The ANALYST

The Journal of the Society for Analytical Chemistry

A monthly International Publication dealing with all branches of Analytical Chemistry

Published for the Society by W. HEFFER & SONS, LTD., CAMBRIDGE

Volume 92 No. 1093, Pages 207 278

April 1967

THE ANALYST THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

EDITORIAL COMMITTEE

Chairman: K. A. Williams

Members:

E. Bishop H. E. Brookes K. R. Capper D I. Coomber W. T. Elwell P. S. Hall J. F. Herringshaw A. G. Hill E. A. Hontoir H. M. N. H. Irving D. Moore G. Nickless A. A. Smales, O.B.E. E. V. Truter T. S. West

The Chairman of the Analytical Abstracts Committee (H. J. Cluley) The Chairman of the Analytical Methods Committee (D. C. Garratt)

and the President and Honorary Officers

President of the Society: A. G. Jones

Hon. Secretary of the Society:

S. A. Price

Hon. Treasurer of the Society: G. W. C. Milner

Hon. Assistant Secretaries of the Society: W. H. C. Shaw, D. W. Wilson

Editor:

J. B. Attrill, M.A., F.R.I.C.

14 BELGRAVE SQUARE, LONDON, S.W.I. Telephone: BELgravia 3258

> Assistant Editor: Miss C. M. Richards, B.Sc.

SUBSCRIPTION RATES

(other than for Members of the Society)

Subscriptions to The Analyst, including Analytical Abstracts, should be sent through a Bookseller or direct to

W. HEFFER & SONS LTD., CAMBRIDGE, ENGLAND

Subscription Rates: The Analyst, Analytical Abstracts and indexes, £15 per annum, post free

The Analyst, with Analytical Abstracts printed on one side of the paper (without index), £15 15s. per annum

The Analyst, with Analytical Abstracts printed on one side of the paper (with index), £17 10s. per annum

Subscriptions are NOT accepted for The Analyst alone

N.B.-Members send their subscriptions to the Hon. Treasurer.

Single copies £1 10s.

Volume 92. No. 1093

April, 1967

April, 1967]

THE ANALYST



iii

THE ANALYST

Heterocyclic Azo Dyestuffs in Analytical Chemistry A Review*

BY R. G. ANDERSON AND G. NICKLESS (School of Chemistry, The University, Bristol 8)

SUMMARY OF CONTENTS

General introduction and scope

1-(2-Pyridylazo)-2-naphthol

General properties Applications as a complexometric indicator Applications as a spectrophotometric reagent Other applications in analytical chemistry

4-(2-Pyridylazo)-resorcinol

General properties

Applications as a complexometric indicator Applications as a spectrophotometric reagent Other applications in analytical chemistry

Other pyridylazo dyestuffs and related compounds

Thiazolylazo and benzothiazolylazo dvestuffs

Miscellaneous heterocyclic azo dyestuffs General

Azo derivatives of 8-hydroxyquinoline

Conclusions

THIS review is concerned with the analytical applications of heterocyclic azo dyestuffs and closely related compounds, in which the heterocyclic atom is at least formally involved in chelation with a metal atom (see example below). The review will, therefore, include all dyes with a heterocyclic atom ortho to the azo group, and also azo-derivatives of 8-hydroxyquinoline. It will, however, exclude certain dyes such as azo dyes of pyrazolone, which chelate through the keto oxygen atom.



The review covers the literature up to the end of 1965, with a few early references from 1966.

* Reprints of this paper will be available shortly. For details see Summaries in advertisement pages.



207

[Analyst, Vol. 92

The earliest references to these heterocyclic azo dyestuffs were concerned with 8-hydroxyquinoline azo dyes as test reagents for cations.^{1,2} In 1951, Liu³ investigated the reactions of 1-(2-pyridylazo)-2-naphthol (PAN) with metal ions. However, the first major paper to be published was by Cheng and Bray⁴ in 1955, who recommended the use of PAN as a complexometric indicator in direct titrations with ethylenediaminetetra-acetic acid (EDTA). In addition, they observed that the chelates of PAN may be extracted into organic solvents, and described a few simple studies on this phenomenon. Initially PAN was used as an indicator, in indirect and direct titrations of metal ions with EDTA.^{5,6,7,8,9} Then about **3** years later applications were also found for the dye as a spectrophotometric reagent, especially for uranium.^{10,11,12,13} Generally, such applications were used in conjunction with solvent extraction procedures. Since then PAN has been used in analytical procedures with about forty-five different metals.

In 1957, Wehber¹⁴ recommended the use of 4-(2-pyridylazo)-resorcinol (PAR) in complexometric titrations, claiming it to be superior to PAN because of the solubility in water of the dye and its chelates. PAR was used in direct EDTA titrations for a variety of metals,^{15,16} being superior to PAN according to Wehber's observations, and also because of its sharper end-points. Pollard, Hanson and Geary¹⁷ used it as a spectrophotometric reagent for cobalt(II), uranium(VI) and lead(II). No solvent extraction was required with this method, and PAR was found to be the most sensitive reagent for cobalt(II), the most sensitive watersoluble reagent for uranium(VI) and the first water-soluble reagent for lead(II). PAR has now been used in analysis for about forty different metals.

Azo dyes of thiazole can be prepared from a very wide range of phenolic substances, and have been used as potential metallochromic indicators.^{18,19,20,21} In addition to these, azo dyes of 8-hydroxyquinoline have been synthesised for use in titrations with EDTA and found to give sharp end-points.^{22,23,24}

Dyes with a PAN-type chelating structure act as tridentate ligands complexing with most metals through the *ortho*-hydroxyl group, the azo nitrogen nearest to the phenolic ring and the heterocyclic nitrogen atom, giving two stable, 5-membered chelate rings.²⁵ They form complexes with ions of small size carrying a large positive charge, such as the titanium group,^{26,27} (similar to salt-forming reagents) and with ions of the heavy metals and transition elements with nearly full d-shells (like other nitrogen-donor chelating agents).^{28,29} These two classes of metals may be compared with class A and class B acceptors, as described by Ahrland, Chatt and Davies.³⁰ These heterocyclic azo dyes will complex well with both types of metal, and this may be regarded as the reason why it has been possible to find analytical uses for them with such a wide range of metals.

Other reviews related to this subject have appeared by Danzuka,³¹ Busev and Ivanov,³² Sommer and Hniličková²⁷ and Hsin-Chien Teng and Shui-Chieh Hung.³³ A short leaflet on some analytical applications of PAR has been published by British Drug Houses Ltd.³⁴

The most important dyes of this class are PAN and PAR, and about 200 papers have already been published concerning applications of these two dyes in analysis alone.

1-(2-PYRIDYLAZO)-2-NAPHTHOL (PAN)

GENERAL PROPERTIES OF THE DYE-

PAN was first prepared by Chichibabin, by coupling sodium 2-pyridyldiazotate with β -naphthol in ethanol under an atmosphere of carbon dioxide.³⁵ Basically the same method is used to prepare the dye today.

PAN is a bright orange solid with a melting-point of 137° C. It is insoluble in water, dilute acids and alkalis, but is soluble in strong acid (pH > 2) to give a yellow - green cation, and in strong alkali (pH > 12) to give a red anion. It is soluble in alcohols, and also to a slight extent in ethers, to give a bright yellow solution, and in concentrated sulphuric acid solution it is violet.



I pH < 2.5

April, 1967]

Abbreviation

The acid dissociation constants have been determined by Pease and Williams,³⁶ who obtained values of 1.9 and 12.2 for pK_{NH} and pK_{OH} , respectively, in 20 per cent. aqueous dioxan with a spectrophotometric method. Corsini, Mai-Ling Yih, Fernando and Freiser³⁷ obtained values of less than 2 and of 12.3 by potentiometric titrations in 50 per cent. dioxan at 25° C. Nakagawa and Wada,³⁸ while studying the solvent extraction behaviour of PAN and the corresponding zinc(II) and nickel(II) chelates, obtained values of 2.9 and 11.5 in aqueous solution (see Table I).

ABBREVIATIONS USED IN THE TABLES

-		
Ext	plana	tion

Sp.				Spectrophotometric determination
Pot.	• •	••		Potentiometric determination
SE.			••	Determination by solvent extraction
log K				Log ₁₀ of stability constant (log ₁₀ K ₁ , log ₁₀ K ₂ , etc.)
EDTA				Ethylenediaminetetra-acetic acid
CHDT.	A			1.2-Cyclohexanediaminetetra-acetic acid
EGTA				Ethyleneglycolbis-(2-aminoethylester)-NNN'N'-tetra-acetic acid
Ext.		• •		Extracted
isoPrO.	н			Isopropyl alcohol
DMF				Dimethylformamide
BuOH				Butanol
pptn.				Precipitation
DBP				Dibutyl phosphate
TBP				Tributyl phosphate
TNOP	0		100	Tri-n-octylphosphine oxide
OD			1.1	Optical density or absorbance
EtOAc			1.1	Ethyl acetate
ш				Ionic strength
IBMK			ere.	Isobutyl methyl ketone
REs				Rare earth elements

TABLE I

DISSOCIATION CONSTANTS OF AZO DYESTUFFS

Dye		рК _{NH}	рКон (para)	pKon (ortho)	Reference
PAN		1.9 (Sp.)		12.2 (Sp.)	36
		<2 (Pot.)		12.3 (Pot.)	37
		2.9		11.5	38
PAR			5.83	12.5	123
		3.1	5.6	11.9	109
		2.3 (Pot.)	6.9 (Pot.)	12.4 (Pot.)	37
		2.69 (Pot. in water)	5.50 (Pot. in water)	12.31 (Sp. in water)	25, 108
		2.41 (Pot. in 50%)	7.15 (Pot. in 50%	13.00 (Sp. in 50%	25, 108
		dioxan)	dioxan)	dioxan)	
PAC	• •	2.60		9.15	143
PAAC		3.84	_	10.16	145
p-PAN		2.54 (Pot.)		10.74 (Pot.)	140
MAAR	• •		5.35	11.99	156
TAR	• •	1.03	6.15	9.5	27
			5·9 (Sp.)	103 (Sp.)	191
			6.4	10.5	178
TAN	• •			9.0 (20% dioxan)	178
				9·8 (60% dioxan)	178
		0.88 (Sp.)		9·10 (Sp.)	195
		2·3 (Sp.)		8.5 (Sp.)	190
BTAN				7.86 (Sp.)	193
TAN 6S	• •	<u> </u>		7.9	21
TAC	• •		_	8.2 (Sp. and Pot.)	189
TAM	••			8.2 (Sp. and Pot.)	189
		3·13 (Sp.)	_	8.65 (Sp.)	169
4MeTAP-ON	Иe	0·77 (Sp.)		7·98 (Sp.)	171
p-TAN	• •		7.19		186
p-BTAN	• •		6.94		186

Note-For space considerations, ionic strength details have been omitted.

The ultraviolet and visible absorption spectra of the dye have been studied as a function of pH, and it has been found that PAN shows hypsochromic and bathochromic shifts on protonation and ionisation, respectively.³⁶ In 20 per cent. aqueous dioxan, the peak

ห้องสมุด กรมวิทยาศาสตร์

Analyst, Vol. 92

wavelengths are at about 440 m μ for the cation, 470 m μ for the neutral molecule and 495 m μ for the anion.

Busev and Ivanov³⁹ have shown that, under various conditions of pH, ionic strength and concentration, PAN shows no evidence of intermolecular association.

Pollard, Nickless and Samuelson⁴⁰ have used thin-layer chromatography to ascertain the purity of commercial PAN and other heterocyclic azo dyes of analytical interest.

Because of the many applications of chloroform to the extraction of PAN chelates, the distribution coefficient of PAN between water and chloroform has been measured.³⁹ A value of 10⁵⁻¹ was obtained, compared with 10⁴⁰ found between carbon tetrachloride and water.⁴¹

The ratio of $\log K_{D Zn(PAN)_{*}}$ has been measured for several solvents. It is fairly constant (about 2) so that the extraction conditions, predicted by D. Betteridge (private communication) from work with carbon tetrachloride or chloroform, may, to a first approximation, be applied to those solvent systems that might be more useful to, or favoured by, the analyst.

PAN forms coloured complexes with most metals. These are red with the alkaline earths, rare earths, Al(III), Sc(III), Y(III), Ti(IV), Zn(II), Cd(II), Hg(II), Ga(III), In(III), Tl(III), Pb(II), Bi(III), Ni(II), Mn(II) and U(VI), etc. With Cu(II), V(IV) and (V), Fe(II) and (III) and Ru(III), they are of varying shades from red to violet, whereas with Co(III), Pd(II) and Pt(II) they are green. The sensitivity of the reagent is low with the alkaline earths. The alkali metals, Ge(IV), As, Se and Te do not react. These reactions are sensitive to changes in solvent, temperature, ionic strength and concentration of metal or ligand. The anion of the metal is not important unless it, itself, has a strong tendency to complex with the metal. The pH of the solution is of great importance, and the minimum pH for chelation with PAN varies from metal to metal. Correct pH control is of absolute importance in all analytical work with PAN.⁴²

Many of these chelates are insoluble in water but can be extracted into various organic solvents. This phenomenon has been investigated in detail by Berger and Elvers,⁴¹ Shibata^{42,43} and Betteridge, Fernando and Freiser.⁴⁴ All of these workers have shown that the formation of the chelates and their extraction into organic solvents is dependent on pH. By the correct choice of pH, organic solvent and masking agents, PAN can be made quite selective as a solvent extraction reagent.

In the course of studying PAN as an analytical reagent, many workers have investigated the compounds formed between the dye and the metal. The most common metal-to-ligand ratios encountered are 1:1 and 1:2. Shibata⁴³ has proposed the following structures for these two types of complex—



It has not always been possible to explain equilibrium results by these structures. There is evidence⁴⁴ for complexes of the type M(PAN)(OH), especially for uranium,⁴⁵ while Stanley and Cheney⁴⁶ reported on Cu(TAR)(OH), which was suggested by potentiometry. The solvent extraction behaviour of nickel(II) and cobalt(II) complexes has not been explained satisfactorily.^{38,44} Other types of complex are rare, and may occasionally occur with ions of high valency. An interesting complex of gallium has recently been reported,⁴⁷ with a metal-to-ligand ratio of 1:5.

Determinations of stability constants and stoicheiometries of many complexes have been made by various workers.^{37,38,45,48,49,50,51} Some values for the stability constants of PAN chelates are given in Table II.

TABLE II

STABILITY CONSTANTS OF THE CHELATES

$$\begin{split} \mathrm{K_1} &= \frac{[\mathrm{ML}]}{[\mathrm{M}] \ [\mathrm{L}]} \ \text{for } \mathrm{M} + \mathrm{L} = \mathrm{ML} \text{ where } \mathrm{L} \text{ is the mono-anionic form of the ligand.} \\ \mathrm{K_2} &= \frac{[\mathrm{ML}_2]}{[\mathrm{ML}] \ [\mathrm{L}]} \ \text{for } \mathrm{ML} + \mathrm{L} = \mathrm{ML}_2 \\ \beta_2 &= \mathrm{K_1} \ \mathrm{K_2} \text{ or } \frac{[\mathrm{ML}_2]}{[\mathrm{M}] \ [\mathrm{L}]^2} \text{ for } \mathrm{M} + 2\mathrm{L} = \mathrm{ML}_2 \end{split}$$

Ion		Ligand	$\log_{10}K_1$	log ₁₀ K ₂	$\log_{10}\beta_2$	Method	Reference
Zn(II)		PAN	11.2	10.5	21.7	Pot.	37
					21.8	SE.	44
			10.9	10.0	20.9	Sp.	38
Cu(II)	••	PAN	~16			Sp.	36
			12.6			SE.	44
			15.5	8.4	23.9	Sp.	50
			17.0			Sp.	139
Ni(II)	••	PAN	12.7	12.6	25.3	Pot.	37
			14.0	13.5	27.5	Sp.	38
Co(II)	••	PAN	> 12			Pot.	37
Mn(II)	••	PAN	8-5	7.9	16.4	Pot.	37
Pb(II)	••	PAR	6.2			Sp.	240
		_	8.6	7.1 (?)		Pot. in water	24
Cu(11)	••	PAR	10.0 (log K)		20.0 ± 1.0		241
$\ln(111)$	••	PAR	9.6 (log K)		$19\cdot2\pm0\cdot2$		241
			13.6		27.0	Sp.	242
TI(III)	• •	PAR	9·8 (log K)	—	19.6 ± 0.2		241
Zn(II)	••	PAR	10.5	6.6	17.1	Pot. in water	25
			11.2	7.8	19.0	Pot. in 50%	25
						dioxan	
			12.4	11.1	23.5	Pot.	37
Cu(II)	••	PAR	11.7			Sp.	123
			14.8	9.1	23.9	Pot. in water	25
			16-4	8.9	25.3	Pot. in 50%	25
						dioxan	
Ni(11)	•••	PAR	$13 \cdot 2$	12.8	26.0	Pot.	37
Co(II)	• •	PAR	10.0	7.1	17.1	Pot. in water	25
			14.8	8.2	23.0	Pot. in 50%	25
						dioxan	
			> 12		—		37
			—		19.7	Sp.	243
Mn(11)	••	PAR	19.7	9.2	18.9	Pot.	37
V(V)	••	PAR	6.5			Sp.	244
$Ta(V) \dots$	••	PAR	5.94			Sp.	118
Nb(V)	••	PAR	6.86	\rightarrow	_	Sp.	118
Th(IV)	••	PAR	7·17 (log K)	100		Sp.	111
U(V1)	••	PAR	12.5	8.4	20.9	Pot. in water	25
			16.2	9.6	$25 \cdot 8$	Pot. in 50%	25
(T (TT)				Contraction Contraction		dioxan	
Zn(11)	••	PAC	8.36	8.30	16.66		144
Cu(II)	••	PAC	13.70	8.30	22.00		144
$N_1(11)$	••	PAC	_		22.14		144
Zn(11)	••	α-PAN			19	Sp.	140
Cu(II)	••	α-PAN			20	Sp.	140
$N_1(11)$	••	α -PAN			23	Sp.	140
$Cu(\Pi)$	••	PAA	5.23	_		Sp.	110
Hg(II)	••	PAA	5.08			Sp.	110
Zn(11)	••	PAA	2.36	—		Sp.	110
Co(11)	••	PAA	3.33			Sp.	110
N1(11)	••	PAA	4.24			Sp.	110
Mn(II)	••	PAA	0.7			Sp.	110
Cu(II)	••	TAR	11.8		_		27
PD(11)	••	TAR	8.4				27
Ln(11)	••	TAR	7.4		_		27
	••	TAR	7.0				27
BI(III)	••	TAR	13.2				27
11(111)	••	TAR	9.4				27
Ga(III)	••	IAR	11.1			\rightarrow	27
In(111)		TAR	10-1				27

Ion		Ligand	$\log_{10} K_1$	$\log_{10} \mathrm{K}_2$	$\log_{10}\beta_2$	Method	Reference
UO,2+		TAR	9.1				191
Cu(II)		TAN	10.8	11.7	22.5	SE.	195
			11.9			Sp.	188
Zn(II)		TAN	9.7	10.0	19.7	SÊ.	195
Co(II)		BTAN	13·4 (log K)				193
Ni(II)		TAC	8.0	8.2	16.2	Sp. and Pot.	189
Ni(II)		TAM	7.3	7.6	14.9	Sp. and Pot.	189
Cu(II)	• •	TAM	6.4	5.4	11.8	·	170
Cu(II)		4MeTAP-OMe	9.8		600 (Carlos - Carlos		173
Zn(II)			5.9				174

TABLE II—continued

APPLICATIONS AS A COMPLEXOMETRIC INDICATOR-

Applications of PAN as a complexometric indicator can be divided into three groups. Direct titrations of metals against EDTA with PAN as indicator—This has been used for the titration of about eleven metals, of which the most important is copper.^{4,52 to 60} The colour change at the end-point is from red or red - violet to yellow or yellow - green. The stability constants of the metal - PAN complexes are high, but EDTA should displace the metal from its PAN complex at the end-point; the reaction, however, is frequently a slow one. This can be improved by heating the solution near the end-point.^{53,60,61} Often in purely aqueous solutions the PAN chelate is present as a fine suspension of solid. Naturally this is not conducive to a fast reaction at the end-point. It has thus been found that the addition of an organic solvent, such as ethanol or acetone, can improve the end-point.⁵⁰ These titrations are sensitive to the effect of pH and use has been made of this to make certain titrations more specific.^{5,61} Otherwise foreign ions may be masked or sometimes reduced to a lower, weakly complexing valency state.^{5,50,61}

Indirect titrations—This method consists in reacting the metal with excess of EDTA and titrating the uncomplexed EDTA with a standard metal solution. Standard copper sulphate is generally used for this purpose, 6,7,8,9 as it produces the sharpest and most clearly defined colour change at the end-point (yellow - green to red - violet). The direct titration of copper is one of the most satisfactory with PAN as indicator. Often heating is required near, the end-point,⁷ and the addition of ethanol is beneficial.⁶¹ The method, first used by Cheng and Bray for the titration of scandium,⁶ has since been used for the titration. Bismuth and thallium(III) have been simultaneously determined by a combination of both methods,⁶² A direct titration at pH 4 to 5 gives the total metal content. Sodium sulphite is then added to reduce the thallium(III) to thallium(I), which does not complex with EDTA at this pH. The liberated EDTA is then titrated with standard copper sulphate solution.

Replacement titrations with copper - EDTA - PAN as indicator—This method is the same as the first method, except that a few drops of PAN and copper - EDTA complex solution are used as indicator. PAN displaces the copper from the EDTA to give a red - violet colour. During the titration the EDTA reacts with the uncomplexed metal in preference to the copper - PAN complex. The end-point is reached when the EDTA reacts with the copper -PAN causing a colour change to yellow. Boiling of the solution at the end-point is usually necessary. The method can be used for metals that form weak complexes with PAN and even for metals that do not react with PAN. The reaction has been used most frequently for the determination of aluminium in a variety of inorganic substances, 63,64,65,66 but has also been used for gallium(III), 14 indium(III), 67 lead(II), 68 vanadium 69 and plutonium. 70 An interesting application is to the analysis of potassium in blood serum. 71 The potassium is precipitated quantitatively as the cobaltinitrite and the cobalt in the precipitate determined by this method.

Table III summarises the applications of PAN to complexometric analysis. Accounts of the use of PAN as an indicator are given elsewhere.^{72,73} In conclusion, it can be seen that as an indicator PAN is more useful in indirect and replacement titrations than in direct titrations, in which its most important application is to the titration of copper. PAN suffers from the disadvantage of being, like its chelates, insoluble in water. Also many solutions require heating during titration with PAN as indicator.

