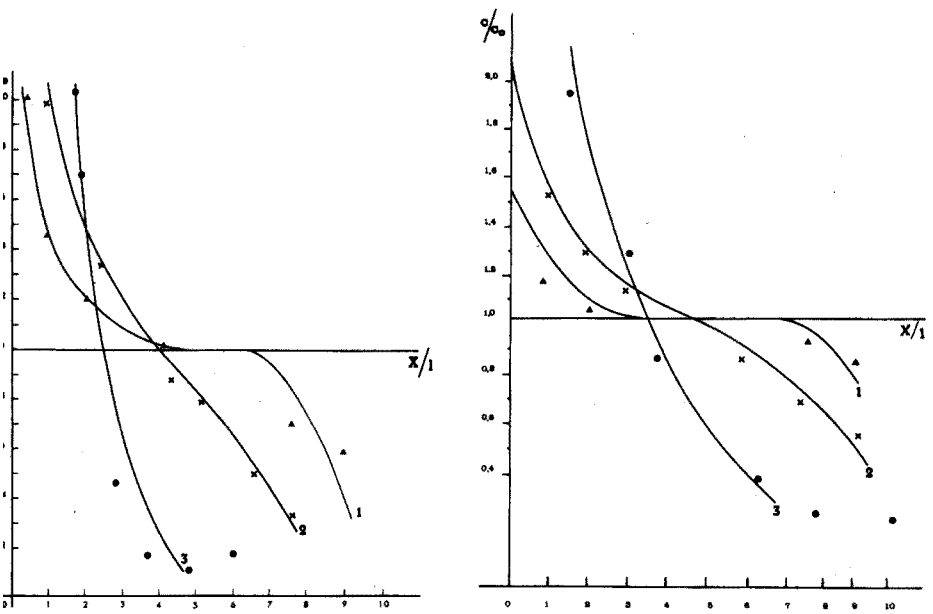
Some preliminary tests showed that even when operating parameters su as travel speed and tube rotation were varied, the zone refining of potassiu thiocyanate, which has a low melting point (175°) and a relatively low thern conductivity, was difficult. The normal artificial cooling methods, such as forced or water, gave unsatisfactory results. For substances of this type which expa considerably on melting, different processes can simultaneously affect the value the distribution coefficient, *K*, in different ways. In the present case, vertical zo refining was selected because a horizontal system with normal cooling gave u satisfactory results. The direction of movement of the test-tube from bottom to t was chosen in order to prevent the quartz container from breaking as a result the expansion of the melted salt. By zone refining under these conditions wi simple air cooling, it was shown that the zinc and copper impurities which we naturally present in the starting salts, accumulated in the upper part of the char *i.e.* they accumulated in the part opposite to the direction of zone travel, with effective distribution coefficient greater than unity ($1 \leqslant K \leqslant 1.1$). Thus, there was inverse segregation which may be due to shrinkage (the thiocyanate expansion melting considerably exceeds 5%).

However, after several passes ($n = 10$), lead and cadmium had not separat significantly at concentrations of *ca.* 10^{-5} wt.%. Under the operating conditio used, an obstacle to further purification could be the high solubility of zone impurities in the part adjacent to the melted zone (Fig. 1) which has a relative high temperature close to the melting point. A severe lowering of the temperatu in zone 3 should ensure concentration of impurities in the molten zone, and th an appreciable improvement of the back-segregation coefficients. In fact, a noticeat

provement in the result of zone refining was obtained by immersing that part the test-tube below the molten zone in liquid air, in a dewar covered with bestos to screen the source of heat from the cold liquid vapors (Fig. 1). In this



. 1. Cross-section of a sketch of the zone-refining apparatus which is in direct contact with the ling dewar. (a) Quartz test-tube; (b) electric heater; (c) reflecting platinum foil; (d) insulating estos cover; (e) liquid air container dewar. (1) Resolidified zone; (2) molten zone of length l; solid zone cooling in liquid air.



2. Theoretical curves of relative solute concentration, c/c_0, plotted as a function of distance in ne lengths, x/l, for $K = 1.2$. (1) Refers to 4 passes, (2) refers to 10 passes and (3) refers to ∞ passes. perimental values are also represented: (▲) after 4 passes, (×) after 10 passes and (●) after 30 passes.

3. Theoretical curves of relative solute concentration, c/c_0, plotted as a function of distance in ne lengths, x/l, for $K = 1.5$. Curve numbers and symbols have the same significance as in Fig. 2.

way K values of *ca.* 1.5 were obtained for Cu and Zn, *ca.* 1.2 for Cd and *ca.* for Pb. The K values obtained for the four metals without cooling in liquid were 1.15, 1.1, 1.0 and 1.0, respectively. Values of K under these conditions w determined by a multipass method, *i.e.* the charge was purified by a large num of passes until it reached an impurity concentration below 10^{-6} wt.%. In purified charge, the quantity of a single cation necessary to bring its concen tion, c_0, to 10^{-5} wt.% was added. Then a fixed number of molten zones w allowed to traverse the initially homogeneous impure solid charge under control operating conditions. The impurity concentration, c, at a distance x from beginning of the charge was then determined. The plot of c/c_0 *versus* x/l (l be the length of the molten zone) gave a curve from which K could be estima using theoretically derived equations for zone refining under ideal conditio (Figs. 2 and 3). It was found that the simultaneous presence of four cations i not alter the value of K. In any case, with the use of such purification proces the final products were single crystals with a volume of some cm^3.

