ANALYTICA CHIMICA ACTA

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SPECTROPHOTOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANTS OF N,N'-BIS(3-HYDROXY-PROPYL)DITHIOOXAMIDE AND N,N'-BIS-(2-HYDROXYPROPYL)DITHIOOXAMIDE

The dissociation constants of N,N'-bis(3-hydroxypropyl)-dithiooxamide and N,N'-bis(2-hydroxypropyl)dithiooxamide were determined by a spectrophotometric method using a weighted least squares technique for the calculations. For N,N'-bis(3-hydroxypropyl)-dithiooxamide a thermodynamic constant pK_1^T of 11.37 was found. At ionic strength $\mu = 1$, $pK_1 = 11.27$ and $pK_2 = 14.29$. For N,N'-bis(2-hydroxypropyl)dithiooxamide, these values were respectively: $pK_1^T = 11.11$; $pK_1 = 10.99$ and $pK_2 = 13.75$.

W. A. JACOB AND M. A. HERMAN,
Anal. Chim. Acta, 33 (1965) 229–236

TRI-*n*-OCTYLPHOSPHINE SULFIDE: A SELECTIVE ORGANIC EXTRACTANT

e

Tri-*n*-octylphosphine sulfide (TOPS) has been investigated as the stationary phase in reversed-phase partition paper chromatographic separations using nitric or hydrochloric acids as the mobile phase. TOPS has also been studied as an extractant for metal ions. Silver, mercury(II), and palladium(II) were found to have R_F values of zero when nitric acid was used as the mobile phase. These same ions were also selectively extracted from aqueous nitric acid solutions. Gold(III), mercury(II), palladium(II), and platinum(IV) were found to have R_F values of zero when hydrochloric acid was used as the mobile phase. However, only gold(III) and mercury(II) were extracted from aqueous hydrochloric acid solutions in liquid–liquid extraction systems. Several separations were successfully performed from 1 M nitric acid.

D. E. ELLIOTT AND CH. V. BANKS,
Anal. Chim. Acta, 33 (1965) 237–244

THE METHOD OF CONCENTRATION-DEPENDENT DISTRIBUTION IN THE QUANTITATIVE USE OF RADIOISOTOPES

PART I. THEORETICAL CALIBRATION CURVES AND COMPARISON TO THE "SUBSTOICHIOMETRIC PRINCIPLE"

The method is based on the utilization of a calibration curve which shows the dependence of the distribution ratio in a two-phase system containing the substance to be determined or a substance reacting with it, on the total concentration of the substance to be determined. The relationship of the proposed method to radiometric titration and to the "substoichiometric principle" in isotopic dilution is discussed. Formulae for the theoretical calibration curves in 4 systems are derived: sorption conforming to the Langmuir isotherm or to the Freundlich isotherm, extraction with a constant quantity of an extracting agent, and sorption or extraction in the presence of a constant quantity of a chelating agent. Theoretical sensitivities are given.

M. KYRŠ,
Anal. Chim. Acta, 33 (1965) 245–256
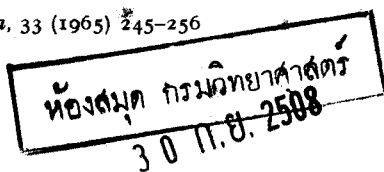
SOME DERIVATIVES OF RHODANINE AS ANALYTICAL REAGENTS

Twenty-two derivatives of rhodanine were investigated as potential spectrophotometric and spot test reagents. Sensitive reactions for silver, gold, copper(I), mercury(II), palladium and some other metals are described. None of the reagents is suitable for spectrophotometry; all but one produce non-extractable, colloidal, metal-ion complexes. The introduction of a sulphonic acid group into the molecule, however, makes the complexes water-soluble.

W. I. STEPHEN AND A. TOWNSHEND,

COULOMETRIC GENERATION OF MOLYBDENUM(V)

Molybdenum(V) was generated at a platinum cathode from 0.7 M molybdenum(VI) in 4 M sulfuric acid. A current efficiency of 99.9% was attained. A limiting current density of 0.05 mA/cm²/mM was found. The formal potential of the Mo(VI)–Mo(V) couple in 4 M sulfuric acid was determined to be *ca.* 0.55 V *vs.* N.H.E. Chromium(VI) solutions were titrated over a wide range of sample size and generating current. Amperometric titration curves were interpreted from current–voltage curves. Titrations could be performed in the presence of oxygen at the 1 μeq. level. The effect of nitrate, perchlorate, orthophosphate, and chloride ions on the titration was determined.

F. J. FELDMAN AND G. D. CHRISTIAN,

THE ATOMIC ABSORPTION SPECTROSCOPY OF CHROMIUM

Conditions were studied for the determination of trace amounts of chromium by atomic absorption spectroscopy. Solution matrix, flame composition, and extraction procedures were the variables studied. A detection limit of 0.006 p.p.m. of chromium was observed with an air–hydrogen flame and methyl isobutyl ketone as the solvent.

F. J. FELDMAN AND W. C. PURDY,

X-RAY SPECTROGRAPHIC DETERMINATION OF TANTALUM IN NIOBIUM BY ELECTRON EXCITATION

An X-ray method is proposed for the determination of tantalum in niobium by direct electron excitation. The optimum excitation conditions for greatest sensitivity are given. The limit of detection for a counting time of 400 sec was found to be 20 p.p.m. The relative standard deviation in the 0.4–5% concentration range was ±2%.

C. J. TOUSSAINT AND G. VOS,

CHARACTERIZATION AND ROUTINE DETERMINATION OF CERTAIN NON-BASIC NITROGEN TYPES IN HIGH-BOILING PETROLEUM DISTILLATES BY MEANS OF LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

Carbazoles, 1,2-benzcarbazoles, and 3,4-benzcarbazoles were identified as major non-basic nitrogen types in a straight-run California gas oil. Indoles and 2,3-benzcarbazoles were found to be absent. A routine procedure using ion exchange, linear elution adsorption chromatography, and ultraviolet spectrophotometric analysis is described for the rapid determination of the indoles, carbazoles, and benzcarbazoles (except N-alkyl derivatives) in straight-run heavy distillates (400 to 1000° F). The relative distribution of various nitrogen types in a number of crude petroleum fractions is reported. In the 600–1000° F boiling range, carbazoles plus benzcarbazoles account for 25 to 70% of the total nitrogen in straight-run samples. Within experimental error, the sum of nitrogen as carbazoles and benzcarbazoles plus bases titratable in acetic anhydride accounts for all of the nitrogen of such samples. The carbazoles and 1,2-benzcarbazoles were clearly identifiable as major components of every crude oil studied.

L. R. SNYDER AND B. E. BUELL,

SEPARATIONS OF ALDEHYDES BY MEANS OF ION-EXCHANGE CHROMATOGRAPHY ON BISULFITE COLUMNS

Mixtures of carbonyl compounds were chromatographed on Dowex-1 columns in the bisulfite form. Sodium bisulfite solutions of increasing concentrations were used as eluants. The studied compounds, including acetaldehyde, formaldehyde, 5-hydroxymethylfurfural, furfural and vanillin, were separated completely from each other. The eluate was also analysed quantitatively.

K. CHRISTOFFERSON,

SUBMICRO METHODS FOR THE ANALYSIS OF ORGANIC COMPOUNDS

THE DETERMINATION OF ACETYL GROUPS

Methods are described for the determination of O-acetyl and N-acetyl groups in 30–80-μg samples of organic compounds. The best general method involved hydrolysis with Wenzel sulphuric acid and distillation of the acetic acid formed, in a small apparatus of the WIESENBERGER type, followed by visual acid–base titration. The overall recovery was 99.1% and the average relative accuracy was $\pm 2.5\%$; accuracy and precision were slightly less satisfactory for alkaline hydrolysis or hydrolysis with phosphoric acid.

A. K. AWASTHY, R. BELCHER AND A. M. G. MACDONALD,

OXIDATION OF ORGANIC COMPOUNDS BY VANADIUM(V)

PART I. MONOHYDRIC ALCOHOLS

The oxidation of various monohydric alcohols with pentavalent vanadium in sulphuric acid medium is described. Optimum conditions for quantitative oxidation and the reaction mechanisms are discussed.

K. S. PANWAR AND J. N. GAUR,

POLAROGRAPHY OF URANYL–MALATE COMPLEXES AT MODERATELY LOW TEMPERATURE

The polarographic behavior of uranyl ion at the dropping mercury electrode was examined in malic acid solution at 15°. The limiting regions of complex formation, polymerization, and reversibility as functions of pH value and ligand concentration were studied. The dimerization of the complexes was demonstrated by the current–voltage curves and conductometric measurements. Three kinds of complex species with metal–ligand ratio of 2:1, 2:2, and 2:3 were identified.

TSAI-TEH LAI AND SONG-JEY WEY,

THE DETERMINATION OF ACTIVE OXYGEN AND IRON(II) IN OXIDE COMPOUNDS

(Short Communication)

G. W. VAN OOSTERHOUT AND J. VISSER,

FAST AND COMPLETE DECOMPOSITION OF ROCKS, REFRACTORY SILICATES AND MINERALS

(Short Communication)

V. S. BISKUPSKY,

SPECTROPHOTOMETRIC DETERMINATION OF TIN WITH RHODAMINE B

(Short Communication)

R. T. ARNESEN AND A. R. SELMER-OLSEN,

DETERMINATION OF LUTETIUM IN AN Al–Lu ALLOY

(Short Communication)

A. BRÜCK AND K. F. LAUER,

SOLVENT EXTRACTION OF BLUE PERCHROMIC ACID BY TERTIARY AND QUATERNARY AMINES

(Short Communication)

M. N. SASTRI AND D. S. SUNDAR,

THE IODOMETRIC ANALYSIS OF MIXTURES OF HYDROGEN PEROXIDE AND LOWER ALKYL PEROXIDES, WITH PARTICULAR REFERENCE TO THE RADIOLYTIC OXIDATION OF METHANE

(Short Communication)

J. A. HEARNE,

SPECTROPHOTOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANTS OF N,N'-BIS(3-HYDROXYPROPYL)DITHIOOXAMIDE AND N,N'-BIS(2-HYDROXYPROPYL)DITHIOOXAMIDE

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(Received December 2nd, 1964)

This paper deals with the results of the spectrophotometric determination of the dissociation constants of N,N'-bis(3-hydroxypropyl)dithiooxamide (3-HPrDTO) and N,N'-bis(2-hydroxypropyl)dithiooxamide (2-HPrDTO).

As reported earlier[1-3], dithiooxamide (DTO) derivatives behave as weak dibasic acids. The dissociation can be given as follows[4]:

$$H_2X \rightleftharpoons H^+ + HX^- \rightleftharpoons 2 H^+ + X^{2-}$$

where:

$$R = -CH_2-CH_2-CH_2OH \quad \text{or} \quad -CH_2-CH-CH_3$$
$$\phantom{R = -CH_2-CH_2-CH_2OH \quad \text{or} \quad -CH_2-CH-}|$$
$$\phantom{R = -CH_2-CH_2-CH_2OH \quad \text{or} \quad -CH_2-CH-}OH$$
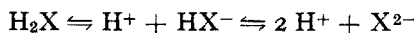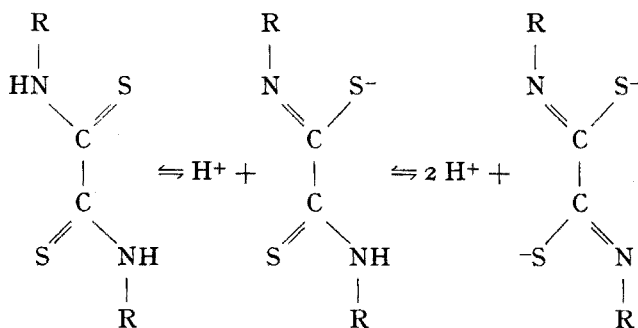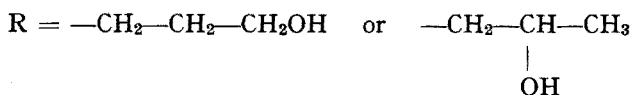
For the estimation of the dissociation constants of weak dibasic acids, spectrophotometric methods have been preferred by several workers[5,6]. The following transformation[3] of the equation giving a general relationship between the optical absorbance and the hydrogen ion concentration was used in this investigation:

$$(\varepsilon_1 - \varepsilon_n) \frac{[H^+]^2}{K_1} + \varepsilon_2 [H^+] + \varepsilon_3 K_2 - \varepsilon_n K_2 = \varepsilon_n [H^+] \tag{1}$$

where $K_1 = (HX^-) [H^+]/(H_2X)$ and $K_2 = (X^{2-}) [H^+]/(HX^-)$; ε_1, ε_2 and ε_3 are the molar extinction coefficients of the species H_2X, HX^- and X^{2-} respectively. ε_n is the apparent extinction coefficient and is obtained from the measurement of the optical absorbance

$$E = \varepsilon_n \cdot L \cdot C_{H_2X}$$

where $L =$ optical path length (cm) and $C_{H_2X} = (H_2X) + (HX^-) + (X^{2-})$.

The value of ε_1 is directly obtained from absorbance measurements at low pH values where $C_{H_2X} = (H_2X)$ and hence $E = \varepsilon_1 \cdot L \cdot C_{H_2X}$. Considering this, eqn. (1) is linear in 4 unknown parameters: $1/K_1$, ε_2, $\varepsilon_3 K_2$ and K_2.

Absorbance measurements at different pH values give a set of equations from which the best estimates for these unknowns are obtained by means of the weighted least squares method[3]. At low pH values, only the first step of the dissociation occurs. Since $K_1 \gg K_2$, the term $K_2(\varepsilon_3 - \varepsilon_n)$ may be neglected in the general eqn. (1).

Equation (1) becomes

$$(\varepsilon_1 - \varepsilon_n) \frac{[H^+]}{K_1} + \varepsilon_2 = \varepsilon_n \tag{2}$$

with only 2 unknowns: $1/K_1$ and ε_2.

Choice of an analytical wavelength

For the calculation of the first dissociation constant K_1 with eqn. (2), the ideal analytical wavelength should be that at which one species absorbs strongly and the other has no absorption at all. This condition, however, is rarely met, and it is therefore necessary to choose a wavelength, where the difference between the extinctions of two successive species is as great as possible and where only a small variation of the absorbance occurs when the wavelength changes. Figure 1 shows the plots of ε_n vs. wavelength for 2-HPrDTO. As can be seen, in a solution of pH = 10.68, a wavelength of 269 mμ would be in agreement with these conditions. However it is seen that with increasing pH value, the minimum shifts to the isosbestic point at about 282 mμ. Therefore measurements were made at different wavelengths between 272 mμ and 275 mμ.

In the case of the simultaneous determination of K_1 and K_2, with eqn. (1), the analytical wavelengths were chosen between the two isosbestic points. To increase the value of $\varepsilon_3 - \varepsilon_n$, somewhat higher wavelengths than in the case of the K_1 determination were chosen, *i.e.* between 275 mμ and 279 mμ.

Solutions of 10^{-4} M of the ligand were used in this investigation, so that all extinctions lay in the most sensitive range of the instrument.

As mentioned earlier[3], the presence of the two isosbestic points (Fig. 1) proves the dibasic character of 2-HPrDTO, since 3 absorbing species must be in solution. A similar plot is obtained for 3-HPrDTO.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a HILGER UVISPEK spectrophotometer. Matched silica cells of 1-cm light path were used.
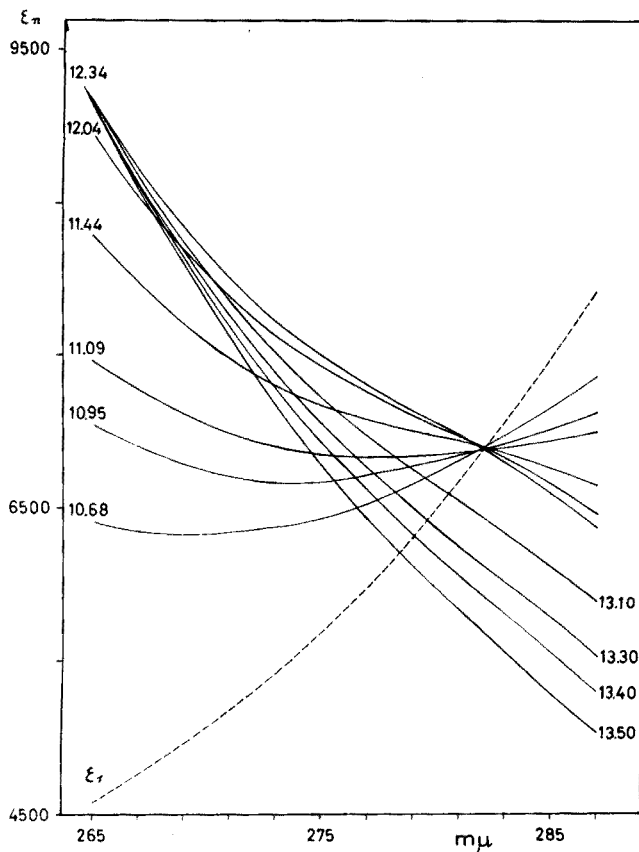
Fig. 1. (1) Apparent molar extinction coefficient ε_n vs. wavelength plot of 2-HPrDTO at different pH values; (2) the dotted line is ε_1 vs. wavelength.

The pH values were determined by means of a lithium glass electrode and a Pye Dynacap pH and millivoltmeter.

All measurements were made at 25°.

Preparation of 3-HPrDTO and 2-HPrDTO

DTO derivatives are generally prepared by WALLACH's reaction[7,8]; one mole of DTO reacts with two moles of 3-amino-1-propanol, or 1-amino-2-propanol, in 95% ethanol. Accordingly, an excess of the aminopropanol was slowly added to a suspension of DTO in ethanol, and the obtained slurry was stirred for several hours without heating. It was left to stand overnight at room temperature.

In the case of 3-HPrDTO the product crystallized from the reaction mixture and was filtered off. To reduce the loss of product, water was added to the filtrates, whereafter the crude acid crystallized. Both yields were purified by recrystallisation from methanol. The purity of the product obtained in these two different ways was examined by infrared spectrophotometry.

TABLE I

DISSOCIATION CONSTANTS OF N,N'-BIS(3-HYDROXYPROPYL)DITHIOOXAMIDE AT DIFFERENT IONIC STRENG

Wave-length (mμ)	$\mu = 0.005$		$\mu = 0.01$		$\mu = 0.05$	
	K_1 $(\times 10^{-12})$	pK_1	K_1 $(\times 10^{-12})$	pK_1	K_1 $(\times 10^{-12})$	pK_1
267	4.72	11.32	4.72	11.33	4.90	11.31
268	4.60	11.34	4.79	11.32	4.97	11.30
269	4.63	11.34	4.75	11.32	4.98	11.30
270	4.57	11.34	4.87	11.31	5.13	11.29
271	4.41	11.36	4.95	11.31	5.17	11.29
272	4.44	11.35	4.90	11.31	5.14	11.30
273						
274						
275						
Mean	4.56	11.34	4.83	11.31	5.06	11.30
Std. dev.		±0.01		±0.01		±0.01

TABLE II

DISSOCIATION CONSTANTS OF N,N'-BIS(2-HYDROXYPROPYL)DITHIOOXAMIDE AT DIFFERENT IONIC STRENG1

Wave-length (mμ)	$\mu = 0.005$		$\mu = 0.01$		$\mu = 0.05$		$\mu = 0.1$	
	K_1 $(\times 10^{-11})$	pK_1	K_1 $(\times 10^{-11})$	pK_1	K_1 $(\times 10^{-11})$	pK_1	K_1 $(\times 10^{-11})$	pK_1
272	0.86	11.07	0.91	11.04	1.00	11.00	1.02	10.99
273	0.82	11.09	0.90	11.05	1.00	11.00	1.03	10.99
274	0.88	11.06	0.91	11.04	0.95	11.02	1.05	10.98
275	0.81	11.09	0.87	11.06	1.00	11.00	1.01	10.99
276								
277								
278								
279								
Mean	0.84	11.08	0.90	11.05	1.00	11.00	1.03	10.99
Std. dev.		±0.01		±0.01		±0.01		±0.01

In the case of 2-HPrDTO, the product did not crystallize from the reaction mixture, not even after longer standing at low temperature. After evaporation of ethanol from the reaction mixture at low temperature, 2-HPrDTO remained as an oily residue. This was dissolved in methanol from which the crude acid was obtained by addition of water. Purification followed in the same manner as for 3-HPrDTO. The elementary analysis gave the following results: found for 3-HPrDTO, 27.70% S, 40.70% C, 6.63% H; found for 2-HPrDTO, 26.48% S, 41.39% C, 6.81% H; theoretical, 27.13% S, 40.65% C, 6.82% H.

$\mu = 0.1$		$\mu = 0.3$		$\mu = 0.5$		$\mu = 1.0$			
K_1 ($\times 10^{-12}$)	pK_1	K_1 ($\times 10^{-12}$)	pK_1	K_1 ($\times 10^{-12}$)	pK_1	K_1 ($\times 10^{-12}$)	pK_1	K_2 ($\times 10^{-15}$)	pK_2
5.11	11.29	5.20	11.28						
5.26	11.28	5.10	11.29						
5.27	11.28	5.01	11.30	6.37	11.20				
5.26	11.28	5.11	11.29	6.48	11.19				
5.42	11.27	5.30	11.28			5.21	11.28	4.89	14.31
5.55	11.26					5.30	11.28	4.84	14.31
				6.77	11.17	5.40	11.27	5.06	14.30
				6.55	11.18	5.48	11.26	4.45	14.36
						5.51	11.26	6.30	14.20
5.37	11.28	5.12	11.29	6.54	11.18	5.38	11.27	5.11	14.29
±0.01		±0.01		±0.01		±0.01		±0.04	

$\mu = 0.25$		$\mu = 0.5$				$\mu = 1$			
K_1 ($\times 10^{-11}$)	pK_1	K_1 ($\times 10^{-11}$)	pK_1	K_2 ($\times 10^{-14}$)	pK_2	K_1 ($\times 10^{-11}$)	pK_1	K_2 ($\times 10^{-14}$)	pK_2
1.11	10.95								
1.11	10.95								
1.11	10.95								
1.10	10.96	1.02	10.99	2.00	13.70	1.03	10.99	1.99	13.70
		1.03	10.98	1.68	13.77	1.02	10.99	1.87	13.73
		1.03	10.99	1.78	13.75	1.04	10.98	1.79	13.75
		1.03	10.99	1.80	13.74	1.04	10.98	1.63	13.79
		0.98	11.01	1.66	13.78	1.03	10.99	1.70	13.77
1.11	10.95	1.02	10.99	1.79	13.75	1.03	10.99	1.80	13.74
±0.01		±0.01		±0.03		±0.01		±0.04	

Solutions

In all measurements, the total concentration of the acid C_{H_2x} was $1 \cdot 10^{-4}\ M$.

Buffer solutions were obtained by mixing adequate amounts of 0.2 M glycine solutions with 0.2 N sodium hydroxide solution as described by KRATZ[9]. Constant ionic strength was obtained by adding sodium perchlorate as an indifferent electrolyte. The measured optical absorbance was corrected for absorption of the solvent, buffer and indifferent electrolyte using a blank containing the same species at the same concentrations.

RESULTS

The results obtained by the described method are summarized in Tables I and II. For the calculation of K_1 eqn. (2) was used for ionic strengths up to $\mu = 0.5$ for 3-HPrDTO, and up to $\mu = 0.25$ for 2-HPrDTO.

For 3-HPrDTO eqn. (1) giving K_1 and K_2 could only be used at ionic strength $\mu = 1$. Indeed, the second dissociation, even at the highest pH values obtainable with lower ionic strengths, was too weak to obtain reliable measurements.

For 2-HPrDTO, K_1 and K_2 could be calculated from the same eqn. at ionic strengths $\mu = 0.5$ and $\mu = 1$.

In Fig. 2, pK_1 values are plotted vs. $\sqrt{\mu}$. Extrapolation to zero ionic strength gave the thermodynamic values: for 3-HPrDTO, $pK_1^T = 11.37$; for 2-HPrDTO, $pK_1^T = 11.11$. When the DEBYE–HÜCKEL[10] equation was applied for the activity coefficient f_i for ionic strengths up to $\mu = 0.1$, a mean value of the thermodynamic pK_1^T was obtained from the formula:

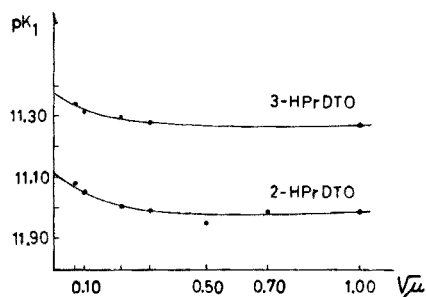$$pK_1^T = pK_1 + \frac{0.505\sqrt{\mu}}{1 + 1.6\sqrt{\mu}} \tag{3}$$

Fig. 2. Extrapolation of the plot of pK_1 vs. $\sqrt{\mu}$ to $\mu = 0$.

TABLE III

CALCULATED VALUES FOR LOG f_i AND THERMODYNAMIC VALUES OF THE FIRST DISSOCIATION CONSTANT K_1^T OF 3-HPrDTO AND 2-HPrDTO OBTAINED FROM EQN. (3), FOR IONIC STRENGTHS UP TO $\mu = 0.1$

$0.505\sqrt{\mu}$	$1 + 1.6\sqrt{\mu}$	$\log f_i$
0.03535	1.112	0.03
0.0505	1.16	0.04
0.1126	1.357	0.08
0.1591	1.504	0.11

μ	3-HPrDTO			2-HPrDTO		
	pK_1	pK_1^T	K_1^T ($\times 10^{-12}$)	pK_1	pK_1^T	K_1^T ($\times 10^{-12}$)
0.005	11.34	11.37	4.26	11.08	11.11	7.76
0.01	11.32	11.36	4.36	11.05	11.09	8.13
0.05	11.30	11.38	4.17	11.00	11.08	8.32
0.10	11.28	11.38	4.17	10.99	11.10	7.94
	Mean	11.37	4.24	Mean	11.09	8.04

where

$$\frac{0.505\sqrt{\mu}}{1 + 1.6\sqrt{\mu}} = \log f_i$$

As can be seen from Table III, the obtained values agreed very well with the extrapolated ones.

SUMMARY

The dissociation constants of N,N'-bis(3-hydroxypropyl)dithiooxamide and N,N'-bis(2-hydroxypropyl)dithiooxamide were determined by a spectrophotometric method using a weighted least squares technique for the calculations. For N,N'-bis(3-hydroxypropyl)dithiooxamide a thermodynamic constant pK_1^T of 11.37 was found. At ionic strength $\mu = 1$, $pK_1 = 11.27$ and $pK_2 = 14.29$. For N,N'-bis-(2-hydroxypropyl)dithiooxamide, these values were respectively: $pK_1^T = 11.11$; $pK_1 = 10.99$ and $pK_2 = 13.75$.

RÉSUMÉ

Les constantes de dissociation du N,N'-bis(3-hydroxypropyl)dithiooxamide et du N,N'-bis(2-hydroxypropyl)dithiooxamide ont été déterminées par une methode spectrophotométrique. Ces constantes ont été calculées par la méthode des moindres carrés pondérée. Il a été trouvé pour 3-HPrDTO une constante thermodynamique $pK_1^T = 11.37$ et pour une force ionique $\mu = 1$, on trouve $pK_1 = 11.27$ et $pK_2 = 14.29$. Pour le 2-HPrDTO ces résultats sont respectivement $pK_1^T = 11.11$; $pK_1 = 10.99$ et $pK_2 = 13.75$.

ZUSAMMENFASSUNG

Die Dissoziationskonstanten von N,N'-bis(3-hydroxypropyl)dithiooxamid und N,N'-bis(2-hydroxypropyl)dithiooxamid wurden mit Hilfe einer spektralphotometrischen Methode berechnet. Die Konstanten wurden nach der Methode der kleinsten Quadrate erhalten unter Berücksichtigung des Gewichtes eines jeden Messpunktes. Hiernach erhielt man für 3-HPrDTO einen thermodynamischen Wert $pK_1^T = 11.37$ während, bei der Ionenstärke $\mu = 1$, $pK_1 = 11.27$ und $pK_2 = 14.29$ gefunden wird. Für 2-HPrDTO betragen diese Werte: $pK_1^T = 11.11$; $pK_1 = 10.99$ und $pK_2 = 13.75$.

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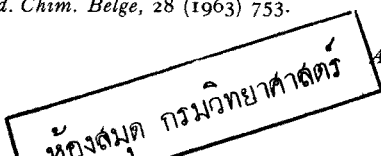
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TRI-n-OCTYLPHOSPHINE SULFIDE:
A SELECTIVE ORGANIC EXTRACTANT*

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The use of trialkylphosphine oxides as extractants for metal ions from aqueous acid solution has been extensively investigated by ROSS AND WHITE[1,2] and ISHIMORI et al.[3]. However, the sulfur analogs of these compounds have received little attention. HITCHCOCK, DEAN AND HANDLEY[4] first reported the investigation of this class of neutral organophosphorus compounds. They found that tri-n-butylphosphine sulfide dissolved in carbon tetrachloride could be used to extract selectively mercury(II) from dilute hydrochloric acid solutions and silver(I) from water. They also stated that silver(I) could be quantitatively extracted from 6 M nitric acid solutions into a solution of triphenylphosphine sulfide dissolved in chloroform.

The sulfur analogs of some trialkyl phosphates have also been reported as selective extractants for mercury(II) and silver(I). HANDLEY AND DEAN[5] found that triiso-octyl thiophosphate and tri-n-butyl thiophosphate dissolved in carbon tetra-chloride were quantitative extractants for mercury(II) and silver(I) from nitric acid. Silver was stripped from the organic phase with either water, dilute sodium hydroxide solution, or dilute aqueous ammonia. WISH AND FOTI[6] used triiso-octyl thiophosphate in carbon tetrachloride to separate silver-111 tracer from rhodium-105 tracer in 8 M nitric acid. The silver was quantitatively stripped from the organic phase by 2 equilibrations with 6 M ammonium hydroxide.

O'LAUGHLIN AND BANKS[7] have reported the use of tri-n-butyl phosphate and tri-n-octylphosphine oxide (TOPO) as stationary phases in the reversed-phase partition paper chromatography of several metal nitrates and chlorides. The similar use of phosphine sulfides has not previously been reported.

The use of tri-n-octylphosphine sulfide (TOPS) as an organic extractant in liquid–liquid extraction systems and as the stationary phase in the reversed-phase partition paper chromatography of various metal nitrates and chlorides is presented in this paper. This study provides a direct correlation between the extracting ability of the thiophosphoryl group and the phosphoryl group in its structural analog, TOPO.

EXPERIMENTAL

Reagents

TOPS was synthesized by a method similar to that used by HITCHCOCK, DEAN AND HANDLEY[4] for the preparation of tri-*n*-butylphosphine sulfide. The reagent was purified by recrystallization from carbon disulfide and also from diethyl ether at dry ice–acetone temperature. The last traces of unreacted sulfur were removed by passing a solution of the reagent in petroleum ether (b.p. 65–110°) through a column packed with chromatographic-grade neutral alumina (Woelm, Eschwege, Germany).

Calculated (found) percentages for $(C_8H_{17})_3P \rightarrow S$: C, 71.58 (71.60); H, 12.77 (12.81); P, 7.69 (7.80); S, 7.96 (8.13).

Procedure

Ten-ml phase volumes were equilibrated for 10 min at room temperature (25°) in separatory funnels using a Burrell "wrist-action" shaker. The aqueous phase was approximately 0.01 M in the metal. The organic phase was a 0.05 M solution of TOPS in cyclohexane, except for the extraction of mercury(II) where nitrobenzene was used as the organic diluent. Complete phase separation was achieved by centrifugation when necessary.

Distribution coefficients were measured by using suitable titration methods, mainly EDTA methods for macro amounts and spectrophotometric methods for micro amounts of the metals.

The experimental techniques described by O'LAUGHLIN AND BANKS[7] were used in the reversed-phase partition paper chromatography studies. The papers were impregnated with TOPS by soaking them in a 0.1 M solution of the reagent in cyclohexane. The cyclohexane was easily removed by evaporation at room temperature. The amount of TOPS on the papers was 1.12 μmoles per cm². Approximately 0.1 μmole of the various metal ions was spotted on the papers.

RESULTS AND DISCUSSION

Reversed-phase partition paper chromatography

The R_F values obtained for the movement of 25 metal nitrates on papers impregnated with TOPS as a function of nitric acid concentration are shown in Table I. Only silver, mercury(II), and palladium(II) were completely retained, while uranium(VI), thorium(IV), and molybdenum(VI) had low R_F values. Bismuth(III) and lutetium(III) showed slight retention. No significant retention was observed for the remaining metals. In general, this behavior was predicted by AHRLAND, CHATT AND DAVIES[8], who divided the periodic table into classes according to acceptor properties. Palladium, silver, and mercury are class 'b' acceptors and thus good sulfur coordinators. They also form insoluble sulfides. Uranium, thorium, and the rare earths are class 'a' acceptors and are better oxygen coordinators. No definite reason can be given for the retention of uranium and thorium. Molybdenum and bismuth are border region acceptors and would be expected to have some affinity for ligands containing sulfur atoms.

The R_F values for the movement of 31 metal chlorides on papers impregnated with TOPS as a function of hydrochloric acid concentration are shown in Table II.

TABLE I

R_F VALUES FOR METAL NITRATES ON TOPS-TREATED PAPERS AS A FUNCTION OF NITRIC ACID CONCENTRATION

Metal	$1\ M$	$3\ M$	$5\ M$	$7\ M$
Bi(III)	0.85[a]	0.78	0.92	0.93
Zn(II)	0.98	0.97	0.99	0.99
Ag(I)	0	0	0	0
Mg(II)	1.0	0.99	1.0	0.98
Cu(II)	0.99	0.98	0.99	0.99
Al(III)	0.98	0.99	0.98	0.99
Ni(II)	1.0	0.98	0.99	0.99
Co(II)	1.0	0.98	0.99	0.99
Fe(III)	0.96	0.99	0.90	0.91
Mn(II)	0.98	0.99	0.98	0.99
Cr(III)	0.98	0.99	1.0	0.99
Cd(II)	1.0	0.97	0.99	0.99
Pb(II)	0.95	0.94	0.96	0.96
Sr(II)	1.0	1.0	0.99	0.99
Hg(II)	0	0	0	0
Pd(II)	0	0	0	0
V(V)	0.96	0.96	0.94	0.94
Mo(VI)	0.45	0.33	0.35	0.33
U(VI)	0.36[a]	0.15[a]	0.07	0.07
Th(IV)	0.33	0.21	0.08	0.08
Ce(IV)	0.98[b]	0.97[b]	0.95	0.98
Y(III)	0.90	0.86	0.90	0.91
La(III)	0.98	0.98	0.95	0.98
Tb(III)	0.92	0.90	0.91	0.95
Lu(III)	0.77	0.74	0.85	0.89

[a] Tailed.
[b] Very small spot remained at start line.

Mercury(II), palladium(II), platinum(IV), and gold(III) were completely retained. Slight retention was observed for molybdenum(VI), tin(II), copper(II), niobium(V), and uranium(VI). In general, the R_F values were found to decrease with an increase in the concentration of hydrochloric acid. Considerably more tailing and streaking was observed when hydrochloric acid was used as the mobile phase than with nitric acid. Tin(II), copper(II), iron(III), gallium(III), indium(III), niobium(V), zirconium(IV), molybdenum(VI), and uranium(VI) showed this type of behavior. The effects of decreasing R_F values, tailing, and streaking can possibly be attributed to retention by the paper, rather than by the stationary phase. The formation of hydrolyzed species, which would tend to increase the movement of the hydrolyzed ion, and kinetic and equilibrium factors may also explain these effects for particular metals.