TABLE III

PAN AS A COMPLEXOMETRIC INDICATOR

Ion		Method	Experimental conditions	Characteristics of method	Reference
Bi(III)	•••	1 1	pH 1 pH 4 to 5	Very specific Simultaneous determination with thallium	245 62
DI (III)		2			61
PD(11)		$\frac{1}{2}$	pH 4.5 to 7.5 In aqueous ethanol pH 5.0	Iron masked with sulphosalicylic	246, 247 8, 9, 61 68
Ga(III)	••	1	pH 2 to 2.6 (70° to 80° C) pH 4 to 5 (70° to 80° C)	acid Fe(III) and Tl(III) interfere	248 249
		2			8
In(III)		3	pH 3·5 pH 2·3 to 2·5	In(III) does not interfere Very specific	67 5
()		ĩ	pH 7 to 8	Interfering ions masked	5
		23	рН 2·5	Ga(III) does not interfere	8 67
		3	pH 2.5 to 2.7	Photometric titration	250
T1(111)		1	pH 4 to 5	Simultaneous determination with bismuth	62
		1	pH 1.8 to 2.0		251
Zn(II)			pH 5 to 6 (70° C)	For analysis of hydrazine	252 4, 53
		2		_	8, 9, 61
		2	pH 5 to 6, excess of EDTA titrated with standard lead solution		253
Cd(II)	••	1	pH 5 to 6	-	4, 53
		1 2	_	In CdS, for analysis of H_2S	107
Hg(II)		2	—	—	8, 61
Cu(11)	••	1	pH 2·5	Addition of organic solvent shar-	4, 53
				Equal amounts of Pb, Mn, Fe and Zn do not interfere in presence of Na S O	
		1		Applications to analysis of copper	52 to 59
		1	рН 6	For standardisation of EDTA solutions	60
		1	pH 4 to 9	Better than with PAR	50
		$\frac{2}{2}$	Acetic acid solutions Aqueous ethanol	_	9 61
Ni(II)		1	pH 4 (50° to 70° C)	Copper masked with $S_2O_3^{2-}$ ions	47
$C_0(U)$		$\frac{2}{2}$		_	8,9 8 9
00(11)	••	3	_	For indirect determination of	71
Fe(III)		9	_	potassium in blood serum	0 61
10(111)		$\frac{2}{3}$	pH 3 (cold)	With aluminium	254
Mn(II)	••	2	—		8
V		$\frac{2}{2}$	_	<u> </u>	8
		3	pH 4·5 to 5 in 33% meth- anol	_	69
AI(111)	••	23	nH 3 (boiling)	_	61 254
		-		Many applications	32, 63 to 66
Mg(II)	••	2	_	_	8, 61 8, 61
Su(II)	••	_	pH 8 (heating)	Excess of EGTA added to solu-	255
				tion and back-titrated with standard Ca(II) solution with Zn - EGTA - PAN as indicator.	
Sc(III)		2	pH 2.5	mg(11) does not interiere	6
Ce(III)	••	1	pH 5 to 6	In rare earth mixtures	256
10(17)	••	-	pH 3 to 4	After separation as iodide	258

TABLE III—continued

	Ion	Method	Experimental conditions	Characteristics of method	Reference
U(VI)		 1	pH 4·4 to 4·6 in 60% iso- propyl alcohol	Many ions do not interfere	259
		2	pH 4.4 to 4.6	Many ions do not interfere	259
Pu		 3	pH 2.5 to 30	-	70
		2	_	Titrated solution masked with F- ions and released EDTA titrated with CuSO ₄ —more specific	70

APPLICATIONS AS A SPECTROPHOTOMETRIC REAGENT-

As PAN and most of its chelates are insoluble in water, applications in this class are generally associated with extraction of the metal into an organic solvent. Normally this is achieved by the use of PAN itself, as upon chelation the metal passes from the aqueous into the organic layer. However, sometimes the extraction is carried out first with a reagent such as tributylphosphate in chloroform for uranyl nitrate, the PAN solution then being added to the organic extract.¹² Solvent extraction has been avoided either by using mixed solvent systems^{47,74,75} or by adding a coagulant such as gum arabic.⁴

In solvent extraction procedures with PAN, it is important that the aqueous solution is at the appropriate pH. Correct pH control can be used to extract one metal in the presence of others.¹⁰ In other cases masking agents can be used to increase selectivity.^{12,76,77,78,79} Back-extraction with acid or an aqueous complexing solution is sometimes possible and has been used for simultaneous determinations of two metals.^{80,81} The choice of solvent is sometimes important. Chloroform is the usual choice, but isopentyl alcohol,⁴ benzene,^{82,83} o-dichlorobenzene,^{11,13} ether^{84,85,86} and carbon tetrachloride⁸² have also been suggested. Addition of strong electrolytes to the aqueous layer has been used to bring about an otherwise impossible extraction.⁷⁸ This effect has been studied in greater detail.⁸⁷ Most PAN complexes have absorption maxima lying between 530 and 570 m μ , but some complexes absorb at longer wavelengths, for instance, vanadium(V) (615 m μ),⁸⁸ cobalt(III) (590 and 640 m μ),^{4,89} palladium(II) (620 and 675 m μ),^{10,76,77} rhodium(III) (598 m μ)⁹⁰ and iron(II) (765 m μ).^{42,43} These metals can be determined in the presence of others because their spectra do not overlap.

Much of the work on solvent extraction procedures has been carried out by Berger and Elvers⁴¹ and Shibata.^{42,43} The applications of PAN as a spectrophotometric reagent are summarised in Table IV. It can be seen that PAN is a useful sensitive reagent finding applications with a wide range of metals. Rigid control of the experimental conditions causes PAN to become a very selective reagent as well.

OTHER APPLICATIONS IN ANALYTICAL CHEMISTRY-

PAN has been used as a chromatographic spray reagent by Pollard, Nickless and Jenkins.⁹¹ The pale yellow background is unobtrusive whereas the spots contrast well, being pink, violet and green. The sprayed chromatograms are stable indefinitely. PAN also has the advantage of being able to detect about forty-five different metals. It has subsequently been used for the detection, after chromatographic separation, of scandium⁹² and the rare earth elements.⁹³ Ion-exchange paper impregnated with PAN has been used for the detection of heavy metals.⁹⁴ An interesting application is the use of PAN and cobalt nitrate solutions for the detection of conjugated steroid glucosiduronates after separation by thin-layer chromatography.⁹⁵

Spot tests for nanogram amounts of heavy metals have been devised by impregnating beads of ion-exchange resin with 1 drop of buffered test solution and 1 drop of PAN solution. Different colours are produced for the various ions.⁹⁶

In ethanolic solutions PAN gives a fluorescent complex with aluminium, and therefore it has been used as a simple qualitative and semi-quantitative test for this metal.^{97,98}

A method for the analysis of uranium has been studied, whereby the metal is precipitated quantitatively from alkaline solution with PAN. The complex is hydrolysed with acid and the absorption of the free PAN produced is measured at 440 m μ . The method is claimed to be 50 per cent. more sensitive than the normal solvent extraction procedure, and to require less stringent conditions.^{99,100}

TABLE IV

PAN AS A SPECTROPHOTOMETRIC REAGENT

		Absorbance	Sensitivity, OD per	General	
Ion	Method	measured at	µg per cm ²	characteristics of method	Reference
Ga(III)	at pH 3.6 to 3.0	$560 \text{ m}\mu$	—		43
		-	0.308	Study of solvent extraction be-	41, 42, 201
	Ext. into CHCl ₃ at pH 4·3	550 mµ	_	haviour For 1 to 15 μ g per 5 ml. Ga(III) extracted from Al(III) previ- ously with isopropyl alcohol as	260
	Aqueous DMF solu- tions at pH 5 to 6	$545~\mathrm{m}\mu$	0.357	Small amount of isopropyl ether added to enhance sensitivity. Cd(II) masked by I ⁻	47
In(III)	Aqueous DMF solu- tions at pH 5 to 6	$545 \text{ m}\mu$	0.214	Simultaneous determination with Ga(III)	47
	<u> </u>		0.132	Study of solvent extraction be- haviour	41, 42, 43, 201, 261
	Ext. into CHCl ₃ at pH 5·4 to 6·7	$560 \mathrm{m}\mu$	0.171	For 5 μ g per ml. Also for simul- taneous determination with Fe(III)	262
	Aqueous dioxan solu- tions at pH 4.3 to 6	550 mμ •0	0.1	1:1 complex soluble in BuOH and isopentyl alcohol	74
Tl(I)	Ext. into CHCl ₃			_	263
Tl(III)	pH 2·2	_		General study	48
Zn(11)	_		0.439	Study of solvent extraction be-	38, 41, 42, 43, 44
	Ext. into isopentyl	$555~\mathrm{m}\mu$	0.42		4
	Ext. into CHCl ₃ at pH 10	540 mµ	_	Ni(II) masked with CN^- . Cd(II) can be back-extracted with Et_2NCS_2Na for simultaneous determination. Fe(II) and $Mn(II)$ should be removed	80
		—	_	In copper	81
	Ext. into CHCl ₃ at pH 6.6	—	_	In iron ores. Other metals re-	264
		—		In nickel and nickel alloys	265
Cd(II)	—	_	0.435	Study of solvent extraction be- haviour	33, 42
	Ext. into CHCl ₃ at pH 8.7 to 10	$555~\mathrm{m}\mu$		<u> </u>	43
	Ext. into CHCl ₃ at pH 10	540 m μ		In nickel. Simultaneous deter- mination with zinc	80
	—	—	_	In copper	81
Hg(11)			0.176	Study of solvent extraction be- haviour	42
	Ext. into CHCl ₃ at pH 6 to 7.5	$560 \mathrm{m}\mu$		—	43
	Ext. into CHCl _s at pH 7.5 to 11.5	555 mµ	0.5	Many ions interfere, but mercury removed by distillation. For up to 5 ug per ml	266
	Aqueous EtOH at pH 6·5 to 8·3	550 m μ		For up to $2.5 \mu g$ per ml. Many ions interfere. Separation described	75
Cu(II)	_	_	—	Study of solvent extraction be- haviour	41 to 44
	Ext. into isopentyl alcohol		0.34	Spectrophotometric studies	36, 49, 267 4
Ag(I)				Study of solvent extraction be- haviour	268
Ni(II)			_	Study of solvent extraction be- haviour	38, 41 to 44
	Ext. into isopentyl alcohol	560 mμ	0.15	Spectrophotometric study	267 4

TABLE IV—continued

Ion	Method	Absorbance measured at	Sensitivity, OD per µg per cm ²	General characteristics of method	Reference
Ni(II)	Ext. into CHCl ₃ at pH 4 to 10 after pptn. of chelate by boiling	570 or 530 mμ	0.85	For 0.2 to $1.5 \text{ m}\mu$ per ml. CCl ₄ and C ₆ H ₆ also used. At pH 4 only Cu(II), Fe(II) and Co(II) interfere. First two masked.	269
	Ext. into CHCl ₃ at pH 5 to 9	575 mµ	_	Co absorbs at 630 m μ and can be simultaneously determined For 0.05 to 1 p.p.m. Simultaneous determination with Mn(II) by back-extraction of latter with acid	270
	Ext. into CHCl ₃	570 m μ		For up to 20 μ g. In presence of cobalt	271, 272
			—	For 5 to 100 p.p.m. In pure Mo and W	273
	<u> </u>	-		In thin films	274
Pd(II)			—	Study of solvent extraction be- haviour	41, 43
	Ext. into CHCl ₃ at pH 2.5	620 and 675 mµ	0.15	Spectrophotometric study For 0-15 to 0.35 mg. Specific at this pH for platinum metals.	$\begin{array}{c} 267 \\ 10 \end{array}$
	Ext. into CHCl ₃ at	678 and 626	0.132	For up to 20 μ g per ml. Co	76
	Ext. into $CHCl_3$ at pH 3.0 to 3.5	$675 \text{ m}\mu$	0.146	In Ti alloys. Interfering ions masked with EDTA	77
Co(II)	-	_		Study of solvent extraction be- haviour	41, 43, 44
	Ext. into isopentyl alcohol	640 mµ	0.29		4
	Aqueous solution Ext. into CHCl ₃ at pH 3 to 6 at	640 mμ 640 or 590 mμ	0.61	Gum arabic added to stop pptn. For 0-1 to 2-4 μ g per ml. 640 m μ more selective. Cu(II) inter- feres	4 89
	—			In thin films	274
	_		_	In molybdenum metal and titan- ium hard materials	275
Rh(III)	Ext. into CHCl3 at pH 5·1	$598 \mathrm{m}\mu$	0.19	For 1.1 to 3.8 p.p.m. Simul- taneous determination with Ir(III). Complex precipitated by boiling with PAN first	90
Ir(III)	Ext. into CHCl ₃ at pH 5·1	$550~\mathrm{m}\mu$	0.056	For 3.6 to 12.5 p.p.m. Simul- taneous determination with Rh(III). Complex precipitated by boiling with PAN first	90
Fe(III)	_	—	0.277	Study of solvent extraction be-	42
	Ext. into CHCl ₃ at pH 4 to 8	$775~\mathrm{m}\mu$		_	43
		_		In thin films	274
Mn(II)	_		1.06	Study of solvent extraction be- haviour	41, 42, 44
	Ext. into ether at pH 9 to 10	$560 \mathrm{m}\mu$	—	_	43
	Ext. into CHCl ₃ from basic solution	$575 \mathrm{m}\mu$	—	Followed by back-extraction with acid for simultaneous deter- mination with Ni(II)	270
			_	In beryllium In Nb, Ta, Mo and W alloys	276 277
v	Ext. into CHCl ₃ at pH 3.5	$615 \mathrm{m}\mu$	0.332	For 9 to 61 μ g. Fe interferes but can be determined simul-	88
	pH 3 in presence of acetone and	560 mµ	—	For 10 to 300 μ g per 50 ml. In steel. Separation of other components described	278
	(1114/2 ³ 2 ⁰ 8 —		-	Study of solvent extraction be- haviour	43

GENERAL PROPERTIES-

		Abaarbaraa	Sensitivity,	Conorol	
Ion	Method	measured at	ug per cm ²	characteristics of method	Reference
7r(IV)	Ext into CHCL				200
21(11)	In organic phase	$555~\mathrm{m}\mu$	0.35	Zr(IV) previously extracted with DBP. For 10 to 65 ug per 25 ml	279
Y(III)	Ext. into CHCl _a	—			200
	Ext. into ether at pH 8.5 to 11	$560 \mathrm{m}\mu$	<u> </u>	—	43
	Ext. into ether at pH 9 to 10	570 mµ	0.76	Can be separated from La(III), Ce(III) and Sc(III). PO_4^{3-} and Zr(IV) interfere	84, 85
REs	Ext. into ether from alkaline solution	530 or 560 mμ		La(III), Ce(III) and Sc(III) not extracted. CCl ₄ , CHCl ₃ and C _e H _e can also be used	82, 86
	pH 3·20 with Cu(II) - EDTA - PAN	530 mµ	_	Following separation by ion- exchange chromatography. RE replaces Cu(II) from Cu- EDTA and Cu(II) reacts with PAN	280
	-	—	-	Study of solvent extraction be- haviour	268
U(VI)	Ext. into CHCl ₃	_		—	200
	_	—		Study of solvent extraction be- haviour	41, 43
	Ext. into o-dichloro- benzene at pH 10	$570 \text{ m}\mu$	0.097	For (0.1 to 5) \times 10 ⁻⁵ mmoles per ml. EDTA masks foreign ions	11
		-	—	In presence of Th(IV) masked with EDTA	13
	UO ₂ (NO ₃) ₂ ext. into TBP - CHCl ₂		_	For 40 to 400 μ g. EDTA useful for masking foreign ions	12
	UO ₂ (NO ₃) ₂ ext. into TNOPO	—	0.092	From plutonium. For 1 to 20 p.p.m. Removal of interfering ions	281, 282
	Red precipitate in NH ₃ solution, ext. into CHCl ₃ if NaCl or Na ₂ SO ₄ added	_	-	EDTA or CN- masks most foreign ions	78
	_		_	In CaF ₂ ; CHDTA masks most foreign ions	79
~				In organic and inorganic materials	283
Sb	Ext. from acid solu- tion containing KI and thiourea with C ₆ H ₆ solution of PA	 AN		_	83
Ca(II)	With Ču - EDTA - PAN			Can be used at lower pH values	284
Pb(II)	At $pH > 6$ in meth- anolic solutions	$530 \text{ m}\mu$	-	For 0.8 to 6.6 μ g per ml. Best with PAN in 50-fold excess	285

TABLE IV—continued

PAN has been used successfully as a mercurimetric indicator for chloride¹⁰¹ (titration of chloride with standard mercury solutions). Titration of mercury with standard chloride solutions is also possible. It is necessary to add ethanol to the titrate.

The dye has also been used in precipitation titrations for anions. Molybdate¹⁰² and tungstate¹⁰³ ions have been determined by titration with standard lead solutions with copper -EDTA - PAN as indicator. The titration reaction is slow and heating is generally required. Sulphate ions have been determined by a similar method,¹⁰⁴ or by precipitation with excess of lead solution and back-titration with EDTA in the presence of copper - EDTA - PAN indicator.¹⁰⁵ Many cations and anions interfere with these titrations. Niobium has been determined by co-precipitation with zinc, and titration of the zinc with copper - EDTA - PAN as indicator.¹⁰⁶ Hydrazine is determined indirectly as it reduces standard thallium(III) solutions to thallium(I). Back-titration of excess of thallium(III) with EDTA and PAN as indicator is then possible.¹⁰⁷

4-(2-PYRIDYLAZO)-RESORCINOL (PAR)

PAR was first prepared by Chichibabin, by coupling resorcinol with sodium 2-pyridyldiazotate.³⁶ Originally the conditions used in the preparation were the same as those for PAN, but in more recent preparations the use of carbon dioxide is dispensed with, and the dye is obtained as the mono-sodium or di-sodium salt.¹⁷ The sodium salts are more water soluble than the free dye itself, and in analysis are used in preference for this reason. The aqueous solutions are orange. The dye as a sodium salt is soluble in acid and alkaline solutions, and to a lesser extent in alcohol. It is insoluble in ether.

Geary, Nickless and Pollard¹⁰⁸ made a complete investigation of the visible spectrum of the dye as a function of pH in aqueous and 50 per cent. aqueous dioxan solutions. They were able to identify the following four chromophoric species—



It is believed that the p-hydroxyl group ionises first, as the o-hydroxyl proton is hydrogenbonded to the azo group. The peak wavelengths of all four forms were found to be as follows—

			Aqueous solution	Aqueous dioxan solution 50 per cent.
I	•••		$395 \mathrm{m}\mu (\epsilon = 15,500)$	420 m μ ($\epsilon = 14,750$)
II	• •		$383 \mathrm{m}\mu (\epsilon = 15,700)$	$392 \text{ m}\mu \ (\epsilon = 15,240)$
III			415 m μ ($\epsilon = 25,900$)	414 m μ ($\epsilon = 23,100$)
IV	•	• •	$485 \mathrm{m}\mu \ (\epsilon = 17,300)$	$502 \text{ m}\mu \ (\epsilon = 17,800)$

Hniličková and Sommer¹⁰⁹ carried out a spectrophotometric study of the dye and established the existence of six chromophoric forms of PAR. In addition to those above, they found H_5R^{3+} ($\lambda_{max.} = 433 \text{ m}\mu$) and H_4R^{2+} ($\lambda_{max.} = 390 \text{ m}\mu$) in 90 and 50 per cent. sulphuric acid. The extra protons are thought to be attached to a hydroxyl group and to the azo group.

Similar to PAN, PAR shows no signs of intermolecular association under most normal conditions met with in analysis.³⁹ The purity of the reagent can be tested by using thin-layer chromatography.⁴⁰

PAR reacts with metals to give red or red-violet complexes. The complex with palladium is green in acid and red in neutral solutions. PAR does not react with the alkali metals, chromium(VI), antimony(III), molybdenum(VI), tungsten(VI) and arsenic(III) or (V). The formation of these complexes is very dependent on pH. Hniličková and Sommer¹⁰⁹ have investigated the formation and stoicheiometry of some metal - PAR complexes as a function of pH, and have shown that in acid solution M(PAR)H was formed, and in alkaline solution, $M(PAR)_2$. Geary, Nickless and Pollard²⁵ measured the stability constants of some metal chelates for the following compounds: PAR, benzeneazo-resorcinol (I), salicylidene-2-aminopyridine (II) and 2-pyridylidene-o-aminophenol (III). Examination of both these



results and those published by Klotz and Ming¹¹⁰ on the chelates of 4-(2-pyridylazo)-dimethylaniline, showed that only the stability constants for **III** were of the same order as those of PAR. The other ligands formed less stable complexes. From this it was concluded that PAR

April, 1967]

chelates with metals through the pyridine nitrogen atom, the azo-nitrogen atom furthest from the heterocyclic ring, and the *o*-hydroxyl group. PAR thus acts as a tridentate ligand forming two stable 5-membered chelate rings, and the commonest chelates are of the type, M(PAR) and $M(PAR)_2$. Other types are rare, but $Th(PAR)_4^{111}$ and $Ga(PAR)_5^{45}$ have been reported.

An interesting and important point to note about the chelation of PAR concerns the ionisation of the two hydroxyl groups. Normally the p-hydroxyl group ionises first, because of the internal hydrogen bonding in the molecule. However, on chelation, which often occurs at pH values lower than either pK_{OH}, protons are released preferentially from the *o*-hydroxyl group. This means that, theoretically, PAR chelates in the thermodynamically unfavoured form—



for which the dissociation constant is not known. Corsini, Mai-Ling Yih, Fernando and Freiser³⁷ considered this problem in calculating the stability constants of metal - PAR chelates, and pointed out that pK_{OH} (ortho) was almost the same for PAR and PAN. They therefore considered it safe to assume that the ionisation of the *p*-hydroxyl group had no effect on pK_{OH} (ortho). The effect of chelation on pK_{OH} (*para*) has also been studied by Corsini, Fernando and Freiser.¹¹² Although the values given by Geary, Nickless and Pollard²⁵ may be open to considerable doubt, following the values given by Corsini, Fernando and Freiser,¹¹² the general approach is in no way invalidated. Further evidence from crystallographic results on the structure of copper-(benzene-azo- β -naphthol)¹¹³ showed that the metal is co-ordinated through the nitrogen atom, alpha to the naphthalene ring. Some values for the stability constants of metal - PAR chelates are given in Table II.

APPLICATIONS AS A COMPLEXOMETRIC INDICATOR—

Wehber¹⁴ was the first to suggest PAR as an alternative to PAN in complexometric titrations. The immediate advantage of PAR over PAN is that this reagent and most of its complexes are water soluble. Thus it is not necessary to add organic solvents to the solution to be titrated. Also in many instances the end-points are sharper, the colour change being from orange - red to yellow. PAR can also be used at lower pH values than PAN. As with PAN, heating of the solution is often necessary.

In most of the titrations the direct method is used. However, back-titration of excess of EDTA with standard lead solutions, with PAR as indicator, has been recommended for aluminium.¹¹⁴ Also standard lead, bismuth and zinc solutions have been recommended for use in back-titrations with PAR.¹¹⁵

Table V summarises the main applications of PAR in EDTA titrations.