It was also found that hydroxyl ions present in the charge at concentratic greater than 10^{-3}% caused breakage of the quartz container after several pas

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ORT COMMUNICATION

e determination of iron(II) in silicate rocks and minerals

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Information regarding oxidation states and reactions in silicate rocks and erals is often obtained by analysing for iron(II) and iron(III). Conventional wet mical analyses have proved most reliable quantitatively. These methods may divided into two main types; either the released iron(II) is determined, or the ess of an oxidant which oxidizes the iron(II) during the decomposition of the nple is measured[1]. The latter type is most commonly used.

One major concern in iron(II) determination is that the precision is often ject to factors such as grinding, moisture control during storage, adequate ing of dissolution procedures, oxidation–reduction control, homogeneity of nple, standardization of titrant and completeness of sample decomposition. tailed accounts of such analytical errors have been given by Brumblay[2] and xwell[1]. Incomplete decomposition and partial oxidation of the sample, however, e proved the most difficult problems. Another problem that often quells neralogical, petrological and geochemical enthusiasm for iron determinations is large amount (0.5–1.0 g or more) of sample required; the relatively small tinum crucibles employed often cause disastrous results, when sample is lost by ling over. In view of these problems, the relatively safe, inexpensive and efficient thod described below was developed. This modified method was tested on some GS standards as well as on some silicate minerals which had been previously lyzed.

The proposed method was based chiefly on earlier methods from the rature[1,3–6], and on that used at the Department of Geology, University of tawa.

cedure

Weigh out accurately 0.1 g of sample powder (−200 mesh or finer grain e is recommended) in a 400-ml Teflon beaker with a well fitting lid. Add 2 ml of distilled water to moisten the powder, followed by 10 ml of (1 + 1) sulfuric d. Bring the contents almost to the boil on an electric hot plate. Displace the of the beaker slightly and add 10 ml of 48–49% (w/v) hydrofluoric acid. Cover beaker again and bring the contents to the boil within 10 s. Adjust the nperature so that the contents boil gently for 20 min. While the sample is being composed, prepare a mixture of 100 ml of freshly distilled water, 5 ml of (1 + 1)

sulfuric acid, 5 ml of saturated boric acid, 5 ml of 85% (w/v) phosphoric a and 5 drops of 0.2% (w/v) sodium diphenylamine sulfonate indicator in a 250 glass beaker. Remove the Teflon beaker from the hot plate by means of a p of tongs, remove the lid, and pour the mixture into the Teflon beaker. Tit immediately with standard 0.025–0.03 *N* potassium dichromate solution until pure green color changes to a grey-green. Then add the potassium dichron solution drop by drop until the first tinge of permanent bright purple appe Constant gentle stirring with a Teflon or glass rod during titration is necessary

Calculation

$$\text{wt.\% FeO} = \left[\left(\text{ml titrant} \cdot N \cdot \frac{71.85}{1000}\right) / \text{wt. of sample}\right] \cdot 100$$

where N = normality of the titrant.

Preparation of chemical solutions and standardization of the titrant well described in the literature (*e.g.* Brumblay[2], Kolthoff and Sandell[3]). Bla and empirical standards are necessary. Potassium permanganate and bari diphenylamine sulfonate can replace the above titrant and indicator.

Results

Two USGS standards BCR-1 and AGV-1, representing high and low F contents respectively, were chosen to test the method. Ten determinations w made on each of the standards; averages, standard deviations (s) and relat standard deviations (s_r) were computed. The results (Table I) from the pres work appear to be somewhat high. Compiled results from the best ten laborato and proposed values by Abbey[7] were the lowest. However, if the rapid oxidat process during experiment is taken into account, a slightly higher value may favorable.

TABLE I

DETERMINATION OF FeO IN BCR-1 AND AGV-1

	Present work			*USGS (wt.%)*	*Abbey[7] (wt.%)*
	wt.%	s^a	s_r^b		
BCR-1	9.10	0.16	1.79	9.08	8.97
AGV-1	2.14	0.11	5.01	2.06	2.02

$^a s = \left(\frac{\Sigma(x-\bar{x})^2}{n}\right)^{\frac{1}{2}}$ $^b s_r = \frac{100 \cdot s}{\bar{x}}$

Four iron-rich pyroxene samples, in duplicate, were analysed by the Mine Constitution Laboratories, Pennsylvania State University, and by the propo method at the University of Ottawa, with the results given in Table II.

Discussion

Many published modifications of the Pratt method[1] have failed to sati

BLE II

TERMINATION OF FeO IN PYROXENES (wt.%)

	P1[a]	*P2*	*P3*	*P4*
ın State[b]	42.28	38.31	33.28	13.35
sent work[c]	42.05	38.36	32.95	13.33

l = orthoferrosilite; P2 = low iron orthoferrosilite; P3 = ferrohypersthene; P4 = ferrosalite.
= 0.04 (J. B. Bodkin, personal communication, 1972). [c] $s = 0.04$, $s_r = 0.13\%$.

need of determining iron(II) oxide in silicate minerals and rocks with high d low FeO content equally well. By these methods, silicate minerals and rocks h low FeO content (*e.g.* < 5 wt.%) consistently yield abnormally high values with high precisions. The present method has minimized this problem. Many oratories, particularly in earth science departments in universities and colleges, y find it worthwhile to use this method owing to the following advantages.

The method is inexpensive. The 400-ml Teflon beakers replace the relatively all conventional platinum crucibles, so that the danger of boiling over and loss sample is minimized. The Teflon beakers are much more stable during boiling d can be easily handled with tongs without contamination. Teflon beakers coast s than half a 15-ml platinum crucible. There is no danger of spilling during nsfer of the decomposed solution for titration, because the cold acid mixture is ured into the hot Teflon beaker containing the sample solution.