Liquid–liquid extraction studies

Distribution coefficients (ratio of molar concentration of metal in organic phase to that in aqueous phase) were measured for certain of those metals having R_F values

TABLE II

R_F VALUES FOR METAL CHLORIDES ON TOPS-TREATED PAPERS AS A FUNCTION OF HYDROCHLORIC
ACID CONCENTRATION

Metal	1 M	3 M	5 M	7 M
Sn(II)	0.86[a]	0.80[a]	0.45[b]	0.54[b]
Pt(IV)	0	0	0	0
Pd(II)	0	0	0	0
Mn(II)	0.96	0.98	0.90	0.90
Zn(II)	0.95	0.97	0.89	0.89
Mg(II)	1.0	0.99	0.93	0.89
Cu(II)	0[c]	0.68[b]	0.78[b]	0.19[b]
Al(III)	0.99	0.99	0.95	0.96
Ni(II)	0.96	0.96	0.90	0.91
Co(II)	0.96	0.96	0.90	0.90
Fe(III)	0.96	0.96[a]	0.59[b]	0.63[b]
Cr(III)	1.0	1.0	0.98	0.95
Cd(II)	0.90	0.90	0.85	0.87
Sr(II)	1.0	1.0	0.99	0.98
Hg(II)	0	0	0	0
Be(II)	1.0	1.0	0.95	0.96
Ga(III)	1.0[a]	1.0[d]	0.44[b]	0.21[b]
In(III)	0.93	0.94	0.90[a]	0.94[a]
Sc(III)	0.97	0.98	0.92	0.95
Ti(IV)	0.96	0.97	0.91	0.94
Nb(V)	0.64[b]	0.38[b]	0.21[b]	0.19[b]
Zr(IV)	0.96[a]	0.97[a]	0.95[d]	0.96[d]
Hf(IV)	0.98	0.99	0.97	0.97
V(IV)	0.95	0.95	0.94	0.94
V(V)	0.92	0.93	0.94	0.93
Rh(III)	0.90	0.90	0.95	0.90
Au(III)	0	0	0	0
Mo(VI)	0.76	0.66[a]	0.71[a]	0.72[d]
U(VI)	0.87	0.86	0.93[d]	0.88[d]
Th(IV)	0.96	0.96	0.97	0.97
Y(III)	0.97	0.97	0.97	0.97

[a] Tailed.
[b] Streak from R_F value given back to start line.
[c] Also streak around R_F of 0.82.
[d] Tailed back to start line.

which indicated possible separations by liquid–liquid extraction. The effect of nitric acid concentration on the distribution coefficients of 13 metal nitrates is shown in Table III. In general, the distribution coefficients agreed with the predictions of AHRLAND, CHATT AND DAVIES[8] and the above reversed-phase chromatography studies. The distribution coefficients for silver were measured by determining the residual silver in the aqueous phase and by stripping the organic phase with 1 M ammonium hydroxide. The residual mercury(II) was determined in the aqueous phase. The organic phase was also analyzed for mercury following destruction of the nitro-benzene by wet oxidation with nitric acid and hydrogen peroxide and successive

TABLE III

DISTRIBUTION COEFFICIENTS[a] FOR EXTRACTION OF METAL NITRATES WITH TOPS AS A FUNCTION OF NITRIC ACID CONCENTRATION

Metal	1 M	3 M	5 M	7 M
Hg(II)	10600	91.7	38.6	26.3
Ag(I)	3740	2110	798	494
Pd(II)	950	180	104	72
Mo(VI)	2.95	3.21	3.34	3.61
Se(IV)	0.0894	0.164	0.101	0.125
Pb(II)	0.00911	0.00403	0.00810	0.00911
Zn(II)	0.00810	0.00707	0.0163	0.0173
Cd(II)	0.00611	0.00304	0.00611	0.00203
As(III)	0	0.00376	0.00527	0.310
Th(IV)	0	0	0.00335	0.0449
U(VI)	0	0	0	0.121
Bi(III)	0	0	0	0
Lu(III)	0	0	0	0

[a] Based on the analytical methods used, the distribution coefficients for Hg(II), Ag(I), and Pd(II) are considered to be accurate to 3 significant figures, while those for the other metals are probably not accurate to more than 2 significant figures.

additions of sodium nitrite until no droplets of the organic solvent were visible. Sodium hydroxide, ammonium hydroxide, and ammonium chloride were unsatisfactory as stripping agents for mercury. Approximately 95% of the mercury was stripped from the organic phase, after extraction from 1 *M* nitric acid, with a pH 6 EDTA–hexamethylenetetramine mixture, which was 0.09 *M* with respect to EDTA. However, the degree of back-extraction decreased sharply as the concentration of nitric acid from which the mercury was originally extracted increased. Sodium cyanide was found to be the most effective stripping agent for mercury. The following distribution coefficients (ratio of molar concentration of metal in the aqueous phase to that in the organic phase) for the stripping of mercury(II) with 0.1 *M* sodium cyanide were obtained as a function of the concentration of nitric acid from which the mercury was originally extracted: 1 *M*, 44.94; 3 *M*, 23.47; 5 *M*, 7.85; 7 *M*, 2.54. The distribution coefficients for palladium(II) were based on the determination of the residual palladium in the aqueous phase. Low, erratic results were obtained for the determination of palladium following destruction of the organic phase by wet oxidation. Sodium cyanide (0.1 *M*) stripped approximately 95% of the palladium from the organic phase, after extraction from 1 *M* nitric acid, but was ineffective at higher concentrations of nitric acid. The distribution coefficients for the other metals investigated in nitric acid media were measured by determining the residual metal in the aqueous phase. Large distribution coefficients were obtained for silver(I), mercury(II), and palladium(II). The extraction of these metals decreased as the concentration of nitric acid increased. A good correlation was obtained between the $(1/R_F - 1)$ values and distribution coefficients for the extraction of molybdenum(VI) from all concentrations of nitric acid. Contrary to the R_F values no extraction was observed for uranium(VI) and thorium(IV), except for some slight extraction at the higher acid concentrations. The

extraction of arsenic(III) increased as the concentration of nitric acid increased. Selenium(IV) showed slight extraction from all acid concentrations, while no significant extraction was observed for lead(II), cadmium(II), zinc(II), bismuth(III), and lutetium(III).

Several separations suggested by the measured distribution coefficients were investigated using 1 M nitric acid. The results are shown in Table IV.

TABLE IV

EXTRACTION OF Ag(I), Hg(II), AND Pd(II) FROM MIXTURES OF METAL NITRATES WITH TOPS FROM 1 M NITRIC ACID

Mixture	Metal added (mmoles)[a]	Metal recovered (mmoles)[a]
Cu(II)	10.34	10.36
Ag(I)	0.101	0.101
Zn(II)	0.0981	0.0987
Ag(I)	0.101	0.101
Pb(II)	7.63	7.58
Ag(I)	0.101	0.101
Pb(II)	7.63	7.63
Zn(II)	0.196	0.195
Ag(I)	0.101	0.101
Pb(II)	7.63	7.60
Hg(II)	0.101	0.0989
Bi(III)	8.18	8.12
Hg(II)	0.101	0.100
Ni(II)	9.90	9.93
Pb(II)	0.0891	0.0889

[a] Determined by same methods used to determine distribution coefficients.

TABLE V

DISTRIBUTION COEFFICIENTS[a] FOR EXTRACTION OF METAL CHLORIDES WITH TOPS AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION

Metal	1 M	3 M	5 M	7 M
Au(III)	6280	12700	14300	13300
Hg(II)	586	112	51	42
Pd(II)	0.222	0.176	0.120	0.0330
Sn(II)	0.147	0.0417	0.00802	0.00802
Ga(III)	0.0134	0	0.0211	0.0211
Mo(VI)	0.00865	0.0108	0.00454	0.00479
Cu(II)	0.00798	0.00697	0.00999	0
As(III)	0.00181	0	0.00272	0.255
U(VI)	0	0.0584	0.0565	0.0183
Fe(II)	0	0	0	0
Fe(III)	0	0	0	0
Pt(IV)	0	0	0	0

[a] Based on the analytical methods used, the distribution coefficients for Au(III) and Hg(II) are considered to be accurate to 3 significant figures, while those for the other metals are probably not accurate to more than 2 significant figures.

The distribution coefficients obtained as a function of hydrochloric acid concentration for 12 metal chlorides are shown in Table V. The distribution coefficients were measured in hydrochloric acid by the same methods that were used in nitric acid. The residual gold(III) was determined in the aqueous phase. Large distribution coefficients were obtained for gold(III) and mercury(II), as expected. The extraction of gold(III) increased slightly as the concentration of hydrochloric acid increased, while that of mercury(II) decreased. No extraction of gold(III) by cyclohexane alone was observed. After equilibration, the color of the organic phase gradually changed from yellow to colorless, indicating that gold(III) may be slowly reduced by TOPS. Contrary to expectation, palladium(II) was only partially extracted, the degree of extraction decreasing with increasing acid concentration. Platinum(IV) was not extracted from any concentration of hydrochloric acid studied. This behavior of palladium(II) and platinum(IV) could possibly be attributed to the strong chlorocomplexes formed by these metals in solution. This may also explain, in part, the lack of significant extraction observed for molybdenum(VI), uranium(VI), copper(II), iron(II and III), gallium(III), and tin(II). Molybdenum, iron, and copper are border region acceptors, while uranium, gallium, and tin are class 'a' acceptors and thus better oxygen coordinators. The extraction of arsenic(III) was found to increase with increasing concentration of hydrochloric acid to about the same extent as in nitric acid.

CONCLUSIONS

Tri-*n*-octylphosphine sulfide is a more selective extractant in hydrochloric acid systems than in nitric acid systems. It is also a more selective extractant than TOPO. The metals extracted by TOPS are either not extracted or only partially extracted by TOPO and *vice versa*. However, there are several similarities between the two extractants. For example, gold was completely extracted by both reagents in liquid–liquid extraction systems. Thorium, uranium(VI), silver, and mercury(II) were nearly completely retained on papers impregnated with TOPO[7], and also on papers impregnated with TOPS, when nitric acid was used as the mobile phase. Similarly, mercury(II), gold, and platinum were completely retained when hydrochloric acid was the mobile phase[7]. Tri-*n*-octylphosphine sulfide appears to be a more generally applicable extractant when used as the stationary phase in reversed-phase partition paper chromatography. Several separations can be performed easily and efficiently with TOPS in either reversed-phase partition paper chromatography or liquid–liquid extraction systems.

SUMMARY

Tri-*n*-octylphosphine sulfide (TOPS) has been investigated as the stationary phase in reversed-phase partition paper chromatographic separations using nitric or hydrochloric acids as the mobile phase. TOPS has also been studied as an extractant for metal ions. Silver, mercury(II), and palladium(II) were found to have R_F values of zero when nitric acid was used as the mobile phase. These same ions were also selectively extracted from aqueous nitric acid solutions. Gold(III), mercury(II), palladium(II), and platinum(IV) were found to have R_F values of zero when hydrochloric acid was used as the mobile phase. However, only gold(III) and mercury(II) were

extracted from aqueous hydrochloric acid solutions in liquid–liquid extraction systems. Several separations were successfully performed from $1\,M$ nitric acid.

RÉSUMÉ

Le sulfure de tri-*n*-octylphosphine est proposé comme réactif d'extraction sélectif, pour la chromatographie de partage sur papier; on utilise les acides nitrique et chlorhydrique comme phase mobile. On a également examiné l'extraction de métaux à l'aide de ce réactif. Avec l'acide nitrique comme phase mobile, on a trouvé des valeurs R_F de 0 pour l'argent, le mercure(II) et le palladium. Seuls l'or(III) et le mercure(II) ont été extraits en solutions HCl, en systèmes d'extraction liquide–liquide. Plusieurs séparations ont été réalisées avec succès en milieu HNO$_3$ M.

ZUSAMMENFASSUNG

Tri-*n*-octylphosphinsulfid (TOPS) wurde als stationäre Phase bei der verteilungspapierchromatographischen Trennung unter Anwendung von Salzsäure als mobile Phase und als Extraktionsmittel für Metallionen untersucht. Silber, Quecksilber(II), und Palladium(II) besassen einen R_F-Wert von 0, wenn Salpetersäure als mobile Phase benutzt wurde. Dieselben Ionen wurden auch selektiv aus wässrigen Salpetersäurelösungen extrahiert. Gold(III), Quecksilber(II), Palladium(II) und Platin(IV) ergaben R_F-Werte von 0, wenn Salzsäure als mobile Phase benutzt wurde. Jedoch wurden nur Gold(III) und Quecksilber(II) aus wässrigen Salzsäurelösungen bei Flüssig–Flüssig-Extraktionssystemen extrahiert. Verschiedene Trennungen wurden erfolgreich aus $1\,M$ Salpetersäure durchgeführt.

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THE METHOD OF CONCENTRATION-DEPENDENT DISTRIBUTION IN THE QUANTITATIVE USE OF RADIOISOTOPES

PART I. THEORETICAL CALIBRATION CURVES AND COMPARISON TO THE "SUBSTOICHIOMETRIC PRINCIPLE"

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Several methods for the determination of trace amounts of elements have been proposed[1-4] that employ a calibration curve given by the dependence of the distribution of the element in a two-phase system upon its overall concentration in both phases.

A typical example[1] is the dependence of barium sorption (traced by radiobarium) by iron(III) hydroxide upon its initial concentration; this can be used for the determination of 10^{-8} g of barium. Sometimes[5,6] the distribution of a certain element can be used as a means of measuring the concentration of another element. Thus, the solubility of silver chloride in terms of radioactivity of the silver in solution depends upon the initial chloride concentration of the aqueous phase employed for the solubility determination. A sensitive method for chloride determination is based[6] on this solubility dependence.

This manner of using radioisotopes in quantitative analysis will be referred to as the method of concentration-dependent distribution.

It is interesting to note[7] that the "substoichiometric principle" proposed first by ZIMAKOV AND ROZHAVSKII[8] and worked out in several interesting papers by STARÝ AND RŮŽIČKA[9,10] (method I) can be considered as a special case of the method of concentration-dependent distribution (method II).

The aim of the present paper is to give theoretical calculations of some calibration curves, which might be of practical interest, to calculate the theoretical optimum conditions and sensitivity of the determinations involved and to compare methods I and II. For reasons resulting from the mathematical treatment given herein, method I will be referred to as method of isolating equal amounts.

In subsequent calculations the ratio of concentrations of substance A in the two phases (distribution ratio) will mostly be used to characterise the distribution. As an arbitrary limit of performance of method II, the concentration of substance A is taken at which the relative error of the sought-for concentration of substance A equals double the relative error of the distribution ratio.

The theoretical concentration limit of method I is fixed as the point where the isolated amount differs by 1% from the theoretical value. In STARÝ AND RŮŽIČKA's

theory a permissible difference of 0.1% is stated, which lowers the theoretical sensitivity by one order of magnitude but provides wider limits for casual pH deviations, undesired shifts in the equilibria of complex formation during separation of the free metal on ion-exchangers (see below), etc.

The definitions of the various symbols used in the subsequent paragraphs are given in Table I.

TABLE I

NOTATION OF SYMBOLS

α	$= V - 0.5X - T$
β_H	— constant for the given extraction agent of chelate (such as EDTA), metal, pH, temperature and excess of masking agent
C_{Me}	— equilibrium concentration of substance Me in the aqueous phase including the hydrolytic products and complexes with foreign masking agents (mole/l)
C_{Me}^{org}	— equilibrium concentration of metal in the non-aqueous phase in a system with a chelate (mole/l)
C_R	— equilibrium concentration of substance H_NR in the organic phase
C_Y	— total equilibrium concentration of all forms of chelate, except the form in which it is combined with metal Me
δ	— maximum allowable relative error in the quantity of isolated substance with method I
ε	$= (\alpha^2 + 2\,VX)^{\frac{1}{2}}$
φ	$= v_0/v_a$ or $\varphi = v/v_a$
G	— total quantity of the substance to be determined in the system in which sorption occurs (moles)
G^{min}	— minimum quantity of substance capable of being determined
G_{Me}, G_R, G_Y	— total amount of metal Me to be determined, of extraction agent H_NR used, and of chelate in the system
k	— constant in Freundlich's isotherm
k'	— constant in Langmuir's isotherm
K	— empirical constant for sorption in dynamic conditions
ξ	— ratio of unreacted extraction agent, $\xi = C_R/G_R \cdot v_0^{-1}$
l	— constant in Langmuir's isotherm
L	$= k'm/v$
m	— amount of sorbent (g)
$[MeR_N]$	— equilibrium concentration of metal in the organic phase
n	— exponent in Freundlich's isotherm ($n > 1$)
N	— number of moles of extractant reacting with one mole of metal Me
q	— distribution ratio in extraction or sorption on ion-exchanger
q_0	— $\lim_{G_{Me} \to 0} q$ (in extraction)
q_∞	— distribution ratio in the system at zero concentration of the chelate or at $G_{Me} \gg G_Y$
T	$= \beta_H \cdot G_{Me}/2\,v_a$
v	— volume of the liquid phase in sorption with the Langmuir or Freundlich isotherm valid; volume of the non-aqueous phase when a chelate is used
v_a, v_0	— volumes of the aqueous and organic phase in extraction
V	$= \beta_H \cdot G_Y/2\,v_a$
x	— equilibrium concentration of the substance subject to sorption in the liquid phase
X	$= 1 + q\varphi$ (system with a chelate)
y	— amount of substance sorbed per unit weight of sorbent (mole/g)
z	$= y/x$

SORPTION OBEYING THE FREUNDLICH ISOTHERM

It has been found in a number of cases[11-13] that the sorption of ions in low concentration conforms to the Freundlich isotherm. In the region where the Freundlich sorption isotherm

$$y = kx^{1/n} \tag{1}$$

is valid, method I cannot be used at all, of course.

For method II:

$$z = y/x = kx^{1/n-1} \tag{2}$$

If we use the equation of substance balance

$$G = x \cdot v + y \cdot m \tag{3}$$

it can be easily derived that:

$$\begin{aligned}
\mathrm{d} \log z/\mathrm{d} \log G &= \frac{\mathrm{d}z}{\mathrm{d}x} \cdot \frac{\mathrm{d}x}{\mathrm{d}G} \cdot \frac{G}{z} = \\
&= -(1 - 1/n)(x^{1-1/n} + km/v)(x^{1-1/n} + km/v \cdot n)^{-1}
\end{aligned} \tag{4}$$

The values v, m, k, n are considered to be constant.

From eqn. (4) it follows that

$$\lim_{x \to 0} |\mathrm{d} \log z/\mathrm{d} \log G| = n - 1 \tag{5}$$

$$\lim_{x \to \infty} |\mathrm{d} \log z/\mathrm{d} \log G| = 1 - 1/n$$

Since $n > 1$, the calibration curve is always steeper in the region of low values of x than in the region of high values; higher values of n lead to steeper calibration curves. Furthermore, it can be easily shown that systems with a high value of k and a relatively small volume of aqueous phase are advantageous for the use of
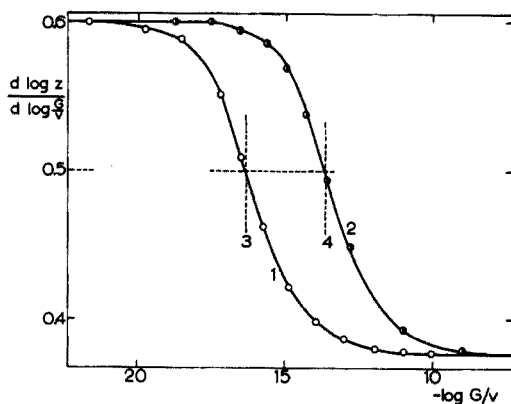

Fig. 1. Slopes of the calibration curves conforming to the Freundlich isotherm ($n = 1.6$). The curves are calculated for varying values of x by eqns. (4) and (5). 1, $km/v = 1 \cdot 10^{-6}$; 2, $km/v = 1 \cdot 10^{-5}$; 3 and 4, upper limit of concentration.

method II. Figure 1 illustrates the slopes of the calibration curves with the chosen value of $n = 1.6$ for two values ascribed to km/v.

As $n \to 1$, the isotherm becomes Henry's law, the value of z does not depend on the concentration of G/v, and the method is unusable.

SORPTION OBEYING THE LANGMUIR ISOTHERM

In systems where the Langmuir sorption isotherm

$$y = \frac{k' x}{l + x} \tag{6}$$

is valid, method II as well as method I can be used since $\lim_{x \to \infty} y = k'$.

For method II, eqn. (3) is again valid, and it can be derived that:

$$\text{d} \log z / \text{d} \log G = \frac{\text{d}z}{\text{d}x} \cdot \frac{\text{d}x}{\text{d}G} \cdot \frac{G}{z} =$$
$$= -[x^2 + x(l + L)][x^2 + 2l\,x + l(l + L)]^{-1} \qquad (7)$$

$\lim_{x \to 0} |\text{d} \log z / \text{d} \log G|$ of course equals 0.

For the minimum value of G/v which still permits the determination, the following convention was proposed above:

$$\text{d} \log z / \text{d} \log G = -0.5 \qquad (8)$$

If the ratio $\omega = x/l$ is introduced into eqns. (7) and (8), we can obtain:

$$L/l = 0.5(1 - \omega^2)(\omega - 0.5) \qquad (9)$$

Equation (3) then gives for the threshold values of G:

$$G^{\min}/v \cdot l = \omega[1 + 0.5(1 - \omega)(\omega - 0.5)^{-1}] \qquad (10)$$

It can be seen that condition (8) can be fulfilled only for ω in the interval from 0.5 to 1. The results of calculations based on eqns. (9) and (10) are given in Fig. 2.
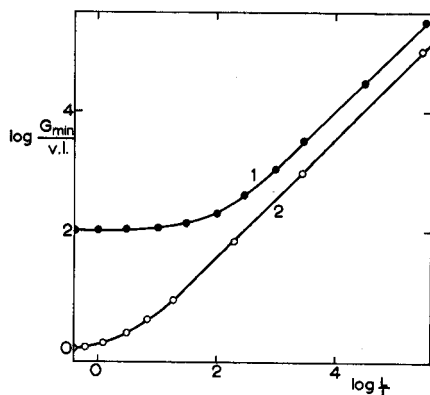

Fig. 2. Limits of applicability of methods I and II in sorption systems obeying the Langmuir isotherm.

It can be seen that systems with values of l and k' as low as possible are desirable.

As the limit condition of applicability for method I instead of eqn. (8), the relation

$$y = (1 - \delta)k' \qquad (11)$$

is valid.

Equation (3) then assumes the form:

$$G^{\min}/l \cdot v = (1 - \delta)L/l + (1 - \delta)/\delta \qquad (12)$$

The limit of applicability of method I, given by eqn. (12), is also shown in Fig. 2 ($\delta = 0.010$). It can be seen that the sensitivity of method II can be more favorable by two orders of magnitude. Consequently, method II is applicable even in concen-

tration ranges where the isolation of equal amounts of substance could no longer be guaranteed, but where the distribution ratio z is still sufficiently dependent on the initial concentration G/v.

EXTRACTION OF SUBSTANCE WITH CONSTANT AMOUNT OF EXTRACTION AGENT IN THE SYSTEM

These systems seem to hold great promise for practical application of method II since they have been frequently and successfully used by STARÝ AND RŮŽIČKA[9,10] in the application of method I.

For an extraction equilibrium involving the extraction of the substance Me with the agent H_NR at a constant pH value, the following relation is true:

$$\beta_H = [MeR_N] \cdot C_{Me}^{-1} \cdot C_R^{-N} \tag{13}$$

If the equilibrium constant of the extraction involved, the pH, the concentrations of the masking agents present in considerable excess, and the stability constants of their complexes with substance Me are known, the value of β_H can be easily computed.

If several reasonable assumptions (identical to those used by STARÝ AND RŮŽIČKA in their theory[10] of method I) are made, we arrive at the total amounts of the substances in question:

$$G_{Me} = C_{Me} \cdot v_a + [MeR_N] \cdot v_0$$
$$G_R = C_R \cdot v_0 + N[MeR_N] \cdot v_0 \tag{14}$$

For the distribution ratio the following relationship is valid:

$$q = [MeR_N] \cdot C_{Me}^{-1} = \beta_H \cdot C_R^N = q_0 \xi^N \tag{15}$$

where

$$q_0 = \lim{}_{G_{Me} \to 0} q = \beta_H (G_R/v_0)^N \quad \text{and} \quad \xi = C_R/G_R v_0^{-1}$$

By combining eqns. (13), (14) and (15), it is possible to obtain the basic equation:

$$G_{Me}/G_R = N^{-1}(1 + 1/q\varphi)(1 - \xi) = N^{-1}(1 + 1/q\varphi)[1 - (q/q_0)^{1/N}] \tag{16}$$

where $\varphi = v_0/v_a$.
For $\xi \ll 1$ eqn. (16) simplifies to:

$$q = (G_A/v_0 N)[(G_{Me} - G_R/N)v_a^{-1}]^{-1} \tag{17}$$

which gives, obviously, the condition of the method of isolating equal amounts.

The curves $\log q = f(\log Me)$, computed from eqn. (16) with $N = 1$ and $N = 3$ for different q_0 values, are shown in Figs. 3 and 4. Each curve includes 3 significant points. One of them is the conventional limit of applicability of method II where d $\log q$/d $\log G_{Me} = -0.5$. Then there is the limit of applicability of method I where $\xi = \delta$. The third point is the limit of the region of substoichiometry ($G_{Me} = N G_R$). It can be clearly seen that method II reaches into the "substoichiometric" as well as into the "superstoichiometric" region and that, theoretically, substantially smaller concentrations of substance Me can be determined by method II than by method I.

Below we shall derive equations for the optimum concentration G_R/v_0 for both methods. The existence of such optimum concentrations can be seen from Fig. 4.
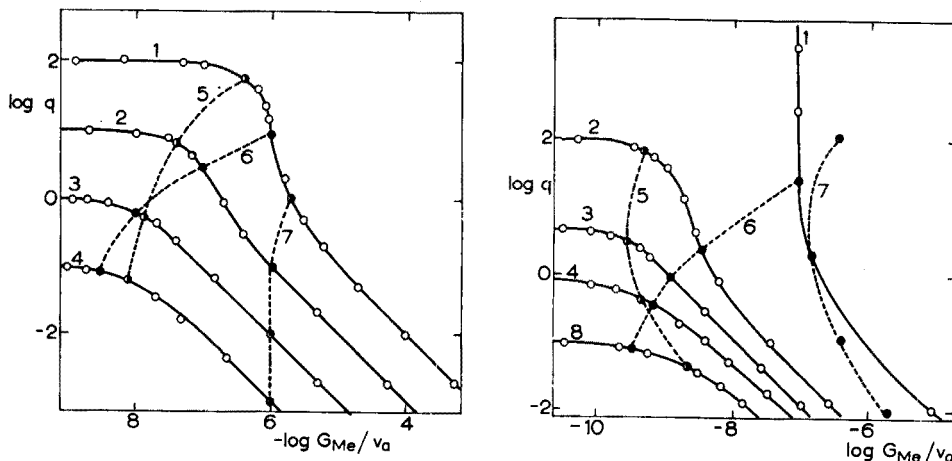
Fig. 3. Theoretical calibration curves for extraction with a constant amount of extraction agent at $N = 1$, $\beta_H = 1 \cdot 10^8$. 1, $q_0 = 1 \cdot 10^2$; 2, $q_0 = 10$; 3, $q_0 = 1$; 4, $q_0 = 0.1$; 5, lower limit of applicability of method II (d log q/d log $G_{Me} = -0.5$); 6, limit of substoichiometry; 7, lower limit of applicability of method I.

Fig. 4. Theoretical calibration curves for extraction with a constant amount of extracting agent at $N = 3$, $\beta_H = 1 \cdot 10^{26}$. 1, $q_0 = 2 \cdot 10^6$; 2, $q_0 = 10^2$; 3, $q_0 = 5$; 4, $q_0 = 0.8$; 8, $q_0 = 0.1$; curves 5, 6 and 7, see Fig. 3.

With method II, the following equation is true for G_{Me}^{min}:

$$-d \log G_{Me}/d \log q = \xi/N(1-\xi) + (q\varphi+1)^{-1} = 2 \tag{18}$$

From eqns. (16) and (18), q can be eliminated and the function $G_{Me}^{min} = f(\xi)$ found; this is the equation of the limit region.

If we put $dG_{Me}^{min}/d\xi = 0$, the value for the minimum value of G_{Me} can be obtained. These mathematical operations lead to the equation:

$$\xi^3(2N^3 + 5N^2 + N) + \xi^2(-6N^3 - 10N^2) + \xi(6N^3 + 5N^2 - N) - 2N^3 = 0 \tag{19}$$

The following roots are meaningful:

N	1	2	3
ξ	0.500	0.76	0.835

The values q and q_0 pertaining to the above ξ values are given in Table II and can be used for a straightforward calculation of the theoretically optimum initial concentration G_R/v, β_H and N being given. The limits of applicability of method II for 3 comparable systems with different N are also given in Table II.

To obtain the limit of method I, it is necessary to substitute $\xi = \delta$ and put $(dG_{Me}/dG_R) = 0$ in eqn. (16). Thus:

$$G_R/v_0 = [(N-1)/\delta^N \varphi\beta_H]^{1/N} \tag{20}$$

The values of the minimum concentrations permitting determination by method I are also given in Table III. The theoretical applicability of method II is seen to be wider by 2 to 4 orders.

TABLE II

COMPARISON OF SENSITIVITIES OF METHOD I AND METHOD II IN EXTRACTION

$(\varphi = 1)$

N	β_H[a]	*Method II*			*Method I, $\delta = 0.01$*			*Method I, $\delta = 0.001$*		
		G_{Me}^{min}/v_a	q	q_0	G_{Me}^{min}/v_a	q	q_0	G_{Me}^{min}/v_a	q	q_0
1	10^8	$9 \cdot 10^{-9}$	0.06[c]	0.1[c]	$1 \cdot 10^{-6}$	0.1	10	$1 \cdot 10^{-5}$	0.1	100
						0.01	1		0.01	10
2	10^{17}	$1 \cdot 10^{-9}$	0.71[b]	1.23[b]	$3 \cdot 10^{-7}$	1	$1 \cdot 10^4$	$3 \cdot 10^{-6}$	1	$1 \cdot 10^6$
3	10^{26}	$3 \cdot 10^{-10}$	3.0[b]	5.0[b]	$3 \cdot 10^{-7}$	2	$2 \cdot 10^6$	$3 \cdot 10^{-6}$	2	$2 \cdot 10^9$

[a] Such β_H values are chosen that for $G_R v_0^{-1} = 10^{-9}$, $q_0 = 0.1$.

[b] These values are independent of β_H and can be used in calculating the sensitivity of method II for unknown β_H.

[c] Read off from Fig. 4.

TABLE III

RANGES OF USABLE VALUES OF LOG G_{Me}/G_Y WHEN EDTA IS USED

$(x = 1.6)$

$\dfrac{d \log q}{d \log G_{Me}}$		$V = 5$	$V = 50$	$V = 500$
0.5	$\log \dfrac{G_{Me}}{G_Y}$	$-0.3-0.7$	$-0.55-0.8$	$-0.55-0.8$
1	$\log \dfrac{G_{Me}}{G_Y}$	Not usable	$-0.33-0.43$	$-0.33-0.46$
Maximum value from the entire calibration curve	$\dfrac{d \log q}{d \log G_{Me}}$	0.95	3.6	12.8

In contrast to method I, a small casual change of pH may cause an error. The error involved can be calculated by calculation of the function d log q/d pH at constant values G_R, G_{Me}, v_0, v_a:

$$d\, \text{pH}/d \log q = 1/N + (1 - \xi)/\xi(q\varphi + 1)$$

The influence of a pH change obviously becomes smaller with increasing G_{Me} values for a given calibration curve.

At the limit of performance of method II, the approximation d log q/d pH $= N$ is true; furthermore, (d log q/d log G_M)$_{pH} = -0.5$, therefore the deviation ΔpH leads to the error $\Delta \log G_{Me} \doteq -2N \cdot \Delta$pH. Obviously the pH value must be maintained strictly, if higher values N, q and ξ are involved.

DISTRIBUTION OF METAL BETWEEN TWO PHASES AT A CONSTANT COMPLEXAN CONCENTRATION

In the method of STARÝ AND RŮŽIČKA[9] the metal–EDTA chelate formed is passed through a column containing a cation-exchanger and the unbound metal is "quantitatively" retained. It is obvious that with a decrease of metal concentration in the solution, part of the complex particles can release the metal ions which are

sorbed subsequently. In order to ensure that all the metal bound in the complex, and only that quantity, is quantitatively isolated, it is necessary to seek suitable conditions experimentally, which is not always easy. Such incomplete separation seems to be reported in the work of LANDGREBE *et al.*[7].

For the application of method II the following experimental arrangement is proposed. The aqueous phase containing a fixed concentration of EDTA (or an analogue) and varying concentrations of the metal is shaken to equilibrium with a non-aqueous phase, which does not take up the metal chelate; pH and the other conditions are kept constant. The distribution ratio with no EDTA present (q_∞) must not depend on the concentration of the metal Me. A change in the distribution ratio q occurs in the region where the concentration of metal G_{Me}/v_a is comparable to the initial concentration of the complexan G_Y/v_a.

If the pH value, temperature and excess of masking agents are kept constant, the following relationships are true:

$$\beta_H = [MeY]/C_Y C_{Me}; \quad q_\infty = \frac{C_{Me}^{org}}{C_{Me}}; \quad q = \frac{C_{Me}^{org}}{C_{Me} + [MeY]} \tag{21}$$

since only 1:1 complexes need be considered with complexans as a rule. The substance balances are as follows:

$$G_{Me} = C_{Me} \cdot v_a + [MeY] \cdot v_a + C_{Me}^{org} \cdot v$$
$$G_Y = C_Y \cdot v_a + [MeY] \cdot v_a \tag{22}$$

If the following definitions are made:

$$\beta_H G_Y/2\, v_a = V; \quad \beta_H G_{Me}/2\, v_a = T; \quad \varphi = \frac{v}{v_a}; \quad q_\infty \varphi + 1 = X;$$
$$V - X/2 - T = \alpha; \quad \sqrt{\alpha^2 + 2\,VX} = \varepsilon,$$

then the equation of the calibration curve can be easily obtained from eqns. (21) and (22):

$$q_\infty/q = 1 + \alpha + \varepsilon \tag{23}$$

For the slope of the calibration curve, the equation is

$$d \log q/d \log G_{Me} = T(\alpha + \varepsilon)/(1 + \alpha + \varepsilon) \tag{24}$$

Some calibration curves, shown in Fig. 5, were calculated by eqns. (23) and (24). For the same value of V, the calibration curve obtained improves as the value of X
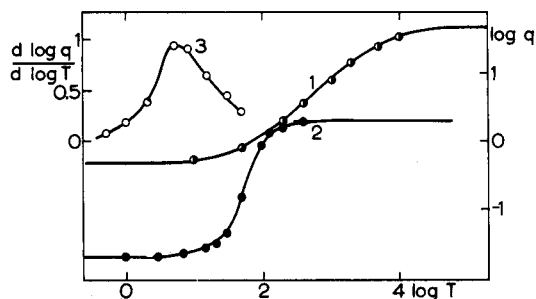

Fig. 5. Theoretical calibration curves when EDTA is used. 1, log q, $V = 50$, $q_\infty = 50$, $X = 100$; 2, log q, $V = 50$, $q_\infty = 2$, $X = 1.6$; 3, d log q/d log T, $V = 5$, $X = 1.6$.

approaches 1. This conclusion is obviously valid generally. As minimum suitable values, the following can be considered $q_\infty \cong 1 \div 3$; $\varphi = 0.2 \div 0.5$; it is therefore recommended to choose experimental conditions corresponding to $X \approx 1.2$ to 2.5.

From eqns. (23) and (24), the limit of applicability of the method as well as the optimum values of T can be computed. The results are listed in Table III.

It can be estimated by the following approximation that for $\delta = 0.001$, method I is approximately 3 orders of magnitude less sensitive than method II, whereas for $\delta = 0.01$ it is less sensitive by two orders.

For the lower limit of applicability of method I, $\delta = C_Y/[\text{MeY}] = 1/C_{Me} \cdot \beta_H = 0.01$. If we put roughly $G_{Me}^{min}/v_a = 2 \cdot C_{Me}$, we may write $G_{Me}^{min}/v_A = 2 \cdot C_{Me} \cdot K = K \cdot 200/\beta_H$, where K is a coefficient $(K > 1)$ expressing the more stringent requirements in view of the non-equilibrium method of separation.

With method II, for $V = 5$, $G_{Me}^{min}/v_a = 10^{-0.3} \cdot G_Y/v_a = 5/\beta_H$. If we assume $K = 2.5$, the difference in sensitivities is two orders. However, the corresponding value of K can be even higher.

Let us calculate the influence of a pH deviation:

$$\frac{d \log q}{d \text{ pH}} = \frac{\partial \log q}{\partial \log q_\infty} \cdot \frac{\partial \log q_\infty}{\partial \log \text{pH}} + \frac{\partial \log q}{\partial \log \beta_H} \cdot \frac{\partial \log \beta_H}{\partial \log \text{pH}}$$

The relationship $\beta_H = \beta_0 B_{Me} \cdot B_Y$ can be used, where β_0 is the true concentration constant of the complex in question

$$\left(\frac{d\beta_0}{d\text{pH}} = 0\right),$$

involving the concentrations of simple ions of the metal and EDTA; B_{Me} and B_Y are related to the values C_{Me} and C_Y, respectively, $i.e.$ to the ion concentrations.

As $\partial \log q/\partial \log q_\infty = 1$ from eqn. (23), the following relationship can be obtained:

$$\frac{d \log q}{d \log \text{pH}} = \overset{(+)}{\frac{\partial \log q_\infty}{\partial \text{ pH}}} + \overset{(-)}{\frac{\partial \log q}{\partial \log \beta_H}} \left(\overset{(+)}{\frac{\partial \log B_Y}{\partial \text{ pH}}} + \frac{\partial \log B_{Me}}{\partial \text{ pH}} \right) \tag{25}$$

The signs over some derivatives indicate whether the derivative can be expected to be of positive or negative value.

The function $\partial \log q/\partial \log \beta_H$ can be derived from eqn. (23):

$$\partial \log q/\partial \log \beta_H = -q \, q_\infty^{-1}[V - T + \alpha\beta^{-1}(V - T) + VX\beta^{-1}] \tag{26}$$

A detailed analysis shows that this function is always negative and its value varies between -1 and 0. The remaining signs are obvious. By using a suitable non-aqueous phase, it is possible to reach almost equal absolute values of the two members in eqn. (25) and a very limited pH effect.

PRECIPITATION REACTIONS

The use of precipitation reactions with method II for trace analysis does not seem to be of great interest, since precipitates with extremely low solubilities exhibit a tendency towards colloidal behaviour, which would involve poor reproducibility of the separation operations. However, if radiometric titration of dilute solutions is

limited by the solubility value, separation of the precipitate causing no difficulties, concentrations of about one order of magnitude lower can be determined by method II[5]. The use of method II is also justified, if the composition of the precipitate is not constant but depends on the initial composition of the solution and if substantial coprecipitation occurs with an adverse effect on the shape of the titration curve, so that the point of equivalence is not easy to determine.

GENERAL REMARKS CONCERNING METHOD II

The selectivity of method II is not substantially different from the selectivity of method I or of precipitation titration, as indicated by the above considerations.

A possible utilization of method II is the determination of the concentration of the carrier in a radioactive preparation of given specific activity, when a preparation of higher specific activity is not available and so the calibration curve cannot be determined in advance by adding the carrier to the second preparation. This difficulty can be overcome in the following way. A system is used in which the distribution ratios depend on the quantity of the radioisotope used and a plot is made of the function $q = f(j)$, where $j = G/G_0$ (G is the amount of radioisotope used and G_0 the minimum amount of radioisotope usable, from the point of view of measurement of radioactivity). Values of $j = 1, 2, 3$ etc. are chosen, and then with the chosen constant amount of radioisotope $G_0 \cdot j_k$ the dependence of the values of q on the amount of the added stable carrier G_C is determined. For equal q values in the two curves, $jG_0 = j_k G_0 + G_C$ and hence $G_0 = G_C/(j - j_k)$. The values of G_0 are calculated for several values of q and the average G_0 is determined. This procedure is more complicated than with method I but substantially lower concentrations can theoretically be determined.