Applications as a spectrophotometric reagent—

Again the immediate advantage of PAR over PAN is the water solubility of both it and its complexes.¹⁷ Spectrophotometric analyses with PAR involving mixed solvent systems or solvent extraction are few and far between.^{116,117} However, butanol has been used to extract excess of PAR from an aqueous phase in order to increase selectivity.¹¹⁸ But normally, although the metal may previously have been extracted to separate it from interfering ions,^{119,120} the analysis is carried out in an aqueous phase.

The sensitivity of PAR for metals is greater than that of PAN, as can be seen by consulting Tables III to VI. In the first application to spectrophotometric analysis,¹⁷ it was reported to be the most sensitive reagent for cobalt, and the most sensitive water-soluble reagent for uranium, being 30 per cent. more sensitive than PAN.

Except in the determination of palladium, all optical densities are measured at wavelengths between 494 and 550 m μ . With PAN, a wider range of wavelengths was used, which gives a greater possibility of choosing a part of the spectrum in which the interference of foreign ions is at a minimum. This increases the selectivity of PAN and makes possible

TABLE V

PAR AS A COMPLEXOMETRIC INDICATOR

Ion	Experimental conditions	General characteristics (all titrations are of the direct method unless otherwise stated)	Reference
Bi(III)	pH 1 to 2	Can also be used in back-titrations	115
		For 4 to 600 μ g per ml. PAR gave better results	286
		than PAN	
	pH 1 to 2	For 2.5 to 64 mg	109
Pb(II)	pH 5 to 9	Can also be used in back-titrations	115
	pH 6.5 to 7	Also used for back-titration of Al(III)	114
	pH 8 to 9.	For 3 to 80 mg	109
Ga(III)	pH 2 to 2.6 (70° to 80° C)	_	248
In(III)	pH 2·3 to 2·5 (60° to 70° C)	Al, Cd, Zn, Mn, Mg and Ca do not interfere	16
		Initial separation into ether from 1.5 N H ₂ SO ₄ and NKI	287
Tl(III)	pH 4 to 5		62
	Weakly acidic	For indirect determination of organic hydrazines	130
Zn(II)	pH 6 to 11.5	Can also be used in back-titrations (pH 5 to 6, 10 to 12)	115
	pH 8 to 9	For 1 to 26 mg	109
Cd(II)	pH 6 to 11.5		115
	pH 8 to 9	For 3 to 80 mg	109
		For the indirect analysis of H ₂ S	107
Hg(II)	pH 3 to 6.9		115
Cu(II)	pH 5 to 11.5	_	115
	pH 5 to 9	Inferior to PAN	50
Ni(II)	pH 5 (90° C)		115
Mn(II)	pH 9		115
Al(III)	pH 3 (100° C)		115
	pH 5 to 7	Indirect method. Excess of EDTA titrated with standard lead solutions. Heat required if excess	114
		of nitrate is present	
REs	pH 6		115
Er(III)	pH 8.5	For $0{\cdot}3$ to $0{\cdot}8$ mg. Other rare earths interfere	288

certain simultaneous determinations. Such methods are not possible with PAR. Also, selective solvent extraction is not applicable. These facts show that PAR is a less selective reagent than PAN, and more involved schemes for the separation or masking of ions are necessary.

Applications are listed in Tables V and VI, and no further comment is required.

OTHER APPLICATIONS IN ANALYTICAL CHEMISTRY-

As a chromatographic spray reagent, PAR is as sensitive as PAN.⁹¹ The reagent has a pale yellow background and the spots stand out with a fairly consistent red colour (vanadium is violet). For the detection of metals on ion-exchange paper, it was noticed that PAR gave a uniform reddish purple colour as opposed to the variety of shades produced by PAN.⁹⁴ As a colour producing reagent, PAR can be used for detecting nanogram amounts of heavy metals absorbed on resin grains.⁹⁶ PAR produces a colour sensitive to 1 μ g with yttrium and zirconium,¹²¹ 0·1 μ g with niobium¹²² and 5 × 10⁻⁴ μ g for copper in a resin spot test.¹²³ The reaction with titanium has been studied more fully.¹²⁴

PAR and methylthymol blue have been used to detect the formation and evaluate the stabilities of peroxy complexes of niobium and tantalum.¹²⁵ The reactions of these metals and titanium, in the presence of hydrogen peroxide with many dyes, including PAR and PAN, have been studied as a function of pH.¹²⁶

The dye has been used as an indicator in precipitation titrations with standard lead solutions, for orthophosphate,¹²⁷ arsenate,¹²⁸ molybdate and tungstate.¹²⁹ PAR has also been used for the indirect determination of organic hydrazine derivatives with thallium(III) ions.¹³⁰

An interesting method involving spectrophotometric titration has been used for copper.¹³¹ The solution containing about 0.1 M copper(II) in 10 ml of acetate buffered medium is titrated against standard PAR solution in 0.05-ml aliquots, the absorption being measured after each addition. A sharp inflection in the titration curve marks the end-point. The method also works for lead and cobalt and does not require a calibration curve.

TABLE VI

PAR AS A SPECTROPHOTOMETRIC REAGENT

			Sensitivity		
		Absorbance	OD per	General	
Ion	Method	measured at	µg per cm ²	characteristics of method	Reference
Pb(II)	pH 10	520 mµ	0.171	For up to 5 μ g per ml Spectrophotometric titration	17 131
	pH 10	$520 \mathrm{m}\mu$	0.19	Separated from interfering ions by extraction into IMBK and back-extracted into NH ₃ solu- tion	119
	pH 9	$512 \mathrm{m}\mu$	0.35	For (C ₂ H ₅) ₂ PbCl ₂ as (C ₂ H ₅) ₂ PbPAR Also for PbCl ₂ in (C ₂ H ₅) ₂ PbCl ₂	. 289
	_		_	Application to steel, brass and bronze	120
Sn(II)	pH 6	514 m μ	0.20	For $(C_2H_5)_2$ SnCl ₂ as $(C_2H_5)_2$ SnPAR	289
Ga(III)	pH 7	504 mμ	1•47	For I to 15 μ g per 25 ml. Many ions interfere	290
	рн 4	530 mµ	_	For up to 1 μ g per ml. Extraction of HGaCl ₄ into ether from 6 N HCl removes most ions except Fe and Sn	291
	pH 4.7 to 6.7	-	_	For 2 to 12 μ g per 50 ml. Up to 600-fold excess of oxalate tolerated	292
	_	-	_	For 6 to 48 μ g per 50 ml. Organic solvents and Br ⁻ ions have no effect	293
	pH 4	$530 \text{ m}\mu$		For 1.0 to 2.0 p.p.m.	294
In(III)	рН 7	$510 \mathrm{m}\mu$	0.753	For 2 to 30 μ g per 25 ml. Many ions interfere	295
		500	0.996	For 5 to 190	201
	pri 3	500 mµ	0.280	Co, Ni, V(V), Zr, Bi, Sn(II), F, NO ₂ ⁻ , P ₂ O ₂ ⁴ and C ₂ O ₄ ²⁻ inter- fere. Separation from these described	290
	pH 4·3 to 6	$500 \text{ m}\mu$	0.5	Cations interfere For 20 to 120 μ g per 50 ml. Or- ganic solvents and Br- ions have no effect	74 293
	рН 7-05	496 mµ	_	Best molar concentrations of metal to ligand are 4.75:5.25. Conditions by Box and Wilson's method ²⁹⁸	297
					242
T1/III)	pH 4	$530 \text{ m}\mu$	-	For 1.0 to 2.0 p.p.m.	294
$C_{\rm II}({\rm III})$	рп 4	517 to 529 m.	in the second	Spectrophotometric titration	294
Ni(II)	pH 8.6 to 10	494 mμ	1.24	For 0.005 to 1.0 μ g per ml. Inter- fering ions masked with EDTA, citrate etc.	299
Pd(II)	In strong acid hea to 70° to 80° C an	at 440 or 630 d m μ	0·172 or 0·0847	44 ions listed as not interfering	116
Co(II)	pH 8	510 m u	0.03	For up to 1.4 ug per ml	17
00(11)		<u> </u>		Spectrophotometric titration	131
	pH 7 to 8	$500 \text{ m}\mu$	0.951	EDTA masks foreign ions	243
	pH 6.8	$510 \mathrm{m}\mu$	0.965	For 4 to 32 μ g per 50 ml. In presence of EDTA only Fe(III) and Ni(II) interfere	300
	pH 6.8 to 8.2	$510 \mathrm{m}\mu$	1.0	In soils, water and plants, citrate and EDTA mask other ions	301
Fe(III)	-				302
Os(IV)	-	$533 \text{ m}\mu$		For 0.3 to 5 μ g per ml	303
V(V)	-		—	In the presence of CHDTA, very specific	304
	pH 5·25 to 6·50	545 mµ	0.69	For up to 1.0 p.p.m. Co, Cu, Ni,	305
	pH 6.5	$540 \text{ m}\mu$	—	For 1 μ g per ml. Many ions inter- fere	306

TABLE VI—continued

		Abcorbanco	OD por	Conoral	
Ion	Method	measured at	ug per cm ²	characteristics of method	Reference
1011			μg per em	In presence of CrO_4^{2-} , $Mo_7O_{24}^{6-}$,	307
Nb(V)	pH 5 to 8 in tartrate media	$550~\mathrm{m}\mu$	—	$WO_4^{2^-}$ and NO_3^- For up to 7 μ g per ml. EDTA masks most metals except V(V)	122
	pH 5.8 to 6.5 in	$540 \mathrm{m}\mu$	_	and $U(VI)$ In presence of Ta(V), Ti(IV) and $Zr(IV)$	118
	pH 5 to 8 in tartrate media	$550~\mathrm{m}\mu$	0.416	For up to 1 p.p.m. CN ⁻ and EDTA mask all ions except U(VI), V(V) and PO ₄ ³⁻ . De-	308
	pH 5 in the presence of 30% H ₂ O ₂			tails for masking these For 2 to 60 μ g per ml. EDTA masks Ti(IV), Zr(IV) and Eq(III)	309
	_	-	—	In steel (without separation from Fe, Cr, Ni, Co, Mo, W, Ti, Al and Zr)	310
	pH 5.5 to 7.0 in tartrate media	$530 \text{ m}\mu$	0.30	In presence of Mo, W, Ti, Al, Fe, Co and Ni	122
	pH 5.5 in oxalate media	540 m μ	0.255	In presence of Mo, W, Zr and U	311
			—	In rocks	312
	pH 5 to 6 in acetate tartrate medium	_		In presence of EDTA or CHDTA only V(V) seriously interferes. Mo, Ti, U and Th interfere in 7 to 10 fold excess	313
Ta(V)	In presence of $C_2O_4^{2-}$, H_2O_2 and BuOH at pH 6 to 8	536 mµ	_	BuOH extracts excess of PAR to prevent reaction with other ions. In presence of Nb(V), Ti(IV) and Zr(IV)	118
	In presence of $C_2O_4^{2-}$ at pH 5.5	$535~\mathrm{m}\mu$	0.0923	For 5 to 80 μ g U, Zr, W, Mo masked with C ₂ O ₄ ²⁻ , Fe masked with EDTA	314
					315
Ti(IV)	In H ₂ O ₂ medium				316
Th(IV)	pH 6·4 to 6·7	—	0.168	CO ₃ ²⁻ , PO ₄ ³⁻ , F ⁻ , NO ₃ ⁻ , C ₂ O ₄ ²⁻ and organic anions forming stable complexes interfere	111
Sc(III)	pH 6 to 7.3	$515 \mathrm{m}\mu$	0.49	For 0.05 to $2.0 \ \mu g$ per ml. Many ions interfere	317
	pH 3.5 to 4.5, $\mu = 0.4$	$530 \text{ m}\mu$	_	Many ions interfere	318
La(III)	pH 5-1	$510 \text{ m}\mu$		_	319
Ce(III)	pH 5-1	$510 \text{ m}\mu$	_		319
Er(III)	pH 8.5	$540 \text{ m}\mu$	(1997)	For 10 ⁻³ to 10 ⁻⁴ g	288
REs		_	—	Conditions for determination of La, Nd, Sm, Gd, Y, Dy and Er	320
TT/TT)	pH 6.2	$515 \mathrm{m}\mu$	0 100	Optimum conditions described	321, 322
U(VI)	pH 8 Aqueous solution at pH 7 to 8	530 mμ 540 mμ	0.100	For up to 60 µg per mi For 0.04 to 16 µg per ml. Masking agents or chromatography re- move all interfering ions	323
Np(V)	pH 9 to 10		0.181		324

OTHER PYRIDYLAZO DYESTUFFS

Although sodium 2-pyridyldiazotate couples with phenols only with difficulty, other pyridylazo dyestuffs have been prepared and used in analytical chemistry.

Sommer and Hniličková,¹⁵ when they reported PAR as a possible metallochromic indicator, also mentioned 2-(2-pyridylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid (PACh) and 2-(2-pyridylazo)-1-hydroxy-8-aminonaphthalene-3,6-disulphonic acid (PA-H). These dyes are less sensitive than PAR, and their applications are more limited. PACh, however, is interesting in that it contains a peri-dihydroxy grouping, a useful chelating system in its own right. Thus two types of chelate formation are possible. Certain metals that form stable chelates with chromotropic acid complex at a lower pH with PACh than with PAR or PAN. It is possible that in these instances chelation is via the two hydroxyl

April, 1967]

groups. PACh, together with 2-(3-pyridylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid has been used for the colorimetric determination of beryllium(II)¹³² and copper(II).¹³³ With beryllium(II) at least, the stoicheiometry of the complexes and the general similarity of behaviour of the two dyes suggests that chelation may only be via the oxygen atoms.

Sommer and Hniličková¹³⁴ have also used 4-(2-pyridylazo)-orcinol (PAO) and 1-(2-pyridylazo)-2,3-dihydroxynaphthalene-6-sulphonic acid (PADNS) as indicators for chelometric titrations. PADNS produces red colours with metals (similar to those of PAN), unlike PACh which produces blue-to-violet colours. Theoretically, PADNS can also complex either like PAN or via the two hydroxyl groups (*cf.* catechol-3,5-disulphonic acid).

Sommer¹²⁴ has reported the reaction of titanium(IV) with several polyphenols and dyes, including 1-(2-pyridylazo)-2,7-dihydroxynaphthalene (2,7-PAN). Except that the extra hydroxyl group makes the dye more water soluble, it is similar to PAN.

7-(2-Pyridylazo)-8-hydroxyquinoline (PAOx), which can be prepared from sodium 2-pyridyldiazotate and 8-hydroxyquinoline, forms coloured complexes with a similar range of metals to those which react with PAN.¹³⁵ However, PAOx chelates at a lower pH than either PAR or PAN. It has been used in the complexometric determination of thallium(III)¹³⁶ and also of copper(II) in alloys.¹³⁷ Theoretically this dye, which has both PAN and 8-hydroxy-quinoline chelating systems, can complex in two different ways, either as a bidentate or tridentate ligand.

Pollard, Nickless and Anderson^{138,139} have synthesised a new series of pyridylazo dyestuffs by coupling 2-hydrazinopyridine with various guinones. They have prepared by this method 4-(2-pyridylazo)-phenol (\dot{p} -PAP), and 2-(2-pyridylazo)-phenol (ρ -PAP). The former is a weak complexing agent, only forming strong colours over a narrow range of pH with metals in groups VIII and Ib, whereas the latter reacts with many cations over a wide range of pH. The behaviour of these two compounds illustrates the relative rôles played by the two hydroxyl groups in PAR. These workers also prepared 2-(2-pyridylazo)-I-naphthol (α -PAN) and some of its water-soluble sulphonated derivatives. This is the compound prepared by Betteridge, Todd, Fernando and Freiser¹⁴⁰ by the Chichibabin and Rjasanzew reaction³⁵ and designated on the basis of a low pK_{OH} value compared with β -PAN, as p-PAN. The evidence provided by D. Betteridge and A. Kawase (private communication) of organic synthesis and infrared spectra leaves no doubt that the compound was incorrectly described. There is, at present, no satisfactory explanation why the pK_{OH} is almost the same value of free 1-naphthol and apparently is not shifted by the hydrogen bonding that would be expected for a hydroxyl group in an ortho position to an azo-group. The reagent reacts with many ions to give complexes, with colours ranging from purple to green, many of which can be extracted. The stability constants are almost the same as those with β -PAN for the same metal ion, a notable exception being copper, which forms a 1:2 complex.¹⁴⁰ The reagent has recently been recommended as an extractive indicator in the titration of EDTA with copper,¹⁴¹ and for the complexometric and spectrophotometric (by solvent extraction) determination of indium.¹⁴² PACh and water-soluble sulphonated derivatives of α -PAN, which is also a derivative of a-naphthol, form blue - violet complexes with many ions, and ionise and chelate at lower pH values than β -PAN. Their properties as chromatographic spray reagents have been discussed.138

Nakagawa and Wada¹⁴³ have prepared 2-(2-pyridylazo)-4-methylphenol (PAC) and investigated its reactions with metal ions. This reagent reacts with a wide range of metals giving blue-to-violet extractable complexes. They have used it for the complexometric determination of copper, zinc, cadmium and lead, for which it appears to be better than PAR or PAN, giving a sharp colour change from violet to yellow at the end-point. The same workers¹⁴⁴ have made a spectrophotometric study of the copper, nickel and zinc chelates and conclude that the reagent acts as a bidentate ligand. However, its behaviour, which is similar to that of 2-(2-pyridylazo)-phenol, suggests to us that it is tridentate.

Gusev and Shchurova¹⁴⁵ have prepared 5-(2-pyridylazo)-2-monoethylamino-*p*-cresol (PAAC) and have used it for the complexometric determination of bismuth, indium and zinc, and for the spectrophotometric determination of thallium and cobalt. They have made a full investigation of the bismuth - PAAC system, and recommend the dye as an indicator for this metal.¹⁴⁶ The reaction of this dye and 3-(2-pyridylazo)-4-ethoxy-6-monoethylamino-toluene with indium has been studied with respect to use in the analysis of this metal.¹⁴⁷

Recently three new dyes have been prepared as possible analytical reagents by coupling

diazotised 2-amino-N-methylanabasine with resorcinol,¹⁴⁸ α -naphthol¹⁴⁹ and β -naphthol.¹⁵⁰ These dyes are similar to their pyridyl analogues, but are more specific. 4-(2-N-Methylanabasineazo)-resorcinol (MAAR) has been used for the complexometric determination of thallium(III),¹⁵¹ indium(III),¹⁵² gallium(III).¹⁵³ and bismuth(III),¹⁴⁸ and also for the spectrophotometric determination of bismuth(III).¹⁵⁴ The reagent's acid dissociation constants have been measured.¹⁵⁵ 1-(2-N-Methylanabasineazo)-2-naphthol (MAAN) has been used for the spectrophotometric determination (in aqueous solutions) of the rare earths¹⁵⁶ and of zinc(II).¹⁵⁷ 4-(2-N-Methylanabasineazo)-1-naphthol (p-MAAN) has been used for the spectrophotometric determination of vanadium(V).¹⁵⁷

Klotz and Ming¹¹⁰ studied the metal complexes of 4-(2-pyridylazo)-dimethylaniline (PAA) and evaluated an order of stability for some common metal ions. The stabilities are low compared with those of PAR, and are of the same order as those of 4-(2-pyridylazo)-phenol.¹³⁹ This dye has found use as an acid - base indicator in non-aqueous media.^{158,159}

Chiswell, Lions and Tomlinson¹⁶⁰ condensed 2-hydrazinopyridine with benzil, acenaphthenequinone and o-phenanthraquinone. For each, only one molecule of hydrazine would condense with the diketone, and the hydrazones obtained reacted with metals in a similar manner to PAR and PAN, forming highly coloured complexes.

Pollard, Nickless and Jenkins⁹¹ prepared a series of pyridylazomethines related to PAR for use as chromatographic spray reagents. These were easily obtained by condensing *o*-aminophenol with pyridine-2-aldehyde and pyridine-2,6-dialdehyde, and by condensing salicylaldehyde with 2-aminopyridine and 2,6-diaminopyridine. The first two give red-tobrown colours with many metals, whereas the second two are far less sensitive.^{25,108} The compound from salicylaldehyde and 2,6-diaminopyridine, however, was found to be selective for copper and iron(III). All of these compounds showed some fluorescence with certain metals.

Pollard, Nickless and Anderson^{138,139} prepared some 2-pyridylhydrazones such as salicylaldehyde-2-pyridylhydrazone, and compared them with the pyridylazo dyestuffs. Although these compounds formed stable metal chelates, the colour changes produced on chelation were not striking. The above-mentioned compound did produce some good fluorescence reactions when used as a chromatographic spray reagent. 2-Pyridylidene-o-aminothiophenol was also prepared^{138,139} and found to be more selective than its oxygen analogue.

THIAZOLYLAZO AND BENZOTHIAZOLYLAZO DYESTUFFS

2-Aminothiazole, unlike its pyridyl analogue, requires no special conditions for diazotisation, and hence thiazolylazo dyes are easily prepared from a wide range of phenols, naphthols¹⁶¹ and other non-phenolic substances.^{162,163} The same is true for 2-aminobenzothiazole.^{164,165} It was inevitable, therefore, that soon after the introduction of pyridylazo dyestuffs as analytical reagents, parallel work should be undertaken on their thiazolyl analogues, as these also will provide a chelating system similar to that of PAN.

In 1958, Boni and Hemmeler¹⁸ coupled diazotised 2-aminothiazole with catechol, resorcinol, phloroglucinol, β -naphthol, chromotropic acid, 8-hydroxyquinoline, alizarin and salicylaldoxime. They showed that the dyes produced could be used for the detection of metals, either in solution or on paper, and worked out qualitative methods for identifying cobalt, copper and zinc, by using 1-(2-thiazolylazo)-2-naphthol (TAN).¹⁹ Later, Hemmeler and Scattolari¹⁶⁶ used 2-(2-thiazolylazo)chromotropic acid (TACh) as an indicator in both direct and indirect titrations of zirconium and thorium.