As long as the boiling is gentle, oxidation of the sample by sulfuric acid is gligible during 20 min. Any dark particles left undecomposed can be easily seen ore titration. After becoming familiar with the procedure, an analyst may easily ndle four samples at a time or even more, within one hour from weighing. automatic titrator would greatly facilitate the titration, but provides no better cision if a rather dilute titrant is used.

Iron(II) oxide in silicates such as orthopyroxenes, clinopyroxenes, amphiboles d almandine garnets, and rocks such as andesite, basalt, basic and mafic nulites, has been determined successfully. As atomic absorption spectrometry is mmonly employed in modern laboratories, total iron can be readily determined gether with other elements in the same solution. Iron(III) can easily be calculated m the total iron and iron(II) contents.

The relatively small amount of saturated boric acid solution used seems equate to take care of the excess of hydrofluoric acid after boiling; amounts up 100 ml made no significant difference to the results. Probably, after 20 min of iling very little hydrofluoric acid is left and the required acidity is maintained. rex glass beakers have been repeatedly used; little damage occurred. However, ger amounts of boric acid might be advisable if cleaning does not immediately low the titration.

As little as 0.05 g of sample has been tested with satisfactory results.

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IORT COMMUNICATION

ɔduct monitoring during the reduction of a nitronaphthalenesulphonic acid

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The reduction of nitro compounds to amines proceeds via nitroso and hydroamine intermediates. These may in part condense to form azoxy compounds, which luce to amine via azo and hydrazo intermediates[1]. Monitoring of the various ction intermediates is thus complex, but has been reported for nitrobenzene[2,3]. is note reports analytical work carried out during a study of the aqueous phase luction of 3-nitronaphthalene-1,5-disulphonic acid to the corresponding amine, ich is one of many aminonaphthalenes used in the manufacture of dyestuffs[4]. e analytical methods described were found to be applicable to reductions by (*a*) alytic hydrogenation and (*b*) aqueous iron (*i.e.* Bechamp process), two procedures ich are widely used in the large scale manufacture of arylamines.

ıterials

The nitro- and aminonaphthalenesulphonic acids used for calibration of the ılytical methods described below were obtained from normal manufacture. Before ; they were purified by appropriate processes of solvent washing, precipitation, rystallization and drying.

Specimen quantities of the following compounds were prepared:

3,3'-Azonaphthalene-1,1',5,5'-tetrasulphonic acid. The amine was diazotized, d converted to the azo compound as described by Hodgson *et al.*[5]. The conjugate d formed on solution in concentrated sulphuric acid showed maximal absorbance 484 nm ($\varepsilon = 2.9 \cdot 10^4$).

3,3'-Hydrazonaphthalene-1,1',5,5'-tetrasulphonic acid. 7.33 g of the azo compund, 1.4 g of 5% palladium–carbon, and 80 ml of water were shaken with drogen at atmospheric pressure, at 40°, for 1.5 h. The filtered product was ·red for 1 h with 14 g of sodium chloride. The resulting solid (3.6 g) was washed :h methanol and dried under vacuum. Proton analysis by n.m.r. detected only hyızonaphthalenetetrasulphonic acid (70% ± 5%) and azonaphthalenetetrasulphonic d (2%). The u.v. spectrum in 0.1 *M* hydrochloric acid or 0.1 *M* sodium hydroxide ɔwed peaks at 255 nm ($\varepsilon = 5.6 \cdot 10^4$), 289 nm ($\varepsilon = 1.9 \cdot 10^4$), and 358 nm ($\varepsilon = 1.1 \cdot 10^4$).

3,3'-Azoxynaphthalene-1,1',5,5'-tetrasulphonic acid. An aqueous solution of ıitronaphthalene-1,5-disulphonic acid (120 ml of 0.2 *M*), reduced to maximal

hydroxylamine concentration, was adjusted to pH 11 with sodium hydroxide. Hydrogen peroxide (100 ml of 20-vol.) was added and the solution was heated to 60–70° for 1 h. After cooling the pH was adjusted to 8, and the solution was stirred with 10 g of sodium chloride. The resulting solid (5.3 g) was washed with methanol and dried under vacuum. The strength by n.m.r. was $71 \pm 5\%$. The u.v. spectrum in 0.1 *M* hydrochloric acid or 0.1 *M* sodium hydroxide showed peaks at 349 nm ($\varepsilon = 2.0 \cdot 10^4$) and 266 nm ($\varepsilon = 2.9 \cdot 10^4$). The u.v. spectrum in concentrated sulphuric acid showed a peak at 390 nm ($\varepsilon = 1.4 \cdot 10^4$).

Analytical procedures

The spectrofluorimetric measurements were made with a Baird-Atomic SF100E spectrofluorimeter. In aqueous solution (neutral or decinormal acid) 3-aminonaphthalene-1,5-disulphonic acid is strongly fluorescent, the wavelength of maximum emission being 441 nm; 3-nitronaphthalene-1,5-disulphonic acid is non-fluorescent under the same conditions. Quenching of the amine, however, became serious at concentrations greater than $5 \cdot 10^{-5}$ mole l^{-1}. To check that neither starting material nor reduction intermediates quenched the fluorescence of the amine, known amounts of the amine were added to samples taken from intermediate stages of the reduction. The amounts added were correctly detected by spectrofluorimetry.