The use of method II rather than method I with a given reagent is only warranted if the sensitivity of method I with the reagent is limited by the stability of the complex in question, or if no reagent is available which meets the requirements of method I for the given concentration level of a particular element. In general the reproducibility of a determination by method II can be expected to be lower than that of method I. This is due to the fact that with method I the basis of the determination is the substoichiometric amount of reagent. Changes of temperature, pH, volumes of phases, etc. within a certain range, are irrelevant. A determination by method II is based on the attainment of an equilibrium state, or on a constant time allowed for reaction to proceed. A casual variation in the factors mentioned necessarily involves an error in the value determined.

On the other hand, it is worth noting that reagents which give more than one complex with the substance to be determined in the concentration range in question can be employed in a procedure by method II, whereas they cannot be used for method I.

In comparing methods I and II, it should be noted that method I is a modification of isotopic dilution, whereas method II is an example of simple tracer methods ("radiometric analysis"[5]) and can only be used in isotopic dilution for determining the amount of substance in the purified fraction as a substitute for gravimetry, colorimetry, etc.

Practical examples[13] of novel applications of method II have been worked

out in our laboratory. By a process of sorption on paper impregnated with Prussian blue a method was developed for determining cesium at the microgram level in presence of large amounts of other alkali metals and calcium.

The author wishes to thank J. Růžička for fruitful discussions and helpful criticism of the present work.

SUMMARY

The method is based on the utilization of a calibration curve which shows the dependence of the distribution ratio in a two-phase system containing the substance to be determined or a substance reacting with it, on the total concentration of the substance to be determined. The relationship of the proposed method to radiometric titration and to the "substoichiometric principle" in isotopic dilution is discussed. Formulae for the theoretical calibration curves in 4 systems are derived: sorption conforming to the Langmuir isotherm or to the Freundlich isotherm, extraction with a constant quantity of an extracting agent, and sorption or extraction in the presence of a constant quantity of a chelating agent. Theoretical sensitivities are given.

RÉSUMÉ

La méthode proposée est basée sur l'utilisation d'une courbe de calibrage, montrant le rapport de coefficient de partage dans un système à deux phases, lors de l'utilisation de radioisotopes en analyse quantitative. On examine la relation de cette méthode avec un titrage radiométrique et avec "le principe substoéchiométrique" en dilution isotopique.

ZUSAMMENFASSUNG

Es wird eine Methode der konzentrationsabhängigen Verteilung beschrieben, wie sie bei der Anwendung von Radioisotopen bei der quantitativen Analyse verwendet wird. Die Methode benutzt eine Eichkurve, die die Abhängigkeit des Verteilungsverhältnisses in einem 2-Phasen-System, das die zu bestimmende Substanz oder eine andere, die mit ihr reagiert, enthält, von der Totalkonzentration der zu bestimmenden Substanz zeigt. Die Beziehung der vorgeschlagenen Methode zur radiometrischen Titration und zu dem "substöchiometrischen" Prinzip bei der Isotopenverdünnung wird diskutiert. Es werden Formeln für die theoretischen Eichkurven von 4 Systemen abgeleitet: die Sorption, die sich nach der Langmuir-Isotherme oder nach der Freundlich-Isotherme richtet, die Extraktion mit einer konstanten Menge eines extrahierenden Reagenzes und die Sorption oder Extraktion in Gegenwart einer konstanten Menge eines Chelatbildners. Theoretische Empfindlichkeiten werden angegeben.

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SOME DERIVATIVES OF RHODANINE AS ANALYTICAL REAGENTS

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Rhodanine and its derivatives have found wide application in the detection and determination of a small group of cations, but there are still many problems associated with their use.

NENCKI[1] noted that rhodanine (I, R=H) precipitated certain metal ions from aqueous solution when he first characterised the compound, but FEIGL[2] was the first to suggest a rhodanine derivative as an analytical reagent. He recommended 5-iso-nitrosorhodanine (II) as a precipitant for mercury and silver ions. Shortly afterwards, FEIGL AND POLLAK[3] introduced rhodanine itself as a selective microgravimetric precipitant for silver ions.

(I)   (II)   (III)
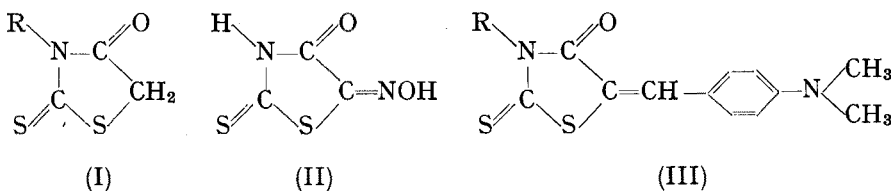
The use of rhodanine derivatives as colorimetric reagents has stemmed directly from FEIGL's introduction of chromophoric groups into the rhodanine molecule[4]. Of 3 derivatives investigated, the now well-known 5-*p*-dimethylaminobenzylidene-rhodanine (III, R=H) was found to be the most sensitive as a spot test reagent for silver(I) ions; 0.5 μg of silver can be detected as a red-violet precipitate or colour. The reagent is also very sensitive, in acidic solutions, towards mercury(I and II), copper(I), gold, platinum and palladium[5]. The *p*-diethyl homologue of the reagent is even more sensitive towards silver ions[6], a direct consequence of the superior auxochromic properties of the diethylamino grouping.

The reactions of 3,5-disubstituted rhodanines are apparently similar to those of 5-substituted rhodanines[7,8]. TURKEVICH[8] found that such reagents, *e.g.* 3-allyl-5-*p*-dimethylaminobenzylidenerhodanine, are highly sensitive colorimetric reagents for palladium, silver, copper(I), etc., the 3-allyl derivative being 5 times as sensitive to silver(I) as the 3-(H) compound. Little is known about this type of reaction; TURKE-VICH AND GEVLICH[7] suggest that it is simply complex formation, but this is an incomplete explanation[9]. Little information is available on the analytical applications of these compounds[8,10].

The very sensitive colour changes associated with the reactions of p-dimethyl- or p-diethylaminobenzylidenerhodanine have been applied in the colorimetric determinations of gold, silver and mercury in acidic solutions[11], silver in an alkaline medium[12], and, indirectly, chloride[13] and cyanide[14]. The methods are unsatisfactory, however, because the coloured complexes are measured as highly dispersed colloids[15,16], and thus their reproducibility depends on strict control of the reaction conditions. SANDELL AND NEUMAYER[17] found that silver 5-p-diethylaminobenzyliderhodanide is apparently less soluble than silver sulphide.

The development of a truly soluble coloured species has been possible in some instances, giving much simpler and more reliable procedures. Gold 5-p-dimethyl-aminobenzylidenerhodanide can be extracted into chloroform[11], and the palladium[18] and platinum(II)[19] complexes are soluble in propionic acid. The silver complex is reported to be slightly soluble in chloroform[17].

This paper describes the reactions of numerous derivatives of rhodanine with a wide range of metal ions, with especial regard to the production of soluble complexes.

EXPERIMENTAL

Reagents

The compounds used are shown in Table I. Most had to be synthesised, and many are new compounds. The syntheses are described elsewhere[20,21]. The reagents are grouped as follows.

Group a: 5-Substituted rhodanines. These were chosen as model compounds to investigate the effect of the 5-substituent on the solubility of their metal complexes.

Group b: 3-Substituted 5-p-dimethylaminobenzylidenerhodanines (III). These were intended for the investigation of the influence of the 3-substituent on the reactions with metal ions.

Group c: 3-Substituted derivatives of Group a.

Group d: Two reagents that differ from 5-p-dimethylaminobenzylidene-rhodanine only in the 2-substituent (=NOH, =O instead of =S).

Reagent solutions

Generally a saturated, acetone solution ($< 10^{-4}$ M) was used.

Buffer solutions

pH 4.7, sodium acetate–acetic acid–water; pH 7.2, 20% (w/v) ammonium acetate solution; pH 9.3, ammonia–ammonium chloride–water; pH 1 was obtained by adding 1 drop of 8 N nitric or hydrochloric acid to the test solution.

Masking agents

Aqueous 0.02 M solutions of acetylacetone, bromide, CDTA, chloride, cyanide, EDTA, malonate, oxalate, propionate, tartrate, thiocyanate, thiosulphate and thiourea, and a 0.02 M glacial acetic acid solution of 8-quinolinol.

Reactions with metal ions

To a solution of reagent (5 drops), buffer solution (2 drops) and water, 1 ml in all, was added a solution of metal ion (1 mg per ml, 1 drop). The mixture was

TABLE I

RHODANINE DERIVATIVES USED IN THE INVESTIGATION

5-Substituent	M.p. (°) uncorr.	Source or synthesis ref.	Ref. to metal ion reactions
Group a			
p-Dimethylaminobenzylidene-		B.D.H.	4-8, 22
p-Nitrobenzylidene-	238 (dec.)	23	—
cycloHexylidene-	168-169	24	8, 25
o-Sulphobenzylidene-	ca. 340	26	22, 26
(2-Thienylidene)-	227-229	27	—
(2-Picolylidene)-	248	28	28
(3-Picolylidene)-	287-288 (dec.)	28	28
(4-Picolylidene)-	284-287 (dec.)	28	28
"Rhodanine red"		29	25
Group d			
5-p-Dimethylaminobenzylidene-thiazolidene-2-oxime-4-one	197 (dec.)	21	—
5-p-Dimethylaminobenzylidene-thiazolidene-2,4-dione	286 (dec.)	33	8

3-Substituent	5-Substituent	M.p. (°) uncorr.	Ref. to synthesis
Group b			
Phenyl-	p-Dimethylamino-benzylidene-	231-234	30[a]
Allyl-	p-Dimethylamino-benzylidene-	131-132	30[a]
n-Propyl-	p-Dimethylamino-benzylidene-	134-135	20
p-Dimethylaminophenyl-	p-Dimethylamino-benzylidene-	260-261	20
(2-Picolyl)-	p-Dimethylamino-benzylidene-	204-205	20
(4-Picolyl)-	p-Dimethylamino-benzylidene-	207	20
(2-Pyridyl)-	p-Dimethylamino-benzylidene-	238-239	20
[2-(3'-Rhodanyl)-ethyl-1-]-	p-Dimethylamino-benzylidene-	179-180	20
Ethylene-1,2-bis-[b]	p-Dimethylamino-benzylidene-	304 (dec.)	20, 31
Group c			
Phenyl-	(2-Thienylidene)-	196-197	32
p-Dimethylaminophenyl-	(2-Thienylidene)-	216-217	21
p-Dimethylaminophenyl-	(3-Picolylidene)-	237-238	21
p-Dimethylaminophenyl-	o-Sulphobenzylidene-	> 260	21

[a] Metal ion reactions, ref. 8.
[b] Insoluble in nearly all solvents, not tested further.

shaken, and the relevant changes were noted. Appropriate masking agents (2–3 drops) were then added in order of increasing complexing strength.

The metal ions investigated were Ag(I), Au(III), Cd(II), Ce(III and IV), Co(II), Cu(I and II), Fe(II and III), Ga(III), Hg(I and II), In(III), Ir(IV), La(III), Ni(II), Os(IV), Pb(II), Pd(II), Pt(IV), Rh(III), Ru(IV), Tl(I), U(VI) and Zn(II).

Solvent extraction procedure for silver

To a solution of reagent (10 drops) was added silver nitrate solution (1 mg Ag per ml, 2 drops). After 5 min, the resulting "solution" was well shaken with the organic solvent (1 ml).

Reactions with metal ions

The reactions of the reagents mentioned in Table I with 26 metal ions were investigated at 4 pH values. Colloidal solutions were detected by the Tyndall effect. The strengths of the complexes were estimated by adding masking agents of increasing strength appropriate to the ion being investigated. The detailed results of these tests are given elsewhere[21].

Group a: These reagents reacted with silver, gold, copper(I) and palladium at pH 1–9.3. Mercury(I) did not react at pH 9.3; mercury(II) reacted only at pH 4.7 and in dilute nitric acid. Platinum(IV) initially gave no reaction with *p*-dimethylamino-benzylidenerhodanine, but gave a sensitive colour change on standing, because of the slow reduction to platinum(II), the reacting species[19]. The yellow-violet change was instantaneous on filter paper, however. Iron(II and III) and copper(II) gave weak reactions with some reagents at pH $\geqslant$ 4.7. Cerium(IV) destroyed the reagents in acidic solution. As would be expected, only 5-*p*-dimethylaminobenzylidenerhodanine, 5-*p*-nitrobenzylidenerhodanine and rhodanine red were sensitive reagents. Copper(I), however, gave a yellow-red change with reagents having no auxochrome, whereas other ions merely intensified the original yellow colour.

The reacting ions formed very strong complexes with this group of reagents, as was shown by the powerful masking agents required for their disruption. As had already been noted[5], the silver complexes were resistant to acidic or neutral cyanide solutions; they required thiourea to reverse the colour change. The gold complexes were similar, but those of mercury(I and II) were somewhat weaker. The palladium rhodanides were not dissociated by any of the complexing agents used.

The only reagent that gave completely water-soluble complexes was *o*-sulpho-benzylidenerhodanine. Its silver, gold, copper(I) and palladium(II) complexes were completely soluble at pH 1–9 at the concentrations used. In the absence of any information to the contrary, one must therefore assume that previous workers[22,26] used more concentrated solutions in finding the silver complex of this reagent "difficulty soluble" or "relatively insoluble".

Group b: In general, these reagents reacted with the same selection of metal ions as did those in Group a, and also, in some instances, with iridium(IV), osmium(IV), lead(II), iron(III), cobalt(II) and copper(II) (Table II). Cerium(IV) again destroyed all the reagents, the oxidation being quicker in acidic solutions. At pH 9.3, they reacted with few metal ions, in some instances only with palladium. Some of the reactions noted were superior, as regards colour intensities and contrasts, to those with *p*-dimethylaminobenzylidenerhodanine. Such reactions are indicated in bold type in

TABLE II

THE REACTIONS OF GROUP b REAGENTS WITH METAL IONS

3-Substituent	pH 1 (HNO₃)	pH 1 (HCl)	pH 4.7	pH 7.2	pH 9.3
Phenyl-	Ag, Au, Cu(I)[a], **Hg(II)**[a], Pd	Ag, Au, Pd	Ag, Au, Cu(I, II), Fe(III), Pd	Ag, Au, Cu(I, II), Pd, Fe(III), Hg(I)	Cu(II), Hg(I)
Allyl-	Ag, **Au**, Cu(I)[a], Hg(I)[a], **Hg(II)**[a], Pd	Ag, Au, Cu(I), Ir, **Pd**	**Ag**, Au, Cu(I)[a], **Pd**	Ag, Au, Cu(I)[a], Pd	**Pd**
n-Propyl-	Ag, **Au**, Cu(I), Hg(I), **Hg(II)**[a], Pd	Ag, Au, Cu(I), Hg(I), Pd	Ag, Au, Cu(I), Pd	Ag, Au, Cu(I), Pd	Pd
p-Dimethylaminophenyl-	Ag, Au, Hg(I), Hg(II)[a], Pd[a], Pt	Ag, Au, Pd[a]	Ag, Au, Os, Pd[a]	Ag, Au, Pd	Ag, Co, Os
(2-Picolyl)-	Au, **Hg(II)**[a], Pd, Pt	Ag, Au, Pd	Ag, Au, Cu(I), Hg(II)[a], **Pd**, Pt	Ag, Au, Cu(I), **Pd**	Pd
(4-Picolyl)-	Ag, **Au**, **Hg(II)**[a], Pd, Pt	Ag, Pd, Pt	Ag, Au, **Cu(I)**, Pd	Ag, Au, Cu(I), Pd	Cu(I), Pd
(2-Pyridyl)-	Ag, Au, **Hg(II)**[a], Ir, Pd[a]	Ag, Au, Ir, Pd[a]	Ag, Au, Cu(I), Hg(II)[a], Ir, **Pd**[a]	Ag, Au, Cu(I), Ir, **Pd**[a]	Ag, Pd[a]
[2-(3'-Rhodanyl)ethyl-1-]-	Ag, **Au**, Cu(I)[a], **Hg(II)**[a], Pd	Ag, Au, Cu(I), Pd	**Ag, Au**, Cu(I), Pb, Pd	Ag, Au, Cu(I), Fe(III)	Ag, Cu(I, II)

[a] Colour fades quickly.

TABLE III

THE MORE SENSITIVE REACTIONS IN TABLE II

3-Substituent	Ion	pH	Colour change[a]
Allyl-	Ag	4.7	Orange → mauve
	Au	1.0 (HNO$_3$)	Pale yellow → deep mauve
	Pd	1.0 (HCl)	Colourless → deep mauve
		4.7	Orange → mauve
		9.3	Orange-yellow → mauve
n-Propyl-	Au	1.0 (HNO$_3$)	Pale-yellow → mauve
(2-Picolyl)-	Pd	4.7	Pale orange → purple
		7.2	Pale orange → mauve
(4-Picolyl)-	Au	1.0 (HNO$_3$)	Pale yellow → mauve[b]
	Cu(I)	4.7	Pale orange → mauve
(2-Pyridyl)-	Ag	4.7	Pale orange → mauve
[2-(3'-Rhodanyl)-	Ag	4.7	Pink → mauve
ethyl-1-]-	Au	1.0 (HNO$_3$)	Pale yellow → deep mauve
		4.7	Pink → deep mauve

[a] The final colours were intense. All the products were colloidal. All the colour changes were reversed by thiourea.
[b] Colour change also reversed by thiocyanate.

Table II, and are described in more detail in Table III. The mercury(II) reaction rarely occurred except in 0.1 N nitric (or sulphuric) acid. Under this condition, it produced a very intense but transient mauve or purple colour with all the reagents; chloride prevented this reaction.

The silver and gold complexes were all very stable, being destroyed only by thiourea in acidic solutions, though also by cyanide in alkaline media. The gold complexes of the pyridine derivatives were rather weaker, and were dissociated by thiocyanate under most conditions. All the palladium complexes were decomposed by thiourea, but by no other masking agents. Thus they are weaker than those with Group a compounds.

In the reactions indicated in Table II, all the coloured products were colloidal. It had been hoped that the complexes would be soluble, positively-charged species of the type $[AgR_n]^+$, the compounds reacting as non-acidic rhodanine derivatives[9]. This is obviously not so. The insolubility of the coloured species therefore precludes the use of any of these compounds as spectrophotometric reagents in aqueous solution.

Variation in the group at the 3-position produced small but noticeable changes in the reactions with metal ions. In general, 3-phenyl, 3-n-propyl- and 3-p-dimethyl-aminophenyl-5-p-dimethylaminobenzylidenerhodanines were somewhat inferior to the other reagents in their colour changes. The joining of two rhodanine residues *via* an ethylene bridge gave a sensitive reagent, but caused no profound change in reactivity. The introduction of pyridine-containing residues into the 3-position eliminated any reaction with mercury(I), but facilitated the reactions with platinum and

TABLE IV

REACTIONS OF PALLADIUM(II) WITH SOME PYRIDINE DERIVATIVES OF 5-p-DIMETHYLAMINOBENZYLIDENE-RHODANINE

pH	3-(4-Picolyl)-	3-(2-Picolyl)-	3-(2-Pyridyl)-
1.0 (HNO₃)	Pale yellow → mauve	Pale yellow → mauve	Pale pink → blue-green[a]
1.0 (HCl)	Pale yellow → pink	Pale pink → mauve	Pale pink → blue-green[a]
4.7	Orange → pale mauve	Orange → intense purple	Orange → intense blue[a]
7.2	Orange → red-orange	Orange → intense mauve	Orange → intense purple[a,b]
9.3	Pale orange → mauve	Orange → mauve	Orange → blue[a]

[a] Colour fades quickly.
[b] Colour change reversed also by cyanide.

iridium. Otherwise, the introduction of another potential coordination position made little difference to the selection of metal ions reacting. Table IV describes in detail the reactions of these pyridine derivatives with palladium.

Group c: The p-dimethylaminophenyl group at the 3-position was not chromophoric, thus none of these reagents gave sensitive colour reactions with metal ions. The sulpho derivative was unstable in water, and could not be investigated further. Neither thienylidene derivative gave a detectable reaction with silver, gold or mercury(II), but the picolylidene compound produced a colloid with silver.

Group d: The oximated compound reacted similarly to 5-p-dimethylaminobenzylidenerhodanine, but the colour intensities were much reduced. It also reacted insensitively with iridium at all the pH values tested. 5-p-Dimethylaminobenzylidenethiazolidene-2,4-dione gave no detectable reaction in solution with any metal ion; on filter paper, however, it gave a pale mauve colour with gold, and a very pale pink with iridium, palladium and platinum.

Attempted solvent extraction of the silver complexes

Each reagent in Groups a and b was reacted with silver ions under the 4 pH conditions, and the solutions were then shaken with the following solvents: hexane, isobutyl methyl ketone, chloroform, di-n-butyl ether, isoamyl acetate and nitrobenzene. The behaviour of the reagents within a group was identical, but there was a marked difference between the two groups.

Group a: No extraction was observed under any conditions; interfacial precipitates were obtained in each case.

Group b: All gave yellow extracts, even when a large excess of silver was present. A radio-tracer ([110]Ag) showed, however, that no silver passed into the organic phase. Only slight (ca. 2%) extraction of silver was observed in the presence of salicylate, a possible ion-association partner for a positively charged silver complex[34]. The aqueous phase became colourless, which seemed to indicate that the complexes were weak, in direct contradiction to their resistance to strong masking agents. It was even possible to extract the reagent from a precipitated complex after it had "aged" for 3 days. Potentiometric (silver electrode) titrations failed to detect any silver binding in 50% aqueous ethanol or aqueous dioxan solution, in accordance with the results of

SOLOV'EV AND SMIRNOVA[35]. KIKUCHI *et al.*[36], however, claim to have detected, by potentiometric techniques, silver binding, albeit weaker than for 3-(H)-rhodanines. Photometric titrations were inconclusive.

DISCUSSION

Many new, sensitive reactions have been discovered, which can be recommended as worthy of development for the detection of silver, gold, palladium, copper(I), platinum and mercury(I and II). These are the reactions summarised in Table II, and especially those in Table III. 3-*n*-Propyl- and 3-(2-picolyl)-5-*p*-dimethyl-aminobenzylidenerhodanines give specific reactions with palladium at pH 9.3, and by the use of suitable masking agents, many other specific reactions could easily be devised.

It is unfortunate that, except in one instance, all the reagents gave colloidal products upon reacting with metal ions. Nor could any of the coloured species be extracted into an organic phase. This, therefore, eliminated the development of any of the compounds as improved spectrophotometric reagents for any metal ions, even though some appear to be more sensitive than FEIGL's reagent. It is of interest, however, that the sulpho derivative gave soluble complexes with silver, gold, copper(I) and palladium. This compound is, unfortunately, not very sensitive, but its existence shows that it should be possible to prepare other rhodanines containing auxochromes, of greater general sensitivity and possessing water-soluble complexes.

The nature of the "complexes" of the 3-substituted rhodanines remains unexplained. Previous work[7,9,35,36], combined with the results noted in this paper and the inability to isolate any metal ion complexes of these compounds, indicates that the reaction is certainly not simple complex formation, and that a much more extensive investigation is necessary before any firm conclusions can be drawn.

SUMMARY

Twenty-two derivatives of rhodanine were investigated as potential spectrophotometric and spot test reagents. Sensitive reactions for silver, gold, copper(I), mercury(II), palladium and some other metals are described. None of the reagents is suitable for spectrophotometry; all but one produce non-extractable, colloidal, metal–ion complexes. The introduction of a sulphonic acid group into the molecule, however, makes the complexes water-soluble.

RÉSUMÉ

Les auteurs ont examiné 22 dérivés de la rhodanine, comme réactifs d'identification et réactifs spectrophotométriques. On décrit des réactions sensibles pour l'argent, l'or, le cuivre(I), le mercure(II), le palladium et quelques autres métaux. Aucun de ces réactifs ne convient pour la spectrophotométrie. L'introduction d'un groupe sulfonique rend les complexes solubles dans l'eau.

ZUSAMMENFASSUNG

22 Derivate des Rhodanins wurden als mögliche spektralphotometrische und Tupfelreagenzien untersucht. Es werden empfindliche Reaktionen für Silber, Gold, Kupfer(I), Quecksilber(II), Palladium und einige andere Metalle beschrieben. Keines der Reagenzien ist für die Spektralphotometrie geeignet. Alle ausser einem ergeben nichtextrahierbare kolloidale Metallionenkomplexe. Die Einführung einer Sulfosäuregruppe in das Molekül macht jedoch die Komplexe wasserlöslich.

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COULOMETRIC GENERATION OF MOLYBDENUM(V)

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Several reducing agents have been generated coulometrically. Included are the generation of iron(II)[1], ferrocyanide[2], iron(II)–EDTA[3], copper(0)[4], copper(I)[5], chromium(II)[6], titanium(III)[7], tin(II)[8], uranium(V)[9] and uranium(IV)[10]. Since many of these reductants are unstable and cannot be used in volumetric titrations, coulometric generation allows the use of unstable intermediates for titrations. In addition, coulometric titrations are sensitive. By having several different reducing agents available, the appropriate system can be chosen to titrate oxidizing agents of varying oxidation potentials. By careful selection of the titrant complex mixtures may be titrated.

The present paper reports on the coulometric generation of molybdenum(V) at a platinum foil cathode. Conditions are described for 100% current efficiency. The intermediate formal potential of the molybdenum(VI)–molybdenum(V) couple makes this a potentially useful selective reducing agent. Titrations can be performed in the presence of oxygen. Estimations of the formal potential of this couple in 4 M sulfuric acid are reported.

Titrations of chromium(VI) have been performed over a wide range of sample size and generating current. The effect of common anions on the titration has been investigated.

EXPERIMENTAL

Reagent grade chemicals were used throughout. Standard chromium(VI) solutions were prepared from primary standard potassium dichromate in the usual manner. The molybdenum(VI) generating solution was prepared by adding 30.9 g of ammonium molybdate to 30 ml of water to make a slurry. The slurry was stirred very rapidly with a magnetic stirrer for 5–10 min. Then 220 ml of 4.5 M sulfuric acid were added and stirring was continued until the precipitate dissolved. Sometimes prolonged stirring (*ca.* 1 h) was required. This resulted in a 0.1 M ammonium molybdate solution in 4 M sulfuric acid (0.7 M molybdenum(V)). Other generating solutions with different concentrations of molybdenum(VI) and/or sulfuric acid were prepared in a similar manner.

Coulometric titrations at 9.65 mA or less were performed with a ChrisFeld Microcoulometric Quantalyzer, Model 6 (ChrisFeld Precision Instruments Corp., Beltsville, Md.). Titrations at greater than 9.65 mA were performed with a Sargent Coulometric Current Source, Model IV (E. H. Sargent & Co., Chicago, Ill.). All

amperometric currents were recorded automatically on a Sargent Polarograph, Model XV. The potential impressed between the indicating electrodes was supplied by this polarograph. Platinum foil generating electrodes were used. A 2 cm² cathode was used unless otherwise stated. The anode (1 cm²) was isolated from the test solution by placing it in a glass tube fitted with a sintered glass frit end; the tube contained sulfuric acid of the same concentration as in the bulk solution as anolyte. Two platinum foil electrodes (1 cm²) were used as indicating electrodes for biamperometric titrations. In amperometric titrations with a single polarized electrode, one of the platinum foil electrodes was replaced by a saturated calomel electrode (S.C.E.). The titration cell was either a 50-ml or a 100-ml beaker. Solutions were stirred with a magnetic stirrer during titrations.

Potential measurements were made with a Leeds and Northrup Potentiometer, no. 8687. Current–voltage curves were recorded on the polarograph.

Procedure

A small, unmeasured amount of chromium(VI) solution was added to the generating solution and was pretitrated to an amperometric end-point break. A potential of 300 mV was impressed between the 2 platinum indicating electrodes. If the amperometric current was erratic, molybdenum(V) was generated for a few minutes and the generating solution was changed. Following pretitration, the sample made 4 M in sulfuric acid, was added and titrated to an end-point break. The excess generation time from the pretitration was added to the end-point value[11].

RESULTS AND DISCUSSION

When molybdenum(VI) was reduced at a platinum cathode a blue color developed which indicated the formation of molybdenum(V). When excess of chromium(VI) was added to this solution, the blue color disappeared until further molybdenum(VI) was reduced to exceed the chromium(VI).

It was evident early in the investigation that a high concentration of both sulfuric acid and molybdenum(VI) was necessary for efficient reduction of the molybdenum. Molybdenum(VI) (0.7 M) was reduced in 4 M sulfuric acid and a current–voltage curve was obtained on the mixture by means of 2 platinum electrodes. A wide plateau of current was recorded from about 200 mV to 800 mV. Thus, a potential difference of at least 200 mV was required to obtain a linear increase in amperometric current in the presence of excess molybdenum(V) (*i.e.*, beyond the end-point of a titration). This was substantiated by titrations of chromium(VI). From these titrations, the sharpest end-points were found when a potential difference of at least 300 mV was used. This is the potential difference used for most of this investigation. The large potential difference required suggests some degree of irreversibility of the molybdenum(VI)–molybdenum(V) couple in this medium.

A typical titration curve is shown in Fig. 1. The initial current reading was generally large and decreased during the titration. At the end-point, a sharp minimum occurred and the current increased linearly beyond the end-point. The end-point was measured at the intersection of the extrapolated final current rise with a line drawn perpendicular to the vertex of the minimum.

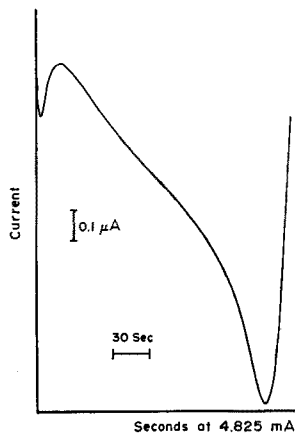The large initial current reading was the result of reduction of chromium(VI)

Fig. 1. Typical titration curve for chromium(VI).

at the indicating cathode and oxidation of water at the anode. This was shown by current–voltage curves obtained *vs.* the S.C.E. using a platinum microelectrode. While chromium(III) exhibited no anodic wave, chromium(VI) yielded a cathodic wave at about + 0.8 V, within *ca.* 200 mV of the anodic oxidation of water. The chromium wave shifted to markedly more negative potentials when the acid concentration was made more dilute. The large potential difference impressed between the platinum indicating electrodes was as great as or greater than the potential difference between these anodic and cathodic processes at the beginning of a titration in high acid concentrations; therefore, a large initial current reading was observed which decreased as the chromium(VI) was used up in the titration. This resulted in a very sharp break at the end-point. As the acid concentration was reduced, the end-point became less sharp because the potential of the chromium(VI) wave shifted to more negative values.

Often, in the first of a series of titrations, the amperometric current was very erratic. If the generating solution was replaced when this occurred, titration curves became smooth. Apparently, initial generation of molybdenum(V) preconditioned the indicating electrodes. Treatment with 6 N nitric acid sometimes helped to precondition the electrodes.

This biamperometric end-point detection could be used over a wide range of molybdenum(VI) and sulfuric acid concentrations. Therefore, the biamperometric titration of chromium(VI) was used to determine the optimum conditions under which 100% titration efficiency could be obtained.

While the molybdenum(VI) concentration was kept constant at 0.7 *M*, the sulfuric acid concentration was varied from 1 to 7 *M* and titrations were performed at 9.65 mA. A plot of titration efficiency *vs.* acid concentration is shown in Fig. 2. An acid concentration of 3 *M* or greater was necessary for 100% efficiency. Results at 7 *M* were not consistent. A concentration of 4 *M* sulfuric acid was used for the remainder of this study.

The limiting current density did not appear to vary linearly with the concentration of molybdenum(VI). It is important that the recommended concentration of
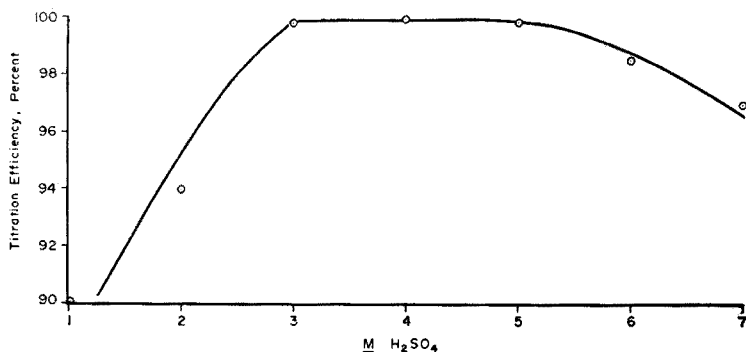
Fig. 2. Titration efficiency as a function of sulfuric acid concentration.

0.7 M molybdenum be used for all titrations. A concentration of at least 0.5 M molybdenum was necessary to form molybdenum(V) quantitatively, even at low currents. At 0.7 M molybdenum(VI) titrations could be performed up to about 50 mA with a 2 cm² generating cathode. With a 1 cm² cathode, a titration efficiency of 99.3% was found at 50 mA. It is recommended that a limiting current density of 0.05 mA/cm²/mM not be exceeded. Titrations were performed satisfactorily at 100 mA by using a 15 cm² electrode (see below). If the limiting current density is exceeded, the reduction is accompanied by formation of hydrogen gas.

After the conditions had been established under which 100% titration efficiency could be obtained, the current efficiency for the reduction of molybdenum(VI) was determined in 4 M sulfuric acid and 0.7 M molybdenum. Molybdenum(V) was generated at 9.65 mA to about 80% of the end-point value before the chromium sample was added. Then generation was continued to the end-point. For a series of 5 titrations the average end-point value was 0.1% greater than was obtained by adding the sample at the beginning of the titration (theoretical value). Therefore, the reduction of molybdenum(VI) occurs at 99.9% current efficiency under these conditions.

Amperometric end-point detection at a single polarized electrode was also investigated. A current–voltage curve for a molybdenum(VI)–molybdenum(V) mixture in 4 M sulfuric acid was recorded *vs.* the S.C.E. The anodic peak of the molybdenum(V) wave occurred at about + 0.8 V. Therefore, it should be possible to perform amperometric titrations with molybdenum(V) at a potential of + 0.9 V *vs.* S.C.E. This was indeed the case. In the titration of chromium(VI), the amperometric current remained small until beyond the end-point when a linearly increasing anodic current resulted. Titration curves, however, were not as sharp as those found using biamperometric end-point detection and therefore this latter system is preferred.

In the current–voltage curve recorded above, the cathodic reduction wave of molybdenum(VI) occurred at about 150 mV more negative than the oxidation wave for molybdenum(V). This confirms the results reported above which indicated a significant irreversibility of this system.

Chromium(VI) samples were titrated using the recommended procedure. Results are shown in Table I. Titrations were performed from 96.5 to 0.965 mA. When the pretitration procedure described was used, it was important that the sample was

TABLE I

TITRATIONS OF CHROMIUM(VI) IN 4 M SULFURIC ACID AND 0.7 M MOLYBDENUM

(The generating cathode was 2 cm² except for titrations at 96.5 mA when a 14 cm² electrode was used)

mg Cr taken	mg Cr found	mA	mg Cr taken	mg Cr found	mA
15.06	15.11	95.6	0.5021	0.5026	9.65
15.06	15.01	95.6	0.5021	0.5016	9.65
15.06	15.10	95.6	0.5021	0.5031	9.65
15.06	15.08	95.6	0.5021	0.5001	9.65
Ave.	15.08		0.5021	0.4986	9.65
Mean error = + 0.013%			0.5021	0.4976	9.65
Std. devn. = 0.046 mg			0.5021	0.5031	9.65
			Ave.	0.5010	
5.032	5.032	48.25	Mean error = − 0.22%		
5.032	5.067	48.25	Std. devn. = 0.0022 mg		
5.032	5.063	48.25			
5.032	5.039	48.25	0.5021	0.5029	4.825
5.032	5.036	48.25	0.5021	0.5004	4.825
Ave.	5.047		0.5021	0.5006	4.825
Mean error = + 0.30%			0.5021	0.5001	4.825
Std. devn. = 0.015 mg			0.5021	0.5033	4.825
			Ave.	0.5015	
0.954	0.948	9.65	Mean error = − 0.12%		
0.954	0.954	9.65	Std. devn. = 0.0015 mg		
0.954	0.954	9.65			
0.954	0.955	9.65	0.05109	0.05064	0.965
0.954	0.962	9.65	0.05109	0.05169	0.965
Ave.	0.955		0.05109	0.05044	0.965
Mean error = + 0.10%			0.05109	0.05169	0.965
Std. devn. = 0.005 mg			Ave.	0.05112	
			Mean error = + 0.059%		
0.954	0.948	4.825	Std. devn. = 0.00052 mg		
0.954	0.953	4.825			
0.954	0.955	4.825			
0.954	0.952	4.825			
0.954	0.953	4.825			
Ave.	0.952				
Mean error = − 0.20%					
Std. devn. = 0.0026 mg					

approximately 4 M in sulfuric acid to prevent dilution of the generating solution acid with a corresponding decrease in titration efficiency.

All the above titrations were performed in the presence of oxygen. Apparently, air oxidation of molybdenum(V) is slow. The fact that air oxidation of reduced molybdenum was negligible indicates that no lower oxidation states of molybdenum were formed since these would be expected to be easily air-oxidized.

The effect of some common anions on the titration was determined. Results are summarized in Table II. Perchlorate and orthophosphate ions had no appreciable effect on the titration. Chloride ions (1 M) did not affect the titration efficiency but did cause a large increase in the initial amperometric current due to oxidation to chlorine at the indicator anode. This resulted in an even sharper break at the end-point if the sensitivity of the polarograph was kept constant. The amperometric current remained off-scale until near the end-point. This effect of chloride ion could be used to advantage to obtain very sharp end-point breaks. Nitrate ion resulted in large positive errors. Apparently, in this highly acidic medium, the molybdenum(V) was

TABLE II
EFFECT OF ANIONS ON THE TITRATION OF CHROMIUM(VI) WITH ELECTROGENERATED MOLYBDENUM(V)
AT 4.825 mA

Anion	Concentration (M)	Theor. sec.	Sec. found
—	—	100.0	99.7
Chloride	1.0	100.0	99.7
Perchlorate	1.0	100.0	99.5
Orthophosphate	1.0	100.0	100.8
Nitrate	0.1	100.0	115.5
Nitrate	1.0	100.0	126.3

partially oxidized by nitrate, resulting in decreased titration efficiency. Thus, nitrate ions must be removed from the sample before titration; this presents no problem since nitric acid is easily volatilized from sulfuric acid.