Jensen^{21,167} prepared thiazolylazo dyes of resorcinol, orcinol, p-cresol, *m*-dimethylaminophenol, β -naphthol and 2-naphthol-6-sulphonic acid. These reagents were used as complexometric indicators, and it was found that in direct titrations they were most useful for cobalt, nickel and copper (addition of ethanol and heating were required for the end-points to be sharpest), although the use of the copper - EDTA - dye system increased the range of titratable metals. 2-(2-Thiazolylazo)-5-dimethylaminophenol (TAM) was found to be a sensitive reagent for the spectrophotometric determination of uranium,¹⁶⁸ and has been investigated further as a possible analytical reagent,¹⁶⁹ especially for copper.¹⁷⁰

Much of the important work on these compounds has been carried out in Japan, in particular by Kawase. Initially, with Yanagihara and Matano, Kawase prepared 2-(4-methyl-2-thiazolylazo)-4-methoxyphenol^{171,172} and used it for the spectrophotometric determination of copper,¹⁷³ zinc,¹⁷⁴ nickel and cobalt,¹⁷⁵ and iron.^{176,177} He then prepared about twenty-three derivatives of 2-(2-thiazolylazo)-phenol¹⁷⁸ and studied their copper complexes,¹⁷⁹ showing

April, 1967]

that two chelates were formed with metal-to-ligand ratios of 1:1, water soluble and suitable for complexometric titrations, and 1:2, soluble in organic solvents and suitable for extraction. Kawase used these dyes for the spectrophotometric determination (with or without extraction) of nickel,¹⁸⁰ cobalt(II)¹⁸¹ and cobalt(III).¹⁸² Of the dyes studied, TAN seemed to be the most useful, and was used for the spectrophotometric determination of zinc¹⁸³ and nickel in chromium,¹⁸⁴ both by extraction into chloroform. Studies on the stability constants and spectra of the metal complexes have shown that the dyes are tridentate.¹⁸⁵ Derivatives of 4-(2-thiazolylazo)-1-naphthol (p-TAN) are almost specific in their reaction towards palladium¹⁸⁶ and p-TAN itself has been used for the determination of this metal by extraction into isopentyl alcohol.¹⁸⁷ Only iron and silver interfere.

Nakagawa and Wada have used azo dyes of thiazole in analysis, for the complexometric determination of copper¹⁸⁸ and nickel,¹⁸⁹ and in solvent extraction.¹⁹⁰ Kaneniwa has also used these dyes in complexometric titrations²⁰ as well as carrying out some spectrophotometric studies on their chelates.^{191,192,193}

Although it has been shown that these dyes act as tridentate ligands.¹⁸⁴ the lower basicity of the thiazole nucleus¹⁹⁴ will cause the chelates to be less stable than their pyridyl analogues. However, this in turn means that the thiazolylazo dves will be more selective.^{190,195} One or two dyes have been shown to be highly selective, such as 1-(6-bromo-2-thiazolylazo)-2-naphthol ("bromobenzothiazo"), a reagent for the solvent extraction of cadmium, 196, 197 and 4-(2-thiazolylazo)-1-naphthol reagent for palladium.^{186,187} The lower stabilities of these chelates also make the dyes particularly useful in EDTA titrations. 18,20,21,166,167,188,189,198,199,200 The dyes and their chelates are less soluble in water than their pyridyl analogues, and are easily extracted into organic solvents. Various workers have studied the solvent extraction of thiazolylazo dye chelates, 169,170,173 to 184,186,187,190,193,195,197,201 Results from these investigations show that, for bivalent ions such as copper, with insoluble dyes, the 1:1 chelate is soluble in water and suitable for use in EDTA titrations and the 1:2 (metal-to-ligand) chelate, which is insoluble in water, can be extracted into organic solvents for spectrophotometric determinations.^{173,174,175,195} As chromatographic spray reagents they are inferior to their pyridyl analogues because the strong orange background colour of the dye causes the chelates to appear less distinct.91

OTHER HETEROCYCLIC AZO DYESTUFFS

By far the most important group of dyes in this class are the azo derivatives of 8-hydroxyquinoline. Very few applications for other heterocyclic azo dyes in analytical chemistry have, as yet, been found. These few will be discussed first.

Pollard, Nickless and Anderson,^{138,139} by condensing a quinone with a heterocyclic hydrazine,²⁰² have prepared a series of pyrimidylazo dyes that they were able to compare with the corresponding pyridyl compounds. The former dyes were found to be superior in several ways for the following reasons—

They are more water soluble.

They are more sensitive towards cations of groups IIa and IIIa of the periodic table.

The bathochromic shifts observed in the visible spectrum on ionisation and chelation of the dyes are larger with the pyrimidyl derivatives.

Pyrimidine is a weaker base than pyridine,¹⁹⁴ and thus the acid dissociation and chelate stability constants were found to be lower. The dyes formed chelates in more acidic solution, and were also found to be more suitable for the titration of copper, giving faster colour reactions at the end-point.

These same workers have also prepared some 8-quinolylazo dyestuffs and hydrazones,¹³⁸,¹³⁹ showing that metals gave sensitive colour reactions only with ligands forming two 5-membered rings on chelation, such as PAR and PAN; but the most stable complexes contained a 5-membered and a 6-membered chelate ring (*cf.* salicylaldehyde-2-pyridylhydrazone^{138,139}). 2-(8-Quinolylazo)-1-naphthol-4-sulphonic acid gives a good colour change with cobalt and iron, and was also found to be a useful fluorescence reagent.

At this point it is interesting to note that Dziomko, Markovich and Zelichenok²⁰³ have

investigated the colour reactions of some multidentate quinazoline derivatives, including some possibly tetradentate ligands of the types shown below—



TABLE VII

THIAZOLYLAZO AND BENZOTHIAZOLYLAZO DYESTUFFS IN ANALYTICAL CHEMISTRY

Dye		Ions	Method	General remarks	References
TAN	••		Indicator	General investigations	18, 20, 21, 167 198 200
		Cu(II)	Indicator	pH 3 to 8	188
			Solvent extraction	General investigations	190, 195
		Zn(II)	Solvent extraction	into CHCl., Absorbance at 600 mu	183
		Ni(II)	Solvent extraction	Also for Zn(11) in Mg and ThO ₂ into CHCl ₂ at pH 7	180
			Solvent extraction	in high purity chromium	184
		Co(II)	Solvent extraction	into \tilde{CHCl}_3 at pH 5 to 9. Absorbance measured at 508 m μ	181
		Co(III)	Solvent extraction	into CHCl ₃ . Absorbance maximum between 600 and 700 m μ	182
		Ag(I), REs	Solvent extraction	General investigations	268
		Co(II), Cu(II), Zn(II)	Detection	_	19
		<u> </u>	Spray reagent	Blue-to-violet colours given by numerous metals	91
TAR	•••		Indicator	General investigations	18, 19, 20, 167, 198
		Cu(II)	Indicator	pH 3 to 8 better than with TAN	188
		REs	Indicator	Better than with PAR	199
		Co(II)	Indicator	— —	181
		N1(11)	Spectrophotometric	Absorbance measured at $473 \text{ m}\mu$, pH 6.0	180
		Nb(V)	Spectrophotometric		325
		_	_	In rocks. Absorbance measured at 550 m μ in an aqueous tartrate medium at pH 5 to 6. Foreign ions masked with EDTA or CHDTA	326
			Spray reagent	Less satisfactory than with PAR	91
TAM			Indicator	General investigations	21, 167
		Ni(II)	Indicator	pH 6 to 10	189
		<u> </u>	Solvent extraction	General investigations	169
		Cu(II)	Solvent extraction	with CHCl ₃ at pH 5 to 10. Absorb- ance measured at 570 m μ	170
		UO_2^{2+}	Spectrophotometric	UO ₂ (NO ₃) ₂ first extracted into IMBK	168
TAC	• •		Indicator	General investigations	20, 21, 167
		Ni(II)	Indicator	pH 6 to 10	189
TADON		0 /11	Solvent extraction	with CHCl ₃ , pH 7	180
TAP-OMe	• •	Co(11)	Indicator		181
4MoTAD O	Ма	Ni(II)	Solvent extraction	with UHU ₃ , pH 7	180
4 Met AP-O	wie	$\overline{7}_{\mathbf{n}}(\mathbf{H})$	Solvent extraction	with isopentul alcohol pH0 Abaseh	173
		ZII(11)	Solvent extraction	ance measured at $612 \text{ m}\mu$	174
		N1(11)	Solvent extraction	with isopentyl alcohol, pH 7 to 9. Absorbance measured at 620 m μ	175
		Co(II)	Solvent extraction	with isopentyl alcohol, pH 7 to 9. Absorbance measured at 607 m μ	176

TABLE VII—continued

Dye		Ions	Method	General remarks	References
		Fe(II)	Solvent extraction	with isopentyl alcohol, pH 5.5 to 7.	176, 177
		Co(III)	Solvent extraction	with CHCl ₃ . Absorbance maximum between 600 and 700 m μ	182
p-TAN			Indicator	General investigations	20
		Pd(II)	Solvent extraction	with isopentyl alcohol. Absorbance measured at $635 \text{ m}\mu$	187
TACh		_	Indicator	General investigations	18, 198
		Th(IV) and Zr(IV)	Indicator	pH 2.5 to 3.0 Th(IV)), 1.5 to 2.5 (Zr(IV))	166
TAN-6S		<u> </u>	Indicator	General investigations	21, 167, 198
TAN-3,6S	••		Indicator	General investigations	198
		Co(II)	Indicator	General investigations	181
		Ni(II)	Spectrophotometric	pH 6.0. Absorbance measured at $515 \mathrm{m}\mu$	180
		Co(III)	Spectrophotometric	· _	182
TAO	••	<u> </u>	Indicator	General investigations	21, 167
BTAN		Co(II)	Detection	For $0.21 \ \mu g$ or more	193
			Spray reagent	Slightly better than TAN	91
BTAR			Spray reagent	Not as good as TAR	91
"Bromoben: thiazo"	zo-	Cd(II)	Solvent extraction	From alkaline tartrate solution into xylene. Absorbance measured at 600 m.	197
BTANa and sulphonat derivative	l ed s	_	Spray reagents	Blue - green spots on a pink back- ground	138
		Cu(II)	Indicator	pH 4.5 to 6. Very good	139
Derivatives of o-TAP		Cu(II)	Indicators and Solvent extraction	General investigations	179
		Ni(III)	Spectrophotometric `	Soluble dyes used in aqueous media	180
		Co(II) Co(III)	Spectrophotometric Spectrophotometric	Others used in solvent extraction	181 182

The pH values between which compounds of this type will extract metals into chloroform have been listed.

Heterocyclic amines containing 5-membered rings are, on the whole, capable of undergoing diazotisation and coupling with phenols.^{204 to 207} However, except for the thiazolylazo dyes, few applications have been found for the products in analytical chemistry.

Kurbatov and Kazarinova²⁰⁸ have prepared 1-(2-thiadiazolylazo)-2-naphthol and measured its acid dissociation constant, which was found to be $7\cdot3$. They recommend its use as an acid - base indicator, stating that it was yellow in acid and pink in alkali.

Dziomko²⁰¹ investigated the solvent extraction of metals with a wide range of chelating agents, including 1-(6-nitro-2-benzothiazolylazo)-2-naphthol, PAN and 2-(2-hydroxyphenyl-azo)-4,5-dimethylimidazole.

Tanaka and Yamauchi²⁰⁹ coupled diazotised 4-amino-5-methylimidazole with β -naphthol and dimethylaniline, and investigated the reactions of the dyes with metals, with regard to their use in complexometric titrations and solvent extraction procedures.

Cherepakhin²¹⁰ has used 3-methyl-5-propylpyrrole-(2-azo-2')-phenol as a reagent for the spectrophotometric determination of cobalt.

AZO DERIVATIVES OF 8-HYDROXYQUINOLINE-

These are easily prepared by coupling the diazotised amine with 8-hydroxyquinoline or one of its derivatives. Coupling takes place either in position 5 or position 7 of the quinoline ring, thus giving rise to two series of compounds.

5-Arylazo-8-hydroxyquinolines—These were the first to be prepared, and have been used mainly as test reagents for the detection of very small amounts of metals.^{1,2,211} to ²¹⁷ Procedures have been described for the detection of bismuth, zinc, mercury, copper, silver, gold, nickel, palladium, chromium, molybdenum, vanadium and magnesium.²⁹ All of these tests are best carried out in nitric acid solution by spotting either on filter-paper or on a white porcelain tile. The test for magnesium is carried out in alkaline solution.

5-(4-Carboxyphenylazo)-8-hydroxyquinoline has been successfully used for the gravimetric determination of zinc and lead, and 5-(2-carboxyphenylazo)-8-hydroxyquinoline has been used for the colorimetric determination of zinc and mercury.²¹⁵ A method has been devised for the indirect determination of metals colorimetrically, by precipitating them quantitatively as their 8-hydroxyquinolinates, dissolving the precipitate in hydrochloric acid and allowing the solution to react with a diazotised amine. The absorption of the dye produced is then measured. The method has been used for the determination of calcium with diazotised sulphanilic and γ -acids,²¹⁸ gallium with diazotised sulphanilic and naphthionic acids²¹⁹ and aluminium with diazotised sulphanilic²²⁰ and naphthionic²²¹ acids. The fact that these dyes complex at low values of pH has been put to good use by Kuznetsov and Fang,²²² who used azo dyes of diazotised picramic acid and dinitroaniline coupled with 8-hydroxy-quinoline for the solvent extraction of zirconium and thorium from acid solutions below the pH at which these metals hydrolyse.

Although these dyes have not found any applications as EDTA indicators, they have been used in mercurimetric titrations for chloride.^{223,224} The most suitable dyes for this purpose were found to be 5-(3- and 4-nitrophenylazo)-8-hydroxyquinoline, and these dyes could also be used for the colorimetric determination of chloride. Both methods are carried out in acidic solution (pH about 2).²²³

8-Hydroxyquinoline violet is 5-(4-nitrophenylazo)-7-nitroso-8-hydroxyquinoline, and can complex either as a derivative of 8-hydroxyquinoline or nitrosonaphthol. It is reported as being specific towards copper and selective towards nickel. Its copper complex is not easily broken up by many common complexing agents, including 8-hydroxyquinoline itself.²²⁵

The acid dissociation and chelate stability constants of 5-(benzeneazo)-8-hydroxyquinoline and 5-(2-, 3- and 4-hydroxyphenylazo)-8-hydroxyquinoline have been measured by Takamoto, Fernando and Freiser.²²⁶ They discussed the results obtained in relation to the position of the aromatic hydroxyl group, and showed that the heterocyclic hydroxyl group ionises at a lower pH than in 8-hydroxyquinoline itself. Chelation also took place at a lower pH than with 8-hydroxyquinoline, and the advantages of this in analytical chemistry were discussed.

7-Arylazo-8-hydroxyquinolines—These are mainly derivatives of 8-hydroxyquinoline-5-sulphonic acid and are used primarily as indicators in titrations, either with EDTA or with standard metal solutions in various applications. 8-Hydroxyquinoline itself will couple either in the 5- or in the 7-position, the dye produced depending on the diazo component and on the conditions of coupling. Sometimes a mixture is obtained and separation of the isomers is necessary.²²⁷ However, with 8-hydroxyquinoline-5-sulphonic acid, coupling can only take place in position 7.

The first workers to use these dyes as indicators for EDTA titrations were Fritz, Lane and Bystroff,²² who coupled diazotised aniline, *p*-chloroaniline, *p*-nitroaniline and α -naphthylamine with 8-hydroxyquinoline-5-sulphonic acid. The dyes thus obtained were suitable for the direct titration of many metals, although the addition of a small calculated amount of copper salt just before the end-point was reached was necessary to ensure a correct result for some of the weaker complexing ions. Within a short time of each other, Guerrin, Sheldon and Reilley introduced 7-(4-sulpho-1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid ("SNAZOXS"),²³ and Fritz, Abbink and Payne introduced 7-(6-sulpho-2-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid²⁴ as indicators for the titration of a wide range of metals with EDTA. These two dyes were found to be similar, and could be used in both direct and indirect titrations. The addition of a small amount of copper salt near the end-point was again sometimes necessary. They could also be used over a wider range of pH than those mentioned previously.²² Busev, Talipova and Skrebkova have since used dyes of this type for the direct titration of gallium,^{228,229} indium^{230,231} and thallium.²³² With 7-arylazo 8-hydroxyquinolines as indicators, the colour change at the end-point is from yellow to orange, red or violet.

oo'-Dihydroxyazo dyes of 8-hydroxyquinoline have been studied by Badrinas,^{227,233}who prepared 7-(2-hydroxy-4-sulpho-1-naphthylazo)-8-hydroxyquinoline and its analogues and recommended them as metallofluorochromic indicators for chelometric titrations.

7-Arylazo-8-hydroxyquinolines have been used as mercurimetric indicators,^{234,235} the best dyes for this purpose being 7-(4-sulphophenylazo)-8-hydroxyquinoline and 7-(2-naphthylazo)-8-hydroxyquinoline. Arsenic has also been determined as arsenate ions by titration with standard lead solutions, with "SNAZOXS" as indicator.¹²⁸

Scandium has been determined spectrophotometrically in aqueous solution with three

azo derivatives of 8-hydroxyquinoline-5-sulphonic acid.²³⁶ The selectivity of the method is low, and the absorbance is measured at $420 \text{ m}\mu$, the free dyes absorbing at $520 \text{ m}\mu$.

The mechanism of chelation of these dyes is interesting, as they can co-ordinate either as an *o*-hydroxyazo dye or as a derivative of 8-hydroxyquinoline. Ishibashi and Yamamoto²³⁷ studied the copper complex of 7-(benzeneazo)-8-hydroxyquinoline-5-sulphonic acid spectrophotometrically, and proposed the following structure for the chelate—



Cherkesov, on the other hand, showed that 7-arylazo-8-hydroxyquinoline in neutral solutions complexed via the hydroxyl group and heterocyclic nitrogen atom (yellow complexes), and in acid solutions via the hydroxyl group and azo nitrogen atom (red complexes). This leaves the heterocyclic nitrogen atom free to be protonated by the acid^{288,239}...



Cherkesov also observed that 5-arylazo-8-hydroxyquinolines only gave yellow chelates with metals, because of the inability of the metal to co-ordinate with the azo group.²³⁹

Heterocyclic azo dyes of 8-hydroxyquinoline have been prepared with diazotised 2-aminopyridine^{135,136,137} and 2-aminothiazole.¹⁸ These have already been discussed, and their behaviour seems to suggest, at least with the pyridine compound, that they complex as derivatives of PAN rather than of 8-hydroxyquinoline.¹³⁵

CONCLUSIONS

The analytical applications of heterocyclic azo dyestuffs, in which the heterocyclic atom is involved in co-ordination with a metal ion, have been reviewed. A few related compounds, whose properties have been compared with those of the azo dyestuffs, have also been included in this review.

The most important dyes of this type are 1-(2-pyridylazo)-2-naphthol for solvent extraction procedures, and 4-(2-pyridylazo)-resorcinol for determinations in aqueous media. These two dyes are also useful as indicators for complexometric titrations, although modified procedures are often required because of slow reactions at the end-point. Some other azo dyes of pyridine have also been prepared, but the same number of uses for them has not as yet been found, despite the fact that some of them show quite promising properties. Because of their ease of preparation, many azo dyes of thiazole have been tested for analytical uses. On the whole they do not appear to be as promising as the pyridylazo dyes, being more strongly coloured themselves, less water soluble and producing less stable complexes. Nevertheless, some specialised applications have been found for these reagents.

Dyes with a PAN-type chelating structure have been shown to complex via the *o*-hydroxyl group, the heterocyclic nitrogen atom and the azo nitrogen atom nearest to the phenolic half of the molecule giving rise to two stable, 5-membered chelate rings. The main characteristic of these dyes is the strong bathochromic shifts observed in their visible spectra on chelation with a wide range of metals. This phenomenon is not observed to the same extent with any related compound in which this chelating structure has been modified.

Several applications have been found for the azo derivatives of 8-hydroxyquinoline as spot reagents and as indicators. These dyes show hypsochromic shifts on chelation, especially if it is the heterocyclic nitrogen atom that is involved in co-ordination.

Heterocyclic azo dyestuffs thus constitute an important and relatively new class of analytical reagents with a wide range of applications. Further research in this field should be fruitful, if directed to investigations on the mechanism of chelation of these dyes and the factors affecting their usefulness in analytical chemistry in order to anticipate the potentials of new dyes, especially dyes containing new heterocyclic systems.

PYRIDYLAZO DYESTUFFS



Position of substitution

	_	10 CO				
Name	Á	в	С	D	E	Abbreviation
4-(2-Pyridylazo)-resorcinol	OH	н	OH	н	н	PAR
1-(2-Pyridylazo)-orcinol	OH	H	OH	H	CH _a	PAO
2-(2-Pyridylazo)-phenol	OH	H	H	н	н	o-PAP
4-(2-Pyridylazo)-phenol	\mathbf{H}	H	OH	H	H	p-PAP
2-(2-Pyridylazo)-4-methylphenol	OH	H	\mathbf{H}	CH ₃	н	PAC
5-(2-Pyridylazo)-2-monoethylamino-p-cresol	OH	н	NHC ₂ H ₅	CH ₃	н	PAAC
4-(2-Pyridylazo)-dimethylaniline	H	H	$N(CH_3)_2$	H	н	PAA
4-(3-N-Methylpiperidyl-2-pyridylazo)-	OH	\mathbf{H}	OH	H	н	MAAR
recordinal*						

* Contains N-CH₃ grouping in 3-position on pyridyl ring.



Position of substitution

Name	A	В	С	D	Е	\mathbf{F}	G	Abbreviation
1-(2-Pyridylazo)-2-naphthol 1-(2-Pyridylazo)-2,3-dihydroxy- naphthalene-6-sulphonic acid	OH OH	H OH	H H	H H	H SO ₃ H	H H	H H	PAN PADNS
1-(2-Pyridylazo)-2,7-dihydroxy- naphthalene	ОН	н	н	H	H	OH	Н	2,7-PAN
4-(2-Pyridylazo)-1-naphthol	\mathbf{H}	\mathbf{H}	OH	\mathbf{H}	H	H	H	p-PAN
1-(3-N-Methylpiperidyl-2-pyridyl- azo)-2-naphthol	OH	Η	н	н	н	Η	н	MAAN
4-(3-N-Methylpiperidyl-2-pyridyl- azo)-1-naphthol*	Η	Η	OH	Η	н	н	Н	p-MAAN

* Contains 🔇

-CH₃ grouping in 3-position on pyridyl ring.



Name	A	В	С	D	E	F	G	Abbreviation	
2-(2-Pyridylazo)-1,8-dihydroxy- naphthalene-3.6-disulphonic acid	OH	SO₃H	н	Η·	SO ₃ H	н	OH	PACh	
2-(2-Pyridylazo)-8-amino-1-naph- thol-3,6-disulphonic acid	OH	SO3H	Н	н	SO ₃ H	н	$\rm NH_2$	PA-H	
2-(2-Pyridylazo)-1-naphthol	OH	H	H	н	H	н	H	α-PAN	
7-(2-Pyridylazo)-8-hydroxyquinoline	OH	H	H	H	H	н	N*	PAOx	
* Cabatilantian of	manht	halama		tom h	- antinal	lima			

* Substitution of naphthalene ring sytem by quinoline.

THIAZOLYLAZO DYESTUFFS



Name	A	В	С	D	Е	F	G	Abbreviation
4-(2-Thiazolylazo)-resorcinol	OH	н	OH	н	н	н	н	TAR
2-(2-Thiazolylazo)-5-dimethylamino- phenol	OH	H	N(CH ₃)	2 H	н	H	H	TAM
2-(2-Thiazolylazo)-4-methylphenol	OH	H	H	CH ₈	H	H	H	TAC
2-(2-Thiazolylazo)-4-methoxyphenol	OH	H	H	OCH,	H	H	H	TAP-OMe
2-(4-Methyl-2-thiazolylazo)-4-meth- oxyphenol	OH	H	н	OCH ₃	н	н	CH3	4-MeTAP-OMe
4-(2-Thiazolylazo)-orcinol	OH	H	OH	H	CH,	H	H	TAO
2-(2-Thiazolylazo)-phenol	OH	H	H	H	н	H	H	o-TAP
4-(2-Benzothiazolylazo)-resorcinol	OH	н	OH	н	н	-	~*	BTAR

* Benzene ring fused across F-G





Position of substitution

* Benzene ring fused to H and I positions.