The polarographic measurements were made with a Cathode Ray Polarograph (Southern Analytical Type A1660) measuring the applied potential against the mercury pool with 1 *M* hydrochloric acid as solvent. The two peaks normally exhibited by nitro compounds in acidic solvents[6] occurred in the case of 3-nitronaphthalene-1,5-disulphonic acid at *ca.* −0.25 and −0.53 V. The former was assigned to reduction of the nitro group to the hydroxylamine and the latter, which was ill-defined and defied accurate measurement, to reduction of the hydroxylamine to amine. As the reaction progressed the peak at −0.25 V decreased, becoming zero after 170 min (see Fig. 1). The peak at −0.53 V persisted to the end of the reaction. Standard additions showed 3-nitronaphthalene-1,5-disulphonic acid to be linearly detected down to $0.5 \cdot 10^{-3}$ mole l^{-1} in reaction samples following those giving no polarographic peak at −0.25 V. This ensured that neither intermediates nor products were interfering with the analysis.

Reaction samples were immediately diluted in pure sulphuric acid, and light absorbance in the wavelength range 350–500 nm was recorded. Samples taken after disappearance of the nitro component showed the characteristic absorption of the conjugate acid of the azonaphthalene, attributed to the azonaphthalene in the sample plus a contribution from disproportionation of the hydrazonaphthalene present. (The isolated 3,3′-hydrazonaphthalene-1,1′,5,5′-tetrasulphonic acid described above partially disproportionated on solution in pure sulphuric acid to give *ca.* 15% azonaphthalenetetrasulphonic acid.) A semi-quantitative estimate of the azoxy compound was possible from the absorbance at 390 nm.

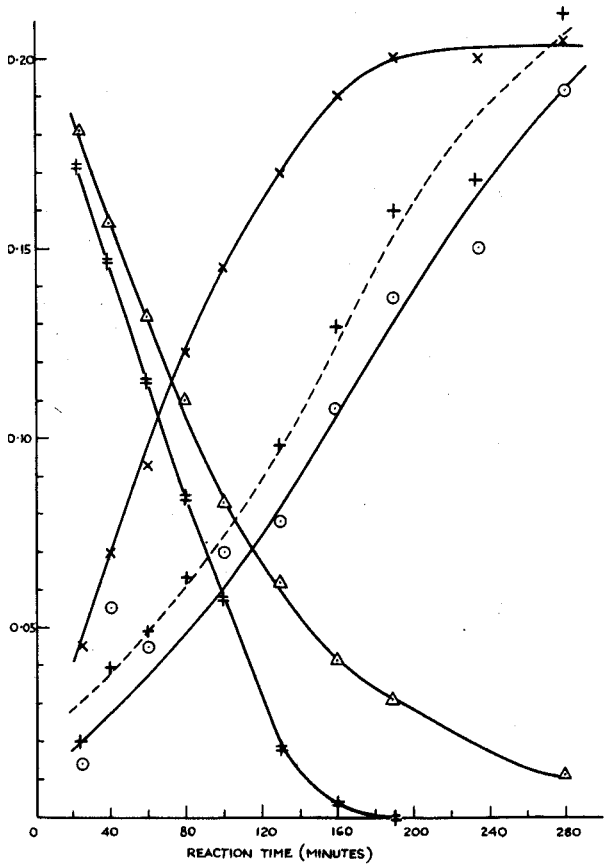
The hydrazo compound was, in the presence and absence of amine, quantitatively oxidized to the azo compound by acidified potassium iodate. Reaction samples (5 ml) were therefore added to 5 ml of 0.05 *M* potassium iodate, and diluted to 50 ml with 0.1 *M* hydrochloric acid; the mixture was diluted with pure sulphuric acid, and the hydrazo concentration in the sample was computed from the azo

tected spectrophotometrically before and after oxidation. Computation for samples th a high hydroxylamine concentration was precluded by the appearance of tensive absorption (λ_{max} = 420 nm) after oxidation, tentatively attributed to the roso compound.

Reaction samples were chromatographed on Whatman 3MM paper and veloped by the butanol-rich layer of a (100 + 100 + 40) butanol–water–concentrated drochloric acid mixture. Where required, individual amine spots from the paper re dissolved in 0.1 *M* hydrochloric acid and the amine was determined spectro-otometrically.

Titanium(III) and nitrite titrations were carried out by standard methods[7]. 3'-Hydrazonaphthalene-1,1',5,5'-tetrasulphonic acid was oxidized to the azo com-und by nitrous acid.

Spectrophotometric measurements were made with a Unicam SP800 instru-nt.



g. 1. Analysis of reaction solution during reduction of an aqueous solution of 3-nitronaphthalene-1,5-ulphonic acid. (∓) Nitro concentration (by polarography); (△) titanium(III) consumption (as nitro uivalent); (×) nitrite consumption (as amine equivalent); (+) amine concentration (by chromato-aphy/u.v.); (⊙) amine concentration (by spectrofluorimetry).

Results and discussion

Figure 1 shows the results obtained from a typical reduction where responses of the various analytical methods are expressed as equivalent con tration of the initial nitro compound or the primary amine. Absorption measurem in pure sulphuric acid showed that accumulation of the azoxy compound was than $3.0 \cdot 10^{-3}$ mole l^{-1}. The maximal azo compound concentration ($2.0 \cdot 10^{-3}$ m l^{-1}) coincided with the disappearance of the nitro compound, and was equival to *ca.* 2% of its initial concentration. The hydrazo concentration in the last samples was less than $1.0 \cdot 10^{-3}$ mole l^{-1}. In the reduction of nitrobenzene, the of reduction of hydrazobenzene is much slower than the other intermedia particularly in the presence of amine[3]. Study of the intermediates encountered in reduction of 3-nitronaphthalene-1,5-disulphonic acid has shown a similar orde reactivity. The level of hydrazo compound quoted above is therefore in cl approximation to its maximum. In this particular example, the total concentrat of azoxy, azo, and hydrazo intermediates was low ($< 5\%$) throughout the reducti

Important features in Fig. 1 are as follows.