The formal potential of the molybdenum(VI)–molybdenum(V) couple in 4 M sulfuric acid was estimated by preparing a solution containing a 1/1 ratio of molybdenum(VI)/molybdenum(V). One-half of the molybdenum(VI) solution was reduced with vanadium(II) formed by passage of vanadium(V) through a Jones reductor. The approximate concentration of each of the molybdenum species was 0.1 M. The potential of this mixture was determined to be + 0.55 V $vs.$ N.H.E. The standard potential of this couple in 2 M hydrochloric acid is reported to be + 0.53 V $vs.$ N.H.E.[12]. Thus, the potential does not vary appreciably between these two acid systems. The formal potential of the molybdenum couple involved in the coulometric reduction of molybdenum(VI) was estimated from a potentiometric titration of cerium(IV) coulometrically. The end-point potential was + 0.98 V $vs.$ N.H.E. The standard potential of the cerium(IV)–cerium(III) couple in 1 M sulfuric acid is + 1.44 V $vs.$ N.H.E. Assuming this to be the formal potential in 4 M sulfuric acid, and using the observed end-point potential, the formal potential of the molybdenum system was calculated to be + 0.52 V $vs.$ N.H.E. The closeness of this value to the measured potential of the molybdenum(VI)–molybdenum(V) couple lends support to the postulation that the major product in the coulometric reduction of molybdenum(VI) is molybdenum(V).

A comparison of the potential of this system with those of other reducing agents generated coulometrically shows that it is intermediate in value and should prove useful as a selective reducing agent. The potential of the iron(III)–iron(II) system, which is more weakly reducing than the molybdenum system, is about + 0.77 V. Nearly all other coulometrically generated reductants are stronger reducing agents than molybdenum(V) with potentials in the order of + 0.3–+ 0.1 V. An exception is the copper(II)–copper(I) couple in hydrochloric acid medium which possesses a potential close to the molybdenum couple (+ 0.51 V). With this system, care must be taken to prevent oxidation of the chloride ions to chlorine by the sample[5]. The molybdenum system does not possess this disadvantage and a wider range of oxidants can be titrated.

SUMMARY

Molybdenum(V) was generated at a platinum cathode from 0.7 M molybdenum(VI) in 4 M sulfuric acid. A current efficiency of 99.9% was attained. A limiting

current density of 0.05 mA/cm²/mM was found. The formal potential of the Mo(VI)–Mo(V) couple in 4 M sulfuric acid was determined to be *ca.* 0.55 V *vs.* N.H.E. Chromium(VI) solutions were titrated over a wide range of sample size and generating current. Amperometric titration curves were interpreted from current–voltage curves. Titrations could be performed in the presence of oxygen at the 1 μeq. level. The effect of nitrate, perchlorate, orthophosphate, and chloride ions on the titration was determined.

RÉSUMÉ

Le molybdène(V) est coulométriquement formé à une électrode de platine, en utilisant une solution de molybdène(VI) 0.7 M dans l'acide sulfurique 4 M; on obtient un rendement en courant de 99.9%. Densité de courant limite de 0.05 mA/cm²/mM. Le potentiel du couple Mo(VI)/Mo(V), dans l'acide sulfurique 4 M est d'environ 0.55 V *vs.* ENH. Des solutions de chrome(VI) ont été titrées. Des courbes de titrage ampérométrique ont été interprétées à partir des courbes courant–voltage. Enfin, on a examiné l'influence des ions nitrates, perchlorates, orthophosphates et chlorures.

ZUSAMMENFASSUNG

Molybdän(V) wurde an einer Platinkathode aus einer 0.7 M Molybdän(VI)-Lösung in 4 M Schwefelsäure erzeugt. Es wurde dabei eine Stromausbeute von 99.9% erzielt und eine Grenzstromdichte von 0.04 mA/cm²/mMol gefunden. Mo(VI)–Mo(V) in 4 M Schwefelsäure besitzt ein Potential von etwa 0.55 V gegen die normale Wasserstoffelektrode. Chrom(VI)-Lösungen wurden titriert. Die Titrationen liessen sich in Gegenwart von Sauerstoff in der Grösse eines Mikroäquivalents durchführen. Der Einfluss von Nitrat-, Perchlorat-, Orthophosphat- und Chloridionen auf die Titration wurde bestimmt.

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THE ATOMIC ABSORPTION SPECTROSCOPY OF CHROMIUM

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In recent years atomic absorption spectroscopy has become an increasingly important tool in trace metal analysis. High sensitivity, ease of sample preparation, and the reduction of interference from associated cations are the chief reasons for this trend. In most cases, however, the concentration of the trace metals, especially in biological samples, is too low to determine directly in aqueous samples.

The use of organic solvents to increase sensitivity has been studied by several workers[1-3]. When solvents miscible with water were used, the small increase in intensity was offset by the accompaning dilution of the sample. ALLAN[2] has made a comprehensive study of extraction into solvents immiscible with water. He found with esters and ketones that there was no absorption due to the solvents and that the flame was steady. He studied the absorption of copper, zinc, manganese, and iron and found a maximum increase of about seven-fold in sensitivity.

ALLAN[3] has also determined the copper content in soil extracts and plant ash. Due to the low concentration levels in these samples he found it necessary to concentrate the copper by chelation with ammonium pyrrolidine dithiocarbamate followed by extraction into methyl isobutyl ketone. WILLIS[1] has studied solvent extraction for the determination of traces of heavy metals in urine. He used ammonium pyrrolidine dithiocarbamate as the chelating agent for lead, mercury, bismuth, nickel, zinc, and cadmium. The chelate was then extracted into methyl *n*-amyl ketone. Although the limit of detection for lead in aqueous solution is about 0.5 p.p.m., by this non-aqueous method it was possible to determine as little as 0.01 p.p.m. of lead with a standard deviation of 0.002 p.p.m. WILLIAMS, DAVID AND IISMAA[4] have studied the chromium content of feces by atomic absorption spectroscopy. They worked over a chromium range of 0.8–70 p.p.m. using aqueous solutions.

The present paper concerns the study of the optimum conditions and the development of a sensitive method for the determination of chromium by atomic absorption spectroscopy. The limit of detection of chromium was studied in water, acetone, ethanol, ether, and methyl isobutyl ketone to find the most suitable solvent. The effect of fuels, fuel pressure, and burner height on the intensity was also investigated.

EXPERIMENTAL

Reagents

Reagent grade chemicals were used without further purification. A standard stock solution containing 50 μg of chromium(VI) per ml was prepared from primary standard potassium dichromate. Working standards of chromium(VI) containing 0.1–10 μg/ml were prepared by dilution of this stock solution just before use. All water used to prepare the standard solutions was distilled through an American Sterilization Co. Spanish Dungeon triple still and was then deionized on a column containing Amberlite IRC-120 cation exchanger plus Amberlite IRA-400 anion exchanger. The water was also distilled from an alkaline permanganate solution in all-glass apparatus to remove any reducing impurities present.

A standard chromium(III) stock solution containing 50 μg/ml was prepared by dissolving chromium metal (99.9%) in concentrated hydrochloric acid which was distilled before use. Working standards of chromium(III) containing 0.1–10 μg/ml were prepared by dilution of the stock solution as above.

Apparatus

All atomic absorption measurements were made with a Jarrel-Ash atomic absorption spectrophotometer (Model 83-000). This model is equipped with 3 Beckman flame spectrophotometer burners to increase the path length; it is designed to allow 5 light passes through the flames. The oxy–hydrogen or air–hydrogen flame was used for these studies. The light source was a chromium hollow-cathode lamp supplied by the Jarrel-Ash Company. All absorption measurements were recorded on the Bristol recorder supplied with the spectrophotometer; the 3479-Å line of chromium was used for measurements. The instrument was operated at maximum sensitivity using scale expansion techniques to increase the signal.

Procedure

A. Direct. In the case where there was no extraction, the solutions were prepared in the organic solvents and aspirated directly into the flame by means of a small porcelain boat.

B. Extraction, Cr(VI). No oxidation was carried out when the chromium was present as chromium(VI). A chilled dichromate solution (*ca.* 10 ml) was added to a 25-ml separatory funnel. Two ml of cold concentrated hydrochloric acid was then added followed by 5 ml of cold methyl isobutyl ketone. The mixture was shaken for about 30 sec and the ketone layer was separated. The ketone solution was then aspirated into the flame. If the solution was too concentrated, it was diluted with additional ketone.

C. Extraction, Cr(III). Two ml of sulfuric acid (approximately 4 M) was added to a chromium(III) solution (*ca.* 10 ml) in a 50-ml beaker which was being gently heated on a hotplate. To this solution was added 0.1 N potassium permanganate until a pink color persisted. The solution was cooled and the extraction was carried out as above.

In this manner standards containing from 0.020 to 0.5 p.p.m. of chromium were prepared and used for a calibration curve to compare the accuracy of the oxidation and extraction methods.

RESULTS AND DISCUSSION

Solvent effects

Most of the common methods for the determination of trace amounts of chromium are colorimetric and depend on the development of a violet color with diphenylcarbazide[5]. The drawbacks of colorimetric procedures at these low levels are well known.

Water, ethanol, ether, acetone, and methyl isobutyl ketone were investigated for use as possible solvents to obtain maximum sensitivity in the determination of chromium. Some typical absorption curves for chromium in methyl isobutyl ketone are shown in Fig. 1 and are compared to curves obtained on the solvent in the
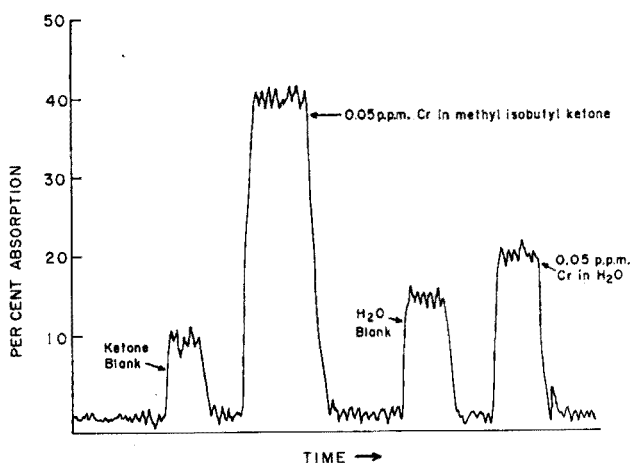
Fig. 1. Typical atomic absorption curves for chromium in water and in methyl isobutyl ketone.

absence of chromium. In all cases, the organic solvent blanks were smaller than the corresponding aqueous blanks.

It has been shown that methyl isobutyl ketone quantitatively extracts chromium(VI) even at very low levels[6]. All extractions in the present work were carried out with this solvent.

The ketone will extract chromium that is present in the hexavalent oxidation state. Therefore, if chromium(III) is present, it must be oxidized to chromium(VI) prior to extraction. There are many reagents available for this oxidation[7]. Potassium permanganate was chosen because the completion of the oxidation is apparent when the pink color persists. This is another advantage of atomic absorption techniques over colorimetric techniques. In the latter, it is necessary to destroy any excess oxidant (without reducing the chromium) since the excess oxidant will react with the diphenylcarbazide reagent. In the present case, extraction of the chromium can be carried out in the presence of excess permanganate without any adverse effects.

The sensitivity of chromium in the various solvents was determined. The

concentration of chromium required to give a 5% absorption above the blank is given in Table I. The absorption due to the blank is also given. The lower limit of detection of 5% was chosen rather than the 1% recommended by most workers; at the high sensitivity settings, the noise level is much greater.

It is evident that maximum sensitivity is obtained in diethyl ether or methyl isobutyl ketone. For practical work methyl isobutyl ketone would be far superior since it quantitatively extracts the chromium and does not dilute the chromium, but concentrates it. The reasons for the great increase in sensitivity of the organic solvents have been discussed previously by ALLAN[2,3].

TABLE I

CONCENTRATION OF CHROMIUM FOR A
5% ABSORPTION ABOVE BLANK

Solvent	Cr concn. (p.p.m.)
Water	0.038
Acetone	0.025
Ethanol	0.030
Ether (diethyl)	0.008
Methyl isobutyl ketone	0.006

TABLE II

RECOVERIES OF CHROMIUM(III)
(Extracted into 5 ml methyl isobutyl ketone)

Cr(III) taken (μg)	Recovery (%)
0.20	94
0.20	93
0.20[a]	102
0.40	96
0.40	94
0.40[b]	55
0.40[b]	60
0.30[c]	91
0.30[c]	89

[a] Two extractions with 5 ml of ketone.
[b] Solution not cooled before extraction.
[c] Extraction into 10 ml of ketone.

Fuel and burner effects

That a flame possesses definite zones differing in temperature and reducing and oxidizing conditions is well known. Therefore, the number of atoms in a sample
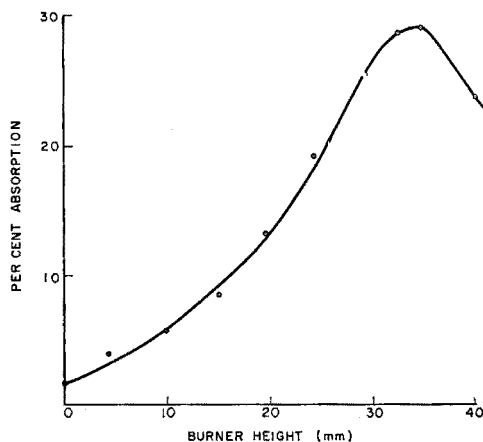
Fig. 2. Relationship between percent absorption and burner height for chromium.

which are in the ground state will be different in the various zones. A maximum is thus expected at a certain height in the flame. A plot of percent absorption *vs.* burner height illustrates this (see Fig. 2).

Both the oxy–hydrogen and air–hydrogen flames were used in this study. It was found that the air–hydrogen flame was much more sensitive in the determinations. This is to be expected from the theoretical principles of atomic absorption spectroscopy. Since absorption occurs in the ground state, it follows that as the temperature of the flame increases, the number of atoms in the ground state decreases causing a decrease in the absorption.

The effects of fuel and air pressure on the absorption were also studied. The results are tabulated in Fig. 3.
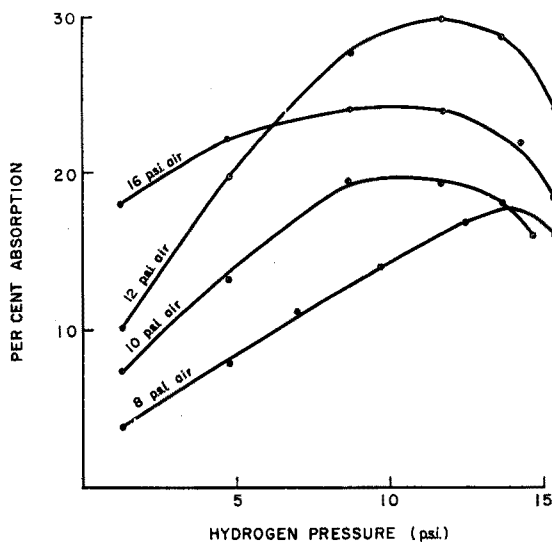
Fig. 3. Relationship between percent absorption and hydrogen and air pressure.

Recoveries

Figure 4 shows the calibration curves for chromium(VI) in methyl isobutyl ketone, chromium(VI) in aqueous solution extracted into methyl isobutyl ketone, and chromium(III) oxidized and extracted into methyl isobutyl ketone. There is generally good agreement among the curves.

Table II shows recoveries of chromium(III) under various conditions. The loss of chromium when it is extracted at higher temperatures is probably due to some partial oxidation of the ketone by the permanganate. This would tend to increase the viscosity, thereby effectively reducing the amount of solvent aspirating in the flame and resulting in apparent loss of chromium. It was observed that when extractions were carried out at higher temperatures, the ketone did indeed become more viscous.
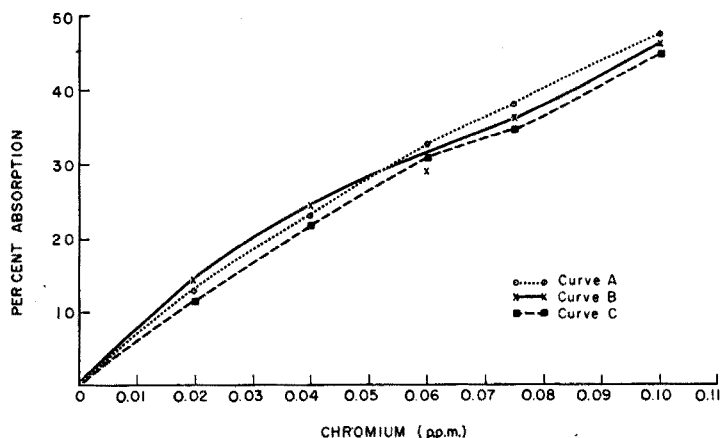
Fig. 4. Calibration curves for chromium in methyl isobutyl ketone. Curve A, Cr(VI) in methyl isobutyl ketone; Curve B, Cr(VI) in aqueous solution extracted into methyl isobutyl ketone; Curve C, Cr(III) oxidized and extracted into methyl isobutyl ketone.

SUMMARY

Conditions were studied for the determination of trace amounts of chromium by atomic absorption spectroscopy. Solution matrix, flame composition, and extraction procedures were the variables studied. A detection limit of 0.006 p.p.m. of chromium was observed with an air–hydrogen flame and methyl isobutyl ketone as the solvent.

RÉSUMÉ

On a étudié les conditions de dosage de traces de chrome, par spectroscopie par absorption atomique. On est arrivé à une limite de détection de 0.006 p.p.m. de chrome, avec flamme air–hydrogène et isobutylcétone comme solvant.

ZUSAMMENFASSUNG

Es wurden die Bedingungen zur Bestimmung von Spuren Chrom mittels der atomaren Absorptionsspektroskopie untersucht. Dabei wurden die Lösungsmatrix, die Flammenzusammensetzung und die Extraktionsverfahren variiert. Es wurde mit einer Luft–Sauerstoff-Flamme und Methylisobutylketon als Lösungsmittel eine Nachweisgrenze von 0.006 p.p.m. Cr gefunden.

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X-RAY SPECTROGRAPHIC DETERMINATION OF TANTALUM IN NIOBIUM BY ELECTRON EXCITATION*

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The determination of traces of tantalum in niobium is of great interest in the atomic energy field, where tantalum is an undesirable element, owing to its thermal neutron-absorption cross-section. Thus during the last 10 years, many X-ray spectroscopic investigations have been made, in order to extend the limit of sensitivity for tantalum as far as possible.

In the niobium–tantalum system, with common analyzing crystals, the second-order K reflection of niobium interferes with the strongest tantalum line, and so a trace determination presents some difficulties. To overcome this, several suggestions have been made. BIRKS AND BROOKS[1] proposed the use of (a) fine collimation to resolve the overlapping second-order Nb line, (b) comparison of the integrated intensity of an unresolved tantalum–niobium doublet with the integrated intensity of a resolved niobium line, and (c) lowering the X-ray tube voltage to excite only the tantalum L spectrum without exciting the niobium K spectrum. BRISSEY[2] used a bent mica crystal to resolve the Ta I Lα I line from the second-order Nb Kα line, but the intensity was only moderate. LUBLIN[3] proposed the use of analyzing crystals which give no second-order reflection, such as germanium and silicon. MEUNIER AND SERGANT[4] utilized the TaI Lγ1 line as the analytical line, but the limit of detection was found to be only 2500 p.p.m. Ta. The lowest limit of detection reported to date[5] is about 250 p.p.m. Ta.

The present investigation was designed in order to discover what limit of detection could be obtained by direct electron excitation. This method consists of placing the sample to be analyzed in the X-ray tube on the surface of the target and analyzing the radiation emitted by the elements. The intensity of the emitted radiation is about 100–1000 times greater than that of the fluorescent radiation. On the other hand, owing to the continuous spectrum, a much higher background is obtained than with the X-ray excitation. Direct emission spectroscopy was first applied to analysis in 1930 by VON HEVESY[6]. More recently this method has been used in electron probe microanalysis[7,8]. However, very few macroanalyses have been made, although the investigations done at the CGR[9,10] and by Fox[11] should be mentioned.

EXPERIMENTAL

Equipment

The apparatus used was a Direct Emission Spectrograph of the "Compagnie Générale de Radiologie", Paris. A demountable tube is used. Metallic or solid samples are placed directly in a slit machined in a normal coppei anode. Since the anode is rotatable under vacuum, 6 different samples can be analyzed successively without breaking the vacuum. Powdered samples are, if necessary, previously mixed with spectrographically pure graphite (to make the surface conducting for the electrons) and pressed to suitable dimensions. Either curved crystals or flat crystal optics can be used.

The vacuum pumping system consisted of a rotating pump (output 2 m³/h), a small mercury diffusion pump (output 8 l/sec), and an oil diffusion pump (output 120 l/sec). Changing from one series of 6 samples to another series was made with an interval of only a few minutes, owing to a bypass and fore-vacuum system. The sample surface irradiated could be chosen between 5 × 1 mm and 1 × 1 mm. For a complete description see BENS[12].

Sample preparation

The metallic samples were cut in small (10 × 16 mm) sheets with a thickness of 1 mm. This sample thickness had to be within ± 0.1 mm, otherwise the distance between the sample and the filament varied too much from one sample to another, causing errors in the intensity measurements. Furthermore, if the sample thickness was much less than 1 mm, the focussing conditions were no longer optimal, resulting in a great loss of intensity. The samples were all polished, using a 50-μ diamond paste, to avoid surface contamination and obtain a better reproducibility. The niobium–tantalum samples were furnished by Pechiney*; these alloys were prepared by fritting the powder mixtures, after which the fritted rods were flattened to a sheet.

Study of optimum conditions

The direct emission spectrograph equipped with the curved crystal optics, scintillation counter and discriminator was used.

The background measured at $\theta = 22.9$ and $\theta = 21.2$ was subtracted from the tantalum $L\alpha$ 1 line, after interpolation. The curved crystal optics gave a net intensity about 3 times greater than the flat crystal. A complete list of the experimental conditions is given in Table I.

TABLE I

APPARATUS AND SPECTROGRAPHIC OPERATING CONDITIONS

Equipment	C.C.R. Direct Emission Spectrograph
Filament	Re
Sample surface irradiated	5 × 1 mm
Excitation conditions	24 kV, 0.1 mA
Crystal	LiF curved, crystal radius $R = 750$ mm
Collimator	1 mm slit before crystal
Detector and operator voltage	Scintillation Counter at 1100 V
Discrimination	Base level: 10 V, window width 40 V
Counting cycle	Fixed time, counting time 100 sec

* Pechiney, Centre de Recherches Métallurgiques de Chambery, France.

To find the optimum excitation conditions in order to detect the minimum possible concentration, the following points were considered. By defining the limit of detection as the peak height above the background which is at least 3 standard deviations of the background[13], one obtains the expression for the limit of detection:

$$LD = \frac{3n}{R\sqrt{BT}}$$

where $R = P/B$, P is the intensity of the peak in counts per sec (cps) after subtraction of the background, B is the intensity of the background in cps, T is the counting time in sec, and n is the concentration of the element in p.p.m.

Thus the excitation conditions where $R\sqrt{B}$ has the greatest value, are optimal for the detection of the lowest possible concentration[14,15]. In Figs. 1 and 2 and in
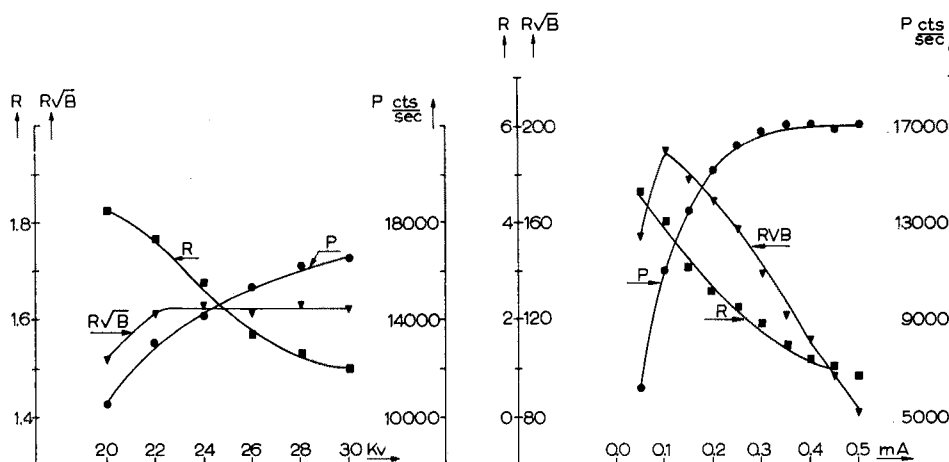
Fig. 1. Effect of anode voltage on sensitivity factor. Electron current constant: 0.1 mA.

Fig. 2. Effect of electron current on the sensitivity factor. Anode voltage constant: 20 kV.

TABLE II

SENSITIVITY FACTORS FOR DIFFERENT DETECTORS

Detector	$\frac{P-B}{B}$	$R\sqrt{B}$	P (cps)
Scint. counter	1.3	120	20,800
Scint. counter+discr.	1.9	143	16,800
Flow + discr.	1.2	54	4,500

Table II this criterion, which may be called the sensitivity factor, is shown together with the peak-to-background ratio and the total peak intensity for different experimental conditions. It can be concluded that excitation conditions of 24 kV and 0.1 mA and the scintillation counter with discriminator should be employed. Figure 1 was obtained by changing the anode voltage in a stepwise manner from 20 to 30 kV, at a constant electron current of 0.1 mA; Fig. 2 was obtained by changing the anode current from 0.1 to 0.5 mA with a constant anode voltage of 20 kV. Figure 1 shows

clearly that when the voltage reaches a value about twice the excitation potential of the Ta L spectrum ($E_V = 11.7$ kV) the sensitivity factor, R_l/B, shows no further significant increase. Although the Nb K spectrum is excited ($E_V = 19.0$ kV) at a tube voltage of 24 kV, the Ta Lα line is still clearly separated from the second-order niobium K line, as can be seen from Fig. 3.
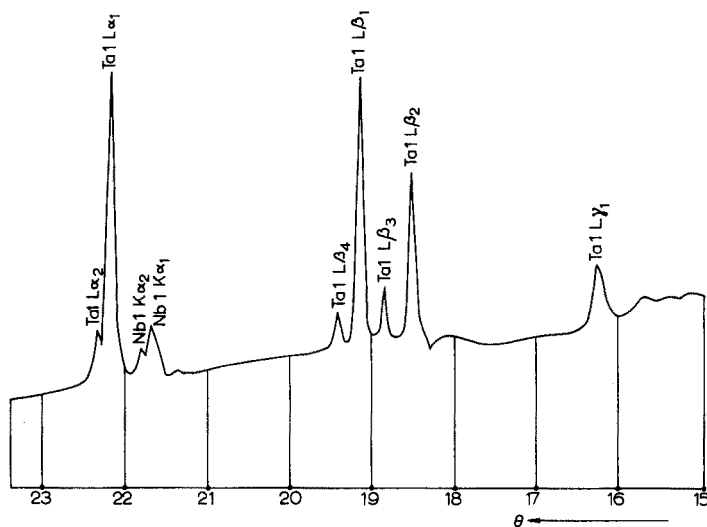

Fig. 3. X-Ray spectrographic chart record obtained from a niobium sample with about 3% of tantalum. Experimental conditions as in Table I except for scintillation counter, 1000 V, scanning speed 4 min/θ, full scale $3 \cdot 10^4$ cps, without discriminator.

RESULTS

Since niobium samples containing tantalum in the trace range (1–1000 p.p.m.) were not available, no calibration curve in the trace range could be established; some "pure" niobium samples which were supplied contained 4000 to 5000 p.p.m. Ta.

However, since the calibration curve obtained for the 0.4–5% Ta region passed through the origin, the limit of sensitivity could be determined, which was the main purpose of the investigation. The limit of detection calculated from the results obtained from a niobium sample containing 4500 p.p.m. of tantalum, with a counting time of 400 sec, was found to be 20 p.p.m. This is about a 12-fold increase in sensitivity compared with the best results reported previously, in which an X-ray fluorescent unit was used.

Quantitative X-ray spectroscopic analysis with electron excitation is becoming popular, but very little is known about the precision, comparison with other methods, analysis time, etc. In the present work, the precision in the 0.4–5% concentration range was found to be ±2%, which appears to be of the same magnitude as that found in X-ray fluorescence analysis[16]. Results obtained by X-ray direct emission spectroscopy showed good agreement with those found by optical emission spectroscopy. The time for a single determination, including sample preparation, was about 1 hour. Polishing the samples was found to be absolutely necessary; the

critical thickness is much smaller than in fluorescence excitation, so that the contribution of the surface layer to the intensity of the fluorescent radiation becomes predominant.

CONCLUSIONS

Direct electron excitation gives a considerable lower limit of detection for tantalum in niobium than X-ray fluorescence. The relatively long analysis time for a single determination (about 1 hour) is principally due to the sample preparation (40 min), as the metallic samples have to be cut in sheets (16 × 10 mm) with a thickness of 1 ± 0.1 mm. This is not a fundamental disadvantage, because the sample holder system can be changed without great difficulty, so that the thickness may vary between 1 and 15 mm; this reduces the complete analysis time to 30 min.

A further difficulty is that a small layer of rhenium is formed on the sample surface during the analysis by evaporation of the filament. However, if all the samples are left for exactly the same time under the electron bombardment, quantitative analyses are readily possible and a good precision can be obtained. The limit of detection for a second series of samples increases slightly if the same standards are used, because of absorption of the radiation by the rhenium layer. Accordingly, for trace analysis, a new set of standard samples should be used with the second series of samples, or the electron bombardment should be carried out on another position of the original standard sample surface. A much better solution to the problem is to deflect the electron beam from a helical rhenium (or tungsten) cathode, situated below the anode as used by HENKE[17]; in this way the contamination by the filament can be eliminated.

SUMMARY

An X-ray method is proposed for the determination of tantalum in niobium by direct electron excitation. The optimum excitation conditions for greatest sensitivity are given. The limit of detection for a counting time of 400 sec was found to be 20 p.p.m. The relative standard deviation in the 0.4–5% concentration range was ±2%.

RÉSUMÉ

Une méthode aux rayons-X est proposée pour le dosage du tantale dans le niobium, par excitation électronique directe. Les conditions d'excitation optimum pour une sensibilité la plus grande sont données. La limite de détection pour un temps de comptage de 400 sec est de 20 p.p.m. La déviation standard relative pour des concentrations de 0.4 à 5% est de ±2%.

ZUSAMMENFASSUNG

Für die Bestimmung von Tantal in Niob wird die Röntgenspektralanalyse mit

Primäranregung vorgeschlagen. Es werden die optimalen Anregungsbedingungen für die grösste Empfindlichkeit angegeben. Die Nachweisgrenze beträgt bei einer Zählzeit von 400 Sek 20 p.p.m. Die Standardabweichung lag im Konzentrationsbereich von 0.4 bis 5% bei ±2%.

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CHARACTERIZATION AND ROUTINE DETERMINATION OF CERTAIN NON-BASIC NITROGEN TYPES IN HIGH-BOILING PETROLEUM DISTILLATES BY MEANS OF LINEAR ELUTION ADSORPTION CHROMATOGRAPHY

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Great interest currently exists in the identification and determination of the various nitrogen compound types occurring in petroleum. This is especially true of the non-basic nitrogen compounds found in high-boiling fractions (400° F+), since these nitrogen compounds generally account for most of the nitrogen in a crude oil. A previous paper[1] from this laboratory has described the identification and routine determination of the non-nitrogen-substituted indoles, carbazoles, and benzcarbazoles (indole derivatives) in cracked petroleum gas oils (400–1000° F). Carbazole[2] and the alkyl carbazoles and indoles[3,4] have also been reported in straight-run petroleum distillates, and the similar occurrence of the benzcarbazoles in heavy straight-run distillates is suggested by analogy. Alternatively, it has been proposed[5] that the non-basic nitrogen compounds in crude oil are primarily amides, on the basis of the titration and chemical reduction of certain Russian crude oils. Compounds of this general type (*e.g.* quinolones, benzquinolones) have since been conclusively identified by COPELIN[6] in the gas oil fraction from a California crude. More recently, OKUNO *et al.*[7] have shown that a number of crude oils from the United States contain large concentrations of non-basic nitrogen compounds other than amides. These latter workers have also proposed a new classification of crude oil nitrogen on the basis of a titration–reduction procedure: strong bases (type A) titratable in acetic acid; additional weak bases (type B) titratable in acetic anhydride; residual non-basic nitrogen (type C), which includes the carbazoles and benzcarbazoles. The type B compounds are further broken down into types B_1, B_2, B_3 according to whether reduction with lithium aluminium hydride converts the original type B compounds into types A, C, or B, respectively.

Our routine procedure for determining the indole derivatives in cracked samples fails when applied to certain straight-run distillates, because straight-run and cracked carbazoles differ in their ultraviolet absorptivities and chromatographic properties. A method for the routine determination of the indole derivatives in straight-run distillates is of obvious interest *per se*, and would assist in resolving the above controversy over the nitrogen types occurring in petroleum. Additionally the direct determination of the indole derivatives in petroleum provides an indirect check on the general validity of the OKUNO *et al.*[7] nitrogen-type procedure, and also furnishes information on the remaining non-basic (type C) nitrogen types in petroleum.

The present paper describes the search for the individual indole derivatives in the gas oil fractions from a California crude oil, the development of accurate routine procedures for determining each of the indole derivative types in straight-run gas oils (400–1000° F), and the determination of the relative amounts of these indole derivatives in several crude oil fractions of interest.

EXPERIMENTAL

Routine determination of indole derivatives in straight-run distillates

   Reagents. These were exactly as described earlier[1].

   Procedure. The indole derivatives (except N-alkyl substituted) in light (400–700° F) straight-run gas oils were determined exactly as in the case of cracked samples (mode A[1]). Nitrogen as carbazoles and benzcarbazoles in heavy (400–1000° F) straight-run distillates was determined as follows. Approximately 0.5 g of sample was weighed into a 5-ml volumetric flask and brought to the mark with benzene. Approximately 0.2 g of the air-dried cation-exchange resin[1] was added. The flask was shaken by hand at 5–10-min intervals for 15–60 min from the time the resin was added, and the supernatant solution was used as sample for the following LEAC separation within 1 h of final shaking. The time required to remove all basic nitrogen from the sample varied with different batches of ion-exchange resin for unknown reasons, and each batch of resin had therefore to be standardized. With any light, catalytically cracked gas oil, the shaking time required for 98% + removal of basic nitrogen (followed by titration) could be determined, and the resulting time used in routine nitrogen-type determinations with that resin batch.

   A portion (250 μl) of the treated sample solution was charged to a dry 400 × 8 mm column of 2% H_2O–Al_2O_3 in the usual manner[8]. Elution was begun with 40% (v/v) methylene chloride–pentane and a 10-ml fraction was collected and rejected. A second 40-ml fraction (B) was collected in a 50-ml flask to which 10 ml of 40% (v/v) methylene chloride–pentane had been added. Eluant was changed to methylene chloride, and a final 100-ml fraction (C) was collected. The ultraviolet (U.V.) absorbance of the B fraction was determined in 1-cm cells at 275, 292, and 305 mμ (A_{275}^B, A_{292}^B, and A_{305}^B) *vs.* 40% (v/v) methylene chloride, and the absorbance of the C fraction was determined at 292 and 305 mμ (A_{292}^C and A_{305}^B) *vs.* methylene chloride. The wt. percent nitrogen as carbazoles in the sample was given by

$$\%N_c = (3.08\,A_{292}^B - 1.23\,A_{275}^B - 1.23\,A_{305}^B)/\text{wt.} + (16.4\,A_{292}^C - 18.1\,A_{305}^C)/\text{wt.} \qquad (1)$$

and the percent benzcarbazoles by

$$\%N_{bc} = (12.2\,A_{305}^C - 3.8\,A_{292}^C)/\text{wt.} \qquad (2)$$

where wt. is the weight in mg of the sample charged to the column (equal to grams of sample in original 5-ml dilution · 50).

   Samples with low nitrogen contents (< 0.05%) and end-points above 900° F may give high results by the present method, due to interference from other sample components. This possibility can be evaluated for such samples from the spectrum of the C fraction between 275 and 300 mμ. An absence of definite absorption maxima at 280 and 292 mμ is evidence for high carbazole and benzcarbazole nitrogen values.

DISCUSSION OF RESULTS

Unsuitability of a previous nitrogen-type method when applied to straight-run heavy distillates

In the routine determination of the indole derivatives in cracked gas oils[1], the sample is first freed of interfering basic nitrogen compounds by cation exchange and the indole derivatives are isolated by microscale linear elution adsorption chromatography (LEAC) over alumina. The resulting indole derivatives fraction is analyzed for each nitrogen type (indoles, carbazoles, benzcarbazoles) by U.V. spectrophotometric analysis. Alternatively, the indole derivatives can be isolated from the sample in weighable amounts by means of similar large-scale separation procedures. Nitrogen type can then be determined either by low-voltage mass analysis or elemental nitrogen analysis on the indole derivative fraction. Table I summarizes the application of each of these procedures to a heavy gas oil fraction (660–1000° F) from a virgin California crude, subsequently referred to as crude oil A. The low-voltage mass analysis of the indole derivatives fraction from this sample is shown in Table II. Alkyl and cycloalkyl carbazoles and benzcarbazoles predominate, as in the case of similar fractions separated from cracked gas oils. The first two non-routine procedures of Table I (mass, elemental nitrogen) gave similar values for total nitrogen as carbazoles plus benzcarbazoles in the sample (0.144, 0.137%). However, the routine procedure for cracked samples gave a low result for carbazole nitrogen. This discre-

TABLE I

ANALYSIS OF NITROGEN TYPE IN THE HEAVY GAS OIL (600–1000° F) FRACTION FROM A CALIFORNIA CRUDE A

Method	Nitrogen (wt-%)		
	Carbazoles	Benzcarbazoles	Sum
Non-routine			
Large scale - mass	0.100	0.044	0.144
Large scale - elemental analysis	—	—	0.137
Routine			
Cracked gas oil method[a]	0.052	0.043	0.095
Straight-run gas oil method[b]	0.083	0.044	0.127

[a] Ref. 1.
[b] Present paper.