231

HO

MISCELLANEOUS REAGENTS







2 - (2 - Pyrimidylazo) - 1 - naphthol



Salicylaldehyde - 2 pyridyl -

hydrazone





2 - (8 - Quinolylazo) - I - naphthol -4 - sulphonic acid







Salicylaldehyde - 8 - quinolylhydrazone

5 - Arylazo - 8 - hydroxyguinolines





7 - (2 - Sulpho - I - naphthylazo) - 8 hydroxyquinoline - 5 - sulphonic acid "SNAZOXS"

References

- Kul'berg, L. M., and Ivanova, Z. V., Zh. Obshch. Khim., 1947, 17, 601; Chem. Abstr., 1949, 43, 597c. Akiyama, T., and Fujii, K., Bull. Kyoto Coll. Pharm., 1954, 2, 10; Chem. Abstr., 1956, 50, 4715g. 1.
- 2.
- 3. Liu, J. Ch.-I., Ph.D. Thesis, University of Illinois, 1951.
- 4.
- 5.
- Cheng, K. L., and Bray, R. H., Analyt. Chem., 1955, 27, 782. Chen, K. L., Ibid., 1955, 27, 1582. Cheng, K. L., and Bray, R. H., Chemist Analyst, 1955, 44, 96 and 98; Chem. Abstr., 1956, 50, 1517d. 6.
- 7. Flaschka, H., and Abdine, H., Ibid., 1956, 45, 2; Chem. Abstr., 1956, 50, 5449b.
- -, Ibid., 1956, 45, 58; Chem. Abstr., 1956, 50, 16538e. 8. -, -
- 9.
- —, ____, Mikrochim. Acta, 1956, 770; Chem. Abstr., 1956, **50**, 9208i. Busev, A. I., and Kiseleva, L. V., Vest. Mosk. Gos. Univ. Ser. Mat. Mekh. Astron. Fiz. Khim., 1958, **13**, 179; Chem. Abstr., 1959, **53**, 11105f. 10.
- Cheng, K. L., Analyt. Chem., 1958, 30, 1027. 11.
- Gill, H. H., Rolf, R. F., and Armstrong, G. W., Ibid., 1958, 30, 1788. 12.
- 13.
- 14.
- Atomic Energy Commission, Chalk River Project, AECL 789, 1959. Wehber, P., Z. analyt. Chem., 1957, 158, 10; Chem. Abstr., 1958, 52, 3590e. Sommer, L., and Hniličková, Naturwissenschaften, 1958, 45, 544; Chem. Abstr., 1959, 53, 6877h. 15.
- Busev, A. I., and Kanaev, N. A., Nauch. Dokl. Vyssh. Shk., 1959, 299; Chem. Abstr., 1959, 53, 16. 18747c.
- 17.
- Pollard, F. H., Hanson, P., and Geary, W. J., Analytica Chim. Acta, 1959, 20, 26. Boni, I. E., and Hemmeler, A., Chimica, Milano, 1958, 34, 443; Chem. Abstr., 1959, 53, 11114f. 18.
- -, Ibid., 1958, 34, 445. 19.

- Kaneniwa, N., Kanazawa Diagaku Yakugakubu Kenkvu Nembo, 1959, 9, 27; Chem, Abstr., 1960, 20. 54, 4541g.
- 91 Jensen, B. S., Acta Chem. Scand., 1960, 14, 927.
- 99
- Guerrin, G., Sheldon, M. V., and Reilley, C. N., Chemist Analyst, 1960, **49**, 36; Analyt. Abstr., 23. 1961. 8. 431.
- Fritz, J. S., Abbink, J. E., and Payne, M. A., Analyt. Chem., 1961, 33, 1381. 24.
- 25.
- 26.
- Geary, W. J., Nickless, G., and Pollard, F. H., Analytica Chim. Acta, 1962, 27, 71.
 Savvin, S. B., Russ. Chem. Revs., 1963, 32, 93.
 Sommer, L., and Hniličková, M., Folia. Přírod. Fak. Univ. J. E. Purkyne v Brne, Chem., 1964, 27 5, 113.
- Reid, E. E., "The Organic Chemistry of Bivalent Sulphur," Chemical Publishing Co., New York, 28
- 1963, Volume V, p. 283. Welcher, F. J., "Organic Analytical Reagents," D. Van Nostrand Co. Inc., New York; Macmillan & Co. Ltd., London, 1947. 29
- 30
- 31.
- Co. L., Londin, 1911, and Davies, N. R., Q. Rev. Chem. Soc., 1958, 12, 265.
 Danzuka, T., Kagaku, 1961, 16, 686.
 Busev, A. I., and Ivanov, V. M., Zh. Analit. Khim., 1964, 19, 1238; J. Analyt. Chem. USSR, 32. 1964, 19, 1150.
- 33. Chien Teng. Hsin. and Chieh Hung, Shui, Chem. Bull. Peking, 1965, 402; Chem. Abstr., 1966, 64, 7337f.
- "4-(2-Pyridylazo)resorcinol Disodium Salt," British Drug Houses Ltd., PAR/9/6302. 34.
- Chichibabin, A. E., and Rjasanzew, M., Zh. Russk. Fiz.-Khim. Obshch., 1915, 47, 1582; Chem. 35 ZentBl., 1916, 3, 229.
- 36. Pease, B. F., and Williams, M. B., Analyt. Chem., 1959, 31, 1044.
- 37
- 38
- Corsini, A., Mai-Ling Yih, I., Fernando, Q., and Freiser, H., Ibid., 1962, 34, 1090. Nakagawa, G., and Wada, H., J. Chem. Soc. Japan, 1963, 84, 639; Chem. Abstr., 1960, 61, 1242h. Busev, A. I., and Ivanov, V. M., Vest. Mosk. Gos. Univ., Ser. II, 1964, 19, 56; Chem. Abstr., 1964, 39 61, 7762d.
- Pollard, F. H., Nickless, G., Samuelson, T. J., and Anderson, R. G., J. Chromat., 1964, 16, 231. Berger, W., and Elvers, H., Z. analyt. Chem., 1959, 171, 185; Chem. Abstr., 1959, 54, 4246c. 40.
- 41.
- Shibata, S., Analytica Chim. Acta, 1960, 23, 367. 42.
- 43. -, Ibid., 1961, 25, 348.
- 44.
- Betteridge, D., Fernando, Q., and Freiser, H., *Ibid.*, 1963, 35, 294. Sommer, L., Ivanov, V. M., and Novotnà, H., *Talanta*, in the press. Stanley, M. W., and Cheney, E. S., *Ibid.*, 1966, 13, 1619. 45.
- 46.
- 47. Cheng, K. L., and Goydish, B. L., Analytica Chim. Acta, 1958, 30, 243.
- 48 Busev, A. I., and Tiptsova, V. G., Zh. Analit. Khim., 1960, 15, 573; Chem. Abstr., 1966, 55, 15223i.
- Shibata, S., Nagoya Kogyo Gijutsu Shikensho Hokoku, 1963, 12, 337; Chem. Abstr., 1964, 60, 1100a. 49.
- Wada, H., and Nakagawa, G., J. Chem. Soc. Japan (Pure Chem. Sect.), 1964, 85, 549; Chem. Abstr., 50. 1965, 62, 1057f.
- Iwamato, T., and Fujimoto, M., Analytica Chim. Acta, 1963, 29, 282. 51.
- Sierra, F., and Asensi, G., An. R. Soc. Esp. Fis. Quim., 1959, B55, 797. Cheng, K. L., Analyt. Chem., 1958, 30, 243. 52
- 53.
- Karminski, W., Chemik, 1958, 11, 401. 54.
- 55.
- Farkas, J., Kohász. Lap., 1960, 93, 427. Lucchesi, C. A., Stearns, J. A., and Hin, C. F., Chemist Analyst, 1959, 48, 9. Miles, Th., Delasanta, A. C., and Barry, J. C., Analyt. Chem., 1961, 33, 685. Chon Tkhek, Li, Punsok Khvakhak, 1963, 2, 51. 56.
- 57.
- 58.
- 59. Budesinsky, B., Chemické Listy, 1956, 50, 1236.
- 60. Iwamoto, T., and Kanamori, K., Analytica Chim. Acta, 1962, 26, 167.
- Lu, Ming-Lien, Liu, Ta-Chun, and Ching, Chih-Ling, Acta Pharmaceutica Sinica, 1963, 10, 436; Chem. Abstr., 1963, 59, 13335h. 61.
- 62.
- 63.
- 64.
- Busev, A. I., and Tiptsova, V. G., Zh. Analit. Khim., 1961, 16, 275; Analyt. Abstr., 1962, 9, 61. Spauszus, S., and Schwarz, C., Neue Hütte, 1962, 7, 180; Analyt. Abstr., 1963, 10, 145. Tikhonov, V. N., Zh. Analit. Khim., 1962, 17, 422; Chem. Abstr., 1962, 57, 11844e. Tikhonov, V. N., and Graninka, Ya., Zav. Lab., 1963, 29, 653; Chem. Abstr., 1962, 57, 3300g. 65.
- 66. Chablo, A., Chemia Analit., 1964, 9, 501; Analyt. Abstr., 1965, 12, 4478.
- 67. Cocozza, E. P., Chemist Analyst, 1960, 49, 46.
- 68. Momoki, K., and Sekino, J., Bunseki Kagaku, [Japan Analyst], 1963, 12, 1149; Chem. Abstr., 1964, 60, 6206b.
- Lassner, E., and Scharf, R., Planseeber. PulvMetall., 1961, 9, 51. 69.
- Brown, W. B., Rogers, D. R., Mershed, E. A., and Amos, W. R., Analyt. Chem., 1963, 35, 1000. 70.
- Flaschka, Holasek, A., and Rosenthal, M., Hoppe-Seyler's Z. physiol. Chem., 1957, 308, 183; Chem. Abstr., 1957, 52, 2999f.
 Welcher, F. J., "The Analytical Uses of Ethylenediamine Tetra-acetic Acid," D. Van Nostrand 71.
- 72. Co. Ltd., London and New York, 1958.
- 73. Meites, L., Editor, "Handbook of Analytical Chemistry," McGraw-Hill Book Company, New York and London, 1963.
- 74. Busev, A. I., and Ivanov, V. M., Izv. Vyssh. Ucheb. Zaved., 1962, 5, 202; Chem. Abstr., 1962, 57, 10521f.
- 75. Ho, Li-Shuh, Shih, Chih-Sheng, and Chiang, Wu, Chem. Bull. Peking, 1965, 253; Chem. Abstr., 1965, 63, 15547a.

- 76. Dono, T., Nakagawa, G., and Hayashi, M., J. Chem. Soc. Japan (Pure Chem. Sect.), 1960, 81, 1703; Analyt. Abstr., 1962, 9, 4231.
- Sawada, T., and Kato, S., Bunseki Kagaku, [Japan Analyst], 1962, 11, 544; Chem. Abstr., 1962, 77 57. 5297hi.
- 78. Shibata, S., Analytica Chim. Acta, 1960, 22, 479.
- Cheng, K. L., Talanta, 1962, 9, 739. 79
- Berger, W., and Elvers, H., Z. analyt. Chem., 1959, 171, 255; Chem. Abstr., 1960, 54, 5341h. 80
- -, Z. anorg. allg. Chem., 1963, 199, 166; Curr. Chem. Pap., 1964, 98. 81.
- 82. Shibata, S., and Ishiguro, Y., Nagoya Kogyo Gijutsu Shikensho Hokoku, 1962, 11, 318; Chem. Abstr., 1962, 57, 6590b.
- 83. Ho. Li-Shu, Shih, Chih-Sheng, and Hu, Chin-Lun, Chem. Bull. Peking, 1965, 56; Chem. Abstr., 1965, 63, 15535d.
- Shibata, S., Nagoya Kogyo Gijutsu Shikensho Hokoku, 1961, 10, 609; Chem. Abstr., 1964, 61, 11309c. —, Ibid., 1961, 712; Chem. Abstr., 1964, 61, 8893b. 84.
- 85.
- -, Analytica Chim. Acta, 1963, 28, 388. 86.
- Zolotov, Yu. A., Alimarin, I. P., and Bagreev, V. V., Trudy Kom. Analit. Khim., 1965, 15, 59; 87. Analyt. Abstr., 1966, 13, 2896.
- Staten, F. W., and Huffman, E. W. D., Analyt. Chem., 1959, 31, 2003. 88.
- Goldstein, G., Manning, D. L., and Menis, O., Ibid., 1959, 31, 192. 89.
- Stokely, J. R., and Jacobs, W. D., Ibid., 1963, 35, 149. 90.
- 91. Pollard, F. H., Nickless, G., and Jenkins, H., in West, P. W., Macdonald, A. M. G. and West, T. S., *Editors*, "Proceedings of the International Symposium on Analytical Chemistry, Birmingham University, 1962," Elsevier Publishing Co., Amsterdam, New York and London, 1963, p. 160. Pang, Shu-Wei, Liu, Chien-Chuan, and Liang, Shu Chuan, Acta Chim. Sinica, 1964, **30**, 160; Chem.
- 92. Abstr., 1964, 61, 7695d.
- 93. Heiniger, C., jun., and Lanzafane, F. M., Analytica Chim. Acta, 1964, 30, 148.
- 94.
- 95.
- Watanabe, H., J. Chem. Soc. Japan (Pure Chem. Sect.), 1965, 85, 513; Chem. Abstr., 1965, 64, 7342c. Crepy, O., Judas, O., and Lachese, B., J. Chromat., 1964, 16, 340. Fujimoto, M., and Iwamoto, T., Mikrochim. ichnoanalyt. Acta, 1963, 655; Chem. Abstr., 1963, 96. 60. 13858f.
- Haworth, D. T., Starshak, R. J., and Surak, J. G., J. Chem. Educ., 1964, 41, 436. Surak, J. G., Herman, M. F., and Haworth, D. T., Analyt. Chem., 1965, 37, 428. U.K. Atomic Energy Authority Report, PG.436(S), Harwell, 1963. 97.
- 98.
- 99.
- 100. Hayes, M. R., and Wright, J. S., Talanta, 1964, 11, 607.
- Ugol'nikov, N. A., and Mar'yanov, B. M., Trudy Tomsk. Gos. Univ., Ser. Khim., 1962, 154, 259; 101. Chem. Abstr., 1964, 60, 6194a.
- Püschel, R., Lassner, E., and Scharf, R., Z. analyt. Chem., 1958, 163, 104. Lassner, E., Scharf, R., and Püschel, R., Ibid., 1959, 165, 29. 102.
- 103.
- 104.
- Püschel, E., Schah, K., and Fuschel, K., 1999, 105, 29.
 Püschel, R., Lassner, E., and Reiser, R., Ibid., 1959, 166, 401.
 Iritani, N., Tanaka, T., and Oishei, H., Bunseki Kagaku, [Japan Analyst], 1959, 8, 30.
 Wakamatzu, S., Ibid., 1960, 9, 587.
 Minami, E., and Watanaki, K., Ibid., 1960, 9, 958.
 Geary, W. J., Nickless, G., and Pollard, F. H., Analytica Chim. Acta, 1962, 26, 575.
 Hailöherri M. and Sommar J. Coll. Control Control Control of the Pollaria. 105.
- 106.
- 107.
- 108.
- 109.
- 110.
- Klotz, J. M., and Sommer, L., Coll. Czech. Chem. Commun., 1961, 26, 2189.
 Klotz, I. M., and Loh Ming, W. C., J. Amer. Chem. Soc., 1953, 75, 4159.
 Busev, A. I., and Ivanov, V. M., Izv. Vyssh. Ucheb. Zaved., Khim. i Khim. Tekh., 1961, 4, 914; Chem. Abstr., 1962, 56, 14922a. 111.
- Corsini, A., Fernando, Q., and Freiser, H., J. Inorg. Chem., Wash., 1963, 2, 224. 112.
- Jarvis, J. A. J., Acta Crystallogr., 1961, 14, 961. 113.
- 114. Langmyhr, F. J., and Kristiansen, H., Analytica Chim. Acta, 1959, 20, 524.
- Wehber, P., Z. analyt. Chem., 1959, 166, 186; Chem. Abstr., 1959, 53, 16804b. Busev, A. I., and Ivanov, V. M., Zh. Analit. Khim., 1964, 19, 232. 115.
- 116.
- Alimarin, I. P., and Han, H. I., Vest. Mosk. Gos. Univ., Ser. II, Khim., 1964, 19, 41; Chem. Abstr., 117. 1964, 61, 12419.
- Alimarin, I. P., and Han, Hsi-I, Zh. Analit. Khim., 1963, 18, 182; Chem. Abstr., 1963, 58, 11950g. Dagnall, R. M., West, T. S., and Young, P., Talanta, 1965, 12, 583. 118.
- 119.
- Ibid., 1965, 12, 589. 120.
- Kallistratos, G., Pfau, A., and Ossowski, B., Analytica Chim. Acta, 1960, 22, 195. 121.
- Belcher, R., Ramakrishna, T. V., and West, T. S., Talanta, 1962, 9, 943. 122.
- 123.
- 124.
- Javanoto, T., Bull. Chem. Soc. Japan, 1961, 34, 605.
 Sommer, L., Z. analyt. Chem., 1960, 171, 410; Chem. Abstr., 1960, 54, 8430d.
 Lassner, E., and Püschel, R., Mikrochim. Acta, 1963, 950; Chem. Abstr., 1964, 60, 9901f. 125.
- -, Ibid., 1964, 753; Chem. Abstr., 1964, 61, 13850d. 126.
- 127. Püschel, R., Ibid., 1960, 352.
- 128. -, Talanta, 1963, 10, 1125.
- 129. Lassner, E., and Schedle, H., Ibid., 1966, 13, 326.
- 130. Berka, A., Z. analyt. Chem., 1963, 193, 276; Chem. Abstr., 1963, 59, 1097a.
- 131. Iwamoto, T., Bunseki Kagaku, [Japan Analyst], 1961, 10, 189; Chem. Abstr., 1962, 57, 4019a.
- 132. Majumdar, A. K., and Chatterjee, A. B., Z. analyt. Chem., 1964, 202, 323; Chem. Abstr., 1964, 61, 2462g.
- 133. -, J. Indian Chem. Soc., 1965, 42, 241.
- 134. Hniličková, M., and Sommer, L., Z. analyt. Chem., 1960, 177, 425; Chem. Abstr., 1961, 55, 11177i.

234

- Busev, A. I., Ivanov, V. M., and Talipova, L. L., Zh. Analit. Khim., 1962. 17. 380: Chem. Abstr., 135. 1962, 57, 6586b.
- 136. Busev, A. I., Talipova, L. L., and Ivanov, V. M., Zh. Vses, Khim, Obshch., 1961, 6, 598; Chem. Abstr., 1962, 56, 5398g.
- 137. Busev, A. I., Ivanov, V. M., and Talipova, L. L., Zh. Analit. Khim., 1963, 18, 33; Chem. Abstr., 1963, 58, 13119b.
- Pollard, F. H., Nickless, G., and Anderson, R. G., Talanta, 1966, 13, 725. 138.
- Anderson, R. G., and Nickless, G., Proc. Soc. Analyt. Chem., 1966, 3, 149. 139
- Betteridge, D., Todd, P. K., Fernando, Q., and Freiser, H., Analyt. Chem., 1963. 35. 729. 140.
- 141. Betteridge, D., Talanta, 1966, 13, 1497.
- 142. Gusev, S. I., and Nikolaeva, E. M., Zh. Analit. Khim., 1966, 21, 166; Curr. Chem. Pap., 1966, 436. Nakagawa, G., and Wada, H., J. Chem. Soc. Japan, (Pure Chem. Sect.), 1962, 83, 1098; Chem. Abstr., 1962, 59, 12143d. 143.
- -, Ibid., 1962, 83, 1190; Chem. Abstr., 1963. 59, 12387f. 144
- Gusev, S. I., and Shchurova, L. M., Zh. Analit. Khim., 1964, 19, 799; Chem. Abstr., 1964, 61, 11304h. 145. -, Ibid., 964; Analyt. Abstr., 1965, 12, 6442. 146.
- 147.
- Gusev, S. I., and Nikolaeva, E. M., *Ibid.*, 1966, **21**, 287. Talipov, Sh. T., and Nigai, K. G., *Ibid.*, 1964, **19**, 851. 148.
- Podgornova, V. S., and Amirkhanova, T. B., Nauchn. Tr., Tashkentsk. Gos. Univ., 1964, 263, 77; 149.
- Chem. Abstr., 1965, 63, 17108g. Talipov, Sh. T., Dzhiyanbaeva, R. K., Chaprasova, L. V., and Gutnikova, R. T., Ibid., 72; Chem. 150. Abstr., 1965, 62, 15425c.
- 151 Talipov, Sh. T., and Nigai, K. G., Zh. Analit. Khim., 1964, 19, 697.
- 152. Talipov, Sh. T., and Abdullaeva, Kh. S., Uzbek, Khim. Zh., 1964, 8, 18; Chem. Abstr., 1965, 62, 9779f
- 153. Abdullaeva, Kh. S., and Talipov, Sh. T., Ibid., 1965, 9, 25; Chem. Abstr., 1965, 64, 5739e.
- Nigai, K. G., Talipov, Sh. T., and Ivanova, I. Ya., Nauchn. Tr., Tashkentsk. Gos. Univ., 1964, 263, 63; Chem. Abstr., 1964, 63, 10664b. 154.
- 155. Talipov, Sh. T., Abdullacva, Kh. S., and Nigai, K. G., Uzbek, Khim. Zh., 1965, 9, 34; Chem. Abstr., 1965, 63, 2365c.
- Dzhiyanbaeva, R. K., Talipov, Sh. T., Chaprasova, L. V., and Serova, A. P., Nauchn. Tr., Tashkentsk. Gos. Univ., 1964, 263, 69; Chem. Abstr., 1965, 62, 15421a. 156.
- 157. Amirkhanova, T. B., Podgornova, V. S., and Shchesterova, I. P., Ibid., 1964, 263, 81; Chem. Abstr., 1964, 63, 4942h.
- 158. Caso, M. M., and Cefola, M., Analytica Chim. Acta, 1963, 29, 127.
- Jasinski, T., and Smagowski, H., Zesz. Nauk., Mat., Fiz., Chem., 1964, 4, 59; Curr. Chem. Pap., 159. 1966, 570.
- 160. Chiswell, B., Lions, F., and Tomlinson, M., Inorg. Chem., 1964, 3, 492.
- 161.
- 162.
- 163.
- Trauman, V., Justus Liebigs Annln Chem., 1888, 249, 31. Morgan, G. T., and Morrow, G. V., J. Chem. Soc., 1915, 107, 1291. Morgan, G. T., Morrow, G. V., and Chattaway, F. D., Chem. News, Lond., 1915, 112, 153. Elderfield, R. C., "Heterocyclic Compounds," Volume 5, John Wiley and Sons, New York; Chapman 164. and Hall, London, 1957, pp. 603 and 604.
- 165. Hunter, R. F., J. Chem. Soc., 1926, 1385.
- Hemmeler, A., and Scattolari, M., Chimica, Milano, 1962, 38, 407; Chem. Abstr., 1964, 60, 11374g. Jensen, B. S., Dansk Kemi, 1963, 44, 35; Chem. Abstr., 1964, 61, 5d. 166.
- 167.
- 168. Sørensen, E., Acta Chem. Scand., 1960, 14, 965.
- Minezewski, J., and Kasiura, K., Chemia Analit., 1965, 10, 21; Chem. Abstr., 1965, 63, 17109g. , , , , Ibid., 1965, 10, 719; Chem. Abstr., 1966, 64, 5756b. 169.
- 170.
- Yanagihara, T., Matano, N., and Kawase, A., Bunseki Kagaku, [Japan Analyst], 1958, 7. 406: 171. Chem. Abstr., 1960, 54, 16288g.
- 172. -, -, Trans. Japan Inst. Metals, 1959, 1, 65; Chem. Abstr., 1961, 55, 19902d.
- -, ---, Bunseki Kagaku, [Japan Analyst], 1958, 7, 500; Chem. Abstr., 1960, 54, 16288g. 173. —, ___, ___, *Ibid.*, 1959, 8, 10; *Chem. Abstr.*, 1961, 55, 10211a. —, ___, ___, *Ibid.*, 1959, 8, 14; *Chem. Abstr.*, 1961, 55, 10211a. —, ___, ___, *Ibid.*, 1960, 9, 344; *Chem. Abstr.*, 1961, 55, 17365g. 174.
- 175.
- 176.
- Matano, N., and Kawase, A., Trans. Japan Inst. Metals, 1962, 4, 151; Chem. Abstr., 1963, 59, 1081h. 177.
- 178. Kawase, A., Bunseki Kagaku, [Japan Analyst], 1962, 11, 621; Chem. Abstr., 1962, 57, 7878d.
- 179.
- —, *Ibid.*, 1962, **11**, 628. —, *Ibid.*, 1963, **12**, 810; *Chem. Abstr.*, 1964, **60**, 6208e. —, *Ibid.*, 1963, **12**, 817. 180.
- 181.
- -, Ibid., 1963, 12, 994; Chem. Abstr., 1964, 60, 4777c. 182.
- 183. -, Talanta, 1965, 12, 195.
- 184. -, Bunseki Kagaku, [Japan Analyst], 1964, 13, 609; Chem. Abstr., 1964, 61, 11325d.
- ____, Ibid., 1964, 13, 553; Chem. Abstr., 1964, 61, 10100a.
 ____, Ibid., 1963, 12, 709; Chem. Abstr., 1963, 59, 11468f. 185.
- 186.
- -, Ibid., 1963, 12, 714; Chem. Abstr., 1963, 59, 12168f. 187.
- 188.
- Wada, H., and Nakagawa, G., Ibid., 1965, 14, 28; Chem. Abstr., 1965, 62, 12419c. Nakagawa, G., and Wada, H., J. Chem. Soc. Japan, (Pure Chem. Sect.), 1964, 85, 202; Chem. 189. Abstr., 1964, 61, 3662g.
- 190. -, ----, Ibid., 1962, 83, 1185; Chem. Abstr., 1963, 59, 9289d.
- 191. Kaneniwa, N., Yoshizawa, F., and Homma, Y., Kanazawa Daigaku Yakugakubu Kenkyu Nempo, 1960, 10, 42; Chem. Abstr., 1960, 55, 23155c.