(*a*) The sum of the concentrations of 3-nitronaphthalene-1,5-disulphonic a (by polarography) and of amine (by nitrite titration) was, throughout the reacti within 10% of the initial 3-nitronaphthalene-1,5-disulphonic acid concentration.

(*b*) The difference between the two "amine" concentrations (*i.e.* that by nitr titration and that by spectrofluorimetry) was throughout within 10% of the mate not accounted for by the sum of the concentrations of the nitro compound (polarography) and amine (by spectrofluorimetry).

(*c*) The difference between the two "amine" concentrations was approximat three times the difference between the two "nitro compound" concentrations (polarography and by titanium(III) titration).

(*d*) Amine concentrations determined by spectrofluorimetry and by pa chromatography–u.v. spectrometry were in close agreement throughout the cou of reduction.

These quantitative relationships clearly demonstrate that during reduction 3-nitronaphthalene-1,5-disulphonic acid, the hydroxylamine intermediate accum ated and thus reacted with nitrous acid[8] (equimolecularly as did the amine produ and titanium(III) (each mole requiring two moles of titanium(III) instead of t six required by 3-nitronaphthalene-1,5-disulphonic acid) in the analytical procedur

The use of spectrofluorimetry here has thus allowed specific monitoring the amine with an ease and accuracy not hitherto reported, and has enabled accura computation of the intermediate hydroxylamine concentrations from the nitrite co sumption. This approach should be applicable whenever it is necessary to monit the reduction of an aromatic nitro compound, because most arylamines give go fluorescence spectra. However, before accurate computation of the hydroxylamine undertaken, an assessment of the hydrazo concentration is necessary, as it al reacts with nitrous acid.

Conclusion

Spectrofluorimetry and nitrite titration allow easy monitoring of the prima amine and hydroxylamine during the reduction of 3-nitronaphthalene-1,5-disu phonic acid. Intermediates derived from the condensation of the nitroso a

ydroxylamine compounds were satisfactorily monitored by spectrophotometry. The ethods of analysis described here are probably applicable to a wide range of omatic nitro compound reductions.

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SHORT COMMUNICATION

Polypropylene bottles in the decomposition of silicate rocks

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The following three methods of dissolving rocks seem to be popular a the basis for the analysis of silicates by flame spectrometry:

1. fusion of the sample with lithium metaborate[1–3] or with mixtures c lithium carbonate and boric acid[4], and solution of the resultant cake in dilut mineral acid;

2. decomposition with hydrofluoric acid in bombs, usually made of PTFE platinum[5–8];

3. a combination of these two procedures[9].

The fusion techniques provide solutions which are suitable for colorimetı analysis[10] and dissolution may be effected more certainly and possibly more rapidly[4] The acid digestion in sealed vessels may improve reliability in the determinatio of certain elements[8] and obviously allows lithium to be determined. Some mineral are however not readily dissolved by this procedure. Combination of the tw dissociation routines overcomes the problem but this results in a fairly time consuming method, expensive of equipment and not readily adapted to batc working.

It is, however, possible to decompose many silicates with hydrofluoric acid a below its azeotropic boiling point[5] and to carry out the dissociation in chea polypropylene and polycarbonate bottles with screwcaps. These vessels are ideall suited to batch working and have been used successfully in this laboratory t produce more than 400 rock solutions. In good conditions about two dozen roc solutions can be produced in about half a normal working day and the mos important control in the rate of solution preparation is evidently the rate c dissociation of component minerals.

Both types of bottle have been employed to investigate the quantity of rock tha can readily be taken into solution, the range of rock types that can be dissolved, an the rates of dissolution of specific minerals. The results of this work are given her together with some comments on matrix interferences.

Experimental

Apparatus. A Pye-Unicam SP 90 atomic absorption spectrophotometer, wit 50-mm nitrous oxide–acetylene and 100-mm air–acetylene burners and standar hollow-cathode lamps, was used for the flame analyses. The photocell output wa

to a voltage/frequency converter and read from a digital frequency counter; photocell output was integrated over periods of up to 10 s. Colorimetric lyses were made with a Pye-Unicam SP 500 spectrophotometer, and residual erial after partial dissolution was identified by infrared absorption spectrophoto-ry (SP 200).

After preliminary trials the most satisfactory polypropylene bottles were found ɔe of 60 ml capacity, with thick walls and wide mouths and deeply threaded w caps. Polycarbonate autoclave tubes of 25 ml capacity with screw caps were) found useful, especially as they could be heated in a domestic pressure ker; the resultant increase in temperature accelerated mineral dissolution.

Recommended procedure. Weigh accurately about 0.100 g of finely ground k or mineral powder (< 300 mesh) into a 60-ml polypropylene bottle. Add ops (0.2 ml) of aqua regia (freshly prepared) and ensure that the acid adequately s the sample. The acid is conveniently added from a 1-ml graduated safety ette. Add 5 ml of 40% (w/v) hydrofluoric acid from a plastic safety pipette. l the bottle with its screwcap and float on the waterbath so that the bottom nm of the bottle is immersed and the upper half of the bottle is out of the direct uence of the steam. This is done by making the holes in the waterbath cover mm larger than the bottle diameter. The temperature of the screwcap should exceed 40–50°. Repeat these steps for each sample in turn.