TABLE II

LOW-VOLTAGE MASS ANALYSIS OF INDOLE DERIVATIVES FROM HEAVY GAS OIL (660–1000 F°) FRACTION, CRUDE A

Compound type	%[a]
-15z (alkyl carbazoles)	30
-17z (cycloalkyl carbazoles)	19
-19z (dicycloalkyl carbazoles)	10
-21 (alkyl benzcarbazoles)	17
-23z (cycloalkyl benzcarbazoles)	10
-25z (dicycloalkyl benzcarbazoles)	5
Other	9

[a] De-isotoped mass data, carbazole/benzcarbazole sensitivity (weight basis) of 1.61 is assumed.

pancy suggests a number of possibilities: (*1*) the U.V. absorptivities for the straight-run and cracked indole derivatives are not identical; (*2*) the elution characteristics of straight-run and cracked samples differ, leading to differing recoveries of straight-run and cracked indole derivatives in the routine chromatographic separation; and (*3*) some other compound types are being recovered in the separation of the indole derivatives, and are interfering (or not reported) in the mass spectral, elemental nitrogen and/or U.V. determinations of the indole derivatives. Each of these possibilities was further investigated.

U.V. absorptivities of straight-run versus cracked indole derivatives. Table III summarizes the analysis of the indole derivatives fraction obtained in the non-routine separation of Table I. Nitrogen-type distribution and/or total nitrogen were obtained by elemental analysis, low-voltage mass analysis, and U.V. analysis

TABLE III

NITROGEN DISTRIBUTION BY VARIOUS METHODS FOR INDOLE DERIVATIVES FRACTION FROM HEAVY GAS OIL (660–1000° F) EX CRUDE A

Nitrogen	*Nitrogen (wt-%)*			
	Elemental[a]	*Mass spectral*[b]	*U.V.*	
			Cracked[c]	*Straight-run*[d]
Carbazoles		3.1	2.5	3.0
Benzcarbazoles		1.4	1.5	1.4
Total	4.3	4.5	4.0	4.4

[a] Kjeldahl.
[b] Based on analysis of Table II.
[c] Using compound type absorptivity data for cracked samples[1]; a_{292} for carbazoles equal $1.48 \cdot 10^4$ cm^2/mole.
[d] Using compound type absorptivity data for straight-run samples (present method); a_{292} for carbazoles equal $1.30 \cdot 10^4$ cm^2/mole.

using absorptivity data previously derived from cracked samples[1]. The U.V. value for total nitrogen (4.0%) was slightly lower than the average of the other two values (4.4%), suggesting some decrease in the U.V. absorptivities of straight-run relative to cracked indole derivatives. It was previously noted that the U.V. absorption coefficient for cracked carbazoles at 292 mμ was somewhat lower than for pure carbazole, presumably because of an effect of alkyl substitution on molar absorptivity. Since straight-run compound types tend to be more heavily substituted than corresponding cracked derivatives[9], the absorptivity of straight-run carbazoles at 292 mμ should be lower still. As shown in Table III, assumption of a lower straight-run carbazole absorptivity at 292 mμ ($1.30 \cdot 10^4$ *vs.* $1.48 \cdot 10^4$ cm^2/mole for cracked carbazoles) gave good agreement with other methods for total nitrogen and individual nitrogen types in this fraction. The latter carbazole absorptivity value was independently checked by isolating a solution of alkyl carbazoles from an 800–900° F fraction from crude A (Fig. 1b), and measuring the absorbance of the 292-mμ band relative to the absorptivities at 275 and 305 mμ. A molar absorptivity at 292 mμ was calculated equal to $1.24 \cdot 10^4$ ($\pm 0.12 \cdot 10^4$) cm^2/mole, in good agreement with the value of $1.30 \cdot 10^4$ derived in Table III. This lowering of the carbazoles 292-mμ absorptivity in straight-run samples significantly affects the accuracy of their analysis by the previous routine method[1].

Recovery of indole derivatives in the routine separation procedure. The elution characteristics of cracked gas oil samples are such that relatively clean separation occurs of the indole derivatives from other sample components during routine separation. As seen in Fig. 2 for the similar elution of the 800–900° F fraction from crude oil A, such is not the case for corresponding straight-run samples. Figure 2 shows the U.V. absorption spectra of several 5-ml fractions taken during initial elution by 40% (v/v) methylene chloride–pentane in the present routine chromato-
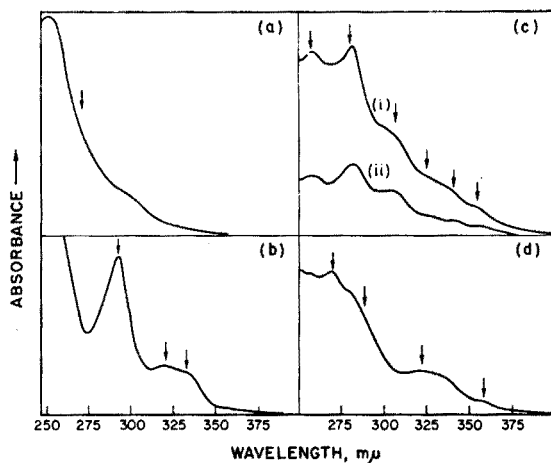
Fig. 1. Ultraviolet absorption spectra of indole derivatives fractions isolated from various distillate fractions of crude A. (a) 475–550° F fraction, first eluted indole derivatives; (b) 700–800° F fraction; (c) 900–960° F fraction, strongly held indole derivatives: (i) original spectrum, (ii) spectrum *versus* that of weakly held indole derivatives; (d) 900–960° F fraction, weakly held indole derivatives *versus* strongly held derivatives.
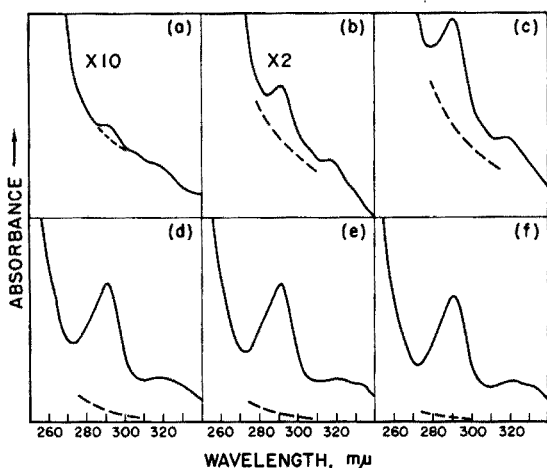
Fig. 2. Ultraviolet absorption spectrum of eluate fractions from routine separation of 800–900° F fraction from crude A. Eluate fractions: (a) 5–10 ml; (b) 10–15 ml; (c) 15–20 ml; (d) 25–30 ml; (e) 35–40 ml; (f) 45–50 ml. — original spectra; - - - estimated spectra of non-carbazole components.

graphic separation procedure. The characteristic absorption maximum of the car-
bazoles at 292 mμ permits us to follow the elution of carbazoles from the column, as
well as the concomitant elution of the initially eluted aromatic hydrocarbons (dashed
curves in Fig. 2). There is clearly considerable overlap of the carbazole and aromatic
hydrocarbon elution bands. This fact greatly complicates the measurement of elution
curves for the various indole derivatives types, and the calculation of recoveries for
use in the routine procedure. Other differences in the compositions of cracked and
straight-run heavy distillates further add to this problem.

As a beginning approximation, the following assumptions were made con-
cerning the initial elution of a straight-run sample by 40% (v/v) methylene chloride–
pentane in the routine separation: (1) indoles and benzcarbazoles are present in
minor amounts in the first 50 ml of eluate; (2) from 5 to 50 ml of initial eluate, the
terminally eluted aromatic hydrocarbons exhibit a constant absorption spectrum
shape between 275 and 305 mμ (for a given sample). The first assumption will be
justified shortly, while the second appears reasonable for a variety of reasons. With
these two assumptions, data such as those of Fig. 2 can be readily converted into
a quantitative carbazoles elution curve. The second 5-ml eluate fraction, which
contains relatively little carbazoles (Fig. 2a), is used to calculate the absorption
spectrum shape for the aromatic hydrocarbons. The carbazoles absorption spectrum
is known, so that the calculation of carbazoles (and aromatic hydrocarbon absorbance
by difference) is then straightforward. Examination of the 5–10-ml eluate fractions,
such as that of Fig. 2a, for several different samples showed close similarity in the
aromatic hydrocarbon shape. Consequently, a general expression for carbazoles
in fractions such as those of Fig. 2 (5–50 ml of eluate) could be derived:

$$\text{moles carbazoles}/5 \text{ ml} = (2.20\ A_{292} - 0.88\ A_{275} - 0.88\ A_{305}) \cdot 10^{-7} \tag{3}$$

A_{292}, A_{275}, and A_{305} refer to the absorbances of the 5-ml fraction at the subscripted
wavelengths.

Carbazoles elution curves were next measured for the routine separation of
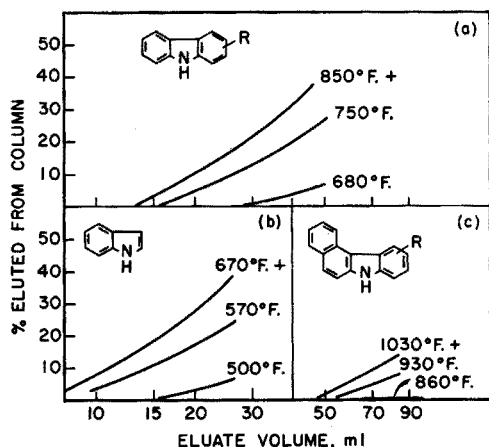
Fig. 3. Experimental and calculated elution curves for indole derivatives of varying average
boiling point in routine separation procedure (initial elution by 40% CH₂Cl₂–pentane). (a) car-
bazoles, expt.; (b) indoles, calc.; (c) 3,4-benzcarbazoles, calc.

several narrow-boiling fractions from crude A. Equation (3) was used for the analysis of the initial 10–40 ml of 40% methylene chloride–pentane. Subsequent eluate was analyzed for carbazoles by means of equations similar to those used in the EXPERIMENTAL section. The latter were in turn derived from previous absorptivity data for the cracked indole derivatives, corrected for the changed absorptivity of carbazoles at 292 mμ (1.30 · 10^4 cm^2/mole). These carbazole elution curves are plotted *vs.* eluate volume (40% (v/v) methylene chloride) in Fig. 3a. The routine procedures for determining the indole derivatives in 700° F+ cracked[1] and straight-run (EXPERIMENTAL section) samples specify initial elution by 50 ml of 40% (v/v) methylene chloride–pentane, with recovery of the indole derivatives in a subsequent CH$_2$Cl$_2$ fraction. Figure 4a summarizes the percentage recovery of carbazoles in the CH$_2$Cl$_2$ fraction
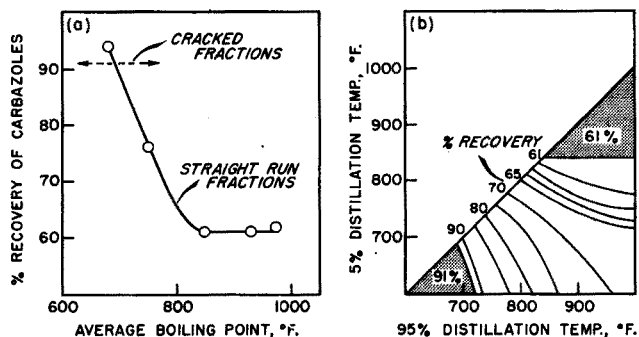
Fig. 4. Experimental recoveries of straight-run alkyl carbazoles in routine procedure for cracked samples (Mode B). (a) narrow-boiling fractions; (b) wide-boiling fractions.

for both straight-run and cracked gas oil fractions, as a function of sample average boiling point in narrow-boiling fractions. The recovery of cracked carbazoles (dashed curve in Fig. 4a) in the routine procedure is constant, while the similar recovery of straight-run carbazoles depends markedly on sample boiling point. *This is a major reason for the failure of the cracked gas oil method in the nitrogen-type analysis of the straight-run sample of Table I.*

For reasons summarized previously, the elution curves and derived recovery figures for routine separation of the straight-run indoles and benzcarbazoles (as in Figs. 3a and 4 for the carbazoles) cannot be directly measured. Other studies[10,11], however, suggest that similar alkyl substitution will result in similar changes in the elution of the alkyl indoles, carbazoles, and benzcarbazoles relative to the unsubstituted derivatives. It can be assumed that similar alkyl substitution exists in the straight-run indoles, carbazoles, and benzcarbazoles as the boiling point of a sample is increased an equal amount above the boiling point of the corresponding unsubstituted indole derivative. It is therefore possible to estimate the elution curves for the indoles and benzcarbazoles from (*a*) the carbazole curves of Fig. 3a and (*b*) the retention volumes of the unsubstituted indole derivatives in 40% methylene chloride–pentane (Table IV). A more detailed analysis suggests that this should be a relatively good approximation. The resulting calculated elution curves are shown in Figs. 3b and 3c. Two important conclusions may be drawn from these curves. First, none of the 3,4-

TABLE IV

RELATIVE SEPARATION ORDER OF THE VARIOUS UNSUBSTITUTED INDOLE DERIVATIVES IN THE ROUTINE PROCEDURE

Compound	Equivalent retention volume, $R°$ (ml/g)	
	40% CH_2Cl_2–pentane [a]	CH_2Cl_2 [a]
Indole	10.6	1.64
Carbazole	18.6	1.98
1,2-Benzcarbazole	76	6.1
2,3-Benzcarbazole	92	5.8
3,4-Benzcarbazole	67	4.6

[a] Eluant.

benzcarbazoles are eluted before 50 ml of eluate, and this will therefore be true for the more strongly adsorbing 1,2- and 2,3-benzcarbazoles. Consequently, the recovery of straight-run benzcarbazoles in the routine procedure will be 100%, as in the case of cracked benzcarbazoles. Second, less than 20% of the indoles or carbazoles in straight-run samples are ever eluted before 15 ml of eluate, and loss of indoles and carbazoles in the first 15-ml fraction may therefore be ignored for most light samples. Consequently, the recovery of straight-run indoles and carbazoles in the routine procedure for light (400–725° F) cracked gas oils, where an initial 15-ml eluate fraction is assumed to elute only the aromatic hydrocarbons from the column, may be assumed close to 100%, as is also true for cracked indoles and carbazoles. Because straight-run samples in the 400–725° F range can be assumed to contain only lightly substituted alkyl carbazoles, the absorptivity of the straight-run and cracked carbazoles in this range can be assumed equal (as their similar elution characteristics (Fig. 3a) suggest). *Consequently, the previous routine procedure for analyzing indole derivatives in light cracked gas oils (400–725°F) should be applicable, without change, for straight-run gas oils.*

Characterization of the routine indole derivatives fraction and identification of individual indole derivatives types in crude oil A. The indole derivatives fraction of Table III, obtained from the 660–1000° F fraction of crude A, corresponds closely to that obtainable in the routine separation. To the extent that we can establish the indole derivatives as predominant in this fraction, we can accordingly discount the possible interference of other sample types in the present routine analysis. The elemental nitrogen and low-voltage mass analysis data (Table III) suggest that 87–91% of the fraction consists of carbazoles plus benzcarbazoles. Neither of these figures rules out the presence of other nitrogen types, however, although the distribution by Z number in Table II strongly suggests that the carbazoles and benzcarbazoles predominate.

A more diagnostic test in this respect is afforded by high-voltage (fragment) mass spectrometry. Examination of the high-voltage mass spectrum of the indole derivatives fraction of Table III showed major fragment peaks only on the expected alkyl and cycloalkyl carbazole and benzcarbazole mass numbers (m/e 180, 194, 208, 222, 192, 206, 220, 230, 244, 258, etc.). The alkyl carbazole fragments on the -16Z series are shown in Fig. 5a, and the alkyl benzcarbazole fragments on the -22Z series are shown in Fig. 5b. The distribution of m/e values is, in each case, exactly that expected for the two compound types in question, by analogy with the mass spectra

of petroleum hydrocarbon and sulfur compound classes. An approximate quantitative analysis of this indole derivatives fraction could be carried out as follows. The high-voltage mass spectra of the carbazoles and benzcarbazoles previously isolated from cracked gas oil fractions were obtained; because of the nature of cracked gas oils, it was possible to obtain quite pure fractions of each nitrogen type. Related high-mass
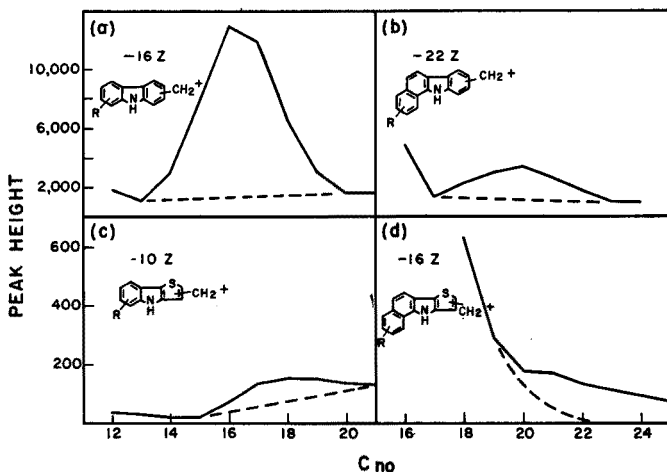

Fig. 5. High-voltage mass-spectral fragment curves for different compound types in indole derivatives concentrate from crude A heavy gas oil, *versus* carbon number. (a) -16z, alkyl carbazole fragments; (b) -22z, alkyl benzcarbazole fragments; (c) -10z, alkyl thiacarbazole fragments; (d) -16z, alkyl thiabenzcarbazole fragments.

spectral fragment data for aromatic hydrocarbon classes found in cracked and straight-run distillates suggested that the fragment sensitivities of the straight-run carbazoles and benzcarbazoles on the fragment masses used would be about 0.8 time as great as for the cracked derivatives. A high-mass fragment analysis for the carbazoles and benzcarbazoles in the indole derivatives concentrate of Table III could then be set up in a straightforward fashion. The resulting analysis of this fraction gave 60 wt-% carbazoles and 38 wt-% benzcarbazoles (98% total).

A further check on the purity of the same indole derivatives fraction is provided by ultraviolet analysis and non-aqueous titration. If an independent value of the 292-mμ absorptivity of carbazoles is used ($1.24 \cdot 10^4$ cm^2/mole, from spectrum of Fig. 1b), it can be calculated that the carbazoles plus benzcarbazoles in the fraction of Table III equal 91%. Similarly, non-aqueous titration with tetrabutylammonium hydroxide gives a value for carbazoles plus benzcarbazoles of 81%. For the preceding 5 independent measures of the sum of carbazoles plus benzcarbazoles in this fraction, 90 (± 8 s.d.) % is obtained, well within the experimental error of the various determinations. It may be concluded that the routine procedure isolates predominately carbazoles and benzcarbazoles in the indole derivatives fraction, and that interference by other sample types to the method is negligible.

Table II and Figs. 1b and 2 confirm the presence of the carbazoles in crude A. The individual benzcarbazole isomers were also sought. The 900–960° F fraction

from crude A was subjected to ion exchange and microchromatographic separation, and several fractions within the indole derivatives band were taken. Previously it was found that the 1,2-benzcarbazoles adsorbed more strongly and concentrated in the elution band tail, while the 3,4-benzcarbazoles were found in the band front. Table IV summarizes the relative elution order of the pure benzcarbazole isomers in the chromatographic system of the routine separation: 3,4-<1,2-~2,3-. This elution order in the cracked gas oils was confirmed, 3,4-benzcarbazoles eluting first, followed by the 1,2-benzcarbazoles. It was previously observed[11] for elution from a less active alumina that 1,2-benzcarbazole was eluted considerably later than the 2,3-isomer. This change in separation order between aluminas of differing activity was relatively slight, and paralleled similar small changes found in the hydrocarbon solutes[12]. As in the case of benzcarbazoles, more active alumina favors the stronger adsorption of the linear hydrocarbon isomers (acenes) relative to non-linear ones.

Figure 1c shows the U.V. spectrum of the most strongly adsorbed portion of the indole derivatives elution band from the 900–960° F fraction. The arrows indicate the band maxima observed in the 1,2-benzcarbazoles from cracked gas oils (and pure 1,2-benzcarbazole). All of the major bands of 1,2-benzcarbazole are clearly visible in Fig. 1c (i). These are brought out more sharply in Fig. 1c (ii), which is the spectrum of the same fraction vs. that of an earlier eluted less strongly adsorbing indole derivatives fraction (so as to correct for the presence of less strongly adsorbing indole derivatives in the strongly adsorbing fraction). It is definitely concluded that the 1,2-benzcarbazoles are present in this crude A. As in the case of benzcarbazoles from cracked gas oils, the 1,2-benzcarbazoles are clearly the predominant benzcarbazole type.

The 2,3-benzcarbazoles are also expected to concentrate in the more strongly adsorbing indole derivatives fractions (as in Fig. 1c). The observed spectra of these fractions clearly rule out the presence of significant amounts of the 2,3-benzcarbazoles (see Fig. 2 of ref. 1) and suggest that little if any of the 2,3-benzcarbazoles are present in this California crude.

The 3,4-benzcarbazoles were sought for in the less strongly adsorbing indole derivatives fractions from the 900–960° F fraction. Their detection in these fractions was more difficult than in corresponding cracked gas oil fractions. Carbazoles and other unknown sample types, which were largely absent in similarly boiling cracked gas oils, gave considerable interference to those straight-run fractions boiling above 800° F which should be rich in 3,4-benzcarbazoles. Figure 1d shows the spectrum of the less strongly adsorbing indole derivatives from the 900–960° F fraction vs. the 1,2-benzcarbazole-rich fraction, so as to cancel out the spectral contributions of the latter isomer. Three of the four absorption bands (arrows) observed in the cracked 3,4-benzcarbazoles are clearly evident in the spectrum of Fig. 1d, and the missing band is a minor one, easily hidden under the spectrum of this fraction. It thus appears that the 3,4-benzcarbazoles are also present in the California crude. The overall spectrum, however, clearly reflects the presence of compound types other than the benzcarbazoles.

As discussed in the next section, the indoles are minor nitrogen types in most crude oils, with their concentrations (if present at all) close to the detection limits of the present routine nitrogen-type method. The presence of indoles in crude A was investigated as follows. Since small amounts of the higher indole derivatives, i.e.

carbazoles, tend to mask the presence of traces of the indoles, a fraction of the California crude was selected (475–550° F) which, on the basis of previous studies with the cracked gas oils, should contain major amounts of the indoles and only traces of the carbazoles. By routine analysis, this fraction contained nitrogen as indoles, 0.0000%; as carbazoles, 0.0004%; as benzcarbazoles, 0.0002%. Microscale separations provided the apparent indole fraction of Fig. 1a, using the previous absorbance subtraction technique. This fraction is clearly a non-indole compound type, representing a minor interference in the indole derivatives fraction for the 475–550° F sample. It is concluded that the indoles do not occur in significant amounts in crude A.

In the aromatic compound classes isolated from sulfur-containing petroleum fractions (such as crude A), thiophene derivatives generally occur in substantial amounts along with hydrocarbons of similar aromatic ring number, *e.g.* alkyl thiophenes with benzenes, alkyl benzothiophenes with naphthalenes, etc. Similarly, COPELIN[6] observed the presence of sulfur-containing analogs of the 2-quinolones in concentrates isolated from a California crude. Thiophene analogs of the carbazoles and benzcarbazoles, if present in crude A, would be expected to concentrate with the other indole derivatives. Figures 5c and 5d show the fragment peaks *vs.* carbon number curves for the *m/e* series corresponding to the thiacarbazoles and thiabenzcarbazoles, respectively. In each case, there is some indication of the presence of the indicated sulfur-containing indole derivatives, although the concentrations of these compound types, if present at all, must be quite small. A final decision on their presence in petroleum must await the application of mass-defect, high-resolution mass spectrometry to fractions similar to that of Table III.

Development of a nitrogen-type method for straight-run heavy distillates

The analysis for indole derivatives in straight-run heavy gas oil fractions (600–1000° F) by the previous cracked gas oil procedure obviously requires modification. First, the differing carbazole absorptivity must be taken into account. Second, the different, and variable, carbazole recovery in straight-run samples must be corrected for. The routine procedure described in the EXPERIMENTAL section was modified so as to measure carbazoles directly both in the normal indole derivatives fraction (methylene chloride), and the preceding eluate fraction which contains carbazoles plus aromatic hydrocarbons. This calculation assumed only that the absorption spectrum shape of the latter aromatic hydrocarbons is reasonably constant from sample to sample, as was experimentally verified in the present investigation. Alternatively, it was possible to use the original cracked gas oil procedure (mode B[1]) and estimate the recovery of carbazoles in the indole derivatives fraction. The carbazoles found in that fraction can be corrected accordingly so as to avoid measuring the carbazoles in the initial methylene chloride–pentane fraction (as in the routine procedure of the EXPERIMENTAL section). For narrow-boiling samples, the data of Fig. 4a can be used for this purpose, while for wide-boiling samples the plot of Fig. 4b was derived from the present investigation.

The present study fully confirms the reliability of the present routine procedure. As seen in Table I, this procedure gives a reasonable check with indole derivatives nitrogen by non-routine procedures. The present nitrogen-type procedure can be carried out on 8 samples in a single 8-h shift, with a standard deviation (% weight)

TABLE V

NITROGEN-TYPE DISTRIBUTION IN THE LIGHT AND HEAVY GAS OIL FRACTIONS FROM SEVERAL CRUDES

Sample	%N										EP^f (°F)
	Light gas oils (400–600°F)				Heavy gas oils (600°F+)				Total		
	I^a	C^b	Type A^c	Total Kjel.	C^b	BC^d	Type B^e	Type A^c	Kjel.	Sum^{b-e}	
Devonian, Canada	$(0.001)^g$	0.000	0.004	0.007	0.047	0.031	0.044	0.053	0.175	0.175	1000
Mississippian, Arizona	$(0.001)^g$	0.002	0.000	0.002	0.022	0.014	0.012	0.013	0.041	0.061	910
Mississippian, Utah	$(0.001)^g$	0.000	0.000	0.001	0.004	0.004	0.006	0.003	0.015	0.017	1000
Permian, Texas	$(0.000)^g$	0.001	0.001	0.002	0.029	0.019	0.016	0.018	0.069	0.082	1000
Cretaceous, New Mexico	$(0.001)^g$	0.000	0.001	0.001	0.012	0.009	0.013	0.015	0.054	0.049	1000
Oligocene, California	0.003	0.001	0.039	0.047	0.056	0.034	0.11	0.115	0.347	0.315	1000
Miocene, California	0.004	0.003	0.040	0.048	0.105	0.028	0.19	0.183	0.553	0.506	890
Miocene, California	$(0.001)^g$	0.002	0.026	0.034	0.064	0.031	0.12	0.142	0.360	0.357	975
Miocene, California (A)	$(0.001)^g$	0.001			0.083	0.044	0.24	0.14	0.45	0.507	1000

a Indole nitrogen by present method.
b Carbazole nitrogen by present method.
c Strongly basic nitrogen; titration in acetic acid.
d Benzcarbazole nitrogen by present method.
e Weakly basic nitrogen; titration in acetic anhydride.
f End-point of heavy gas oil.
g Within experimental error of zero.

of $\pm$ 0.005 for carbazole nitrogen and $\pm$ 0.002 for benzcarbazole nitrogen. Adsorbent linearity was noted for sample sizes of 10–100 mg (crude oil A). As an additional check on accuracy, the various heavy gas oils of Table V were reanalyzed by the alternative procedure (mode B, cracked gas oil method[1]) of ignoring carbazole nitrogen in the 40% methylene chloride–pentane fraction, and then estimating, and correcting for recovery from Fig. 4b. Nitrogen as carbazoles for these 9 samples by the 2 procedures showed a standard deviation (% weight) of $\pm$ 0.004. Similarly, 100° F distillation fractions from the heavy gas oil of Table I were analyzed for nitrogen type and the composited results compared with the total heavy gas oil: carbazole nitrogen, 0.088% (composite), 0.086% (gas oil); benzcarbazole nitrogen, 0.037% (composite), 0.043% (gas oil).

Nitrogen-type distribution in petroleum distillates

The present LEAC procedure permits the direct determination of nitrogen present as indole derivatives in most crude distillates. This in turn allows us to determine the relative importance of the indole derivatives as crude nitrogen types and to evaluate the apparent controversy over amides as crude constituents. Comparison of the indole derivatives nitrogen values with type C nitrogen (by difference) for a number of samples also provides a further test of the validity of the nitrogen-type classification scheme of OKUNO *et al.*[7]. Finally, information can be obtained on the relative occurrence of non-basic (type C) nitrogen compounds other than the indole derivatives. Nine different crude oils covering a wide range in estimated geologic age and source locations within North America were selected for this purpose. The light (400–600° F) and heavy (600° F+) gas oil portions from these crudes were analyzed for various nitrogen types: indole derivatives, type A, and types B plus C in the case of the light gas oils; indole derivatives and types A, B, and C in the case of the heavy gas oils. These results are summarized in Table V. The light gas oils all contain very little type B+C nitrogen compared to the heavy gas oils; determination of the various non-basic nitrogen subtypes (or even of total type B+C nitrogen) is therefore relatively imprecise, and these light gas oil data do not permit a good discussion of the relative distribution of non-basic nitrogen types, or of the validity of the procedure of OKUNO *et al.* Measurable indole concentrations are observed for two of the light gas oils of Table V, but their actual presence in these samples was not confirmed by further separation and analysis. Since the indoles should reach a concentration maximum in the 400–600° F boiling range (by analogy with cracked samples, and by extension to straight-run samples on the basis of the carbazoles, Table VII), it is concluded from the light gas oil data of Table V that the concentration of nitrogen as indoles in heavier distillates and residues is generally minor (0.000–0.004 wt-%).

The heavy gas oil data of Table V conclusively demonstrate the widespread occurrence of the carbazoles and benzcarbazoles in crude petroleum. The carbazoles plus benzcarbazoles invariably account for more than a third of total type B+C nitrogen. The postulate[5] that amides (type B) are the only important non-basic nitrogen type in crude petroleum is therefore not generally warranted. The sum of nitrogen as strong bases, weak bases, carbazoles, and benzcarbazoles is generally in good agreement with total nitrogen values (Kjeldahl) for these fractions. The standard deviation (wt-% nitrogen) between experimental total nitrogen values and the sum of these 4 nitrogen types is only $\pm$ 0.02, which is close to the experimental reproducibil-

ity of the various nitrogen-type determinations; these deviations are randomly distributed. The agreement of total nitrogen values with the sum of nitrogen-type determinations suggests that the titration of nitrogen as strong and weak bases is a reliable analytical procedure, generally free from non-nitrogen interferences, and that type C compounds other than the indole derivatives are largely absent from crude heavy gas oils; that is, such nitrogen types as the nitriles, phenanthrolines, indoloquinolines, and phenazines, all of which contain one non-basic (type C) nitrogen per molecule, and all of which have been reported in petroleum or processed petroleum fractions[13-15], are not present in petroleum distillates in other than trace quantities. In this connection it is worth comparing some cracked gas oil fractions analyzed previously. Table VI summarizes indole derivative analyses of 3 of these fractions, along with nitrogen as types A and B by titration. Since the light gas oil fraction contains significant indoles, and since these also titrate as type B nitrogen to the extent of 65–80%[7], the type B nitrogen figure must be corrected for indoles so as not to report indole nitrogen twice. Again, as in the case of the straight-run fractions of Table V, the cracked gas oils of Table VI show the sum of nitrogen types determined as indole derivatives, strong bases, and weak bases about equal to total nitrogen. We conclude that other type C nitrogen compounds, *e.g.* phenazines, nitriles, etc. are present in these cracked gas oils in only trace amounts, if at all.

TABLE VI

NITROGEN-TYPE DISTRIBUTION IN CATALYTICALLY CRACKED GAS OIL FRACTIONS

Fraction	% N					Total	
	I[a]	C[b]	BC[c]	Type A[d]	Type B[e]	Kjel.	Sum I, C, BC, A, B
Light FCC gas oil (433–660° F)	0.040	0.064	0.001	0.048	0.055 0.026[f]	0.186	0.179[f]
Heavy FCC gas oil (426–744° F)	0.004	0.191	0.017	0.037	0.017 0.014[f]	0.285	0.263
825–850° F	0.000	0.020	0.299	0.056	0.045	0.455	0.418

[a] Indole nitrogen by present method.
[b] Carbazole nitrogen by present method.
[c] Benzcarbazole nitrogen by present method.
[d] Strongly basic nitrogen; titration in acetic acid.
[e] Weakly basic nitrogen; titration in acetic anhydride.
[f] Corrected for indoles titrating as type B nitrogen (est. 73% titration).

The possible interference of carbazoles and benzcarbazoles to the type B nitrogen titration was studied, and on the basis of experiments to be reported in detail later it was clear that no more than 10–15% of the carbazoles and benzcarbazoles were titrated in acetic anhydride. Quite possibly, no interference of this type exists, in agreement with the lack of interference of pure carbazole in the acetic anhydride titration procedure. The possibility of thermal rearrangement of weak bases (type B) in the original crude (to carbazoles and benzcarbazoles) during the preparation of the samples of Table V was also considered, since it could be argued that reactions of this type might explain the contradictions in the present *versus* previous[5] studies. Crude A and all of its distillation fractions were titrated for strong

and weak bases, and total nitrogen determined. Weak bases constituted 71% of the type B + C nitrogen in the original crude. Composite recoveries of total nitrogen, strongly basic (type A) nitrogen, and weakly basic (type B) nitrogen in the distillation fractions and residue were 103, 101, and 94%, respectively. It is therefore apparent that little if any conversion between nitrogen types A, B, and C occurred as a result of distilling the crude.

In agreement with the studies of OKUNO et al.[7] and BEZINGER et al.[5], the strong bases in the samples of Table V were, within experimental error, completely unacetylated in the acetic anhydride titration procedure, indicating only tertiary nitrogen bases in these samples (e.g. pyridines, quinolines, etc.).

The distribution with boiling point of the indole derivatives in the straight-run California gas oil is shown in Table VII, and compared with the distribution of these

TABLE VII

COMPARISON OF NON-BASIC (TYPES B+C) NITROGEN TYPE IN CRACKED AND STRAIGHT-RUN GAS OILS versus BOILING POINT

| Boiling point range (°F) | % N | | | | | | | |
| | Straight-run[a] | | | | Cracked[b] | | | |
	I[c]	C[d]	BC[e]	NB[f]	I[c]	C[d]	BC[e]	NB[f]
400–500	0.000	0.000	0.000	0.003	0.04	0.00	0.00	0.08
500–600	(0.001)	0.002	0.000	0.015	0.07	0.01	0.00	0.11
600–700	(0.004)	0.034	0.000	0.085	0.02	0.25	0.00	0.31
700–800	—	0.106	0.006	0.235	——	0.17	0.07	0.29
800–900	——	0.072	0.046	0.260	—	0.01	0.29	0.41
900–960	—	0.097	0.071	0.363	——	—	0.41	——
960–1000	—	0.092	0.114	——				

[a] Crude A.
[b] Ref. 1.
[c] As indoles.
[d] As carbazoles.
[e] As benzcarbazoles.
[f] Experimental non-basic (total minus basic equal types B+C).

nitrogen types in a cracked gas oil related to crude A. The indole derivatives in the fractions boiling above 600° F account for 40–50% of type B+C nitrogen in the straight-run sample, and 70–90% in the cracked sample. Indoles constitute 50–80% of type B+C nitrogen in the 400–600° F cracked fractions, but less than 10% in corresponding straight-run fractions. Whereas carbazoles do not occur in appreciable amounts in cracked samples boiling above 800° F, in straight-run samples the carbazole content is reasonably constant from 700 to 1000° F. Figure 6 summarizes the distribution of these various straight-run nitrogen types vs. boiling point, with the residual distillation fraction (1000° F+) included. Although the carbazoles and benzcarbazoles cannot be determined in this residual sample because of the boiling point limitation (400–1000° F) on the routine procedure, it seems reasonable that the higher indole derivatives constitute much of the type C nitrogen in the crude residue. The ratio of indole derivative nitrogen to type B + C nitrogen holds relatively constant at 45–48% in the 700–1000° F fractions of crude A, and is 36% in the residue (by difference).

Application of the present and previous nitrogen-type methods has also been made to hydrotreated products of reduced nitrogen content (10–300 p.p.m. nitrogen). On the basis of the U.V. spectra of recovered indole derivatives fractions from these samples it appears that these nitrogen-type methods give accurate results for hydro-
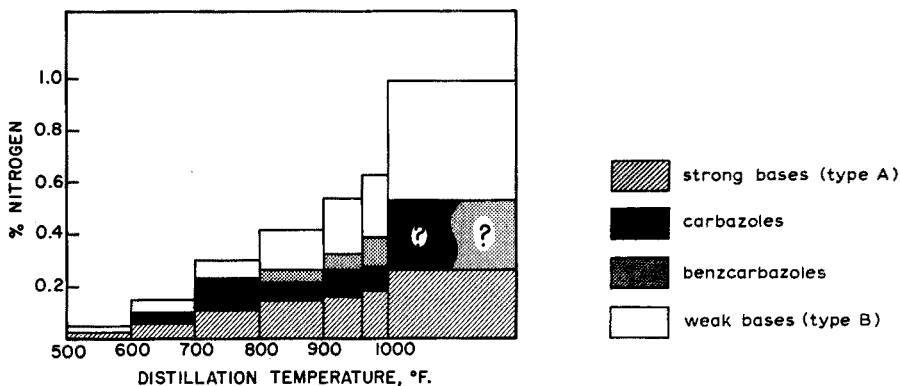
Fig. 6. Distribution of nitrogen type *versus* boiling point for crude A.

treated samples as well. Samples derived from straight-run feeds must be analyzed by the present method, and products from catalytically cracked feeds by the previous procedures[7]. Proportionately larger sample sizes must be charged to the routine separation procedures.