- Kaneniwa, N., Yoshizawa, F., and Homma, Y., Ibid., 1960, 10, 48. 192
- 193. -, Ibid., 1960, 10, 52.
- Albert, A., Goldacre, R., and Phillips, J., J. Chem. Soc., 1948, 2240. 194.
- 195.
- Navratil, O., Colln Czech. Chem. Commun., 1964, 29, 2490. Brudz, V. G., Drapkina, D. A., Smirnova, K. A., Doroshina, N. I., Sidenko, Z. S., and Chizhova, 196. G. S., USSR Patent No. 146,088, 1962; Chem. Abstr., 1962, 57, 9219a.
- 197. Drapkina, D. A., Brudz, V. G., Smirnova, K. A., and Doroshina, M. I., Zh. Analit. Khim., 1962, 17, 940; Chem. Abstr., 1963, 58, 9617c.
- 198. Svoboda, V., and Spolana, N. E., Talanta, 1960, 4, 201.
- Hung, Shui-Chief, and Jen, Hung-Te, Acta Chim. Sinica, 1965, 31, 91; Chem. Abstr., 1965, 62, 199. 15421b.
- 200.
- Havir, J., and Vřestál, J., Chemické Listy, 1966, 60, 64. Dziomko, V. M., Trudý Vses. Nauchno-Issled. Inst. Khim. Reakt., 1963, 25, 183; Chem. Abstr., 201. 1964, 61, 1241a.
- Zincke, Th., and Bindewald, H., Ber. dt. chem. Ges., 1884, 3026. 202.
- Dziomko, V. M., Markovich, I. S., and Zelichenok, S. L., Trudy Vses. Nauchno-Issled. Inst. Khim. 203. Reakt., 1963, 25, 47; Chem. Abstr., 1964, 61, 6373c.
- 204. Quilico, A., Gazz. Chim. Ital., 1931, 61, 970.
- 205.
- Reilly, J., Teegan, J., and Carey, M., Nature, 1947, 159, 643. Putokhin, N. I., and Yakovlev, V. I., Dokl. Akad. Nauk SSSR, 1954, 98, 89; Chem. Abstr., 1955, 206. 49, 12431d.
- 207. Goerdeler, J., and Deselaers, K., Chem. Ber., 1958, 91, 1025.
- Kurbatov, D. I., and Kazarinova, N. F., Izv. Sib. Otdel. Akad. Nauk SSSR, 1958, 94; Chem. 208. Abstr., 1959, 53, 9886g.
- 209. Tanaka, H., and Yamauchi, O., Chem. Pharm. Bull, Tokyo, 1964, 12, 1268; Chem. Abstr., 1965, 62, 2225h.
- 210. Cherepakhin, A. I., Zh. Analit. Khim., 1966, 21, 502.
- Gutzeit, G., and Monnier, R., Helv. Chim. Acta, 1933, 16, 233. 211.
- -, Ibid., 1933, 16, 478. 212.
- 213. -, Ibid., 1933, 16, 484.
- Boyd, T., Degering, E. F., and Shreve, R. N., Ind. Engng Chem. Analyt. Edn, 1938, 10, 606. 214.
- Das, R., and Sircar, S. S. G., J. Indian Chem. Soc., 1955, 32, 679. 215.
- Gutzeit, G., Monnier, R., and Bachoulkova-Brun, R., C. R. Séanc. Soc. Phys. Hist. Nat. Genève, 1933, 50, 203; Chem. Abstr., 1934, 28, 33325. 216.
- Fresenius, W., Analyt. Chem., 1934, 96, 433; Chem. Abstr., 1934, 28, 36839. 217.
- 218. Armeanu, V., and Costinescu, P., Revue Chim. Buc., 1960, 11, 343; Chem. Abstr., 1963, 58, 1902a.
- 219.
- Srivastava, T. N., and Singh, N., Indian J. Appl. Chem., 1964, 27, 150. Mellan, I., "Organic Reagents in Inorganic Analysis," Blakiston Co., Philadelphia, 1941, p. 241. 220.
- Schams, O., Mikrochemie, 1938, 25, 16. 221.
- Kuznetsov, V. I., and Fang, Ming-O, Zh. Neorg. Khim., 1960, 5, 1375; Chem. Abstr., 1961, 55, 2339b. 222.
- Mustafin, I. S., and Sivanova, O. V., Izv. Vysh. Ucheb. Zaved., Khim. i Khim. Tekh., 1962, 5, 875; 223. Chem. Abstr., 1963, 58, 13133h.
- 224. Sivanova, O. V., Sb. Nauch. Rab. Stud., Saratovsk. Gos. Univ., 1962, 94; Chem. Abstr., 1963, 59, 8100c.
- Steigmann, A., J. Soc. Chem. Ind., Lond., 1947, 66, 353; Chem. Abstr., 1948, 42, 1525e. 225.
- Takamoto, S., Fernando, Q., and Freiser, H., Analyt. Chem., 1965, 37, 1249. 226.
- 227.
- Badrinas, A., Talanta, 1963, 10, 704. Busev, A. I., Talipova, L. L., and Skrebkova, L. M., Zh. Analit. Khim., 1962, 17, 180; Analyt. 228. Abstr., 1962, 9, 4605.
- Busev, A. I., Skrebkova, L. M., and Talipova, L. L., Ibid., 1962, 17, 831; Chem. Abstr., 1963, 229. 58, 9621a.
- 230.
- Busev, A. I., and Talipova, L. L., Ibid., 1962, 17, 447; Chem. Abstr., 1962, 57, 14427b. , , , Vest. Mosk. Gos. Univ., Ser. II, Khim., 1962, 17, 73; Chem. Abstr., 1962, 57, 6603c. 231.
- -, Uzbeksk. Khim. Zh., 1962, 6, 24; Chem. Abstr., 1962, 57, 15799i. 232.
- 233. Martinez, F. B., Badrinas, A., and Bonza, A. P., Infción. Quím. Analít Pura Apl. Ind., 1960, 14, 151; Chem. Abstr., 1962, 57, 2828d.
- Cherkesov, A. I., Materialy (Dvatsaat Vlorgy) Nauchn. Konf. Saratovsk. Gos. Ped. Inst. Fac. 234. Estesvozn., Fiz., Mat., Saratovsk, Sb., 1961, 91; Chem. Abstr., 1963, 58, 9624c.
- 235. -, Zav. Lab., 1961, 27, 1447; Chem. Abstr., 1962, 56, 10884f.
- 236. Busev, A. I., and Lunina, G. E., Zh. Analit. Khim., 1965, 20, 1069; Chem. Abstr., 1966, 64, 5748g. Ishibashi, M., and Yamamoto, Y., Bull. Inst. Chem. Res. Kyoto Univ., 1953, 31, 280; Chem. Abstr., 237. 1954, 48, 12111f.
- Cherkesov, A. I., Dokl. Akad. Nauk SSSR, 1962, 142, 1098. 238.
- -, Zh. Analit. Khim., 1962, 17, 16; Chem. Abstr., 1962, 57, 4002b. 239.
- 240. Kristiansen, H., and Langmyhr, F. J., Acta Chem. Scand., 1959, 13, 1473.
- Dwivedi, C. D., Munshi, K. N., and Dey, A. K., J. Inorg. Nucl. Chem., 1966, 28, 245. Hniličková, M., Colln Czech. Chem. Commun., 1964, 29, 1424. 241.
- 242.
- Busev, A. I., and Ivanov, V. M., Zh. Analit. Khim., 1963, 18, 208; Chem. Abstr., 1963, 58, 13118e. 243.
- Babko, A. K., Volkova, A. I., and Get'man, T. E., Zh. Neorg. Khim., 1966, 11, 374; Chem. Abstr., 244. 1966, 64, 13736g.
- Busev, A. I., Zh. Analit. Khim., 1957, 12, 481; Chem. Abstr., 1958, 52, 1841g. Pashinkin, A. S., and Novoselova, A. V., Zh. Neorg. Khim., 1959, 4, 2657. 245.
- 246.
- Zlomanov, V. P., Popovkin, B. A., and Novoselova, A. V., Ibid., 1959, 4, 2661. 247.

- 248 Busev, A. I., and Skrebkova, L. M., Izv. Sib. Otdel. Akad. Nauk SSSR, 1962. 57; Chem. Abstr., 1963. 58. 5032g.
- Busev, A. I., and Tiptsova, V. G., Zh. Analit. Khim., 1960, 15, 698. 249
- 250. Kitagawa, H., Bunseki Kagaku, [Japan Analyst], 1959, 8, 594.
- Busev, A. I., and Tiptsova, V. G., Zh. Analit. Khim., 1958. 13. 180. 251
- 252. Berka, A., and Busev, A. I., Analytica Chim. Acta, 1962, 27, 497.
- Kawahata, M., Motidzuki, H., Kadziyama, R., and Isi, M., Bunseki Kagaku, [Japan Analyst], 1962, 11, 748. 253.
- 254 Flaschka, H., and Abdine, H., Z. analyt. Chem., 1956, 152, 77; Analyt. Abstr., 1957, 4, 414.
- Nakagawa, G., Tanaka, M., and Wada, H., Bull. Chem. Soc. Japan, 1963, 36, 320; Chem. Abstr., 255. 1963, 59, 13b.
- Konkin, V. D., and Zhikareva, V. I., Sb. Trudy. Ukr. Nauchno-Issled. Inst. Metal., 1964, 444; Chem. Abstr., 1965, 62, 5887h. 256.
- 257 Busev, A. I., Kiseleva, L. V., and Cherkesov, A. I., Zav. Lab., 1958, 24, 13; Chem. Abstr., 1958, 52, 18086d.
- 258. Busev, A. I., Ivanov, V. M., and Tiptsova, V. G., Ibid., 1962, 28, 799; Analyt. Abstr., 1963, 10, 585.
- 259.
- Lassner, E., and Scharf, R., Z. analyt. Chem., 1958, 164, 398. Suzuki, T., Bunseki Kagaku, [Japan Analyst], 1963, 12, 655; Chem. Abstr., 1963, 59, 9308g 260.
- Babko, A. K., and Kish, P. P., Dopov. Akad. Nauk URSR, 1961, 1323; Chem. Abstr., 1962, 56, 261. 10900f.
- 262. Shibata, S., Analytica Chim. Acta, 1960, 23, 434.
- 263. Schweitzer, G. K., and Norton, A. D., Ibid., 1964, 30, 119.
- Pohl, H., Z. Erzbergbau Metalhuttenw., 1963, 16, 18; Chem. Abstr., 1963, 58. 9628f. 264
- 265. Andrew, T. R., and Nichols, P. N. R., Analyst, 1965, 90, 161.
- 266. Ho, Li-Shuh, Kuo, Ching-Nan, Shih, Chih-Sheng, and Chiang, Wu, Chem. Bull. Peking, 1965, 250; Chem. Abstr., 1965, 63, 17135f.
- 267. Pease, B. F., Diss. Abstr., 1958, 18, 1236; Chem. Abstr., 1958, 52, 12652e.
- Navrátil, O., Colln Czech. Chem. Commun., 1966, 31, 2492. 268.
- 269. Dono, T., Nakagawa, G., and Wada, H., J. Chem. Soc. Japan, (Pure Chem. Sect.), 1961, 82, 590; Chem. Abstr., 1961, 55, 20781c.
- Shibata, S., Nimii, Y., and Matsumae, T., Nagoya Kogyo Gijutsu Shikensho Hokoku, 1962, 11, 275; Chem. Abstr., 1962, 57, 4024d. 270.
- 271. Nakagawa, G., and Wada, H., Bunseki Kagaku, [Japan Analyst], 1961, 10, 1008; Chem. Abstr., 1963, 58, 6182fg.
- ., J. Chem. Soc. Japan, (Pure Chem. Sect.), 1963, 84, 636; Chem. Abstr., 1964, 61, 1260c. 272.
- 273. Püschel, R., and Lassner, E., Mikrochim. Acta, 1965, 17; Chem. Abstr., 1965, 62, 12434e.
- Cheng, K. L., and Goydish, B. L., Michrochem. J., 1963, 7, 166; Chem. Abstr., 1963, 59, 12167d. 274.
- 275. Püschel, R., Lassner, E., and Illaszewicz, A., Chemist Analyst, 1966, 55, 40.
- 276. Pollock, E. N., and Zopatti, L. P., Analytica Chim. Acta, 1963, 28, 68.
- 277. Penner Donaldson, E. M., and Inman, W. R., Talanta, 1966, 13, 489.
- Wakamatsu, S., Bunseki Kagaku, [Japan Analyst], 1960, 9, 284; Analyt. Abstr., 1962, 9, 3227. Rolf, R. F., Analyt. Chem., 1961, 33, 125. 278.
- 279.
- 280. Inczedy, J., Nemeshegyi, G., and Erdey, L., Acta Chim. Hung., 1965, 43, 1; Chem. Abstr., 1965, 62, 15421c.
- 281. Baltisberger, R. J., Analyt. Chem., 1964, 36, 2369.
- Anderson, D. L., and Smith, H. E., U.S. Atomic Energy Commission Report, RL-SA-38, 1965. 282.
- 283.
- Camera, V., Medna Lav., 1961, 52, 59; Analyt. Abstr., 1962, 9, 3190. Vishnu, and Srivastava, V. K., Curr. Sci., 1962, 31, 330; Chem. Abstr., 1963, 58, 5028f. 284.
- 285. Negoiu, D., Kriza, A., and Baloiu, L., Anal. Univ. C.I. Parhon, 1964, 13, 165; Chem. Abstr., 1966, 64, 14951g.
- 286. Gattow, G., and Schott, D., Z. analyt. Chem., 1962, 188, 10; Chem. Abstr., 1962, 57, 11846f.
- 287. Sayun, M. G., and Tikhanina, S. P., Zav. Lab., 1962, 28, 544; Analyt. Abstr., 1963, 10, 69.
- 288. Enmov, I. P., and Ivanov, V. M., Zh. Analit. Khim., 1960, 15, 750; Analyt. Abstr., 1962, 9, 598.
- 289. Pilloni, G., and Plazzogna, G., Analytica Chim. Acta, 1966, 35, 325.
- Hagiwara, K., Nakane, M., Osumi, Y., Ishii, E., and Miyake, Y., Bunseki Kagaku, [Japan Analyst], 290. 1961, 10, 1374; Chem. Abstr., 1962, 56, 14917b.
- Hniličková, M., and Sommer, L., Z. analyt. Chem., 1963, 193, 171; Chem. Abstr., 1963, 59, 16g. 291.
- Tsintsevich, E. P., Ivanov, V. M., and Tsabel, V. A., Vest. Mosk. Gos. Univ., Ser. II, Khim., 1963, 18, 54; Chem. Abstr., 1964, 60, 2319e. 292.
- 293. Ivanov, V. M., Tsintsevich, E. P., and Ghorokova, A. N., Ibid., 1964, 19, 69; Chem. Abstr., 1964, 61, 8886f.
- 294. Dwivedi, C. D., Munshi, K. N., and Dey, A. K., Chemist Analyst, 1966, 55, 13.
- 295. Hagiwara, K., and Muraki, I., Bunseki Kagaku, [Japan Analyst], 1961, 10, 1022; Chem. Abstr., 1965, 63, 14033c.
- Kish, P. P., and Orlovskii, S. T., Zh. Analit. Khim., 1962, 17, 1057; Chem. Abstr., 1963, 58, 13122f. 296.
- 297. Spitsyn, V. I., Granovsky, Y. V., Komissarova, L. N., Borisova, A. P., and Savich, I. A., Vest. Mosk. Gos. Univ., Ser. II, Khim., 1965, 20, 50; Chem. Abstr., 1965, 63, 5221f. Box, G. E. P., and Wilson, K. B., J. R. Statist. Soc., Ser. B, 1951, 13, 1.
- 298.
- Shijo, Y., and Takeuchi, T., Bunseki Kagaku, [Japan Analyst], 1965, 14, 511; Chem. Abstr., 1965, 299. 63, 17136f.
- 300. -, Ibid., 1964, 13, 536; Chem. Abstr., 1964, 61, 10025f.
- 301. Golobov, A. D., and Vakhramaeva, N. A., Pochvovedenie, 1965, 81; Chem. Abstr., 1965, 62, 13831d.
- 302. Takeuchi, T., and Shijo, Y., Bunseki Kagaku, [Japan Analyst], 1965, 14, 930.

- Negoiu, D., Kriza, A., and Teodoscu, I., Anal. Univ. Buc., Ser. Stiint. Nat., chim., 1963, 12, 107: 303. Chem. Abstr., 1966, 64, 8922h.
- 304 Budevski, O., and Dzhonova, L., Talanta, 1965, 12, 291; Chem. Abstr., 1965, 62, 7110d.
- 305 Shijo, Y., and Takeuchi, T., Bunseki Kagaku, [Japan Analyst], 1965, 14, 115; Chem. Abstr., 1965, 63, 3619c.
- 306 Kawahate, M., Mochizuki, H., Kajiyama, R., and Ichihasi, K., Ibid., 1965. 14. 348: Chem. Abstr., 1965. 63. 2383f.
- 307. Geary, W. J., and Larsson, C. N., in Shallis, P. W., Editor, "Proceedings of the SAC Conference, Nottingham, 1965," W. Heffer & Sons Ltd., Cambridge, 1965, p. 455. Belcher, R., Ramakrishna, T. V., and West, T. S., *Talanta*, 1963, **10**, 1013.
- 308
- 309.
- Elinson, S. V., and Pobedina, L. I., Zh. Analii. Khim, 1963, 18, 189; Chem. Abstr., 1963, 58, 11950c. Elinson, S. V., Pobedina, L. I., and Rezova, A. T., Zav. Lab., 1965, 31, 1434; Chem. Abstr., 1966, 310. 64, 7358f.
- 311. . Zh. Analit. Khim., 1965, 20, 676; Chem. Abstr., 1965, 63, 15548g.
- Patrovsky, V., Chemické Listy, 1965, 59, 1464; Chem. Abstr., 1966, 64, 10392c. 312.
- 313. -, Talanta, 1965, 12, 971.
- Elinson, S. V., and Rezova, A. T., Zh. Analit. Khim., 1964, 19, 1078. 314.
- 315 Kajiyama, R., and Watanabe, M., Bunseki Kagaku, [Japan Analyst], 1966, 15, 153.
- Jieh-Chun, Li, and Shuen Ming, Cheng, Scientia Sin., 1965, 14, 144. 316.
- Busev, A. I., and Chang, Fang, Vest. Mosk. Gos. Univ., Ser. II, Khim., 1960, 15, 46; Talanta, 1962, 9, 101; Chem. Abstr., 1961, 55, 24385e. Sommer, L., and Hniličková, M., Analytica Chim. Acta, 1962, 27, 241. 317.
- 318.
- Spacu, P., Antonescu, E., and Plostinaru, S., Revue Roum. Chim., 1964, 9, 121; Chem. Abstr., 1964. 319. 61, 10296c.
- Wang, S. Y., Mou, S. F., and Liang, S. C., Scientia Sin., 1964, 13, 522; Chem. Abstr., 1964, 61, 2475b. 320.
- Munshi, K. N., and Dey, A. K., Analyt. Chem., 1964, 36, 2003. 321.
- Busev, A. I., and Ivanov, V. M., Vest. Mosk. Gos. Univ., Ser. II, Khim., 1960. 15, 52; Chem. 322. Abstr., 1961, 55, 8152.
- 323. Florence, T. M., and Farrar, Y., Analyt. Chem., 1963, 35, 1613.
- Chudinov, E. G., Zh. Analit. Khim., 1965, 20, 805; Chem. Abstr., 1966, 64, 1324n. 324.
- Patrovsky, V., Talanta, 1965, 12, 971. 325.
- -, Chemické Listy, 1965, 59, 1464; Chem. Abstr., 1966, 64, 10392c. 326.