When the first sample has been heated for at least 1 h, remove it from the erbath and cool it quickly to room temperature. Add 3–5 g of boric acid ighed to the nearest mg) and about 30 ml of distilled water. Transfer the ution to a 100-ml flask and dilute to the mark. Repeat in turn for the aining samples. The boric acid may dissolve slowly but usually the crystals ain for but a few minutes. If clear plastic volumetric flasks are available the ture of fluorides and rock solution may be transferred to the flask with a diluting ution containing the boric acid and any required flame buffer or releasing nt. The final volume of the solution naturally depends upon the composition he sample, but the total concentration of dissolved salts should be as low as sible. For routine purposes, dilution of 25 ml of the stock solution to 50 ml pled with rotation of the burner as necessary gives rapid and satisfactory results.

ults and discussion

In initial tests, four standard rocks, a granite, a dolerite, a calc-silicate hornfels, a garnet mica schist, were treated with various combinations of mineral acids 40% (w/v) hydrofluoric acid. After digestion for various periods of time at ° and cooling, boric acid was added in the proportion of 1 g for each ml of rofluoric acid[8]. The mixtures were then diluted to 100 ml and allowed to clear out further heating. All four rocks dissolved readily and up to 300 mg was olved completely in 1 h. The rate of dissolution was found to be most affected by hydrofluoric acid concentration and it was usually best to keep the mineral acid tent to a minimum, a mixture of 5 ml of hydrofluoric and 0.2 ml of aqua regia ving an efficient combination.

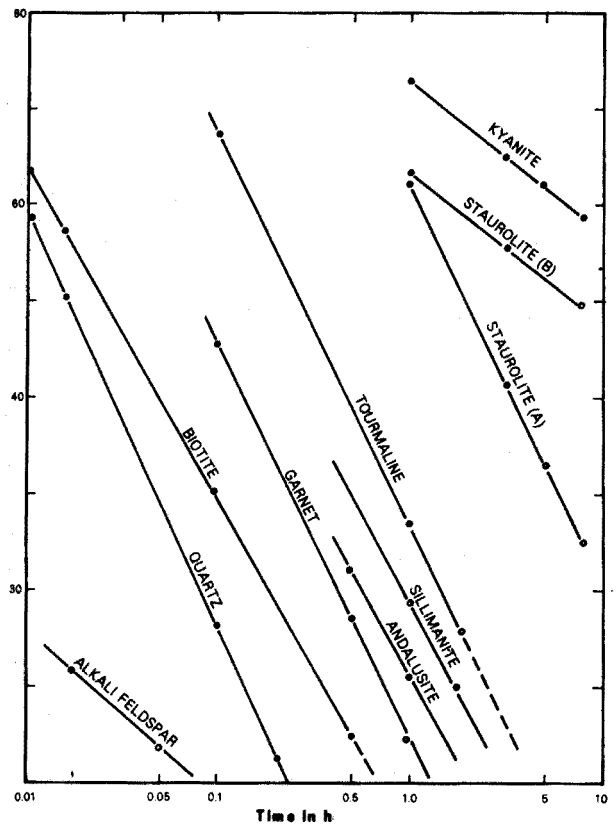
The four rocks were then treated in 100-mg portions with acid mixtures of composition for periods of from 1 min to 1 h. The products were then diluted 100 ml as before. The residue was removed by filtration and identified by

infrared absorption spectrography. The solutions were analysed by colorimetric and atomic absorption spectrometry. The results of these analyses showed that the constituent minerals of the four rocks each had specific and different rates of decomposition. Feldspars were destroyed in less than 5 min and other minerals were broken down in the order olivine, amphibole, quartz, pyroxene, mica, and garnet; the garnet requiring about 50 min for dissolution.

The method was applied to a large number of very varied rocks and for most samples digestion for 1 h proved sufficient. The rocks dissolved included igneous rocks composed of various combinations of quartz, alkali-feldspar, plagioclase, micas, amphiboles, clino and orthopyroxenes, olivines, iron oxides and sulphides, chlorites, serpentine minerals, epidotes, carbonates, and a wide range of accessory minerals. Metamorphic rocks containing the minerals listed for igneous rocks were readily dissolved but some difficulties were experienced with some rocks containing garnets, staurolite, kyanite and tourmaline. No difficulty was found in decomposing clay, silt, or carbonate-rich sediments.

In order to specify more precisely the capacity of the decomposition technique to break down silicate minerals, various quantities of several minerals were digested for various periods. The following minerals could be dissolved in quantities of at least 0.1 g in 1 h or less by the recommended acid mixture: alkali-feldspars, plagioclases, feldspathoids, quartz, biotite, muscovite, phlogopite, chlorite, hornblende, actinolite, epidote minerals, diopside, augite, olivine, calcite, dolomite, illite, kaolinite, montmorillonite, magnetite and ilmenite. Some difficulty was experienced in achieving a satisfactory rate of dissolution for pyrite, garnets, andalusite, sillimanite, kyanite, staurolite, tourmaline, and hypersthene. These minerals were therefore ground as finely as possible by hand (to about 2 μm particle size) and 0.025-g portions were treated with various acid mixtures for periods of up to 10 h. Pyrite was found to dissolve readily if the aqua regia content was increased to 1 ml. All the other minerals responded to finer grinding. Garnet and hypersthene could then be decomposed in 1 h with the recommended acid mixture, and the remaining minerals showed an increase in the proportion decomposed. Increase of the time of digestion produced an increase in the percentage decomposition; the proportion undecomposed reduced linearly with the logarithm of the time (Fig. 1). Andalusite, sillimanite, and tourmaline could be dissolved after less than 5-h digestion, but kyanite and staurolite remained after 10 h. Varying the proportion and type of mineral acid did not accelerate the decomposition of these minerals; garnet dissociation was slightly accelerated by the presence of an additional 1 ml of concentrated sulphuric acid but greater quantities of sulphuric acid or nitric acid caused the polypropylene to become discoloured, shortened the useful life of the bottles considerably, and gave no further increase in rate of decomposition. For staurolite and kyanite increase in the quantity of mineral acid, including hydrochloric and sulphuric acids, produced markedly less rapid attack. It is evident that more than 30-h digestion would be necessary to decompose 0.025 g of staurolite and very much longer for kyanite. Rocks containing these minerals must be regarded for practical purposes as "insoluble" by this acid digestion.