Interferences in high-boiling low-nitrogen distillates

Subsequent to the above work, the present method was applied to a 600–950° F distillate from a Heidelberg crude oil described by OKUNO et al.[7]. This crude oil was of particular interest because the latter workers found no type C nitrogen (*i.e.* carbazoles, benzcarbazoles) by their titration procedure. This observation is in marked contrast to the data for the crude oils of Table V. Preliminary analyses of the 600–950° F fraction showed 0.039 wt-% total nitrogen by Kjeldahl, 0.014 and 0.056 % type A and B nitrogen by titration, and 0.028 to 0.038% nitrogen as carbazoles plus benzcarbazoles by the present LEAC method (depending upon whether carbazoles in the B fraction were measured or estimated). Obviously the titration procedure, and possibly the LEAC analysis, were giving high results on this sample. The possibility of interference to the LEAC analysis was emphasized by examination of the spectrum of the C fraction between 275 and 300 mμ. Whereas the C fractions from the heavy gas oils of Table V all showed clear peaks at 280 (benzcarbazoles) and 292 mμ (carbazoles), the C fraction from the Heidelberg heavy gas oil was virtually devoid of fine structure between 275 and 300 mμ. Detailed non-routine analyses for indole derivatives in the Heidelberg sample were carried out as for the heavy gas oil from crude A. The average of high-voltage mass spectrometry, non-aqueous titration, and elemental analysis for nitrogen in the indole derivatives fraction indicated only 0.01 ± 0.01 % nitrogen as carbazoles plus carbazoles in the original Heidelberg heavy

gas oil. The nature of the interference to the LEAC analysis was next clarified by carrying out routine LEAC nitrogen-type analyses on 100° F wide distillation fractions from the Heidelberg crude. The C fraction spectra for distillates boiling below 900° F all resembled the fractions obtained with other crudes, appearing free from interference. The major carbazole absorption bands were clearly evident in the C fractions from the 600–800° F distillates, as were the 1,2- and 3,4-benzcarbazole bands in the C fraction from the 800–900° F distillate. The C fraction from the 900–1000° F distillate, however, showed quite intense absorption totally devoid of maxima between 275 and 300 mμ. Clearly, some new compound type, present in the 900° F + fractions, was interfering with the routine LEAC determination of nitrogen type. When the analyses for nitrogen type in the lower boiling fractions were compared with the data of Table VII, it could be estimated that the total nitrogen as carbazoles and benzcarbazoles in the 600–950° F Heidelberg distillate equaled 0.011%. This value is in good agreement with the average of non-routine determinations.

The possibility that some of the LEAC nitrogen-type results for the low nitrogen crudes of Table V might similarly be in error was next considered. An obvious check on this possibility is the comparison of the sum of nitrogen types *versus* total nitrogen by Kjeldahl, for low *versus* high nitrogen content samples. A significant interference problem would show up as high nitrogen-type results for low nitrogen crudes, and low nitrogen-type results for high nitrogen crudes. For the 5 heavy gas oils of Table V with total nitrogen contents above 0.1%, the ratio of the sum of nitrogen types to total nitrogen is 0.99. For the 4 samples with lower nitrogen contents, the same ratio is 1.17. Thus, the results for the low nitrogen samples appear to be 18% high, indicating some interference in either the LEAC procedure or titration method. On balance, we conclude that interference in the LEAC nitrogen-type procedure is not generally important, but should be kept in mind when analyzing samples which boil above 900° F and have nitrogen contents below 0.05–0.1 %. In any case, serious interference of this type can be verified by examination of the C fraction spectrum as above.

SUMMARY

Carbazoles, 1,2-benzcarbazoles, and 3,4-benzcarbazoles were identified as major non-basic nitrogen types in a straight-run California gas oil. Indoles and 2,3-benzcarbazoles were found to be absent. A routine procedure using ion exchange, linear elution adsorption chromatography, and ultraviolet spectrophotometric analysis is described for the rapid determination of the indoles, carbazoles, and benzcarbazoles (except N-alkyl derivatives) in straight-run heavy distillates (400 to 1000° F). The relative distribution of various nitrogen types in a number of crude petroleum fractions is reported. In the 600–1000° F boiling range, carbazoles plus benzcarbazoles account for 25 to 70% of the total nitrogen in straight-run samples.

Within experimental error, the sum of nitrogen as carbazoles and benzcarbazoles plus bases titratable in acetic anhydride accounts for all of the nitrogen of such samples. The carbazoles and 1,2-benzcarbazoles were clearly identifiable as major components of every crude oil studied.

RÉSUMÉ

Carbazoles, 1,2-benzocarbazoles et 3,4-benzocarbazoles ont été identifiés, comme types azotés non basiques majeurs dans une essence de Californie. Les indoles et les 2,3-benzocarbazoles sont absents. Une méthode de routine, utilisant échangeur d'ions, chromatographie par adsorption (élution linéaire) et analyse spectrophoto-métrique, est décrite pour le dosage rapide des indoles, carbazoles et benzocarbazoles. Les carbazoles et 1,2-benzocarbazoles sont nettement identifiables comme consti-tuants majeurs de chaque huile brute examinée.

ZUSAMMENFASSUNG

Carbazole, 1,2-Benzcarbazole und 3,4-Benzcarbazole wurden als die Haupt-typen nichtbasischen Stickstoffs in einem kalifornischen Gasöl identifiziert. Indole und 2,3-Benzcarbazole wurden nicht gefunden. Es wird ein Routineverfahren be-schrieben, das Ionenaustauscher, die lineare Elutions-Adsorptions-Chromatographie und ultraviolette spektralphotometrische Analysen zur schnellen Bestimmung von Indolen, Carbazolen und Benzcarbazolen (ausser N-Alkylderivaten) in schweren Destillaten (400–1000° F) verwendet. Über die relative Verteilung verschiedener Stickstofftypen in einer Anzahl von Rohölfraktionen wird berichtet. Im Siedebereich von 600–1000° F tragen Carbazole und Benzcarbazole etwa 25–70% zum Gesamtstick-stoff der Proben bei. Die Carbazole und 1,2-Benzcarbazole waren klar identifizierbar als Hauptkomponenten eines jeden Öls, das untersucht wurde.

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SEPARATIONS OF ALDEHYDES BY MEANS OF ION-EXCHANGE CHROMATOGRAPHY ON BISULFITE COLUMNS

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SAMUELSON *et al.*[1-4] have demonstrated that various carbonyl compounds are retained quantitatively by ion-exchange resins in the bisulfite form. The carbonyl compounds were recovered by elution with eluants such as sodium chloride and sodium carbonate. Certain ketones were separated from aldehydes by elution with hot water or carbonate buffers. These separations were based upon the lower stability of the α-hydroxysulfonic acids corresponding to the ketones. No systematic work on the chromatographic separation of aldehydes was carried out.

The first work on the chromatographic separation of aldehydes by means of ion-exchange resins in the bisulfite form was carried out by HUFF[5]. In this work, bisulfite solutions of increasing strength were used as eluants. The bisulfite ions in the eluant prevent the decomposition of the α-hydroxysulfonate ions which are eluted in the order of increasing ion-exchange affinity.

In the present work the same principle was adopted. The aim of the investigation was to find suitable conditions for the separation of some aldehydes which are formed during the sulfite cooking of wood.

EXPERIMENTAL

Apparatus

The chromatographic columns used had an inner diameter of 10–11 mm. The resin bed had a height of 20–41 cm, and rested on a sintered-glass disc. The space below the disc was filled with glass wool.

A B-D Cornwall Luer-Lok Syringe (1.000 $\pm$ 0.001 ml), with a metal pipet holder was used to feed in the solutions of the aldehydes.

The eluant was delivered to the column top at a constant flow-rate by a piston-type micro pump. The eluate was collected in fractions by means of a time-actuated fraction collector.

Reagents

Formaldehyde, about 35% (Merck).
Acetaldehyde, Laboratory Reagent (BDH).
5-Hydroxymethylfurfural (Fluka).
Furfural, p.a. (Merck).
Vanillin, Laboratory Reagent (BDH).

Bisulfite solutions (0.1–0.8 M) were prepared from sodium pyrosulfite, p.a. (Merck) on the day of use.

The resin, Dowex 1-X8, was used in 2 wet-bead sizes, 100–200 mesh and 150–300 mesh. The fractions were obtained by hydraulic classification[6]. Before the conversion to the bisulfite form, the resin was purified as recommended by SAMUELSON[7].

Preparation of column, absorption and elution

The resin was converted to the bisulfite form in a beaker by successive treatments with a saturated bisulfite solution. The slurry was then allowed to settle in the column and the treatment with bisulfite was continued until the last traces of chloride were removed. The excess of bisulfite was decreased by washing the column with water. Washing with one column-volume of water lowered the bisulfite concentration of the effluent to less than a hundredth.

The sample solutions, less than 20 ml in total, were fed in at the top of the column with the syringe and allowed to drain by gravity. If not otherwise mentioned, aqueous solutions were used. The column walls and the resin bed were washed with small portions of water, the total amount of which was noted.

In the elution step bisulfite solutions of different concentrations were forced through the column at a constant flow-rate ranging from 0.24 to 0.95 ml/cm²/min in the different experiments. The eluate, taken up in test tubes, was weighed out, and the density of the eluant was corrected for. The size of the eluate fractions varied between 3 and 25 ml.

In experiments where step-wise elution was used the elution was interrupted and the solution above the resin and in the tubings sucked off and replaced by the desired eluant.

Analytical methods

Suitable methods for the determination of formaldehyde, furfural and vanillin in bisulfite solutions were described in a previous paper[8]. Acetaldehyde was estimated as proposed by STOTZ[9]. In control experiments, the presence of bisulfite had no effect upon the determination. 5-Hydroxymethylfurfural was determined analogously to furfural, but the absorbance was measured at the wavelength 283 mμ. The molar absorptivity was found to be 15,800 [$cf.$[10,11]].

RESULTS AND DISCUSSION

Influence of particle size and pretreatment

In chromatographic work it is highly desirable that the peak elution volume ($\bar{v}$) is reproducible. Upon washing with water a bisulfite resin can be successively transformed into its sulfite form. As a consequence of this transformation, sulfurous acid was detected in the eluate even after the column had been washed with 25 column-volumes of water. Moreover, traces of oxygen present in the water can affect an oxidation to sulfate ions. Excessively large amounts of washing water should therefore be avoided.

Experiments were carried out with furfural in order to study the reproducibility of the peak elution volume, which was calculated as the number of column-volumes, $\bar{v}/X$, of eluant required to elute the maximum of the elution band. Results obtained with resins of 2 different particle sizes are summarized in Table I. From

TABLE I

ELUTION OF 60 μmoles OF FURFURAL FROM DOWEX I-X8 [HSO_3^-, II $\times$ 210 mm] WITH 0.4 M SODIUM BISULFITE

Particle size (mesh)	Washing before loading[a] (column-volumes)	Flow-rate (ml/cm²/min)	$\bar{v}/X$ (column-volumes)	β (ml)	Recovery (%)
100–200	I	0.24	12.2	41	88.0
100–200	3	0.24	12.2	42	98.3
100–200	5	0.24	12.2	40	95.2
100–200	3[b]	0.24	12.1	40	86.2
150–300	0[c]	0.47	12.2	31	94.3
150–300	I	0.47	11.9	31	97.1
150–300	3	0.47	11.9	35	98.8
150–300	3[b]	0.47	11.8	34	88.8

[a] After loading, the column was washed with one column-volume of water.
[b] The furfural was added in 0.4 M sodium bisulfite.
[c] The resin was conditioned with 0.4 M sodium bisulfite before loading.

this Table it is seen that the peak elution volume was not affected to a detectable extent when the amount of washing water was varied between I and 5 column-volumes. Similarly, a moderate amount of bisulfite in the sample solution had no detectable influence.

As can be seen from Table I a decreased particle size is a great advantage, resulting in a lowering of the width of the elution band (β). The flow-rate was made twice as high in the experiments with the finer resin particles, but a variation ranging between 0.23 and 0.70 ml/cm²/min appeared to have no detectable effect upon β. The width was measured at the height of $0.368 \cdot c_{max}$ [cf.[7]].

The aim of the experiments reported in Table I was to obtain reliable determinations of the peak elution volume and of the width of the elution curves. For this reason, a large number of small fractions (5.5 ml) were taken and analyzed. The errors which occurred when the recovery of furfural was determined in these experiments were therefore larger than those which would occur in experiments where larger fractions were taken.

Influence of eluant concentration

The influence of a change in the eluant concentration on the elution of formaldehyde was investigated. Column sizes of 10 $\times$ 78 mm and II $\times$ 200 mm were used with eluant concentrations of 0.1, 0.2, 0.4 and 0.8 M sodium bisulfite; the flow-rates were respectively 0.8 or 0.35 ml cm^{-2} min^{-1}, and the resin size was 100–200 mesh. The columns were previously treated with saturated bisulfite solution and washed with 2 column-volumes of water before and after the addition of the aldehyde. When the logarithm of the distribution constant was plotted against the negative logarithm of the eluant concentration, a linear relationship was found to exist. For the above cases, a straight line with a slope of unity was obtained. The same slope was observed also in experiments with acetaldehyde, 5-hydroxymethylfurfural, furfural and vanillin. In systems where an ion exchange occurs between ions of the same

charge the slope of the straight line should be equal to unity[7]. Hence these results confirm that the separation method used in this work is based upon an elution of α-hydroxysulfonate ions and not upon an elution of liberated carbonyl compounds. Plots of this type are valuable as an aid in predicting the position of the elution bands at various eluant concentrations.

Separation of acetaldehyde and formaldehyde

To ensure a complete uptake of these compounds which may polymerize, the effluent was tested [*cf*.[1]]. A bisulfite column (Dowex 1-X8, 100–200 mesh, 10 × 78 mm) was washed with 2 and 5 column-volumes of water before the addition of each of the aldehydes. Afterwards, the column was washed with 10 portions of water, each containing one column-volume. Formaldehyde could be detected only in the first fraction and amounted to less than 1%, but acetaldehyde could not be found in the effluent.

In order to arrive at suitable separation conditions, individual elution runs were performed. Acetaldehyde was eluted in maximum concentration from 20–41-cm columns after the passage of 4.3–4.5 column-volumes of 0.2 M sodium bisulfite, and formaldehyde was eluted after 6.0–6.3 column-volumes. The band width (β) for both acetaldehyde and formaldehyde was 18 ml on a 20-cm column with the particle size 100–200 mesh, when the eluate was collected in 6.4-ml fractions. To effect a proper separation, a sufficient difference in peak elution volume would be brought about if a 30-cm column were chosen [*cf*.[12]].

The result of a chromatography run with 46 μmoles of acetaldehyde and 126 μmoles of formaldehyde on such a column is reproduced in Fig. 1. As can be seen, a clean separation was obtained.

Acetaldehyde and formaldehyde have earlier been chromatographed on a 9.5 × 600 mm column[5]. Insufficient data on the separation were given, but consider-
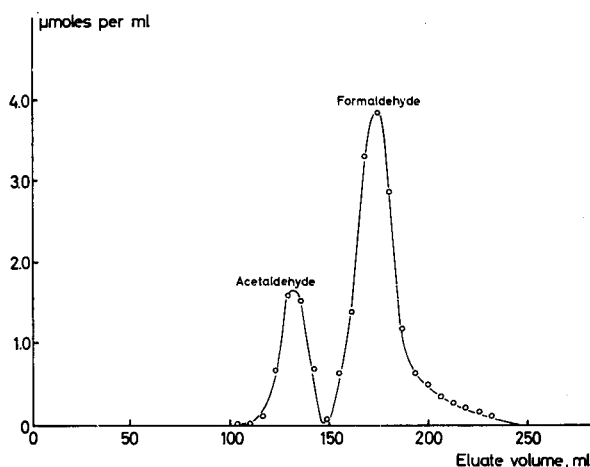
Fig. 1. Chromatography of acetaldehyde and formaldehyde on Dowex 1-X8 in bisulfite form. Column size: 11 × 300 mm; bead size: 100–200 mesh; eluant: 0.2 M NaHSO$_3$; flow-rate: 0.27 ml/cm^2/min; fraction size: 6.4 ml.

ing the large column length, the difference of about 30 ml in peak elution volume seems to be too small to effect a complete separation, even if the eluate fractions were chosen to be only 3 ml.

Separation of 5-hydroxymethylfurfural and furfural

5-Hydroxymethylfurfural was not studied in separate elution runs. In a preliminary chromatography run, 61 μmoles of 5-hydroxymethylfurfural and 60 μmoles of furfural were added to a 1.1 × 21.5-cm column of Dowex 1-X8 (HSO$_3^-$, 150–300 mesh). Before and after the addition of the aldehydes, the resin was washed with 2 column-volumes of water. The separation was incomplete. A better result could perhaps have been achieved with smaller eluate fractions. Instead, the column
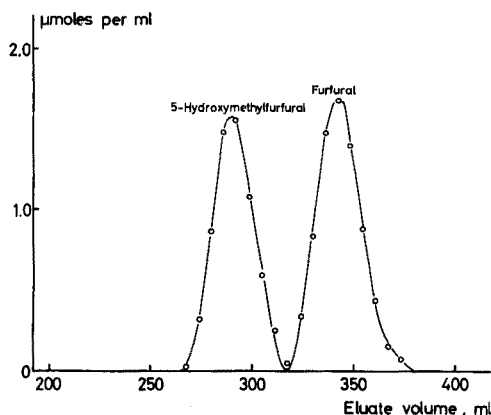
Fig. 2. Chromatography of 5-hydroxymethylfurfural and furfural on Dowex 1-X8 in bisulfite form. Column size: 11 × 300 mm; bead size: 150–300 mesh; eluant: 0.4 M NaHSO$_3$; flow-rate: 0.27 ml/cm^2/min; fraction size: 6.3 ml.

length was increased to 30 cm, whereby an acceptable separation was obtained (Fig. 2), with the peaks eluted after 10.1 and 11.9 column-volumes, respectively, of 0.4 M sodium bisulfite.

Separation of formaldehyde, furfural and vanillin

Vanillin was found to be held very strongly by the resin. Experiments performed with a 1.0 × 7.5-cm column of Dowex 1-X8 (HSO$_3^-$, 100–200 mesh) and some different bisulfite solutions showed an increased elution effect in the following order: 0.4 M (pH 3.5) <0.4 M (pH 5.6, adjusted with sodium hydroxide) <0.8 M (pH 3.6). The band width (β) was found to be very large for the most effective of these eluants for a 7.5-cm long column (about 100 ml for eluate fractions of 3 ml). When longer columns were used 10–20% (by volume) of ethanol was added to the solution of 0.8 M sodium bisulfite in order to suppress the van der Waals forces[13], whereby the band width decreased below 100 ml.

Three compounds, 25 μmoles of formaldehyde, 21 μmoles of furfural and 20 μmoles of vanillin, were separated on a 1.1 × 30-cm column. The resin was washed with one column-volume of water before and after the addition of the aldehydes.

This run was performed not only to separate these easily separable compounds, but also to discover where to change the eluant to obtain sharp peaks. The range of use of each eluant is made clear in Fig. 3.
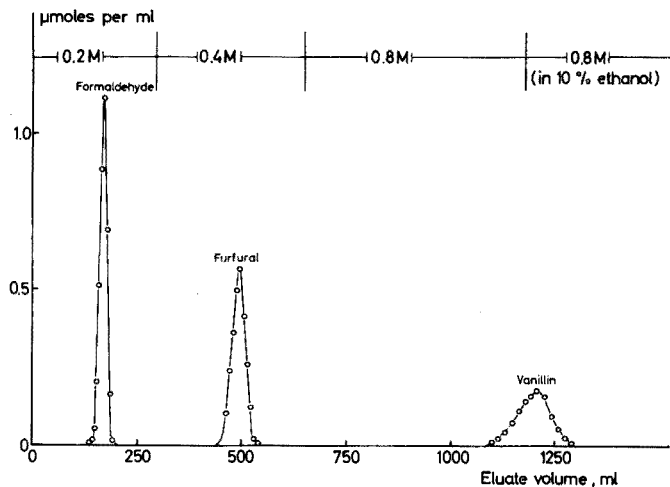
Fig. 3. Chromatography of formaldehyde, furfural and vanillin on Dowex 1-X8 in bisulfite form. Column size: 11 × 300 mm; bead size: 100–200 mesh; eluants: 0.2, 0.4, 0.8 M NaHSO$_3$ and 0.8 M NaHSO$_3$ in 10% ethanol; flow-rates: 0.26, 0.30, 0.24 and 0.22 ml/cm^2/min; fraction sizes: 6, 8, 6 and 6 ml.

Separation of acetaldehyde, formaldehyde, 5-hydroxymethylfurfural, furfural and vanillin

Figure 4 shows a run with 126 μmoles of formaldehyde, 46 μmoles of acetaldehyde, 61 μmoles of 5-hydroxymethylfurfural, 60 μmoles of furfural and 50 μmoles of vanillin, performed on a 1.1 × 41-cm column of Dowex 1-X8 (HSO$_3$⁻, 150–300 mesh). The resin was washed with 2 column-volumes of water before and after the addition of the aldehydes. The separations between acetaldehyde and formaldehyde and between the 2 furfurals were more distinct in this run than in earlier runs with shorter columns.

The last chromatography run was repeated, but fractions of 19.4 ml were collected. The compounds were determined quantitatively with the following result: acetaldehyde 101.0%, formaldehyde 98.4%, 5-hydroxymethylfurfural 90.8%, furfural 91.8% and vanillin 96.8%. As shown in Fig. 4, the chromatographic separation of the 5 aldehydes was complete. The deviations between the added and found amounts of aldehydes are explained by errors in the spectrophotometric analyses of the eluate fractions.
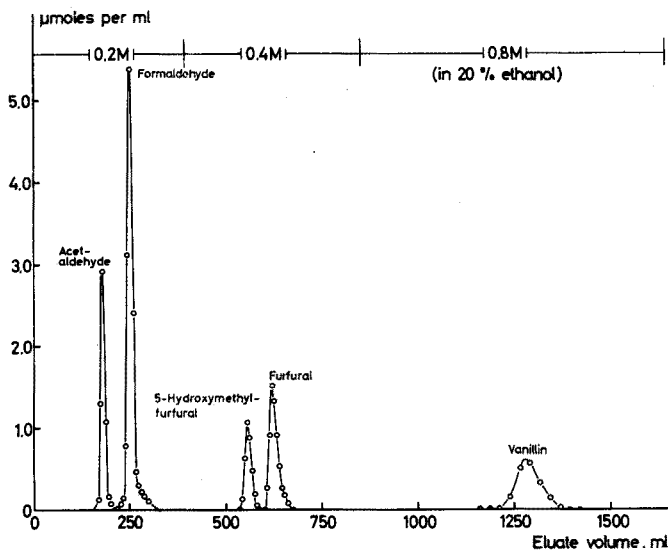
Fig. 4. Chromatography of acetaldehyde, formaldehyde, 5-hydroxymethylfurfural, furfural and vanillin on Dowex 1-X8 in bisulfite form. Column size: 11 × 410 mm; bead size: 150–300 mesh; eluants: 0.2 and 0.4 M NaHSO$_3$, and 0.8 M NaHSO$_3$ in 20% ethanol; flow-rates: 0.27, 0.27 and 0.52 ml/cm^2/min; fraction sizes: 6.5, 6.4 and 25 ml.

SUMMARY

Mixtures of carbonyl compounds were chromatographed on Dowex-1 columns in the bisulfite form. Sodium bisulfite solutions of increasing concentrations were used as eluants. The studied compounds, including acetaldehyde, formaldehyde, 5-hydroxymethylfurfural, furfural and vanillin, were separated completely from each other. The eluate was also analysed quantitatively.

RÉSUMÉ

On décrit une méthode de séparation d'aldéhydes par chromatographie sur colonnes de Dowex-1 (forme bisulfite), avec élution au moyen de solutions de bisulfite de sodium de concentrations croissantes. Les composés étudiés comprenant acétaldéhyde, formaldéhyde, hydroxy-5-méthylfurfural, furfural et vanilline ont été séparés complètement les uns des autres.

ZUSAMMENFASSUNG

Mischungen von Carbonylverbindungen wurden mit Dowex-1-Kolonnen in der Bisulfitform chromatographiert. Als Elutionsmittel wurden Natriumbisulfit-lösungen mit ansteigenden Konzentrationen verwandt. Die untersuchten Verbindungen Acetaldehyd, Formaldehyd, 5-Hydroxymethylfurfural, Furfural und Vanillin wurden vollständig voneinander getrennt. Die Eluate wurden quantitativ analysiert.

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SUBMICRO METHODS FOR THE ANALYSIS OF ORGANIC COMPOUNDS

THE DETERMINATION OF ACETYL GROUPS

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The determination of acetyl groups was for many years one of the least satisfactory methods in microanalysis, until WIESENBERGER[1] improved the accuracy very considerably, mainly by introducing various refinements in the distillation apparatus. Despite this advance the method can provide difficulties with new compounds because it depends essentially on the saponification process being completely quantitative; and this is often a function of time, the particular saponification reagent chosen and the particular characteristics of the compound.

When the development of a method for the determination of acetyl on the submicro scale was being considered, we had had no experience of this type of distillation on this minute scale of operation, and it was thought that there would be many difficulties; accordingly, other possible approaches were first examined.

It has been reported[2,3] that saponification with aqueous alkali, followed by passage of the solution through an ion-exchange column, yields satisfactory results on the micro scale; the acetic acid in the eluate is titrated either alkalimetrically or iodimetrically. Attempts were made to adapt this method to the submicro scale[4,5].

With a resin bed of Zeo-Karb 225 (100–200 mesh; 30 × 5 mm), it was possible[5] to carry out ion exchange of the 1-ml hydrolysate and recover microgram amounts of acetic acid quantitatively with 2.5 ml of wash water. The Amberlite CG-120 and IR-120 resins gave very high recoveries, as did the Zeo-Karb unless regeneration was done with great care. However, when hydrolysis of standard glucose pentaacetate was done with 4–5 N sodium hydroxide at 100°, exceedingly high values for acetyl were obtained; these were eventually traced to reaction products other than acetate which gave titratable acids on passing through the ion-exchange column. When hydrolysis was done at room temperature, results were much better. Hydrolysis with 0.5 N barium hydroxide in silica tubes at 110° for 45 min was then tested and satisfactory results were obtained for various N-acetyl compounds (Table I). But the time of hydrolysis and the excess of barium hydroxide present proved extremely critical with other compounds, *e.g.* *p*-acetaminophenol and 2-acetamino-5-nitrobenzotrifluoride. Further investigation of this method was therefore abandoned; full details of the above procedure can be found elsewhere[5].

FEIGL[6] has described a spot test for O-acetyl based on pyrohydrolysis; the compound is mixed with manganese(II) sulphate tetrahydrate and is then heated;

TABLE I

SUBMICRO ALKALINE HYDROLYSIS AND ION-EXCHANGE METHOD

Compound	Wt. taken (μg)	Acetyl calcd. (%)	Acetyl found (%)	Recovery (%)
Phenacetin	37.47	24.02	24.7	102.9
	53.01		23.4	97.5
Acetanilide	44.17	31.84	32.2	101.1
	64.39		32.0	100.5
p-Bromoacetanilide	42.88	20.11	19.5	96.9
	57.55		20.6	102.4
m-Trifluoromethyl-	45.36	21.19	20.0	94.4
acetanilide	61.27		21.2	100.0

acetic acid is detected in the evolved vapours. Attempts were made to apply this reaction quantitatively[7], but low results were always obtained (70–90%). Superheated steam was then tried, various reagents being mixed with the test compound; sodium hydrogen sulphate proved to be the most effective reagent. Good results were obtained for a very limited number of compounds but others gave high results and it was concluded that secondary decomposition occurred. Even if a wide range of O-acetyl compounds had proved amenable to this process, the method would still have been limited in scope, for N-acetyl compounds produced only a fraction of the theoretical amount of acetic acid[7].

At this stage it appeared that saponification, followed by distillation was the only remaining means of attacking the problem. Because the WIESENBERGER apparatus had given good service on the micro scale for many years, a small version of this apparatus was constructed.

Known amounts of acetic acid were distilled from volumes of solution scaled down proportionately from the micro scale, but the results were unsatisfactory. About 10 ml of distillate had to be collected to ensure complete distillation of the acetic acid, and at this dilution accurate titration was not possible. The conditions for distillation were varied, and eventually conditions were established which ensured that quantitative distillation of acetic acid could be achieved in a distillate of not more than 3 ml. In the course of this work it was found advantageous to use the same condenser for refluxing and for distillation. This was readily done by adjusting the condenser to the upper or lower position by simply turning it on the ground joint.

For saponification, aqueous 4 N sodium hydroxide, Wenzel sulphuric acid or phosphoric acid was used.

EXPERIMENTAL

Apparatus

The conventional WIESENBERGER apparatus (British Standard 1428: Part C. 2: 1954) was scaled down to the dimensions shown in Fig. 1. The inner tube of the condenser was of silica. The capacity of the flask was 20 ml, compared with the 65-ml capacity of the micro-scale flask. A boiling tube (7.5 × 1.5 cm) was used for collection of the distillate. The flask required regular cleaning with chromic acid.
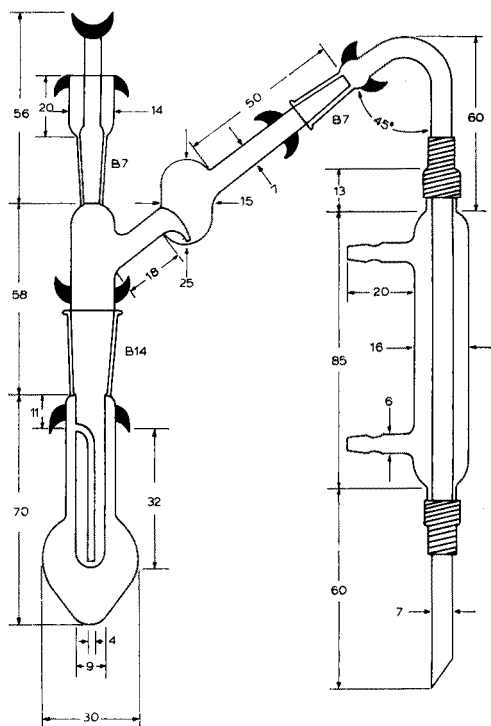
Fig. 1. Modified WIESENBERGER apparatus for submicro analysis (all dimensions in mm).

Reagents

4 N Sodium hydroxide. A standard ampoule (B.D.H., Ltd.) for preparation of 1 N sodium hydroxide was diluted to 125 ml instead of 500 ml.

Wenzel sulphuric acid. This was prepared and purified by the method of WIESENBERGER. Concentrated sulphuric acid (100 ml M.A.R.) was added, whilst cooling, to 210 ml of distilled water in a 750-ml round-bottom flask. This mixture was refluxed for 1 h, and then allowed to cool. The distillation head of an acetyl micro-apparatus was inserted in the neck of the flask and attached to the condenser. The contents of the flask were brought to the boil, and 10 ml of distillate were collected and discarded. Another 5 ml of distilled water were added through the funnel into the flask and a further 5 ml of distillate were collected in a clean 25-ml measuring cylinder. This process was continued until 25 ml of distillate had been collected, and then the liquid was transferred to a clean silica 100-ml conical flask and titrated with 0.01 N sodium hydroxide. A further 25 ml of distillate was collected, adding 5 ml of water to the acid before distilling off each successive 5 ml, so that the volume of liquid in the flask remained virtually constant. Each 25 ml of distillate should require not more than 0.02 ml of the alkali for neutralization. If a higher value was obtained, distillation was continued until the volatile acids had been completely removed. The acid solution was then cooled to room temperature and stored in a glass-stoppered bottle fitted with a dust-cap.

Phosphoric acid. Approximately 100% phosphoric acid (100 ml, B.D.H., Ltd.) and 100 ml of distilled water were mixed together and refluxed for 1 h. Any volatile products were removed as described above.

Glass-distilled water freed from dissolved carbon dioxide by boiling was used throughout.

Procedure

Transfer 30–80 μg of sample (weighed on an Oertling QO1 quartz fibre balance) to the flask and add 0.5 ml of saponifying agent. Add two platinum tetrahedra to promote even boiling and assemble the apparatus, after moistening all the joints with 2–3 drops of water, so that the condenser is in the upper position. Place 0.5 ml of water in the cup round the stopper. Immerse the lower portion of the flask in a phosphoric acid bath so that the level of the solution is slightly below the level of the acid bath. Raise the temperature to 150°–155° (alkaline saponification) or 165–170° (acid saponification), and heat for 30 min (sulphuric acid saponification), 30–60 min (alkaline saponification) or 60 min (phosphoric acid saponification). Longer heating periods may be necessary for some compounds, but the above times are applicable to a wide range of materials.

Remove the bath and allow to cool for a few minutes. The spray-trap empties during this time. Mark the flask with a glass-marking pencil at the 0.5-ml mark (acid saponification) or at the 1.0-ml mark (alkaline saponification). Turn the condenser to the lower position. If alkaline saponification has been used, add 0.5 ml of Wenzel sulphuric acid and allow 1.0 ml of water to flow into the flask in two 0.5-ml portions. If acid saponification has been used, proceed in the same way but omit the acid. Place the receiver in position at the end of the condenser. Wash the flask free from phosphoric acid and wipe dry.

Distil over the free flame (2–2.5 cm high) of a micro-burner until the condensate just reaches the condenser. Remove the flame so that the trap empties, then start the distillation again. Continue the distillation until the mark is *nearly* reached (*i.e.* 0.7 ml or 1.2 ml). Add a further 0.5 ml of water and distil. Repeat this operation until 2.75–3.0 ml of distillate have been collected.

The total time of distillation should occupy 5–6 min including the initial distillation which occupies about 2 min.

Transfer the receiver tube to a magnetic stirrer, insert a teflon-covered stirring bar and pass carbon dioxide-free nitrogen for about 10 sec. Whilst still passing nitrogen, add 250 μl of 0.01 N alkali from an Agla buret and 0.1 ml of ethanolic 0.1% phenolphthalein indicator. Back-titrate with 0.01 N hydrochloric acid from an Agla buret until the solution just becomes colourless, but a faint pink tinge remains in the bubbles. The end-point is most easily seen under close "daylight" lighting.

Determine the blank on the various reagents by following the whole procedure without a sample. The blanks are usually about 3 μl, occasionally rising to 5 μl. Check the sodium hydroxide solution against the standard 0.01 N hydrochloric acid with each series of determinations.

RESULTS AND DISCUSSION

There is a degree of uncertainty in the standard textbooks about the type of

hydrolysis — acid or alkaline — which is most appropriate for N-acetyl and O-acetyl compounds. Accordingly a selection of materials was hydrolysed by aqueous $4 N$ sodium hydroxide, Wenzel sulphuric acid and diluted phosphoric acid. Representative results are shown in Table II. Unless otherwise indicated, acid hydrolysis with sulphuric acid at $165-170°$ required a period of 30 min, as did alkaline hydrolysis at $150-155°$, whereas hydrolysis with phosphoric acid at $165-170°$ required not less than 1 h. Sample weights of 30–80 μg were used in all cases.

TABLE II

SUBMICRO DISTILLATION METHOD

Compound	Acetyl calcd. (%)	% Acetyl found		
		H_2SO_4	H_3PO_4	$NaOH$
Phenacetin	24.0	24.8	24.2	24.2
		23.7	24.4	23.3
Acetanilide	31.8	31.6	31.0	32.7
		31.3	31.5	31.6
Acetylglycine	36.7	36.1 [a]	35.9	33.3
		35.0 [a]	36.2	32.1 [a]
1-Acetyl-3-methylurea	37.1	37.3	36.2	28.1
		35.9	36.9	29.8 [a]
N-Acetyl-DL-methionine	22.5	23.4	22.0	23.1
		21.7	21.9	22.6
N-Acetyl-DL-tryptophan	17.5	18.3	17.0	16.0
		16.9	16.8	18.3
N-Acetyl-DL-leucine	24.8	24.3	25.6	25.5
		24.8	24.3	25.4
Acetaminophenol	28.4	28.8	—	—
		29.3	—	—
Pentaacetylglucose	55.1	54.2	54.3	54.5
		57.2	55.5	55.4
Hexaacetylmannitol	59.5	58.3	58.9	59.8 [a]
		60.5	60.7	58.3
Tetraacetyl-D-galactose-diethyldithioacetal	37.9	39.1 [b]	39.4 [b]	39.4 [b]
		37.2 [b]	42.8 [b]	37.3 [b]
		36.5 [b]		
Acetovanillone	25.9	26.3	23.4	1.1
		25.2	26.2	

[a] Saponification for 1 h
[b] See text.

Hydrolysis with phosphoric acid possessed no apparent advantages over the other methods; the method with Wenzel sulphuric acid appeared to be the most generally reliable. The only compounds which gave slightly more consistent results on alkaline hydrolysis were pentaacetylglucose and hexaacetylmannitol. Several compounds, e.g. acetylglycine, 1-acetyl-3-methylurea and acetovanillone, were not quantitatively hydrolysed by $4 N$ sodium hydroxide. Alkaline hydrolysis also had the disadvantage that a precipitate formed during the acidification before distillation; probably the precipitate consisted of sodium sulphate and silicic acid. Its presence made the handling of the distillation step rather critical.

With sulphuric acid, acetylglycine gave low and variable results after hydrolysis for 30 min, but satisfactory results after 1–1.5 h; extension of the hydrolysis to 2 h produced no further improvement. Acetylsalicylic acid (aspirin) gave very variable results in all cases, as happens on the micro scale.

One compound containing sulphur, tetraacetyl-D-galactose-diethyldithioacetal, was tested and gave very high recoveries under the usual conditions. The results were improved considerably when 1 mg of mercuric sulphate was added before the distillation, though they still tended to be high.