Received October 18th, 1966

The Determination of Plutonium in Refractory Materials by Electrometric Methods after Dissolution by Fusion with Ammonium Hydrogen Sulphate

By G. W. C. MILNER, A. J. WOOD, G. WELDRICK AND G. PHILLIPS

(Analytical Sciences Division, Atomic Energy Research Establishment, Harwell, Didcot, Berks.)

A fusion with ammonium hydrogen sulphate at 400° C has been developed for the dissolution of refractory materials containing plutonium dioxide. On cooling, each melt is leached with sulphuric acid to produce a solution suitable for analysis for plutonium by electrometric methods. Plutonium concentrations (about 2 mg per ml) are determined either by a potentiometric titration based on the reduction of plutonium(VI) to plutonium(IV), or by a controlled-potential coulometric method, the $Pu^{3+} - Pu^{4+}$ couple being used. Both techniques are suitable for the accurate determination of plutonium with a precision of better than 0.20 per cent. (coefficient of variation) for about 5-mg amounts or less. The behaviour of many other elements in these methods has been studied in some detail.

The fusion technique has been found to be suitable for the dissolution of several refractory materials, including samples of $PuO_2 - UO_2$ fired at 1550° C, and also samples of $PuO_2 - ThO_2$ produced by the ignition at 900° C of the carbides of these elements coated with pyrolytic graphite. The determination of the plutonium contents of these samples was then completed directly by the electrometric methods.

CERAMIC materials containing plutonium are being studied as potential fuels for nuclear reactors, and oxide and carbide systems are being investigated for this purpose. In this work specimens are prepared to cover a wide range of compositions, and final materials are then checked by chemical analysis. With oxide samples, difficulties can occur in the chemical analysis because of the refractory nature of plutonium dioxide, particularly after ignition at temperatures greater than 850° C. Many of the oxide samples for analysis had been ignited at temperatures greater than 850° C, and some reached 1550° C in the ignition process. In the analysis of carbides for plutonium, the usual practice is to ignite them to oxide to remove carbonaceous matter before proceeding with the dissolution. The temperature in this process can be controlled at less than 850° C. The present methods for the dissolution of low-fired plutonium dioxide include the use of various acids, such as nitric acid *plus* hydrofluoric acid,¹ halogen acids,² or perchloric acid and hydrochloric acid at high pressures,³ but, unfortunately, these methods are unsatisfactory for the complete dissolution of high-fired plutonium dioxide. A need occurred therefore for the development of new methods of dissolution that were compatible with the solution requirements of the techniques for the plutonium determination.

In earlier work⁴ a sodium peroxide sinter was developed for the dissolution of plutonium dioxide, and differential spectrophotometry proved to be suitable for the determination of the plutonium content of the resulting solution. The differential spectrophotometric method requires, however, that the plutonium concentration is not less than 2 mg per ml, and that at least 15 ml of solution are available for each determination. Electrometric methods for plutonium offer the advantage of improved precision for smaller concentrations, but they are more readily applied to solutions in sulphuric acid medium. Controlled-potential coulometry is suitable for the determination of 4-mg amounts of plutonium in M sulphuric acid with a precision of 0.25 per cent.,⁵ whereas a potentiometric titration procedure⁶ can be used for the determination of 2 to 10-mg amounts in M sulphuric acid with a precision of 0.1 per cent. Both techniques have been applied successfully to the analysis of cermet and alloy samples that could be dissolved in mineral acids, but their application to solutions produced by the sodium peroxide sinter technique proved less suitable. A fusion with ammonium hydrogen sulphate has been recommended by Feldman⁷ for the dissolution of small amounts (about 2 mg) of plutonium dioxide, and the results of preliminary experiments with this
technique in our laboratory were encouraging. The complete dissolution of plutonium dioxide, ignited at 1350° C, was achieved by fusing with ammonium hydrogen sulphate at 520° C and extracting the cooled melt with M sulphuric acid. Moreover, the resultant solution was suitable for analysis by electrometric techniques. In fact, the behaviour of this type of solution in controlled-potential coulometry was superior to that of solutions prepared by other methods. The further development of this procedure for the dissolution of larger amounts of high-fired plutonium dioxide was therefore undertaken, and the results of this investigation are reported here.

EXPERIMENTAL

FUSION CONDITIONS WITH AMMONIUM HYDROGEN SULPHATE FOR THE DISSOLUTION OF PLUTONIUM DIOXIDE—

Feldman succeeded in dissolving 2-mg amounts of an impure specimen of plutonium dioxide by fusing it with ammonium hydrogen sulphate in a small quartz beaker. This technique needed scaling up, however, before it could be used successfully for the dissolution and analysis of oxide samples containing plutonium. The feasibility of achieving this was tested on a sample of finely powdered plutonium dioxide that had been ignited at 1350° C. A suitable sample weight (about 100 mg) was mixed with 2 g of ammonium hydrogen sulphate in a glass beaker, and then the covered beaker was heated at 500° to 520° C on a hot-plate for 2 hours. Visual examination of the melt at this stage indicated that a little unattacked plutonium dioxide remained, and so more ammonium hydrogen sulphate (2 g) was added and heating was continued for a further $1\frac{1}{2}$ hours. On cooling, the melt was leached with sulphuric acid, and the solution was diluted to 50 ml to give a solution M in sulphuric acid. The plutonium content was determined by analysing suitable volumes of solution by the electrometric techniques. The following results, expressed as percentage recoveries, assuming stoicheiometric PuO₂₋₀₀, showed that the plutonium dioxide was dissolved completely by the above fusion procedure.

		Plutonium taken, mg	Plutonium found, mg	Recovery, per cent.	Coefficient of variation, per cent.
Coulometry	•••	9·966	9·964	100·0	0.17 (2 determinations)
Potentiometry		3·986	3·983	99·9	0.15 (8 determinations)

Information on the efficiency of the fusion with time was next obtained by carrying out experiments with fusion times of 30 minutes, 2 hours and 4 hours. The resultant solutions were then analysed for plutonium content by potentiometry. The following results showed that although 99 per cent. of the plutonium dioxide is dissolved after 2 hours, a fusion time of 3 to 4 hours is needed for complete dissolution—

Time of fusion		Plutonium taken,	Plutonium found,	Recovery,	Coefficient of variation,
		mg	mg	per cent.	per cent.
30 minutes		3.074	2.924	95.1	0.16 (6 determinations)
2 hours		3.621	3.596	99.3	0.22 (6 determinations)
4 hours		3 ·260	$3 \cdot 260$	100.0	0.08 (6 determinations)

Although ammonium hydrogen sulphate boils quietly at 520° C, losses of reagent from a covered beaker eventually cause the melt to evaporate to dryness, and care is needed to prevent this from taking place. There is also a risk of some loss of plutonium resulting from carry-over in the spray. It was considered that these problems might be overcome by using a lower temperature for the fusion and a condenser to deal with any spray. Tests showed that ammonium hydrogen sulphate remained in the molten state even at 400° C, and so dissolution experiments with plutonium dioxide were carried out at this temperature. The plutonium dioxide and ammonium hydrogen sulphate mixture was placed in a 50-ml conical flask and an air condenser, 5 inches in length, was fitted. A small watch-glass was used to cover the open end of the air condenser. Under these conditions it was possible to take 200 mg of plutonium dioxide into solution with 5 g of ammonium hydrogen sulphate, provided that the fusion process was allowed to proceed for 3 hours or longer. A little difficulty was experienced with the removal of the air condenser, but this was overcome by moistening the ground-glass joint with M sulphuric acid and allowing it to stand for some time before removing. The condenser was washed with M sulphuric acid and the washings were added

240

April, 1967] REFRACTORY MATERIALS BY ELECTROMETRIC METHODS

to the sample solution before making up to volume (100 ml). A series of plutonium determinations carried out by potentiometric titration following this dissolution technique gave a mean recovery of 100.0 per cent., with a coefficient of variation of 0.20 per cent.

METHOD

APPARATUS-

Conical flasks-Capacity, 50 ml, fitted with C19 ground-glass joints.

Glass tubes, 5 inches long and 0.5 inch i.d.—Fitted with C19 ground-glass cones to serve as air condensers.

Grade A 100-ml graduated flasks.

Controlled-potential coulometer^{8,9}—Fitted with a digital voltmeter (type LM1010–2, Solartron Laboratory Instruments Ltd., Chessington, Surrey).

Electrolysis cell for coulometry—As described previously.⁵ Automatic potentiometric titrator.⁶

REAGENTS-

Ammonium hydrogen sulphate-B.D.H. laboratory reagent.

Silver(II) oxide—Prepare by adding 100 ml of 3 per cent. w/v potassium persulphate to 10 ml of 10 per cent. w/v silver nitrate. Allow to stand for 1 hour. Filter the precipitate, wash well with water and allow it to dry in a desiccator.

Sulphuric acid, 9 M and M.

Silver sulphate, 1 per cent. w/v in M sulphuric acid.

Cerium(IV) sulphate, 0·1 N in M sulphuric acid—Standardise potentiometrically against 0·1 N potassium dichromate.⁶

Ammonium iron(II) sulphate, 0.025 N in M sulphuric acid—Standardise against cerium(IV) sulphate.

Potassium dichromate, 0.1 N—Dissolve 4.903 g of potassium dichromate (dried at 110° C) in water and dilute to a volume of exactly 1 litre at 20° C.

Use AnalaR reagents, including the distilled water.

RADIOCHEMICAL SAFETY-

Operations on dry samples containing plutonium dioxide, up to the point of complete dissolution, should be conducted in a glove-box. Aliquot portions for completion of the analysis may be handled in a fume cupboard with an efficient extraction and filtration system.

PROCEDURE-

Prepare a solution (100 ml) of the sample to contain 1 to 2 mg of plutonium per ml by transferring a suitable weight of sample to a 50-ml conical flask and adding 2 g of ammonium hydrogen sulphate. Fit an air condenser, and cover its open end with a small watchglass. Stand the flask on a small temperature-calibrated hot-plate, and adjust the rheostat to raise the melt to 400° C. Maintain at this temperature for at least 3 hours, and add more ammonium hydrogen sulphate if the melt solidifies. Then cool the flask, moisten the ground-glass joint with M sulphuric acid and allow to stand (preferably overnight). Carefully remove the air condenser and wash it with M sulphuric acid, adding the washings to the flask. Allow the melt to dissolve and add more M sulphuric acid for this purpose, if necessary. Transfer the solution to a 100-ml graduated flask and dilute to the mark with M sulphuric acid. Take suitable aliquots containing about 4 mg of plutonium for determination by either potentiometric titration or controlled-potential coulometry as follows.

Potentiometric titration—Transfer the aliquot of sample solution to a 15-ml squat beaker, and adjust the solution to be 2 to 3 ml in volume and M in sulphuric acid. Add 3 ml of 1 per cent. silver sulphate solution, and then 25 mg of finely powdered silver(II) oxide. Stir the mixture and allow it to stand for 5 minutes. Add two further portions (25 mg each) of silver(II) oxide at intervals of 5 minutes, and allow to stand for a total of 20 minutes while agitating at frequent intervals. Then cover the beaker with a watch-glass and warm it at 95° C for 5 minutes to destroy the excess of oxidant. Cool, rinse the watch-glass and beaker with 1 ml of water, and then add 3 ml of 9 M sulphuric acid. Accurately add 2 ml of 0.025 N ammonium iron(II) sulphate solution to reduce plutonium(VI) to plutonium(IV), and leave some reagent in excess (Note 1). Place the electrode system, consisting of a platinum electrode and an S.C.E. in the sample solution, and allow the potential to stabilise while stirring the solution smoothly. Dip the end of the Agla burette in the solution and slowly titrate the excess of iron(II) with standard 0.1 N cerium(IV) sulphate solution with the automatic potentiometric titrator. Calculate the plutonium content of the sample from the expression—

Plutonium, mg =
$$\frac{(C - B) N \times 239 \cdot 1 \times V}{A \times 2}$$

where C is the titre for the total ammonium iron(II) sulphate added,

B is the titre of the iron(II) in excess,

N is the normality of the cerium(IV) sulphate solutions,

A is the volume of the aliquot taken for analysis, and

V is the total volume of the sample solution.

Note 1-

The strength of the ammonium iron(II) sulphate should be such that the titration of the excess will require less than 0.5 ml of 0.1 N cerium(IV) sulphate. This is because the total capacity of the burette is 0.5 ml.

Coulometric determination—Transfer the aliquot of sample solution to the coulometer cell, and add sufficient M sulphuric acid to cover the working electrode. Remove oxygen from the solution by passing a stream of nitrogen through it. Then reduce the plutonium to the tervalent state by electrolysing at a potential of +0.30 volt against an S.C.E. until the current attains a low constant value ($\leq 10 \mu A$). After adjusting the coulometer to zero, carry out the quantitative oxidation of plutonium to the quadrivalent state by electrolysing at +0.70 volt against an S.C.E. until the cell current reaches its previous low value ($\leq 10 \mu A$). Correct the digital-voltmeter reading, Q, for a blank determination carried out in exactly the same way with only M sulphuric acid in the cell. Calculate the weight of plutonium from the expression—

Plutonium, mg =
$$\frac{Q \text{ (corrected)} \times F \times 239 \cdot 1 \times V}{96.487 \times A}$$

where F is the calibration factor in millicoulombs per millivolt for the coulometer range used, and V and A are the same as for the potentiometric titration.

THE BEHAVIOUR OF OTHER OXIDES IN THE SOLUTION PROCESS-

In experiments to study the behaviour of other oxides, a suitable weight of each oxide in the range 50 to 200 mg was transferred to a 50-ml flask, then 2 g of ammonium hydrogen sulphate was added and the fusion carried out. Several oxides gave clear melts which produced complete solutions in M sulphuric acid. Oxides in this category included B_2O_3 , CeO_2 , CuO, HgO, MnO₂, MoO₃, NiO, NpO₃, ThO₂ (ignited at 2000° C), UO₂, U₃O₈, V₂O₅ and ZrO₂. The clear melts of a few oxides failed to give clear solutions in M sulphuric acid. These oxides included beryllium oxide, niobium pentoxide, silicon dioxide, tantalum pentoxide, titanium dioxide and tungsten trioxide (WO₃). This difficulty was overcome with beryllium oxide, niobium pentoxide and titanium dioxide by extracting the melts with concentrated sulphuric acid before diluting with water. The melts of tungsten trioxide and silicon dioxide failed to produce clear solutions.

The oxides of barium, calcium and lead did not produce clear melts, and insoluble sulphates of the elements precipitated from M sulphuric acid solutions. Calcium sulphate was incompletely precipitated under these conditions. The oxides of the rare earths were unattacked during the ammonium hydrogen sulphate fusion, but clear melts could be obtained by including ammonium nitrate in the fusion mixture. The oxides of iron and magnesium were also unattacked by ammonium hydrogen sulphate, and ammonium chloride was needed to achieve clear melts. The resultant solutions containing chloride and nitrate ions required evaporating to fumes of sulphuric acid to remove these constituents before proceeding with the plutonium determination.

INTERFERENCES IN THE PLUTONIUM DETERMINATION-

As many oxides of other elements are dissolved by the solution procedure developed for plutonium dioxide, a knowledge of the behaviour of these elements in the electrochemical procedures for plutonium is important. Possible interfering elements are those that are able to undergo oxidation - reduction reactions similar to plutonium. However, as the redox reaction for plutonium is not the same in both procedures, elements interfering in the potentiometric method may not necessarily interfere in the coulometric method. The behaviour of elements in these methods was therefore considered separately with the following results.

POTENTIOMETRIC TITRATION-

Any element capable of oxidation by silver(II) oxide and then reduction by iron(II) will give high results for plutonium by this method. Elements in this category include chromium, cerium, vanadium and manganese, and the first three react quantitatively. Manganese is oxidised to permanganate by silver(II) oxide, but then precipitation of manganese dioxide occurs during the destruction of excess of oxidant. Lloyd and Pickering¹⁰ have reported that when manganese in sulphuric acid solutions is not fully oxidised by silver(II) oxide, the remaining manganese(II) ions reduce permanganate with the precipitation of manganese dioxide.

From electrochemical considerations there should be negligible interference from many elements. No difficulties were encountered from equal amounts of the following elements in the determination of plutonium at the 4-mg level: B, Be, Bi, Ca, Cu, Eu, Mg, Nd, Ni, Sm, Ti, Th, U and Zr. The presence of mercury made the precision of the determination worse, and low results were obtained in the presence of equal amounts of molybdenum, niobium and tantalum. These elements were precipitated on heating the solution to destroy excess of silver(II) oxide and removed some plutonium from solution. Difficulties might be expected from elements precipitating as sulphates from M sulphuric acid, and although quantitative results were obtained for plutonium in the presence of an equal amount of calcium, some plutonium was carried down on the sulphate precipitates of lead and barium. In the case of iron, iron(III) sulphate was precipitated on fuming the solution with sulphuric acid to remove chloride ions. Unfortunately this precipitate did not re-dissolve in M sulphuric acid, and it retained some of the plutonium on it.

At a 10:1 ratio of the oxide of the other element to plutonium dioxide, the list of elements causing no interference is reduced to boron, copper, magnesium, thorium, uranium and zirconium. It proved impossible to produce satisfactory solutions for the increased amounts of bismuth, europium, neodymium, samarium and titanium, and although nickel gave a clear solution initially, a precipitate began to form fairly soon after preparation. Both beryllium and mercury gave satisfactory solutions. However, the titration curves were poorly defined in the presence of beryllium, and the precision of the plutonium determination was poor. Mercury also caused inferior titration curves with a positive bias of a few per cent. for the determination of plutonium. With calcium, the increased amount of calcium sulphate precipitated from solution at the 10:1 ratio resulted in the removal of some plutonium from solution, and hence interference in the determination.

CONTROLLED-POTENTIAL COULOMETRY-

This technique is more specific for plutonium than the potentiometric titration, and earlier work⁵ showed that no interference occurred from chromium, molybdenum, thorium, titanium and uranium in the analysis of alloys, cermets and ceramic materials. Interference from electro-active elements is limited to those that undergo oxidation - reduction reactions in the voltage range required for the plutonium determination (*i.e.*, +0.3 to +0.7 volt against an S.C.E.), and possible interfering and non-interfering elements can be identified by reference to tables of standard potentials of half-reaction for the elements.

Iron, mercury, silver and vanadium were considered to be the elements most likely to cause difficulty in the electrolysis. The E'_0 value for the Fe^{2+} - Fe^{3+} couple is almost identical with that for the Pu^{3+} - Pu^{4+} couple, and so interference from this element is serious. Mercury interfered seriously by depositing as the metal on the platinum electrode during the electrolysis. It also proved difficult to determine the completion of the plutonium determination under these conditions. Similarly, silver caused difficulties by reducing to the metal and plating on the working electrode. For vanadium, E'_0 values for the various couples are +0.119 volt against an S.C.E. for V^{3+} - VO^{2+}_{2+} , and +0.76 volt against an S.C.E. for VO^{2+}_{2-} - VO^{4-}_{2+} , and clearly interferences can be expected in the plutonium determination on electrolysing at +0.7 volt against an S.C.E. This was confirmed experimentally in the analysis of a synthetic solution with a 1:1 ratio of plutonium dioxide to vanadium pentoxide, as a high background current persisted at +0.7 volt, resulting in a plutonium recovery of about 105 per cent. Investigations with a pure vanadium solution showed that VO^{2+}_{2+} ions oxidised slowly at +0.7 volt, but that

this reaction did not take place on reducing the voltage to +0.62 volt against an S.C.E. It was concluded that it should be possible to oxidise Pu^{3+} to Pu^{4+} to 99 per cent. completion at +0.62 volt against an S.C.E. and avoid interferences from vanadium. This was attempted experimentally with satisfactory results, a recovery of 99.9 per cent. being obtained for plutonium in the 1 + 1 mixture of plutonium dioxide with vanadium pentoxide on correcting for the 1 per cent. plutonium unoxidised at this potential.

From electrochemical considerations most of the remaining elements should not interfere. Investigations were therefore limited to those elements with E'_0 values fairly near to the voltage range for the plutonium determination, and to those elements hydrolysing or precipitating from solution. From elements in the first category, copper was found to give no interference with plutonium for 1:1 and 10:1 ratios of its oxide to plutonium dioxide, and although bismuth did not interfere at a 1:1 ratio of the oxide, it proved impossible to produce satisfactory solutions for a 10:1 ratio of bismuth trioxide to plutonium dioxide.

In the second category of elements, work by Shults¹¹ indicated that difficulties might arise from elements not in true solution in M sulphuric acid. This worker reported interference from zirconium, even in small amounts, in the coulometric determination of plutonium. The nature of this interference was similar to that from organic matter in causing extended titration times and hence poor results. This behaviour was identified as being caused by fouling of the electrode by hydrolysed zirconium in the solution. In consequence, any element that can hydrolyse from M sulphuric acid containing ammonium sulphate may cause difficulty in the plutonium determination. Niobium and tantalum could be included in the same category as zirconium. The interference of zirconium was confirmed by us. A small positive bias was obtained for a 1:1 ratio of the oxides, and this increased to about 10 per cent. for a 10:1 ratio of zirconium dioxide to plutonium dioxide. For freshly prepared solutions of niobium and tantalum, negligible interference occurred for 1:1 ratios of each oxide to plutonium dioxide. At 10:1 ratios of niobium pentoxide or tantalum pentoxide to plutonium dioxide, however, it proved impossible to prepare satisfactory solutions. The difficulties with elements forming insoluble sulphates (e.g., barium, calcium and lead) were the same as for the potentiometric titration method. Beryllium resulted in a slight positive bias being obtained for plutonium. This was caused by a persistent background current occurring during both the reduction and oxidation of plutonium.

RESULTS

A standard plutonium solution was used to test the procedures and to give information on accuracy and precision. It was prepared from a sample of high purity plutonium dioxide that had been ignited at 1300° C to produce stoicheiometric $PuO_{2\cdot00}$. This material was ground to a fine powder and 200 mg were taken for dissolution by fusing with ammonium hydrogen sulphate at 400° C. The recoveries for plutonium shown in Table I were obtained by both the coulometric and potentiometric titration methods. The mean recovery values and the precisions (coefficients of variation) obtained for the determinations by both procedures were considered to be satisfactory.