Garnet-rich rocks may require heating with the acid mixture for some hours; 0.1-g portions of separated garnets were completely decomposed in 10 h. Similar precautions clearly are required for rocks containing andalusite, sillimanite and



g. 1. Approximate rates of dissolution of silicates. Curves relate to attack in 60-ml polypropylene ›ttles with 5 ml of hydrofluoric acid and 0.2 ml of aqua regia except for staurolite (B) where 5 ml ılphuric acid was added to the reagent.

›urmaline. Experience with rocks, however, indicates that decomposition may be ;hieved in a 1-h digestion provided that the garnet, andalusite, sillimanite or ›urmaline content is less than about 10% of the rock.

The use of polycarbonate autoclave tubes in a domestic pressure cooker creases the rate of decomposition by a factor of three. These vessels however, 'e less convenient to use than the polypropylene bottles and they slow the 'eparation of batches of rock solution. However, they are particularly valuable the analysis of small quantities of minerals.

he influence of boric acid on absorbance

It has been stated[8] that the boric acid-rich solutions produced by this chnique of decomposition provide a good matrix for atomic absorption analysis ith relatively few matrix interferences[6]. This is generally supported by the 'esent work. The absorbances for silicon, aluminium and manganese were, however, ightly affected by variation in the quantity of boric acid present in the solution. alcium was even more strongly influenced by the concentration of boron and an crease in boric acid content from 4 to 5 g per 100 ml almost halved the

calcium absorption. This effect was not removed by adding strontium or by usi the nitrous oxide–acetylene flame. Thus the quantity of boric acid had to accurately measured. Strontium has been found to enhance considerably the sig obtained from silicon, aluminium, calcium and manganese; it was found benefic to bring the strontium concentration to about 3000 p.p.m.[9] either on diluting 100 ml or in a subsequent dilution. However, the use of strontium did not entir remove matrix interferences in the determination of silicon and aluminium, and t use of closely matching standards to minimize these interferences was preferred.

A further difficulty was encountered in the use of the nitrous oxide burn in nebulizing these solutions with large salt concentrations. In order to redu salting up of the burner and mixing chamber it was desirable to reduce the s content to about 3%. This could be achieved by using 0.6 g of boric acid per of 40% (w/v) hydrofluoric acid; this amount of boric acid allowed glassware to used in dilutions provided that the dilution was carried out expeditiously[8].

Numerous schemes[6–9,11,12] for the analysis of solutions of this kind have be given and it is not intended to discuss such schemes here. It is perhaps wor noting however, that we successfully used the molybdenum blue colorimetric meth for silicon, 2,2-bipyridyl for total iron, and tiron for total iron and titaniu determination on the solutions. In addition, the solutions were used for the flar emission determination of sodium and potassium, and for atomic absorpti determinations of silicon, aluminium, titanium, total iron, manganese, magnesiu calcium, lithium, zinc and beryllium.

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OK REVIEWS

H. Swift and E. A. Butler, *Quantitative Measurements and Chemical Equilibria*, H. Freeman and Co., San Francisco, 1972, xviii + 719 pp., price $12.50.

Anyone familiar with Professor Ernest Swift's books and publications in ılytical chemistry will be interested in this new book written in collaboration h Professor Eliot Butler of Brigham Young University. A great protagonist of systematic approach to qualitative analysis, Professor Swift acknowledges that undergraduates now are given instruction in this branch of practical chemistry l that more emphasis is being given to the quantitative aspects of chemical ılysis at an earlier stage in their chemistry courses. The need, therefore, exists a text which fills the gap left by the omission of qualitative analysis and vides a suitably instructive text to introduce the freshman student to the techniques l methods of quantitative chemical analysis.

The present book contains five main sections dealing successively with eral chemical principles, equipment and techniques, gravimetric measurements l methods, titrimetric measurements and methods, electrical and optical methods; eral appendices list useful equilibrium data and other physical constants. mplete procedural details are given for a fairly conventional range of quantitative rcises; indeed, the details are quite elaborate in most instances, and there may n be a danger of over-elaboration. However, where instructors' time is short, the th of detail may be very advantageous to the average beginning student. More phasis is given in the book to titration processes and a useful feature is the ntion given to the use of a simple weight burette. The availability of top-pan ances has made gravimetric titrimetry a practical process for most undergraduate rses. When one considers that the foundations of titrimetry were based on weight ations, it seems all the more relevant to instruct the student in the use of the ght burette.

This is an interesting and instructive book. It manages to retain a very sical image of quantitative analysis whilst providing a more modern platform olution equilibria on which to practise it. Most teachers, particularly at freshman mistry level, will find it to contain a great deal of useful material which can dily be incorporated into their own quantitative chemistry courses. Moreover, s well written, well-presented and very moderately priced–attributes which too books possess these days.

W. I. Stephen (Birmingham)

Guide to Modern Methods of Instrumental Analysis, Edited by T. H. Gou Wiley–Interscience, New York, 1972, xii+495 pp., price £7.75.