The distillation step was the most critical part of the procedure. The volume of the distillate had to be kept low, otherwise detection of the end-point of the final titration became difficult. By following the recommended technique it was possible to recover the acetic acid quantitatively in a volume of 2.5 ml of distillate; distillation and titration of a further 2.5 ml gave a result equivalent to a similar blank determination.

TABLE III

COMPARISON OF METHODS

Hydrolysing agent	No. of samples	No. of results	Average recovery (%)	Average relative error (%)
Wenzel H_2SO_4	12	43	99.1	2.5
1 : 1 H_3PO_4	12	37	98.2	2.6
4 N NaOH	11	24	98.7	3.1

The average recoveries by the 3 hydrolysis procedures were calculated; compounds for which a particular type of hydrolysis was obviously unsuitable were, of course, omitted. The results (Table III) indicated that hydrolysis with sulphuric acid was slightly preferable to the other procedures. In general, results should lie within ± 5% of the theoretical 100% recovery; this is approximately the same accuracy as is generally obtained on larger scales of working.

SUMMARY

Methods are described for the determination of O-acetyl and N-acetyl groups in 30–80-μg samples of organic compounds. The best general method involved hydrolysis with Wenzel sulphuric acid and distillation of the acetic acid formed, in a small apparatus of the WIESENBERGER type, followed by visual acid–base titration. The overall recovery was 99.1% and the average relative accuracy was ±2.5%; accuracy and precision were slightly less satisfactory for alkaline hydrolysis or hydrolysis with phosphoric acid.

RÉSUMÉ

Les auteurs décrivent des méthodes pour le dosage des groups O-acétyl et N-acétyl dans des échantillons de substances organiques de 30–80 μg. La meilleure

méthode générale comprend hydrolyse avec acide sulfurique Wenzel, distillation de l'acide acétique formé dans un petit appareil, de type WIESENBERGER, et titrage acide–base visuel. Exactitude moyenne relative: $\pm 2.5\%$. L'exactitude et la précision sont un peu moins bonnes avec hydrolyse alcaline ou hydrolyse au moyen d'acide phosphorique.

ZUSAMMENFASSUNG

Es werden Methoden zur Bestimmung von O-Acetyl- und N-Acetyl-Gruppen in Proben organischer Verbindungen von 30–80 μg beschrieben. Die beste allgemeine Methode verwendet die Hydrolyse mit Wenzel-Schwefelsäure und die Destillation der Essigsäure. Die Essigsäure wird in einer kleinen Apparatur nach WIESENBERGER gebildet und anschliessend mit einer Base titriert. Die Gesamtausbeute beträgt 99.1%, die durchschnittliche Richtigkeit $\pm$ 2.5%. Richtigkeit und Genauigkeit sind bei der Alkalihydrolyse oder der Hydrolyse mit Phosphorsäure etwas schlechter.

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OXIDATION OF ORGANIC COMPOUNDS BY VANADIUM(V)

PART I. MONOHYDRIC ALCOHOLS

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Vanadium(V) has been employed for the determination of certain inorganic compounds[1], but systematic studies of its use for the oxidimetric determination of organic compounds has not so far been made. Oxalic acid[2] has been used for the standardisation of vanadate solutions in 50% sulphuric acid. The oxidation of indigo[3] and hydroquinone[4] by vanadate solutions using oxalic acid as catalyst has been reported by RAO *et al.* Tartaric acid can be oxidized by refluxing with a vanadate solution under suitable conditions[4]. WEST AND SKOOG[5] have reported the use of vanadium(V) solutions in the oxidimetric determination of certain hydroxy acids and polyhydric alcohols. Recently, WATER AND LITTLER[6] have made a qualitative survey of the oxidation of a variety of organic compounds by vanadium(V) in order to study the mechanisms of the reactions.

Quantitative oxidations of monohydric alcohols with vanadium(V) do not so far appear to have been attempted. It was therefore thought worthwhile to study the oxidation of these and other organic compounds purely from an analytical aspect. Recently, oxidative determinations of some organic compounds were reported[7] and the present paper is part of a series intended to provide a systematic study.

EXPERIMENTAL

Preparation of vanadate solution

A standard solution of vanadium(V) was prepared by dissolving the requisite amount of sodium metavanadate (E. Merck) in the minimum amount of A.R. sulphuric acid and diluting to the required volume with distilled water. The solution was standardized against standard iron(II) solution in the presence of N-phenylanthranilic acid indicator.

Preparation of alcohol solution

The alcohols used were of the purest grade available and were further purified by refluxing with calcium oxide followed by distillation. Standard 0.02 M solutions of the alcohols in water were prepared.

Procedure

The reaction mixture consisted of an aliquot of vanadate solution to which sufficient sulphuric acid and distilled water were added to give the required acidity. This solution was cooled before addition of alcohol and the final volume in each case

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was 50 ml. The solution was refluxed for a definite time on a water bath, after which it was cooled and the excess of vanadate was back-titrated, after dilution, with standard iron(II) solution in the presence of N-phenylanthranilic acid indicator. The temperature of the reaction mixture was about 90°.

RESULTS

Oxidation of methanol

The oxidation of methanol proceeded with the consumption of 4 equivalents of oxygen per mole of the alcohol, corresponding to the formation of formic acid. It was observed that under similar conditions formic acid did not undergo any appreciable oxidation even after refluxing for 12 h. A blank was always run along with the reaction mixtures.

As indicated in Table I, the oxidation of methanol to formic acid stage required about 6 h under the optimum conditions.

Oxidation of ethanol

There was negligible oxidation of ethanol at room temperature but on refluxing oxidation occurred. In first 1–3 h, depending upon the acidity, ethanol consumed about 6 equivalents of the oxidant; up to this stage oxidation was fast compared to that of methanol. However, further oxidation was slow. At an overall acid concentration of 10.8 N, the oxidation was complete in about 8 h, a mole of ethanol consuming 10 equivalents of oxidant; it was observed that no further oxidation then occurred. This supports the earlier view[7] about the oxidation of acetaldehyde. The oxidation route followed by ethanol appears to involve formation of acetaldehyde, which then undergoes oxidation as described previously. Probably at high acidity the glyoxal resists oxidation and hence only 6 equivalents of oxidant per mole of ethanol are consumed (*cf.* oxidation with alkaline permanganate[1]). A qualitative test for formic acid was given by the reaction mixture in the case where 10 equivalents were consumed.

Oxidation of n-propanol

Oxidation of *n*-propanol with vanadium(V) required 7 equivalents of oxidant per mole. The results indicated that no single reaction course was followed, although they were quite reproducible. When the reaction mixture was exposed to sunlight or to the light of a 1000 W tungsten filament lamp, 4 equivalents of oxidant per mole of alcohol were used (see Table I). This corresponded to the formation of propionic acid which resisted oxidation under these conditions.

Oxidation of isopropanol

As in the case of other alcohols, almost no oxidation occurred in the cold. On refluxing 8 equivalents of the oxidant were consumed per mole of the alcohol (Table I). This corresponded to the oxidation of the alcohol to a mole each of acetic acid, formic acid and water.

Oxidation of n-butanol

The oxidation of *n*-butanol in the dark at ordinary temperature was very

TABLE I

OXIDATION OF MONOHYDRIC ALCOHOLS WITH VANADIUM(V) [a]

| Overall concentrations | | | Time of completion (min) [a] | | | | | | | | |
Acid (M)	Vanadate (N)	Alcohol (M)	MeOH	EtOH	n-PrOH	iso-PrOH	n-BuOH	iso-BuOH	sec-BuOH	tert.-BuOH	n-AmOH
10.8	0.04	0.002	480	120	240	120	120	120	45	240	90
9.0	0.04	0.002	480	120	120	210	120	180	60	360	120
7.2	0.04	0.002	—	180	240	—	240	240	90	480	180
9.0	0.08	0.002	360	60	60	90	120	120	45	240	90
9.0	0.02	0.002	600	120	240	300	—	—	—	—	—
9.0	0.04	0.004	480	180	120	240	120	—	—	—	—
9.0	0.04	0.001	360	60	60	180	120	90	45	240	120

[a] Time of completion refers to the heating time required for oxidation up to the stage given in the text.

slow. Even at very high acid concentrations, only about 5 equivalents of the oxidant were consumed in about 24 h, but the reaction was not quantitative. However, on refluxing 10 equivalents of the oxidant were consumed per mole of the alcohol, which corresponded to the oxidation of *n*-butanol to the propionic acid stage; no further oxidation then occurred.

Oxidation of isobutanol

In the oxidation of isobutanol with vanadium(V), at refluxing temperatures 8 equivalents of the oxidant were consumed per mole of the alcohol. This suggests that the alcohol was oxidized to one mole each of acetone, carbon dioxide and water; acetone was observed not to undergo oxidation under these conditions.

Oxidation of sec.-butanol

The oxidation of *sec.*-butanol with vanadium(V) on heating was rapid compared with that of other isomeric alcohols; this may be the case with other secondary alcohols also. Fourteen equivalents of the oxidant were consumed per mole of the alcohol; this corresponded to the formation of a mole each of acetic acid, formic acid, carbon dioxide and water. Under the optimum conditions the reaction was complete in about 45 min (Table I).

Oxidation of tert.-butanol

tert.-Butanol was oxidized on refluxing, with the consumption of 12 equivalents of the oxidant per mole. This corresponds to oxidation to one mole of acetic acid and 2 moles of formic acid.

Oxidation of n-amyl alcohol

After about 24 h this alcohol consumed 4 equivalents of oxidant at ordinary temperature; this corresponded to the formation of the corresponding carboxylic acid. On refluxing, the reaction was quite fast and proceeded further, 12 equivalents of the oxidant per mole being consumed. This agreed with oxidation up to the formation of butyric acid, which resisted further oxidation under similar conditions. Under optimum conditions the reaction was complete in about 90 min.

DISCUSSION

It was observed that the oxidation of monohydric alcohols, which is usually slow at room temperature, was accelerated appreciably by heating and by increasing acid concentration[5]. In most cases, the reactions followed definite courses but these were different for different alcohols.

Unlike some oxidations with other reagents, the oxidation of primary alcohols with vanadium(V) usually involved removal of one carbon atom and a carboxylic acid containing a carbon atom less than the alcohol was produced. The fatty acids were quite resistant to further oxidation under the conditions described.

The occurrence of C–C bond cleavage in the oxidation of alcohols and aldehydes has been reported by various workers. BARNARD AND KARAYANNIS[8] reported the formation of fatty acids containing one carbon atom less than the parent alcohols in oxidation with dichromate. CONANT AND ASTON[9] reported the production of

acetone in the oxidation of isobutyraldehyde with dilute acidic dichromate solution. WATERS[10] also observed acetone to be the oxidation product of isobutyraldehyde in oxidation with acidic vanadate solution.

The elimination of one carbon atom during the oxidation indicates that such oxidations do not follow the same course as oxidations with permanganate. A close examination of the data for the oxidation of the alcohols and aldehydes indicates that the C–C bond is not broken until the aldehyde stage is reached, $i.e.$ the reaction

$$RCH_2OH \xrightarrow{(O)} R.CHO$$

proceeds stoichiometrically, but the subsequent reaction cannot be represented by the equation

$$R.CHO \xrightarrow{(O)} R.COOH$$

The oxidation is facilitated by an increase in the overall acidity, thus it seems probable that the C–C cleavage occurs via the enolisation of the aldehyde, a process which is acid-catalysed.

The formation of carboxylic acids containing one carbon atom less than the parent alcohol, suggests that the attack occurs at the α-carbon atom and the following mechanism appears reasonable.

$$R.CH_2CH_2OH \xrightarrow{(O)} R.CH_2CHO$$

$$R.CH_2CHO \xrightarrow{\text{enolisation}} R.CH=CH(OH)$$

$$\downarrow {\substack{\text{hydroxylation} \\ H_2O+(O)}}$$

$$R.CH(OH).CHO \longleftarrow R.CH-CH-OH$$
$$\qquad\qquad\qquad\qquad\qquad HO \quad OH$$

$$\downarrow (O)$$

$$R.CO.CHO \xrightarrow{(O)} R.COOH + CO_2$$

The first step is the oxidation of the alcohol to the corresponding aldehyde. The aldehyde then undergoes enolisation followed by hydroxylation of the double bond, forming an α-hydroxyaldehyde hydrate, which then loses a water molecule forming an α-ketaldehyde. The α-ketaldehyde is then decarboxylated to give the lower carboxylic acid.

The above mechanism is supported by a detailed study of the oxidation of ethanol, its various oxidation products and related compounds; acetaldehyde was observed to consume 8 equivalents of the oxidant, thus being oxidized to the formic acid stage. Glycolic acid and glyoxal behaved similarly. A study of the oxidation of ethyl acetate and ethyl acetoacetate was also undertaken and it was observed that these required respectively 10 and 18 equivalents of the oxidant per mole of the ester. This suggests that the two esters were oxidized to a mole each of acetic and formic acids along with carbon dioxide and water (1 mole of each in the case of ethyl acetate, and 3 moles of carbon dioxide and 2 moles of water in the case of ethyl acetoacetate).

Methanol was an exception as it yielded only formic acid. Abnormal behaviour was also shown by n-propanol.

Oxidation of secondary alcohols did not follow a generalized pattern. Isopropanol produced one mole each of acetic acid, formic acid and water; yet acetone cannot be assumed to be the intermediate product because the oxidation of acetone was much slower under identical conditions. In the case of *sec.*-butanol, a mole each of acetic acid, formic acid and carbon dioxide were formed.

The only representative tertiary alcohol studied was *tert.*-butanol, which was oxidized to a mole each of acetic acid and water and 2 moles of formic acid.

The oxidation of alcohols with vanadate solution can be employed for the oxidimetric determination of these alcohols and for purity control.

SUMMARY

The oxidation of various monohydric alcohols with pentavalent vanadium in sulphuric acid medium is described. Optimum conditions for quantitative oxidation and the reaction mechanisms are discussed.

RÉSUMÉ

Les auteurs ont examiné l'oxydation de divers alcools par le vanadium(V), en milieu sulfurique. Les conditions optima d'oxydation quantitative et le mécanisme de la réaction sont donnés.

ZUSAMMENFASSUNG

Die Oxydation verschiedener einwertiger Alkohole mit Vanadium(V) in schwefelsaurem Medium wird beschrieben. Optimale Bedingungen für die quantitative Oxydation und der Reaktionsmechanismus werden diskutiert.

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POLAROGRAPHY OF URANYL–MALATE COMPLEXES AT MODERATELY LOW TEMPERATURE

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In a previous study of the effect of temperature on the polarographic behavior of uranyl–malate complexes[1], remarkably different characteristics were found to exist between the temperature ranges of 9.1°–21.5° and 28.5°–48.5°. At the lower temperature range, a partial polymerization to form a dimer occurred. However, when the temperature was increased above 21.5°, the dimer began to depolymerize to a monomer and a complete depolymerization was confirmed at the temperature range of 28.5° to 48.5°. In the previous article[1] the discussion was concentrated on the higher temperature range, by using a normal operating temperature of 30° $\pm$ 0.1°. In a continuation of the investigation of the polarographic behavior of uranyl–malate complexes at the lower temperature range of 9.1°–21.5°, the present paper extends the discussion from a constant ligand concentration (0.1 M) and constant pH value (4.5) to widely varying conditions of ligand concentration and pH value at a constant temperature of 15°.

EXPERIMENTAL

The current–voltage curves were obtained with a Fisher Elecdropode as described previously[1]. In this case, however, the temperature was maintained at 15° $\pm$ 0.1° instead of at 30° $\pm$ 0.1°.

Viscosity measurements were carried out with an Ostwald viscometer which was thermostatted at 15° $\pm$ 0.1°. The densities of the polarographic solutions were also measured at 15° with a hydrometer.

An Industrial Instruments conductivity bridge Type RC with a cell having a cell constant of 0.13 was used for the conductometric titration.

The preparation and standardization of malic acid and uranyl perchlorate solutions were the same as given in our previous paper[1].

A 0.2 M sodium perchlorate solution was used as a supporting electrolyte and Triton X-100 (0.002% solution) was used as a maximum suppressor.

RESULTS AND DISCUSSION

Diffusion currents

All reduction waves had diffusion-controlled limiting currents with $i_d/h^{\frac{1}{2}} =$ 0.660 $\pm$ 0.005 for variations of the mercury head from 88.7 to 44.0 cm. A constant value of $i_d/C = 4.27 \pm 0.04$ was also obtained at pH 4.5 and ligand concentration

0.1 M, where C is the concentration of uranyl ion. This indicates that the U(V)–malate complexes were stable toward disproportionation in the electrode reduction.

As shown in Fig. 1, the diffusion current gradually decreased with increasing concentration of ligand. However, two constant values of $i_d \eta^{\frac{1}{2}}$, 5.2 and 4.9, were obtained for malic acid concentrations ranging from 0.04 M to 0.70 M, and from 0.85 M
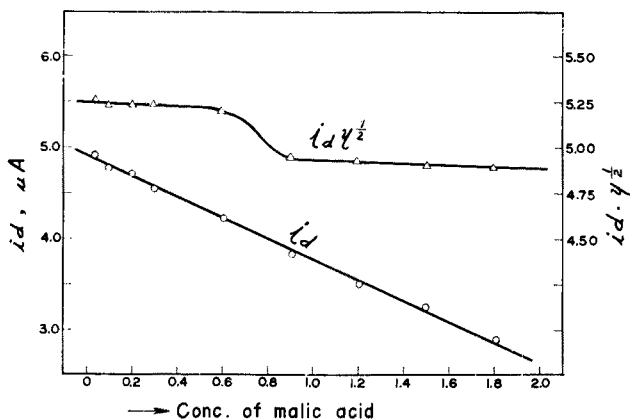
Fig. 1. Correction for the effect of viscosity on diffusion current (1.0 mM UO$_2$(ClO$_4$)$_2$, 0.2 M NaClO$_4$ and 0.002% Triton X-100 at pH 3.0 and 15°).

to 1.80 M, respectively, after the correction for viscosity effect due to the increment of reagent concentration. This reveals that the Ilkovic–Stokes-Einstein equation[2] is valid and two kinds of chelate species with constant composition must have existed at the respective reagent concentrations mentioned above.

Limits of complex formation, polymerization and reversibility

The plots of the limiting regions of complex formation, polymerization, and reversibility as functions of pH value and concentration of complexing agent are shown in Fig. 2. Region A, an area of no reaction, was demonstrated by the identity of the half-wave potentials with that of simple uranyl ion, −0.18 V $vs.$ S.C.E.[3]. In region B, all polarograms had a mean value of 0.059 V of $E_{1/4} - E_{3/4}$ for one-electron reversible reduction. However, in region C the $E_{1/4} - E_{3/4}$ values were 0.041 to 0.055 V. The deviation from the theoretical value for one-electron reversible reduction was attributed to the polymerization of the complexes[4].

The degree of polymerization was evaluated from eqns. (1) and (2) which were given by the authors[4].

$$\frac{E_{1/2} - E_{7/8}}{E_{1/8} - E_{1/2}} = \frac{243 + 602 \ (b/a)}{243 \ (b/a) + 602} \tag{1}$$

$$E_{1/4} - E_{3/4} = \frac{1}{b} 0.028 \ (1 + b/a) \tag{2}$$

where a and b are the values in the electrode reaction

$$b M_a X_p{}^{(am - pl)} + abne = a M_b X_q{}^{(b(m-n) - ql)} + (bp - aq) X^{-1} \tag{3}$$
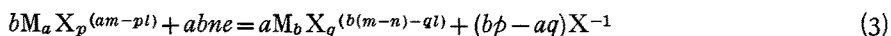
The data obtained are presented in Table I, in which the partial dimerization of the complexes was evidenced by a and b values greater than unity. The higher the pH value, the greater the ligand concentration needed for dimerization; the pH region for polymerization shrinks gradually with increases in the malic acid concentration.
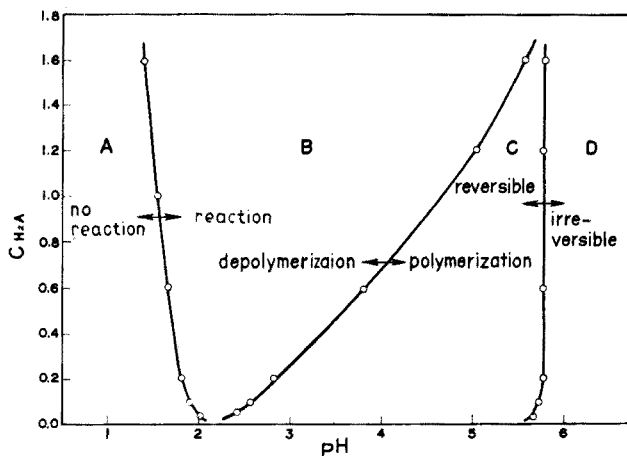
Fig. 2. Limits of reversibility, complex formation, and polymerization (1.0 mM $UO_2(ClO_4)_2$, 0.2 M $NaClO_4$ and 0.002% Triton X-100).

TABLE I

DEGREE OF POLYMERIZATION IN VARIOUS POLAROGRAPHIC SOLUTIONS

pH value	$E_{1/4}-E_{3/4}$	$\dfrac{E_{7/8}-E_{1/2}}{E_{1/2}-E_{1/8}}$	b	a
$C_{H_2A}=0.04\ M$				
2.0	0.058	0.98	1.00	1.00
3.0	0.041	0.96	1.45	1.30
5.7	0.041	0.95	1.45	1.32
$C_{H_2A}=0.10\ M$				
2.6	0.059	0.99	1.00	1.00
3.6	0.041	0.88	1.45	1.32
5.8	0.041	0.95	1.40	1.40
$C_{H_2A}=0.20\ M$				
2.8	0.059	1.00	1.00	1.00
3.6	0.041	1.04	1.40	1.32
5.4	0.041	1.00	1.40	1.40
$C_{H_2A}=0.60\ M$				
3.8	0.058	1.02	1.00	0.97
4.3	0.046	1.05	1.30	1.18
5.3	0.047	1.05	1.28	1.16
$C_{H_2A}=1.20\ M$				
4.6	0.058	1.00	1.00	1.00
5.1	0.050	1.03	1.20	1.09
5.5	0.051	1.04	1.19	1.08
$C_{H_2A}=1.60\ M$				
1.8–5.8	0.058	1.00	1.00	1.00

When the pH was above 5.8 (in region D, Fig. 2) a maximum still persisted on the waves, even though the amount of Triton X-100 (0.002%) added was doubled, and the waves observed were all irreversible on account of their extremely high $E_{1/4}-E_{3/4}$ value of 0.085 V.

Dimerization evidenced by conductometry

Further proof for the dimerization of the complexes at lower temperature was obtained by conductometric measurements (Fig. 3).

As shown in curve 1 of Fig. 3, two kinds of monomers with metal–ligand ratios of 1:1 and 1:2 were confirmed at 30°. However, at 15°, polymerization occurred, forming 3 kinds of dimeric species with metal–ligand ratios of 2:1, 2:2, and 2:3 in
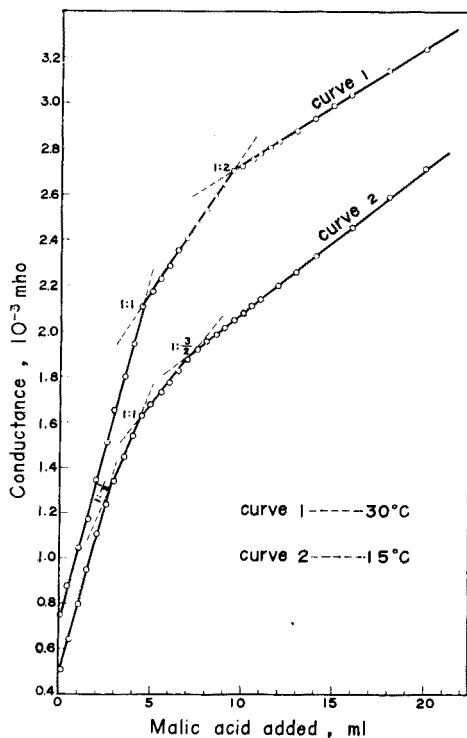
Fig. 3. Conductometric titration (5.0 ml of 10 mM UO$_2$(ClO$_4$)$_2$ + 160 ml of H$_2$O + x ml of 10 mM malic acid).

which the metal ion was in excess, equivalent, and insufficient to the ligand, respectively. Obviously the lower temperature favored the polymerization of the complexes, and the results obtained by conductometry agreed with those of the polarographic studies mentioned above.

Effect of pH and ligand concentration

The effects of pH value and ligand concentration on the half-wave potential were studied over the pH range 1.8–5.8. It is obvious from Fig. 4, that at pH 4.5 the

$-E_{1/2}$ values decreased with increasing malic acid concentration when the malic acid concentration was lower than 1.2 M, indicating a gain in ligand of the reduced species in the reduction. However, when the malic acid was above 1.2 M, the $-E_{1/2}$ values increased with increasing ligand concentration, revealing a loss of ligand in the reduction.
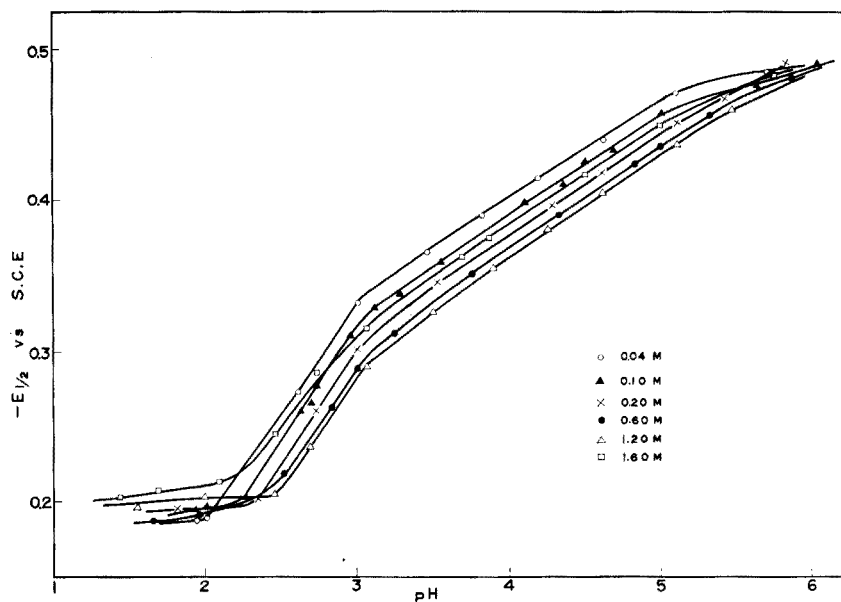
Fig. 4. Plots of $-E_{1/2}$ vs. pH (1.0 mM UO$_2$(ClO$_4$)$_2$, 0.2 M NaClO$_4$, and 0.002% Triton X-100).

When the pH was lower than 1.8, the lack of reaction between uranyl ion and malic acid was demonstrated by the fact that there was no shifting of the half-wave potentials.

Above pH 5.6, the curves were essentially superimposed. This shows that the half-wave potential was independent of the ligand concentration, and that the ligand number of the uranium(VI) was the same as that of uranium(V).

The number of hydrogen ions involved in the electrode reduction were found to be 2,1 and 0 for the pH ranges 1.80–3.00, 3.00–5.00, and 5.00–5.80, respectively, as evidenced by the slope of $\Delta E_{1/2}/\Delta$pH, -0.12, -0.06, and -0.01.

SUMMARY

The polarographic behavior of uranyl ion at the dropping mercury electrode was examined in malic acid solution at 15°. The limiting regions of complex formation, polymerization, and reversibility as functions of pH value and ligand concentration were studied. The dimerization of the complexes was demonstrated by the current–voltage curves and conductometric measurements. Three kinds of complex species with metal–ligand ratio of 2:1, 2:2, and 2:3 were identified.

RÉSUMÉ

Les auteurs ont examiné le comportement polarographique de l'ion uranyle à l'électrode à gouttes de mercure, en milieu acide malique à 15°. On a examiné : limites de formation du complexe, polymérisation, et réversibilité en fonction du pH et de la concentration en "ligand". La dimérisation des complexes est démontrée par courbes courant–voltage et mesures conductométriques. Trois espèces de complexes ont été identifiées, avec rapport métal–ligand 2:1, 2:2 et 2:3.

ZUSAMMENFASSUNG

Das polarographische Verhalten von Uranylionen an der tropfenden Quecksilberelektrode wurde in äpfelsaurer Lösung bei 15° geprüft. Die Grenzbereiche für die Komplexbildung, die Polymerisation und die Reversibilität als Funktion des pH-Wertes und der Ligandenkonzentration wurden untersucht. Die Dimerisation des Komplexes wurde durch Stromspannungskurven und konduktometrische Messungen veranschaulicht. Drei Komplexe mit einem Metall–Liganden-Verhältnis von 2:1, 2:2 und 2:3 wurden identifiziert.

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SHORT COMMUNICATIONS

The determination of active oxygen and iron(II) in oxide compounds

In investigations of oxide materials it is often desirable to have accurate information about the average valency of the ions of Fe, Mn, Co, Ni, Cu and other elements. For this purpose many analytical methods are known, *e.g.* the determination of active oxygen in manganese oxide, manganese dioxide, nickel and cobalt oxide[1] and the determination of iron(II) in magnetite.

Very recently a method for the determination of iron(II) in ferrites was described in which a hot phosphatocerate solution is used as a solvent[2].

Although these methods are very useful, their applicability is limited. Methods for the determination of "active oxygen" are quite different from those for the determination of iron(II). Moreover, for these methods the sample must be in a finely divided form; this may lead to errors from unwanted oxidation during the pulverization operation.

These difficulties can be overcome by the method which is described below; this was developed in 1947, and published as a short note in a thesis in 1954[3]. Since that time it has been used with very good results for routine work in research on magnetic materials, ferrites and oxidic semiconductors.

The oxide material is dissolved in hydrochloric acid to which a small amount of iron(II) has been added. If the sample contains active oxygen due to the presence of iron, manganese, cobalt, nickel or lead in the trivalent or tetravalent state, part of the iron(II) solution is oxidized. The iron(II) chloride is finally titrated with cerium(IV) sulphate solution.

It was found possible to dissolve lumps of ferrites and oxidic material in 6 N hydrochloric acid in sealed glass tubes at elevated temperatures; it is necessary to exclude air by filling the tube with nitrogen. It is known that hydrochloric acid can contain small amounts of chlorine, especially when it is stored for a while. If the amount of iron(II) in the sample is very small it is possible that no iron(II) will be found at all. Therefore a known small amount of iron(II) is added to the acid and a blank determination is performed.

Reagents

6 N Hydrochloric acid + 0.2 N iron(II) chloride. Dissolve 11.2 g of pure iron in 6 N hydrochloric acid. Make up to 1 l with 6 N hydrochloric acid. Store the solution in the reservoir of a micro-buret as described below.

6 N Hydrochloric acid + 0.01 N iron(II) chloride. Dissolve 0.56 g of pure iron in 6 N hydrochloric acid. Make up to 1 l with 6 N hydrochloric acid. Store the solution in the reservoir of a micro-buret as described below.

Distilled water, oxygen-free. Boil distilled water for several minutes. Cool.

Nitrogen. Oxygen-free.

Cerium(IV) sulphate solutions, 0.01 N and 0.05 N. These were prepared in the usual way and standardized against As_2O_3.

Apparatus

The micro-burets used were 5-ml burets from Metrohm (type E 274). The outlet arm was fitted via a ball and socket joint to a small silver reductor column[4] (10 × 1.5 cm), below which the outlet tube was drawn to the normal diameter for a buret tip.

Pyrex tubes (external diameter *ca.* 12 mm, internal diameter *ca.* 9.6 mm and length *ca.* 250 mm) sealed at one end, were cleaned with a saturated solution of CrO_3 in concentrated sulphuric acid. The chromic–sulphuric acid was rinsed out carefully with water and the tubes were then washed with a dilute solution of iron(II) sulphate, before final rinsing with distilled water.

Heating blocks were constructed from aluminium blocks (30 × 30 × 6 cm); in each block, 8 holes of length 25 cm and diameter 1.5 cm, were drilled. Each block was placed on an electric hot-plate for heating.

General precautions

(*a*) Ferrites should not be powdered before dissolving, otherwise there is a chance of oxidation by air.

(*b*) The amount of sample may be increased or decreased as required.

(*c*) Some ferrites should be heated at 300° for complete dissolution.

(*d*) Tubes which are not properly sealed can explode violently on heating, especially at 300°. Therefore the aluminium heating block should be placed in a cage of iron wire with bricks in front of the holes. When the tubes are taken out of the aluminium block, and during all further handling of them, safety goggles should be worn.

Determination of active oxygen

Weigh exactly *ca.* 100 mg ($= a$) of ferrite sample, and transfer to a Pyrex tube. Flush the tube with a stream of nitrogen for several minutes by means of a glass capillary reaching to the bottom of the tube; remove the capillary. Add an exactly measured quantity of 6 *N* hydrochloric acid + 0.2 *N** iron(II) chloride solution from the micro-buret. This quantity should be between 4 and 6 ml. The solution should not wet the upper wall of the tube. Flush the tube with a stream of nitrogen, the capillary nearly reaching to the surface of the solution; remove the capillary. Make a constriction in the tube at the open end by means of a blowpipe. The inner diameter of the constriction should be a little wider than the outer diameter of the capillary. Flush the tube with a stream of nitrogen, the capillary nearly reaching to the surface of the solution to expel any oxygen.

Seal the tube. Cool. Fill a second Pyrex tube with nitrogen and add exactly the same amount of 6 *N* hydrochloric acid + 0.2 *N* iron(II) chloride solution. Flush with nitrogen and seal as described above.

Place both tubes in the holes of the aluminium heating block. Place bricks in front of the holes and heat the block to 100°. If, after an hour, the pieces of ferrite are not dissolved, raise the temperature to 150°, or even to 300° (see point (*d*) above).

Take the tubes out of the block. Put 25 ml of 2 *N* sulphuric acid into a 300-ml conical flask and drive the air out of the flask by adding about 100 mg of sodium

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* For traces of active oxygen lower concentrations of $FeCl_2$ are used with advantage.

hydrogen carbonate. When the evolution of carbon dioxide has ceased, add another 100 mg of sodium hydrogen carbonate. Meanwhile open the tube by scratching the tube with a glassknife or file and pressing the heated end of a glass rod on the scratch. Transfer the solution to the conical flask while the carbon dioxide is still being evolved. Rinse the tube with oxygen-free distilled water.

Add 1.0 ml of 0.0025 M ferroin solution by means of a pipet and titrate with 0.05 N cerium(IV) sulphate solution until the indicator colour changes from red to light blue (V ml).

Carry out the blank in the same way (V_0 ml).

Calculation. The ferrite contains:

$$\frac{(V_0 - V) \cdot t \cdot 8}{a} \cdot 100 = \% \text{ active oxygen.}$$

where t = titre of the cerium(IV) sulphate solution.

Determination of iron(II)

Weigh exactly about 100 mg ($= a$) of ferrite, and transfer to a Pyrex tube. Flush the tube with a stream of nitrogen as before, and remove the capillary. Add an exactly measured quantity (4–6 ml) of 6 N hydrochloric acid + 0.01 N iron(II) chloride solution from the micro-buret. Carry on exactly as described in *Determination of active oxygen.*

Titrate the sample after addition of 1.0 ml of 0.0025 M ferroin solution with 0.01 N cerium(IV) sulphate solution (V ml).

Carry out the blank in the same way (V_0 ml). The ferrite contains: $(V - V_0) \cdot t \cdot$ 55.85/100 = % divalent iron.

The reproducibility of the blank determination is about 0.02 ml of standard solution.

The sensitivity is 0.002 mg of active O or 0.01 mg of Fe(II).

If the sample is small (a few milligrams) or the active oxygen or iron(II) content is very low, it is advantageous to use 0.001 N iron(II) chloride and cerium(IV) sulphate solutions. The end-point of the titration should then be detected potentiometrically. In this case, the sensitivity is 0.0005 mg of active O or 0.003 mg of Fe(II).

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Fast and complete decomposition of rocks, refractory silicates and minerals

Present methods for the decomposition of rocks and minerals are not entirely satisfactory for application to many geological and geochemical investigations. One of the recent works of this kind, by SHAPIRO AND BRANNOCK[1,2], was reviewed by HOOPS[3] who established that decomposition by the recommended procedure (H_2SO_4 + HF) was not complete and some constituents of the rocks, such as andalusite, kyanite, sillimanite, corundum, tourmaline, rutile, garnet, staurolite, zircon, spinel, graphite, gold and pyrite remained undecomposed.

CHEAD AND SMITH[4] commented on the use of ammonium fluoride by various workers and found that molten ammonium fluoride was a good flux for decomposition of some refractory silicates (quartz, orthoclase, feldspar, beryl, Fe-tourmaline). They suggested this method for the determination of silica in a glass sand. Recently the use of ammonium fluoride was recommended again by KUZNETSOV AND TANANAEV[5], and by LITEANU AND BIAN[6]. However, ammonium fluoride cannot be regarded as a universal flux because attempts to decompose such substances as sillimanite, kyanite, zircon, rutile, some refractory ceramic material (British Firebrick Standard No. 268) were ineffective.

CLAUD[7], considering different methods of decomposition of silicates and oxides, described a very effective procedure using potassium fluoride, sodium pyrosulphate, sulphuric acid, hydrofluoric acid and sodium sulphate, but unfortunately this method excludes determination of the common alkali metals.

In the recent literature connected with this problem, lithium tetraborate was mentioned as a very effective decomposing agent. WANG[8] and WELDAY et al.[9] suggested the use of lithium tetraborate as a flux for X-ray spectrography and emission spectroscopy of silicates. In view of the absence of satisfactory methods in this field an attempt was made to find a fast, complete and simple procedure for the decomposition of a wide range of rocks, minerals, and refractory ceramic materials in such a way that it would be possible to determine all the main elements of silicates, namely, sodium, potassium, calcium, magnesium, iron, aluminium, titanium and many minor elements. Silicon is determined separately by a simple, rapid and accurate procedure developed in our laboratory[10]. Numerous fluxes were investigated and it was found that decomposition of rocks, refractory silicates and minerals was rapid and complete if the material was fused with a mixture of lithium fluoride and boric acid at ca. 800–850° in a platinum crucible. Lithium tetraborate which is formed on heating the mixture proved to be an efficient flux. The fluoride removed silica as silicon tetrafluoride, while boron and excess fluoride were eliminated by addition of concentrated sulphuric acid and heating. The solution after dilution with water, addition of hydrochloric or nitric acid and boiling, was clear and normally did not require filtering. Elements forming insoluble sulphates, e.g. barium, or precipitates in acid solutions such as rare earths, niobium, tantalum or tungsten were removed by filtration. It should be stressed however that even in this latter case full dissolution of the sample was achieved and if necessary such precipitates could be rendered soluble by some normal chemical method.

Experimental

In a platinum crucible of capacity 25–30 ml mix 2 g of boric acid and 3 g of lithium fluoride (A. R. Grade). Make a small hollow in the mixture, place in 0.5 g of finely ground sample (100 mesh) and cover it by gently tapping the sides of the crucible (there is no need to mix sample with the mixture). Cover the crucible with a lid and heat it gently for 2–3 min over a small gas flame of a Meker burner. Gradually increase the flame to bring the contents of the crucible to the melting point and heat it for 10 min on the full flame. In the presence of graphitic and/or sulphide material the crucible should be opened periodically to permit oxidation. Cool the crucible quickly in water by half immersing in a stream of tap water; add 10 ml of concentrated sulphuric acid and gently heat on an asbestos plate over a Bunsen or a Meker burner until bubbles of gas are evolved. Regulate the heating so that the evolution of gas from the covered crucible is not so vigorous that loss of sample will result. When the evolution of gas has ceased, increase the temperature until copious fumes of SO_3 appear and maintain this for 2–3 min (heating with sulphuric acid should take about 30 min). Cool the crucible in *ca.* 150 ml of water in a 250-ml beaker, add 5 ml of concentrated hydrochloric or nitric acid and boil both crucible and lid until all contents are dissolved and the liquid is clear (in the presence of much aluminium and calcium (*ca.* 40–45%) it takes about 10–15 min).

This procedure was used for the decomposition of a variety of substances and the following all gave total fusion. In many cases material normally regarded as quite intractable fused in 5 min *e.g.* zircon, sillimanite, topaz.

Minerals included the following: zircons, spinel, corundum, rutile, kyanite, sillimanite, tourmaline, staurolite, garnet, topaz, tantalite, biotite. Rocks such as varieties of basalts, granite, standard rocks such as G-1, W-1, dolerite D-1, granite A.S.G. (A.N.U.), graphitic schists with pyrite, fossil wood, peridotite, and basic rocks with high chromium content caused no difficulty. Ceramics such as British Chemical Standard Firebrick No. 269, Basic slag No. 174/1, and Burnt refractory standard sample No. 76 were also decomposed satisfactorily.

By analysing the listed substances, using different methods no interference was observed in determination of such elements as sodium, potassium, calcium, magnesium, iron, aluminium, titanium.

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Spectrophotometric determination of tin with rhodamine B

Rhodamine B has been recommended as a colorimetric reagent for antimony[1-8], gallium[9] and gold[10]. The complexes formed are usually extracted into benzene or isopropyl ether. Small amounts of tin are reported to have no influence. When the extraction is performed with ethyl acetate, however, it has been shown that small amounts of tin(IV) give positive interference.

In the present paper rhodamine B is proposed as a reagent for the spectrophotometric determination of small amounts of tin. As the reagent is not specific, preliminary separations may in some cases be necessary. Small amounts of tin may then easily be determined.

Experimental

Apparatus. A Zeiss spectrophotometer model PMQ II with 1.000-cm cells provided with lids was used for determination of optical densities. The extractions were performed in ordinary separatory funnels. A common centrifuge (3000 rev./min) was used to remove dispersed water from the organic layer.

Reagents. All chemicals used were of reagent grade. 0.02 M solutions of rhodamine B were prepared by dissolving 9.58 g in water and diluting to 1 l. 0.001 M solutions of tin(IV) were prepared by dissolving 0.1187 g of tin metal in 100 ml of concentrated hydrochloric acid and diluting to 1 l with distilled water. To oxidize the tin, chlorine was passed through the solutions. Excess of chlorine was removed by nitrogen. The ethyl acetate was reused after treatment with sodium bicarbonate, water, calcium chloride and finally distillation.

Absorption curves. If a solution of rhodamine B and hydrochloric acid is treated with ethyl acetate, the organic layer becomes red. If tin(IV) is present the intensity of the colour increases. It was found necessary to measure the optical density against a blank. Figure 1 shows the absorption curve, which exhibits maxima at 522.5
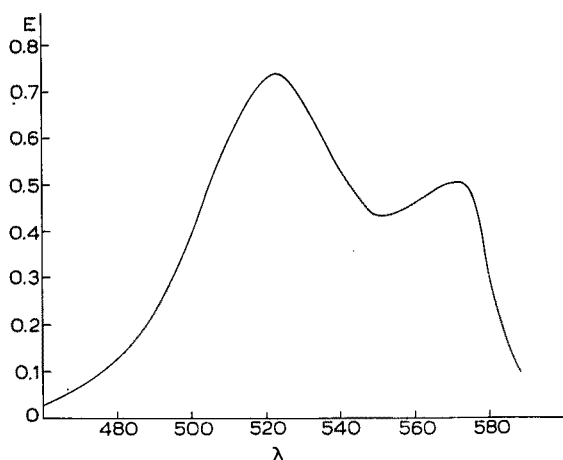
Fig. 1. Absorption curve of the tin–rhodamine B complex in ethyl acetate (0.2374 mg Sn, 47.9 mg rhodamine B in 20 ml 2 N HCl extracted into 20 ml of ethyl acetate).

and 572.5 mμ and a minimum at 550 mμ. When the tin concentration was increased, the maximum at 522.5 mμ and the minimum at 550 mμ were displaced a little towards lower wavelength values, while no displacement could be detected for the maximum at 572.5 mμ.

Effect of hydrochloric acid concentration. Extractions were performed in the presence of varying amounts of hydrochloric acid. Figure 2 shows the optical densities against the concentration of acid in the aqueous phase.
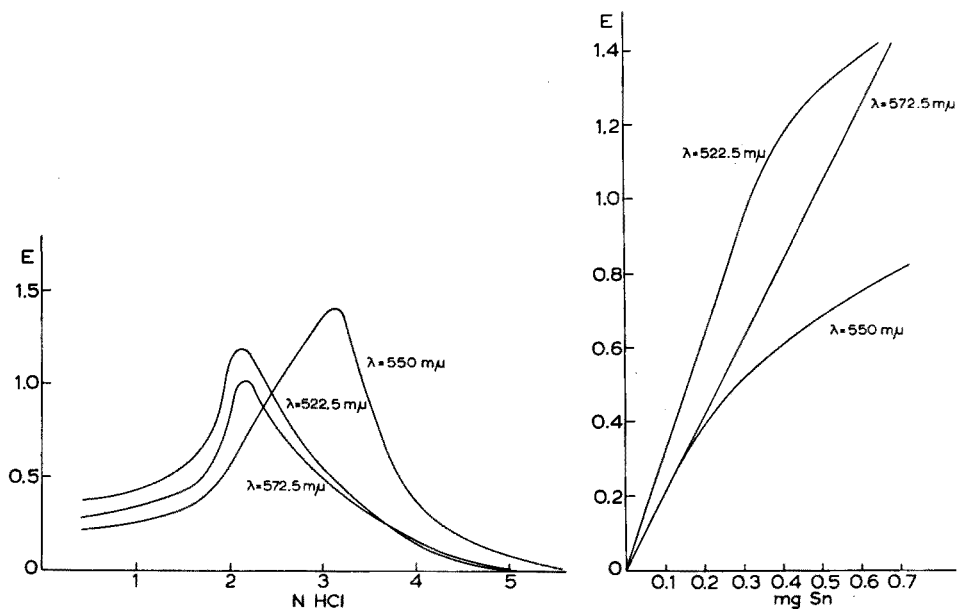
Fig. 2. Extractability of rhodamine B–tin complex as a function of the hydrochloric acid concentration (0.3561 mg Sn, 47.9 mg rhodamine B and varying amounts of hydrochloric acid extracted into 20 ml ethyl acetate). The optical densities were measured against blanks at 522.5, 550 and 572.5 mμ.

Fig. 3. Standard curve of the tin–rhodamine B complex in ethyl acetate measured against a blank at 522.5, 550 and 572.5 mμ.

When the acid concentration was too low, the sensitivity was low and the separation of the two layers proved difficult. However, an excessive concentration of acid accelerated the decomposition of ethyl acetate and thus made the system unstable. Hence, an acid concentration of 2 N was chosen even though the sensitivity was greatest at about 3.4 N at 550 mμ. As the acid concentration was increased, the colour intensity decreased for both the complex and the blank. Above an acid concentration of 6 N in the aqueous phase there was no difference between them.

Beer's law. For the verification of Beer's law the optical densities for the rhodamine B–tin complex were measured for different tin concentrations at 522.5, 550 and 572.5 mμ against a blank. An excess of rhodamine B was used, and the acid concentration was kept constant at 2 N. The time of contact of the organic and aqueous

phases was always kept constant and the organic layer was centrifuged before the optical densities were measured. Figure 3 shows the optical density plotted against the tin concentration. Nearly straight lines were obtained at 522.5 and 572.5 mμ for tin concentrations up to 0.3 and 0.7 mg of tin per 20 ml, respectively. Above these concentrations the optical densities fell off and Beer's law was not obeyed. Still the extinctions were reproducible within 6%. The optical densities were found to be constant for at least 1 h.

Procedure. Rhodamine B solution (5 ml) was added to the tin solution and diluted to 20 ml with hydrochloric acid. The aqueous phase, which at this point had an acid concentration of 2 N, was treated with 20.0 ml of ethyl acetate. The mixture was shaken for 1 min and then the layers were allowed to separate (about 2 min). Some of the organic phase was removed by a pipet and centrifuged and the optical densities were measured at 522.5, 550 and 572.5 mμ against a blank prepared in the same way, but without tin. The optical densities should be measured within 1 h. The ethyl acetate should not be allowed to stay in contact with the aqueous phase longer than necessary, because of decomposition.

Interferences. Mercury(II), iron(III), antimony(III or V), zinc or bismuth added to 0.356 mg of tin caused changes in the colour and serious interferences if the additions were 10 times the tin content; the optical densities were then increased more than 20%. When the zinc addition was only one tenth of the tin content the interference was negligible. The change in the colour may be due to complex formation with rhodamine B. Sodium nitrate or oxalic acid (10 mg) caused some increase (10%) in the optical densities when added to 0.356 mg of tin.

The following compounds did not interfere when added to 0.356 mg of tin in the amounts given: 100 mg of Na_2SO_4, EDTA, NH_4Cl, NaCl, KCl, $CaCl_2$, $MgCl_2$, $NiCl_2$ or $AlCl_3$; 50 mg of $NaAsO_2$ or Na_2HAsO_4; 10 mg of NaH_2PO_4, $CuCl_2$, $CoCl_2$, $PbCl_2$, $CrCl_3$, $CdCl_2$.

Experiments indicated that tin(II) was oxidized during the extraction and was therefore determined as tin(IV) complex with rhodamine B.

Application to alloys

The proposed method was tested on 2 alloys containing: (I) 10.6% tin, 84.9% copper, 3.5% lead and 1.0% zinc; (II) 11.7% tin, 87.9% copper and 0.4% zinc.

The alloy (0.1 g) was dissolved in 5.0 ml of concentrated hydrochloric acid and 10 drops of 30% perhydrol. After the alloy had dissolved the solution was diluted to 100 ml. Aliquots (3 ml) were added to 5 ml of rhodamine B solution, 3.25 ml of

TABLE I

DETERMINATION OF TIN IN ALLOYS

	Weight (g)	522.5 mμ		550 mμ		572.5 mμ	
		E	% Sn	E	% Sn	E	% Sn
I	0.1061	0.825	8.3	0.542	10.2	0.681	10.5
I	0.1042	0.864	8.9	0.528	10.0	0.663	10.5
II	0.1000	0.905	9.7	0.521	10.3	0.683	11.2
II	0.1038	0.900	9.3	0.526	10.0	0.689	10.9

concentrated hydrochloric acid and 8.75 ml of distilled water. The hydrochloric acid concentration should then be 2 N. The extraction with ethyl acetate was performed as in the procedure given above. The results are given in Table I.

The measurement of the optical density at 550 or 572.5 mμ gave satisfactory results, while the tin contents found from measurements at 522.5 mμ were too low, perhaps because of interfering elements.

Discussion

The commonest reagents for colorimetric determination of tin are dithiol, phenylfluorone and haematoxylin. According to SANDELL[11] none of these is entirely satisfactory. They are not specific, and for some purposes not sensitive enough. With regard to the method with rhodamine B, the same reservations might be taken. This method, however, is faster and easier to perform. Methods based on the reducing power of tin(II) are very sensitive but the influence of other reducing materials is evident.

Elements which interfere in the determination of tin by rhodamine B, have to be removed. Fractional distillation, as described by ONISHI AND SANDELL[12], should be satisfactory for the separation of tin from mercury, bismuth, zinc, iron and antimony.

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Determination of lutetium in an Al–Lu alloy

A rapid and reasonably accurate method for the determination of lutetium in an Al–Lu alloy down to about 1% lutetium had to be developed. One of the commonest methods for the determination of the rare earths in aluminum is the pre-

cipitation of the rare earths as fluorides[1]. This method is time-consuming and one must keep in mind that soluble fluoride complexes could be formed[2]. Titrations with ethylenedinitrilotetraacetic acid (EDTA) have been used for the determination of the rare earths[3,4]. FRITZ et al.[5] used arsenazo as an indicator for determining the rare earths in the presence of other metals; the ratio of rare earth to aluminum was 1:1 or 1:2. Metallochromic indicators of the sulfonphthaleinnitrilodiacetic type, such as xylenol orange, which were introduced by PRIBIL et al.[6], are among the most useful for EDTA titrations. Xylenol orange may be used as an indicator in the titration of bismuth, thorium, scandium, lead, lanthanum, zinc and mercury. Ethylenedinitrilotetraacetic acid itself is a very unselective reagent; masking is the commonest method for eliminating interferences. Several well-known agents are available for masking aluminum, e.g., ammonium fluoride, triethanolamine, pentan-2,4-dione and sulfosalicylic acid. The latter seemed to be the most suitable for the required titration, which was to be performed in a slightly acidic medium. Because of their close similarity in chemical behaviour, the stability constants of the rare earth complexes with EDTA vary gradually from $1.9 \cdot 10^{-15}$ for lanthanum to $8.7 \cdot 10^{-20}$ for lutetium[7], hence only the sum of the rare earths can be determined. The Al–Lu alloys that had to be analysed were prepared from high purity lutetium (99.9%) and aluminum (99.99%), so that no interference from other elements was expected.

Apparatus and reagents

A microburet of 1 ± 0.0002 ml capacity was used; all pH measurements were made with a combined glass–calomel electrode. The reagent-grade chemicals required in this procedure were obtained from the UCB (Union Chimique Belge).

Standard EDTA solution. Dissolve 18.6 g of disodium(ethylenedinitrilo)tetraacetate dihydrate in 1 l of twice-distilled water and store in a polyethylene bottle. Standardize against a standard zinc solution with eriochrome black T as indicator[8].

Standard lutetium solution. Dissolve lutetium oxide (99.9%) in 6 N hydrochloric acid and dilute to obtain a solution containing approximately 0.1 mg Lu/ml.

Standard aluminum solution. Dissolve 2 g of aluminum metal (99.99%) in 6 N hydrochloric acid and dilute to 1 l with twice-distilled water.

All other solutions were prepared with twice-distilled water.

Procedure

Take an appropriate amount of the Al–Lu alloy to be analysed (about 2 mg of Lu should be present) and dissolve it under reflux in 6 N hydrochloric acid. After dissolution, transfer the solution quantitatively to a 200-ml beaker and mask the aluminum with an appropriate amount of aqueous 20% (w/v) sulfosalicylic acid solution. Any iron present can be masked with ascorbic acid. Adjust the total volume to about 100 ml with twice-distilled water. The pH of the solution should be about 1 at this moment. Add concentrated ammonia solution (d = 0.9) until the pH is ca. 5, and then adjust the pH to 5.5 (pH meter) with a dilute (1:99) ammonia solution. Add 10 drops of aqueous 0.2% (w/v) xylenol orange solution and titrate with standard EDTA solution, taking the sharp color change from red to yellow as the end-point.

The results obtained by the described procedure are shown in Table I. It is clear that good results can be obtained for concentrations of over 1% of lutetium in aluminum.

TABLE I

ANALYSIS OF Lu–Al MIXTURES

Lu in Al given (%)	No. of detns.	Relative standard deviation	Lu in Al found (%)
4.97	8	0.5	4.95
3.80	8	0.8	3.82
1.95	9	0.8	1.945
0.98	10	1.1	0.99

To obtain a sharp end-point and good results, the following points are essential: (1) the pH of the solution must be adjusted with ammonia solution instead of hexamethylenetetramine; (2) the pH of the solution at the start of the titration must be 5.5 ± 0.1; (3) 0.5 ml of the masking agent must be present for each milligram of aluminum.

The authors are indebted to MM. VAN HENGEL and REYNDERS for much of the practical work done.

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Solvent extraction of blue perchromic acid by tertiary and quaternary amines

The quantitative extraction of blue perchromic acid by tri-*n*-butyl phosphate in benzene has been reported earlier[1,2]. The blue compound is quite stable in this solvent and chromium can be determined by this extraction method. Further studies have shown that long-chain tertiary and quaternary amines can also be used for the quantitative extraction of the blue compound. The results are presented in this paper.

Tertiary amines as extractants

Materials. A pure sample of tri-*n*-octylamine (T. Schuchardt) was used without further purification. All other materials were of analytical grade. The solvents were purified by conventional methods.

Extraction procedure. The solution containing the requisite quantities of potassium dichromate and acid was cooled to about 5°, as well as the hydrogen peroxide solution. The solutions were mixed (20 ml) in a 100-ml separatory funnel and the blue perchromic acid formed was extracted with two 10-ml portions of 0.01 *M* tri-*n*-octylamine (pretreated with an equal volume of 0.1 *N* acid) in benzene, also cooled to about 5°. The combined organic layers were thoroughly shaken with 5 ml of 10% potassium hydroxide solution and the chromate formed was extracted with redistilled water. The chromate solution was boiled to decompose hydrogen peroxide and acidified and the chromium present was determined iodometrically. The reaction between dichromate and hydriodic acid at such low concentrations was very slow but the addition of oxalate ions made the reaction instantaneously quantitative[3] and the liberated iodine could be determined accurately.

TABLE I

EFFECT OF ACIDITY (SULPHURIC ACID)

(Concentration of chromium = 0.04158 mg-atom; concentration of hydrogen peroxide = 1.8 meq.)

Acidity (N)	% Extraction	Acidity (N)	% Extraction
0.0025	91.0	0.06	99.0–100.0
0.005	92.3	0.075	96.7
0.0075	93.3	0.10	95.7
0.01	95.5	0.25	91.2
0.025	95.7	0.50	79.2
0.035	99.0–100.0	1.00	28.1

Effect of acidity. It was found that sulphuric acid was the best medium for the extractions. As can be seen from Table I, quantitative results (99–100% recovery) were obtained in the range 0.035 to 0.06 *N* sulphuric acid. About 98% extractions were obtained in the case of hydrochloric acid while very poor extractions were observed with perchloric acid.

TABLE II

EFFECT OF HYDROGEN PEROXIDE CONCENTRATION

(Concentration of chromium = 0.04158 mg-atom; acidity = 0.05 *N* H_2SO_4)

H_2O_2 present (meq.)	% Extraction	H_2O_2 present (meq.)	% Extraction
0.1546	90.00	2.090	95.65
0.3092	92.40	3.402	94.56
0.6184	94.56	4.640	93.48
1.0822	96.74	9.276	92.40
1.5440	99.0–100.0	12.368	89.13
1.960	99.0–100.0	15.460	88.00

Effect of hydrogen peroxide concentration. The effect of the hydrogen peroxide concentration on the percentage extraction was studied in detail. It can be seen from Table II that almost quantitative results were obtained in the range 1.54 to 1.96 meq. of hydrogen peroxide.

Nature of the extracted species. In order to determine the nature of the extracted species, a series of solutions containing 2–10 mg of tri-*n*-octylamine in benzene (20 ml), were prepared and pretreated with 0.1 *N* sulphuric acid. The cooled aqueous mixture (20 ml) contained 0.0832 mg-atom of chromium as dichromate, 1 ml of 1 *N* sulphuric acid and 1.8 meq. of hydrogen peroxide. The perchromic acid formed was thoroughly shaken with 20 ml of the cooled amine solution. The chromium extracted into the organic phase was determined in each case and the distribution coefficient (D_M) calculated. A plot of log D_M *vs.* log C_{amine} gave a straight line with a slope of
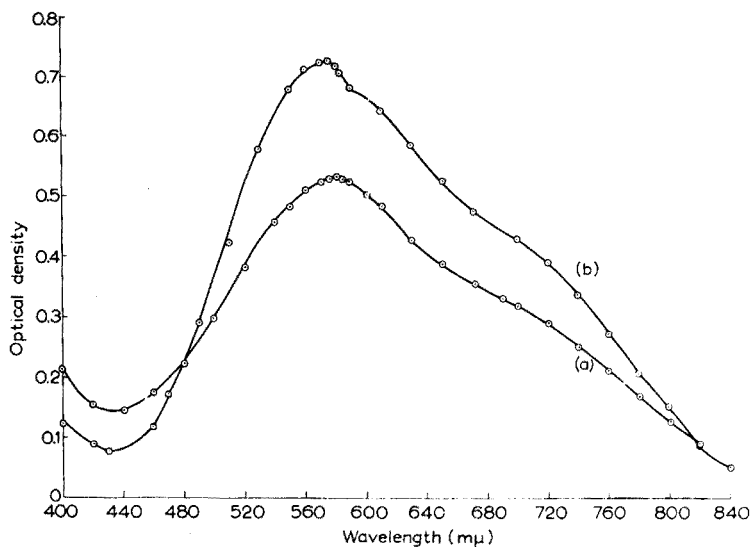
Fig. 1. Absorption spectra of the blue perchromic acid extracts with: (a) tri-*n*-octylamine (0.02084 mg-atom Cr); (b) Aliquat-336 (0.02377 mg-atom Cr).

1.14, which indicates a 1 : 1 ratio between the amine and chromium, present in the extracted species[4].

Interferences. Large quantities of copper, cobalt and nickel did not interfere in this extraction procedure, while vanadium, molybdenum and tungsten caused interference.

Colorimetric determination. The absorption spectrum of the tri-*n*-octylamine extract of the blue perchromic acid (Fig. 1, curve a) showed an absorption maximum at 580 mμ with no decrease in optical density for about 60 min. In view of this stability, it was possible to carry out a direct photometric determination on the colored extract at 580 mμ. The Beer–Lambert law was obeyed up to a maximum concentration of 100 μg of chromium per ml in the extract.

Quaternary amines as extractants

The use of quaternary ammonium compounds as substitutes for tertiary amines for extraction purposes has been discussed by several workers[5,6]. In the present work, it was observed that the quaternary ammonium compound, methyltricaprylammonium chloride (Aliquat-336) in chloroform readily extracted the blue perchromic acid.

Materials. A sample of Aliquat-336 (methyltricaprylammonium chloride; General Mills, Inc.) was used without further purification as a 1% (v/v) solution in chloroform. All other reagents were of analytical grade.

Procedure. The volumetric procedure adopted in extractions with amines for the determination of chromium could not be employed in this case, since the back-extraction of chromium into the aqueous phase was not quantitative. Hence, the direct photometric determination of the blue extract was utilised. The spectrum of the Aliquat-336 extract of the blue perchromic acid indicated an absorption maximum at 575 mμ (Fig. 1, curve b). The Beer–Lambert law was obeyed in the concentration range 0–90 μg of chromium per ml in the organic extract. The blue color of the extract was stable for at least 10 h at room temperature (27°), and only about 2.5% decrease in optical density was observed even after 24 h.

The formation of the blue perchromic acid and its extraction with Aliquat-336 were carried out as described above (*Extraction procedure*); the overall acidity for the formation of perchromic acid was 0.05–1 N in hydrochloric acid and about 3.5 meq. of hydrogen peroxide was added. The combined portions of the Aliquat-336 extract were then mixed and centrifuged for 2–3 min. The extract was made up to 25 ml with the clear Aliquat-336 solution. The optical density of the solution was measured at 575 mμ. The chromium present was determined with the help of a calibration curve previously prepared according to the same procedure.

The interferences were the same as in the case of the tertiary amine.

Nature of the extracted species. The composition of the extracted species was determined by the log–log method[4] and by the extraction isotherm method[7]. Both methods indicated a 1:1 ratio between chromium and methyltricaprylammonium cation in the extracted species.

Discussion

It is evident from the results reported that tertiary and quaternary amines extract the blue perchromic acid quantitatively. The stability of the extracts is sufficiently high to allow a direct photometric determination of chromium. The stability of the Aliquat-336 extract in particular is extremely high and is comparable to that of TBP-extract of the blue perchromic acid[1,2].

The structure of the blue perchromic acid has been investigated by several workers[8] and conclusive evidence has been put forward for the assignment of the molecular formula, CrO_5 to this compound. It has been suggested[9] that the stabilisation of this molecule is due to coordination by a donor molecule (*e.g.*, water, ether, pyridine, TBP, etc.), the degree of stability varying with the nature of the latter.

It is generally agreed[6] that the tertiary and quaternary amines act as extractants by an anion-exchange mechanism. Since the blue perchromic acid is readily extracted by tertiary and quaternary amines, one has to envisage the formation of

an anionic species from the essentially neutral CrO_5 molecule under the experimental conditions.

With regard to the spectra of the tri-*n*-octylamine and the Aliquat-336 extracts of the blue perchromic acid (Fig. 1), it is interesting to note that the absorption at 720 mμ reported in the case of TBP-extract[9] is absent, although the absorption maximum at 580 mμ remains unchanged. This suggests the existence of a different species in the amine extracts.

In view of the above facts, the formation of an anionic species such as CrO_5X^- ($X^- = Cl^-$ or HSO_4^-) (*cf.* CrO_3Cl^- [10]), may be contemplated under the experimental conditions. Work is in progress on this aspect.

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The iodometric analysis of mixtures of hydrogen peroxide and lower alkyl peroxides, with particular reference to the radiolytic oxidation of methane

The reaction of peroxides with excess potassium iodide in acid solution has been shown to be first order, and the rate to be characteristic of the peroxide used[1-5]. Rate constants for the reaction of hydrogen peroxide, methyl hydroperoxide, ethyl hydroperoxide, diethyl peroxide, and *tert.*-butyl hydroperoxide with excess potassium iodide in McIlvaine's buffer have been recorded by CADLE AND HUFF[4].

More recently JOHNSON AND SALMON[5] have described the use of a buffered iodide reagent, containing molybdate as a catalyst[7], to characterise methyl hydroperoxide as a product of the radiolytic oxidation of methane.

The present communication presents a study of the reaction of this reagent with mixtures of hydrogen peroxide, methyl hydroperoxide, dimethyl peroxide and ethyl hydroperoxide.

Materials

Methyl hydroperoxide was prepared by the method of MINKOFF[8], ethyl hydroperoxide by the method of WALLING AND BUCKLER[9], and dimethyl peroxide by the method of HANST AND CALVERT[10]. For purposes of comparison methyl hydroperoxide and ethyl hydroperoxide were also prepared by the γ-irradiation of 10% oxygen–methane and oxygen–ethane mixtures, the gases being "research grade" quality. The gas mixtures at 76 cm Hg and 25° were given a dose of $8.6 \cdot 10^{19}$ eV per g of mixture, the source (^{60}Co) used giving a dose rate of $4.3 \cdot 10^{17}$ eV/g/min in these mixtures. The product was extracted by shaking with 10 ml of distilled water and the yields of molecules of peroxide per 100 eV were $G_{CH_3OOH} = 2.0$ and $G_{C_2H_5OOH} \sim 0.3$.

All materials used were Analar grade.

Procedure

The iodide reagent[6] consisted of 2 solutions: (a) 66 g of potassium iodide, 2 g of sodium hydroxide and 0.2 g of ammonium molybdate per litre; and (b) 20 g of potassium hydrogen phthalate/l. Equal volumes of (a) and (b) were mixed and then combined with an equal volume of the peroxide solution. Optical density changes at 350 mμ and 20° were then measured against a reagent blank, using thermostatted silica cells, stoppered to minimise contact with air. Reaction was complete within about 5–8 h.

Beer's law was not obeyed above $[OD]^{1cm} = 0.8$. For measurements below this limit an extinction coefficient $\varepsilon = 24600$ was used, and a calibration curve was used for optical densities from 0.8 to 1.7.

Results

First-order plots obtained for reaction of the reagent with prepared mixtures of hydrogen peroxide, methyl hydroperoxide, dimethyl peroxide and ethyl hydroperoxide at 20°, showed the following characteristics.

(a) With mixtures of hydrogen peroxide and methyl hydroperoxide a plot was obtained which became linear after the first few minutes of reaction. Extrapolation of this linear portion back to zero time led to a positive intercept value for $\ln a/(a - x)$ from which the concentration of hydrogen peroxide could be calculated (see Fig. 1). This behaviour followed from the fact that the rate constant for the reaction with hydrogen peroxide is greater by a factor of about 4. In the absence of hydrogen peroxide the plot was linear through the origin (see (e) below).

(b) Dilution of methyl hydroperoxide solutions below $3.3 \cdot 10^{-5}$ M in the reagent led to the formation of hydrogen peroxide. The total amount of peroxide remained constant on dilution, but the relative amount of hydrogen peroxide produced increased with increasing dilution, obeying approximately the following relationship to the total peroxide concentration over the range of dilutions studied (see Fig. 1).
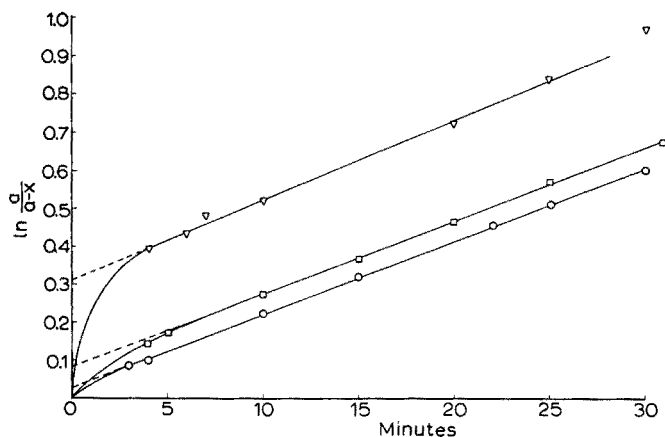
Fig. 1. Methyl hydroperoxide. Effect of dilution in iodide reagent on first-order plot. Concentration of peroxide: $\triangledown$ $1.51 \cdot 10^{-6}$ M; $\square$ $1.18 \cdot 10^{-5}$ M; $\circ$ $2.49 \cdot 10^{-5}$ M.

$$10^6 [H_2O_2] = -4.9 \log [R_2O_2] - 22.0$$

where $[H_2O_2]$ is the hydrogen peroxide molarity, and $[R_2O_2]$ is the total peroxide molarity.

(c) Dimethyl peroxide reacted only slowly with the reagent and when in admixture with methyl hydroperoxide resulted in no definite end-point for the reaction even after 24 h. With equimolar quantities and making an estimate of the final optical density, a first-order plot gave a curve, passing through the origin, with an initial slope of 0.015 (min^{-1}) decreasing to 0.0045 (min^{-1}) at ca. 80% reaction.

(d) Dilution of dimethyl peroxide solutions to $<10^{-4}$ M led to the formation of methyl hydroperoxide and then hydrogen peroxide.

(e) Ethyl hydroperoxide prepared by the radiolysis of oxygen–ethane mixture
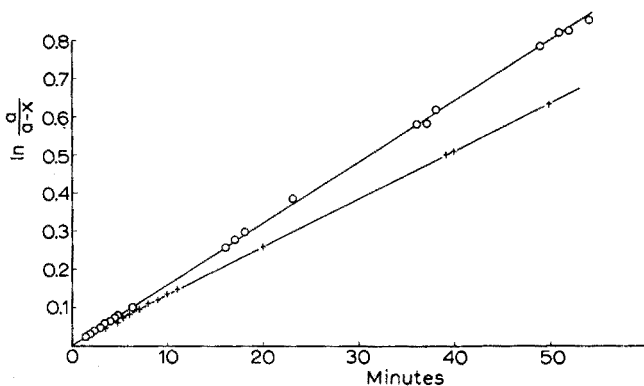
Fig. 2. Methyl and ethyl hydroperoxide. First-order plot at 20°. $\circ$ CH$_3$OOH, $k = 0.016$; $+$ C$_2$H$_5$OOH, $k = 0.0125$.

gave a linear first-order plot $k = 0.0125$ (min^{-1}) at 20°. Ethyl hydroperoxide prepared by the method of WALLING AND BUCKLER[9] gave a plot which although initially curved (0.015) had a final slope of 0.0128 (min^{-1}). This curvature probably indicates the presence of more than one peroxide.

In comparison, purified methyl hydroperoxide, and also the peroxide prepared by radiolysis, gave a linear first-order plot with $k = 0.017 \pm 0.002$ (min^{-1}) at 20°.

In Fig. 2, the result for a synthesised sample of methyl hydroperoxide is compared with ethyl hydroperoxide produced radiolytically. The ratio of the rate constants $k_{CH_3OOH}/k_{C_2H_5OOH} = 1.28$ is similar to that calculated (1.33) from the data of CADLE AND HUFF[4] obtained at 30° in buffered solution at pH 4 with an initial potassium iodide molarity of 0.14 and without the addition of any catalyst (molybdate).

For purposes of analysis the values of these rate constants are too close to allow the estimation of small amounts of ethyl in methyl hydroperoxide and *vice versa*. A mixture containing 6 parts of methyl to 1 of ethyl hydroperoxide gave a first-order plot indistinguishable from that for pure methyl hydroperoxide.

Conclusions

Hydrogen peroxide can be identified and estimated when in admixture with any or all of the above peroxides provided that the dilution of these is not so low as to form additional hydrogen peroxide. This proviso is particularly important in the analysis of alkyl peroxides, since otherwise it might be erroneously concluded that hydrogen peroxide was present in the original mixture.

Mixtures of one of the hydroperoxides with small amounts of the other two alkyl peroxides cannot be resolved and the first-order plots show no detectable change from the pure material. The presence of appreciable quantities of dimethyl peroxide leads to a marked non-linearity in the first-order plot, and renders the method useless for quantitative determination of all but hydrogen peroxide. Mixtures of methyl and ethyl hydroperoxide are not easily distinguished from the pure materials.

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BOOK REVIEW

I. P. ALIMARIN AND N. PETRIKOVA, *Inorganic Ultramicroanalysis*, translated from the Russian by M. G. HELL, International Series of Monographs on Analytical Chemistry, Vol. 15, Pergamon Press, Oxford–London–New York–Paris, 1964, xv + 151 pp., price 40 s.

Powers of ten, either positive or negative, tend to have an hypnotic effect on the lay public, and where ultramicroanalysis is concerned, unfortunately, many scientists are not very far removed from "lay public". Analytical chemists have, of course, been conditioned over the past fifteen years to the casual use of terms down to 10^{-13} g or even lower. This, however, has usually been in the context of instrumental analysis, where the actual amounts of sample handled (meaning, in general, the volumes of solution) are of classical size. But suggest to the "average" analytical chemist that he should start off with a sample of 1 μg or 100 nl, and he loses interest: this in spite of the fact that the 10^{-12}-g measurement of spectrochemical or activation analysis *may* drop below the present limit of ultramicroanalysis by several powers of ten (though this statement takes no account of the, as yet, little probed question of precision).

It is around sixty years — in the inorganic field — and fifty years — in the organic field — since chemists were viewing with suspicion the highly specialised craft of microanalysis. It is salutary to view the field of analytical chemistry today and to note how many of these "highly specialised" techniques have become common practice.

Microchemistry, then, which in 1920 was regarded as the field of the dedicated, is now a commonplace adjunct of the properly equipped analytical laboratory. Ultramicroanalysis could be said to have reached, in 1940, a stage comparable to microanalysis in 1920. In 1965 we ought to have come to terms with it. We ought, indeed, to be looking further: the 2-mg sample of the 1920's, the 2-μg sample of the 1940's, ought to have led to the 2-ng sample of the 1960's. But this has not yet happened. Therefore one welcomes the translation of this book by Professor ALIMARIN and Dr. PETRIKOVA as a stimulant to further development. Professor ALIMARIN rightly acknowledges his indebtedness to BENEDETTI–PICHLER as the visionary who was one of the first to see that such flights of fancy might be actualities. But he and his colleagues have done much to translate the fancy into fact; and we can only be grateful that his experience has now been made readily available to the English-speaking world.

Those already familiar with ultramicro techniques in analytical chemistry will have ordered this book, probably even before the publication date. Those who still regard those techniques as part of an esoteric mystery should buy the book and try to discover what it has to teach them. The occasional infelicities in translation (*cf.* p. 16!) should not deter the open-minded reader from getting a new view on some of the future possible achievements of analytical chemists.

C. L. WILSON (Belfast)

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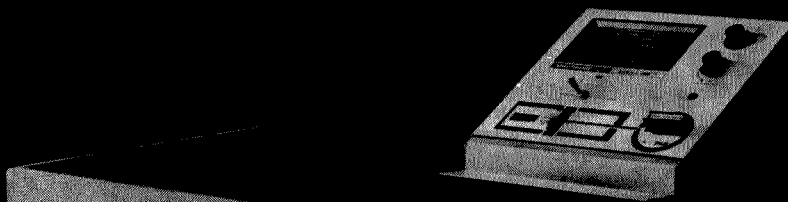Until you see the Spectronic 600 E.

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