This latest addition to the long list of books which discuss instrument methods of analysis is directed to the professional chemist rather than the beginn The topics have been selected by the criteria of a wide field of application a moderate financial requirement. The coverage is gas chromatography, hig resolution liquid chromatography, thin-layer and paper chromatography, g permeation chromatography, visible and u.v. spectrometry, i.r. and Ram spectroscopy, n.m.r., e.s.r., m.s., g.c.–m.s., electroanalytical methods, and therm gravimetric analysis. Each topic is dealt with by a different expert.

The discussion in the chapters on various optical methods are at a theoretic rather than practical level, and notably succeed in one of the book's general air of ensuring that the reader will not be upstaged in the use of jargon by the young generation or by instrument purveyors. The discussions of separation methods a excellent. Electroanalytical methods are described at a lower level of erudition th the other topics.

The editor promises further volumes on other techniques if readers w cooperate by buying the present book. He deserves to be encouraged, for his approa is refreshing.

A. M. G. Macdonald (Birminghai

Günther Kraft et Joseph Fischer, *Indikation von Titrationen*, Walter de Gruyt Berlin, 1972, xii+304 pp., Werkstoff DM 58.–.

Ouvrage original, car il est, à ma connaissance, le premier traitant d propriétés et de l'utilisation des indicateurs pour l'ensemble des méthod titrimétriques.

Dans chaque cas, après une étude théorique succinte et sans dévelo pements inutiles, le principe de la méthode est décrit, ainsi que l'appareillage et mode de détection du point final de la titration.

Tout cela est fort bien fait, clairement exposé, sans détails inutil La présentation, l'impression, tout concourt à en faire un livre "sympathiqu facile à consulter. D'autant plus que les auteurs donnent des exemples d'applicati judicieusement choisis, ce qui fait qu'en peu de temps il est possible d'acquérir l notions fondamentales de telle ou telle méthode titrimétrique.

Tout au plus, pourrions-nous faire deux petites critiques: l'étude de la précisi et de la sensibilité de certains dosages aurait pu être développée. D'autre pa il est regrettable que les auteurs n'aient pas établi une table alphabétique d matières.

Les principaux chapitres sont: les indicateurs optiques (Optische Indikatio tant visuels que photométriques. Les indicateurs radiométriques, chapitre très cou et qui aurait pu être développé davantage, d'autant plus qu'un des auteurs e spécialisé dans ce domaine. Le chapitre 3 parle d'indicateurs thermométriqu (enthalpiques) et le suivant traite des indicateurs potentiométriques. Viennent ensui

ndicateurs voltamétriques, ampérométriques, conductométriques et oscillomé-
ues. Notons encore que, parmi les indicateurs potentiométriques, les auteurs
it pas oublié les électrodes dites sélectives.

Donc, un livre fort utile et qui engagera le chimiste à utiliser toujours
antage les méthodes physico-chimiques de titration et singulièrement les
hodes d'électro-analyse.

Denys Monnier (Genève)

e Galan, *Analytical Spectrometry*, Adam Hilger Ltd., London, 1971, viii+279
price £6.00.

Analytical spectrometry is a wide-ranging field, and this textbook encompasses
ecular absorption spectrometry, infrared spectrometry, flame spectrometry, arc
spark emission spectrometry, X-ray spectrometry, activation analysis, n.m.r.
:trometry and mass spectrometry. The various techniques are described at a level
:h is designed for students in technical colleges, but would also be appropriate
university undergraduates with an interest in analytical chemistry.

The first chapters contain discussions of electromagnetic radiation and atomic
molecular spectra, which help to indicate the essential unity of all the methods
ussed in later chapters. The smooth development of this approach to the subject
ptical spectrometry is perhaps disrupted by the chapter on monochromators for
optical region, and this chapter might be omitted in a preliminary reading of
book, though it should be studied carefully at some stage.

As an introductory text, this should be very valuable to students in providing
ible background information with just sufficient theory. The final chapter on
ction of methods is worthy of study even by more advanced workers.

A cheap paperback edition would be very welcome.

A. M. G. Macdonald (Birmingham)

ANNOUNCEMENT

The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy

The 25th Pittsburgh Conference on Analytical Chemistry and Appl Spectroscopy will be held at the Cleveland Convention Center, Cleveland, Oh U.S.A., March 4–8, 1974. An estimated 350 papers on all aspects of Analyti Chemistry and Spectroscopy will be presented. Symposia on the following subje are being arranged:

Recent developments and trends in clinical chemistry
Great moments in analytical chemistry and spectroscopy
Remote sensing of environmental air pollutants
The role of analysis in consumer chemistry
Recent advances in selective ion electrodes
Symposium on applied liquid chromatography
Monitoring of water pollutants: for abatement, for prevention, for econom
Symposium on computerized laboratory systems (ASTM)
Symposium on matrix isolation spectroscopy
Coblentz society award symposium

Papers are not restricted to these topics and original papers on all aspects Analytical Chemistry and Spectroscopy are invited.

Authors wishing to present papers at the Conference should submit thr copies of a 150-word abstract to: Richard S. Danchik, Program Chairma 1974 Pittsburgh Conference, Alcoa Laboratories, Alcoa Center, Pennsylvania 150 U.S.A.

Abstract forms are available from the Program Chairman. The names a complete addresses of all authors should be included with submitted abstrac the name of the person who will present the paper being underlined. The fi date for receipt of abstracts is October 1, 1973.

In addition to the program of technical papers, more than 275 compani both foreign and domestic, will be represented at the Exposition of Mode Laboratory Equipment, the largest exposition of analytical instrumentation a related materials in the world. Reservations for exhibit space should be directed Robert W. Baudoux, Exposition Chairman, U.S. Steel Corporation, Resear Laboratory, M.S. 57, Monroeville, Pennsylvania 15146 U.S.A.

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CONTENTS

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