TABLE I

Results for plutonium after dissolution of plutonium dioxide with ammonium hydrogen sulphate

Method of determination	Plutonium taken, mg	Mean recovery, per cent.	Coefficient of variation, per cent.	Number of determinations
Potentiometric	 2.818	100.0	0.18	6
	3.654	100.1	0.19	6
	4.135	100.0	0.10	6
Controlled-potential				
coulometry	 5.181	99-96	0.09	8
2	5.691	99.95	0.18	5
	6.180	99-95	0.10	6

The value of this method of dissolution for samples containing refractory plutonium dioxide has recently been demonstrated in this laboratory for the analysis of $PuO_2 - UO_2$ samples and PuC - ThC spheres coated with graphite. In a metallurgical study of $PuO_2 - UO_2$ fuels it was necessary to determine the plutonium contents of a series of refractory

samples covering a range of compositions from 70 per cent. $UO_2 - 30$ per cent. PuO_2 to 99 per cent. $UO_2 - 1$ per cent. PuO_2 . All of the materials in this work had been sintered at a temperature of 1550° C either in argon, or in a mixture of carbon dioxide and carbon monoxide. The ammonium hydrogen sulphate fusion procedure proved to be satisfactory for the dissolution of all samples, and the controlled-potential coulometric and the potentiometric titration methods were applicable to the analysis of the resultant solutions. Although uranium caused no interference, slight difficulty was encountered from iron in the analysis of samples at the 1 per cent. level of plutonium dioxide by controlled-potential coulometry. These samples were found to contain iron as an impurity, and a correction was needed for the iron in solution. Results for plutonium from the analysis of samples in this range of compositions are given in Table II. Very good agreement was found to occur between the results for plutonium by both methods of analysis.

TABLE II

The determination of plutonium in refractory PuO₂ - UO₂ ceramic samples

			Plutonium conte per c	ent by analysis, ent.
		Sample weight,	ىمىتىسىسىم	
Nominal composition	Sample conditions	mg	Potentiometric	Coulometric
PuO2, 30% - UO2, 70%	Sintered at 1550° C in argon	248.9	25.4	25.4
PuO ₂ , 15% - UO ₂ , 85%		562.2	13.2	13.2
$PuO_2, 10\% - UO_2, 90\%$	Sintered at 1550° C in carbon monoxide - carbon dioxide	489.0	9.06	9.00
PuO2, 1% - UO2, 99%	Sintered at 1550° C in argon	901.9	0.98	0.99*
	* Result corrected for in	ron in solution.		

For the analysis of the PuC - ThC spheres, which had been fired at 1500° C in an inert atmosphere during preparation, it proved necessary to ignite the samples at 900° C in air to remove the graphite coating and oxidise all carbonaceous material. This resulted in a refractory mixture of PuO₂ - ThO₂ for subsequent analysis for plutonium. In the analysis of a typical sample, 1.0077 g of sample was ignited to give 0.3746 g of oxide, which was then dissolved in ammonium hydrogen sulphate to give 100 ml of solution. Aliquots (5 ml) containing about 2.23 mg of plutonium were taken for analysis by the electrometric methods with the following results for the percentage of plutonium in the coated spheres.

- Potentiometric method: 13.6 per cent. of plutonium, with a coefficient of variation of 0.6 per cent. for three results.
- Coulometric method: 13.5 per cent. of plutonium, with a coefficient of variation of 0.2 per cent. for four results.

The suitability of the above method was confirmed on a synthetic sample with a similar composition. A recovery of 99.92 per cent. was obtained for the plutonium by the coulometric method as a mean of six results, with a coefficient of variation of 0.07 per cent.

CONCLUSIONS

Fusion with ammonium hydrogen sulphate has proved to be a successful method for dissolving refractory plutonium dioxide, either alone or in the presence of other refractory oxides. The need to reduce the sample to a fine state of subdivision and to mix it thoroughly with the fusion mixture, which is so essential for the sodium peroxide sinter, is unnecessary for the ammonium hydrogen sulphate fusion. As a consequence the latter method is readily applicable to very high-fired materials that cannot be dissolved completely by the sodium peroxide sinter. However, the ammonium hydrogen sulphate fusion is not rapid by comparison with the peroxide sinter, but the resultant solution is more suitable for the determination of plutonium by electrometric methods. Although a glove-box is necessary for the hydrogen sulphate fusion, the solution can then be transferred to a fume cupboard and the determination completed there because of the small amount of plutonium needed for the electrometric methods. This gives greater flexibility in handling sample solutions after dissolution. By comparison, the sodium peroxide sinter followed by differential spectrophotometry must be carried out completely in a suite of glove-boxes because of the higher concentrations of plutonium involved.

We thank Mr. I. G. Jones for assistance in some of the preliminary experiments.

References

- 1. Katz, J. J., and Seaborg, G. T., "The Chemistry of the Actinide Elements," Methuen and Co. Ltd., London; John Wiley and Sons Inc., New York, 1957, p. 279.
- Ltd., London; John Wiley and Sons Inc., New York, 1957, p. 279.
 Cleveland, J. M., J. Inorg. Nucl. Chem., 1964, 26, 1470.
 Kolthoff, I. M., and Elving, P. J., Editors, "Treatise on Analytical Chemistry," Interscience Publishers Inc., New York, 1962, Part II, Volume 9, p. 251.
 Milner, G. W. C., Crossley, D., Jones, I. G., and Phillips, G., Analyst, 1965, 90, 732.
 Phillips, G., and Milner, G. W. C., in Shallis, P. W., Editor, "Proceedings of the SAC Conference, Nottingham, 1965," W. Heffer & Sons Ltd., Cambridge, 1965, p. 240.
 Milor G. W. C. Wood A. L and Cassie G. F. I. K. Atomic Energy Authority Research Report

- Milner, G. W. C., Wood, A. J., and Cassic, G. E., U.K. Atomic Energy Authority Research Report, AERE-R 4975, H.M. Stationery Office, London, 1965. 6.
- Feldman, C., Analyt. Chem., 1960, 32, 1727. 7.
- Rockett, J. J., U.K. Atomic Energy Authority Research Report, AERE-R 3784, H.M. Stationery Office, London, 1961.
 Milner, G. W. C., and Edwards, J. W., U.K. Atomic Energy Authority Research Report, AERE-R 3772, 8.
- 9. H.M. Stationery Office, London, 1961.
- Lloyd, C. P.; and Pickering, W. F., Talanta, 1964, 11, 1409. 10.
- 11. Shults, W. D., Ibid., 1963, 10, 833.

Received November 30th, 1966

The Spectrophotometric Determination of Ampicillin

By J. W. G. SMITH, G. E. DE GREY AND V. J. PATEL (Beecham Research Laboratories, Clarendon Road, Worthing, Sussex)

A method is described for the determination of Ampicillin (α -aminobenzyl penicillin) based on the spectrophotometric measurement at 320 m μ of a compound formed by acid degradation of the penicillin at 75° C in the presence of buffer solution at pH 5·2 and a trace of a copper salt. Results obtained on samples of Ampicillin, Ampicillin Trihydrate and Ampicillin Sodium show good agreement with those recorded by the cup-plate microbiological method.

FOLLOWING the isolation of the penicillin nucleus, 6-aminopenicillanic acid in 1959, several semi-synthetic penicillins with a wide range of antibacterial properties have become available in this country (Table I).

SEMI-SYNTHETIC PENICILLINS

Several methods have been published for the determination of these compounds. The British Pharmacopoeia monographs for Ampicillin and Ampicillin Trihydrate specify a procedure based on the cleavage of the β -lactam ring to the corresponding penicilloic acid by controlled hydrolysis with standard alkali. This method is also included in the B.P. monographs for Cloxacillin Sodium and Methicillin Sodium, and in the B.P.C. monograph for Phenethicillin Potassium. The B.P. monographs for Cloxacillin Sodium and Methicillin Sodium also include additional assays based on chlorine and methoxyl determinations, respectively. An iodimetric assay procedure has been specified for Ampicillin Sodium B.P.

Alternative methods have been examined in these laboratories with a view to establishing a routine general procedure that would be applicable to the assay of large numbers of samples and, if possible, specific for the intact penicillin molecule in the presence of 6-aminopenicillanic acid, side-chain compounds and the usual penicillin degradation products.

The method selected for detailed study was that originally described by Herriott¹ and later modified by Stock² and by Holbrook.³ Herriott found that benzylpenicillin could be determined by acid degradation under controlled conditions of pH, time and temperature to a stable intermediate with an absorption maximum at 322 m μ . Stock recognised this intermediate as the penicillenic acid, and showed that reproducible results could be obtained by incorporating trace amounts of a copper salt in the buffer solution. The method was further investigated by Holbrook and has been applied by Weaver and Reschke⁴ to the determination of Methicillin Sodium.

Our preliminary experiments indicated that an intact penicillin molecule was essential for this determination. No acid degradation products, as indicated by absorption maxima above 300 m μ , were observed when solutions containing 6-aminopenicillanic acid side-chain compounds and penicilloic acids were subjected to acid treatment for prolonged times and at elevated temperatures. The method, therefore, appeared promising for the determination of the semi-synthetic penicillins. It was, however, realised that the experimental conditions described for benzylpenicillin and Methicillin might not be applicable to all of the compounds in Table I, in view of their different stability characteristics in acidic solution. It was clearly necessary to examine each penicillin individually to determine optimum assay conditions. This paper describes the work carried out in these laboratories to establish a suitable assay procedure for Ampicillin.

Method

Reagents-

Copper sulphate solution—Dissolve 3.93 g of copper sulphate pentahydrate in water, and dilute to 1 litre.

Buffer solution pH 5·2—Mix together 464 ml of 0·1 M citric acid solution and 536 ml of 0·2 M disodium hydrogen phosphate solution. Adjust the pH, if necessary, to 5·2 \pm 0·05 with the citric acid or disodium hydrogen phosphate solution. To 15 ml of the copper sulphate solution add the mixed buffer at pH 5·2 to a volume of 1 litre.

(1 ml of this solution contains $15 \mu g$ of copper.)

TABLE I

SEMI-SYNTHETIC PENICILLINS

			s	
R ₁ —C	O-NH	H-CH-	$-\acute{C}H$ $C(CH_3)_2$	
		co-	–N—–CH.COOR ₂	
Compound			R ₁	R_2
Phenethicillin Potassium	••	••	C ₆ H ₅ OCH	K
			CH,	
Propicillin Potassium	••		C ₆ H ₅ —O—CH—	K
			CHCH.	
Ampicillin	••		C ₆ H ₅ —CH —	н
			I NH-	
Ampicillin Trihydrate			C ₆ H ₅ —CH—	H.3H ₂ O
) NH	-
Ampicillin Sodium			C _e H ₅ CH	Na
			VOCH.	
Mathiaillin Cadium			\prec .	No LL C
Methicilini Sodium	••	••	\checkmark	Na.n ₂ C
			∕OCH₃	
Cloxacillin Sodium	••	••	< <u></u>	Na.H ₂ C
			N C—CH ₃	
			\ ₀ /	
Phenbenicillin Potassium		••	C ₆ H ₅ —O—CH—	
			l CeHe	K

PROCEDURE-

Prepare a solution of the sample in distilled water at a concentration of about 1.0 mg per ml of Ampicillin. Place 2.0 ml of this solution into a 100-ml calibrated flask and dilute to volume with the pH 5.2 buffer solution. Transfer 10.0 ml of this solution to a calibrated test-tube, lightly stopper the tube and place in a thermostatically controlled bath at 75° C. After exactly 30 minutes, remove the tube from the bath and cool to room temperature in ice. If necessary, adjust the volume to 10.0 ml with water and determine the optical density at 320 m μ in a 1-cm cell with the unheated buffered Ampicillin solution in the reference cell. Determine the Ampicillin concentration of the original sample by reference to a calibration graph prepared by carrying out the above procedure on known dilutions of the standard Ampicillin preparation.

EXPERIMENTAL

A Hilger H999 Ultrascan recording spectrophotometer was used for most of the experimental work described, and a Unicam SP500 instrument was used for measuring optical densities during subsequent routine assays. Unless otherwise stated, all experiments were performed on buffered solutions containing a nominal Ampicillin concentration of $20 \,\mu g$ per ml.

April, 1967]

WAVELENGTH OF MAXIMUM ABSORPTION-

Under the specified conditions of assay, Ampicillin was found to develop an absorption maximum at $320 \text{ m}\mu$ (Fig. 1). Under other assay conditions studied, the wavelength was found to vary in the range 320 to $340 \text{ m}\mu$.



Fig. 1. Ultraviolet absorption spectrum of degraded Ampicillin; pH 5.2, temperature 75° C, 15 μ g per ml of copper in buffer solution, 30 minutes' heating time



Fig. 2. Time of heating; pH 5.2, 15μ g per ml of copper in buffer solution

TIME OF HEATING-

Under the optimum conditions of pH, temperature, Ampicillin and copper concentration, the absorption at 320 m μ increases with time to a maximum at 30 minutes (Fig. 2). During the following 40 minutes at 75° C, it was found that the optical density decreased slowly at about 0.2 per cent. per minute. The solution held at room temperature after reaction for 30 minutes at 75° C was found to exhibit the same optical density for 1 hour.

Effect of pH on absorption at 320 mµ-

The effect of pH on the absorption at 320 m μ , at a temperature of 75° C, was examined with phosphate - citrate buffer solutions in the pH range 2.5 to 7.5. Copper sulphate reagent was added to all buffer solutions to produce a copper concentration of 15 μ g per ml. The optimum pH of 5.2 was selected from these observations (Fig. 3).



EFFECT OF COPPER CONCENTRATION-

Fig. 4 illustrates the effect on the optical density of varying the copper concentration in the pH 5.2 buffer solution within the range 0 to 30 μ g per ml. A copper concentration of 15.0 μ g per ml in the buffer solution was selected.



Fig. 5. Effect of temperature

EFFECT OF TEMPERATURE-

The optimum temperature of 75° C was selected from a series of results obtained by heating a 20 μ g per ml solution of Ampicillin at pH 5.2 for 30 minutes at temperatures in the range 50° to 100° C (Fig. 5).

BEER'S LAW-

Buffered solutions of the standard Ampicillin at a range of concentrations up to and including 50 μ g per ml were assayed by the specified procedure. Beer's law was obeyed over the range (Fig. 6). A working concentration of 20 μ g per ml of Ampicillin in the buffer was selected for optimum sensitivity.



Fig. 6. Beer's Law; pH 5.2, temperature 75° C, 15 μ g per ml of copper in buffer solution, 30 minutes' heating time

RESULTS

Table II shows results obtained by the specified procedure on routine samples of Ampicillin, Ampicillin Trihydrate and Ampicillin Sodium. The results are expressed in terms of the free acid and are compared with those recorded by the quadruplicate (8×8 Latin square) cup-plate microbiological assays (*B. Subtilis* A.T.C.C. 6633 as assay organism) with fiducial limits of error (P = 0.95) estimated as ± 3 per cent. of the quoted average potencies.

250

TABLE II

COMPARISON OF SPECTROPHOTOMETRIC AND BIOLOGICAL ASSAYS Expressed as up per mg of Ampicillin

Expressed as μ_g per mg or minpler	
--	--

Compoun	d	Sample No.	Spectrophotometric assay	Bioassay	
Ampicillin		 1	964	961	
-		2	967	960	
		3	958	962	
		4	976	971	
		5	978	970	
		6	978	990	
Ampicillin Trihydrate		 7	755	755	
		8	778	773	
		9	811	815	
		10	814	810	
		11	829	830	
		12	823	825	
		13	837	834	
		14	838	840	
		15	846	844	
		16	847	845	
		17	847	837	
		18	851	845	
Ampicillin Sodium		 19	765	770	
		20	790	793	
		21	830	833	
		22	837	834	
		23	852	857	
		24	851	844	

The spectrophotometric assay results quoted in Table II represent the mean of duplicate determinations. A standard deviation of less than 1 per cent. was indicated.

DISCUSSION

The method described is considered to be the most specific at present available for the direct chemical determination of Ampicillin. As no interference has been observed due to 6-aminopenicillanic acid and α -aminobenzylpenicilloic acid, the structure



appears to be essential for the reaction to proceed. Thus the spectrophotometric method is clearly more specific than procedures based on the determination of either the β -lactam ring, *e.g.*, alkaline or penicillinase de-activation, iodine absorption or hydroxamate colour formation, or the side-chain entity.

The optimum assay conditions for Ampicillin, *i.e.*, pH, temperature, time of heating and wavelength of measurement, differ somewhat from those specified in previous papers for benzylpenicillin and Methicillin Sodium (Table III).

TABLE III

ASSAY CONDITIONS FOR AMPICILLIN, BENZYLPENICILLIN AND METHICILLIN

Compound			Wavelength, mµ	рН	Temperature, °C	Time of heating, minutes	Penicillin concentration in buffer, µg pcr ml
Ampicillin			320	5.2	75	30	20
Benzylpenicillin	• •	• •	322	4.6	100	15	40 to 50
Methicillin	••	••	330	3 ·8	70	30	i.u. per ml 10

Assay conditions for Ampicillin, Benzylpenicillin and Methicillin

The importance of copper in the reaction has been confirmed. The optimum copper concentration in the pH 5.2 buffer for the Ampicillin assay (15.0 μ g per ml) is considerably higher than that found by Stock² for benzylpenicillin, *i.e.*, 0.33 μ g per ml. The effect of

varying the copper concentration in the Methicillin Sodium assay was not reported by Weaver and Reschke,⁴ but a figure of 0.5 μg per ml in the buffer solution was specified; in the absence of added copper, a lower absorptivity was obtained.

The method is simple and accurate, and because of the stability at room temperature of the solution after reaction many samples can be assayed simultaneously. The procedure should be amenable to automation, and this aspect is currently being investigated, together with the possibility of extending the method to the assay of the other semi-synthetic penicillins listed in Table I.

The procedure described for Ampicillin has been used in these laboratories for the routine assay of samples covering a wide potency range. The method has given satisfactory reproducibility and results have shown good agreement with those recorded by the cup-plate bioassay method.

References

Herriott, R. M., J. Biol. Chem., 1946, 164, 725. Stock, F. G., Analyst, 1954, 79, 662. 1.

- 2.
- 3. Holbrook, A., J. Pharm. Pharmac., 1958, 10, 762.
- 4. Weaver, W. J., and Reschke, R. F., J. Pharm. Sci., 1963, 52, 362.

Received November 9th, 1966

252

An X-ray Spectrographic Method for Determining Barium

BY S. A. PROKOPOVICH AND E. R. MCCARTNEY

(Department of Ceramic Engineering, School of Chemical Technology, The University of New South Wales, Kensington, N.S.W., Australia)

An X-ray spectrographic method is described in which a Philips 50-kV universal X-ray spectrograph with a chromium tube is used for the quantitative trace analysis of barium in aqueous solutions. The method involves the use of the barium $L\alpha_1$ line, and is suitable for concentrations of up to at least 0.5 per cent. w/w of barium. A limit of detection of 0.002 per cent. w/w of barium is achieved. The extension of the method to the neighbouring elements in the periodic table is suggested.

SEVERAL methods have been developed for the X-ray spectrographic analysis of barium in various systems. Davis and Van Nordstrand¹ have described the determination of barium, calcium and zinc in lubricating oils, Lewis and Goldberg² have determined barium, titanium and zinc in sediments, Gulbransen³ has developed a procedure for the analysis of barium in barite ores, and Toussaint and Vos⁴ have used X-ray spectrometric determinations for barium in ion-exchange clay effluents.

The purpose of the present work was to investigate yet another approach to the quantitative determination of barium with a view to lowering the practical limit of detectability, thus permitting the extension of the useful range of the trace analysis. The system of interest in this investigation was the filtrate, resulting from the hydrothermal formation of barium titanate, and consisting of the solution of barium hydroxide in water. The barium hydroxide solution is difficult to handle owing to the rapid absorption of carbon dioxide from air, and it was expected that the X-ray spectrographic analysis of the filtrate solutions, immediately acidified with the hydrochloric acid, would enable more convenient handling of the reaction filtrates and result in a considerable time saving.

INSTRUMENTATION

The equipment used in this work was a Philips 50-kV universal X-ray spectrograph provided with a pulse height discriminator. In the preliminary work, tungsten and chromium X-ray tubes were used in conjunction with the scintillation and flow proportional counters and lithium fluoride and pentaerythritol analysing crystals. However, the final combination and the operating conditions that were found to give the most satisfactory results are—

X-ray tube		 	Chromium
Tube operated at		 	44 kV, 22 mA
Analysing crystal		 	Lithium fluoride
Parallel blade collimation	ator	 	480 μ , 10 cm long
Counter		 	Flow proportional
Analytical line		 	$BaL_{\alpha_{1}}$, 87.13° (2 θ)
X-ray path		 	Air
Counting technique		 	Fixed count
Pulse height discrim	inator	 • •	Adjusted to give maximum P/B ratio
i unse mengine unserini	macor	 ••	hujustou to give maximum 1/12 futto

EXPERIMENTAL

Preliminary work carried out with the scintillation counter, lithium fluoride crystal and tungsten indicated that the BaK_{α_1} line is not a satisfactory choice owing to the very high background in this angular region, which results in a low peak-to-background ratio. The high background intensity encountered when analysing liquid specimens is caused by scattering of the white continuum from the light elements of which most liquids consist. The pulse height discrimination for BaK_{α_1} was found to be ineffective, as scattered radiation from the tungsten tube is about the same wavelength as the line of interest.

254 PROKOPOVICH AND MCCARTNEY: AN X-RAY SPECTROGRAPHIC [Analyst, Vol. 92]

The BaL_{α_1} line is, then, the logical choice because the background in this region is much lower, resulting in an increased P/B ratio. A flow proportional counter was selected for the analysis of BaL_{α_1} radiation (2.775 Å) as it is very sensitive to radiation softer than 2.3 Å. The use of the chromium tube under these conditions resulted in the net intensity of the BaL_{α_1} line being about three times larger than for the tungsten tube at the same loading, and the peak height discriminator was found to be effective for both. Results with the pentaerythritol crystal were similar to those obtained when using lithium fluoride, with essentially the same P/B ratio. However, because of the temperature dependence of the pentaerythritol crystal and also because the full range of the data for it was not available, a lithium fluoride crystal was selected.

PROCEDURE-

The Perspex cells for the analysis of liquids were made from standard Perspex sample bottles (1³/₈ inch in diameter), provided with tightly fitting polythene lids. The bottles were shortened to about 1¹/₈ inch in height, and were provided with a supporting circular edge made of $\frac{1}{4}$ -inch thick Perspex. New bottoms were glued on and holes, 1 inch in diameter, were cut in the polythene lids. The Mylar foil was placed on the top of the bottle, and the lid was slid over, thus forming a satisfactory seal.

The reaction filtrate was found to contain no titanium; this permitted direct determination of barium. A barium calibration graph was prepared by using barium hydroxide solutions containing fixed amounts of hydrochloric acid in a given volume. Standards were checked by chemical analysis. The ratio technique was used to take care of fluctuations of the instrument sensitivity that occurred over a period of time and that may have invalidated the calibration graph. For this purpose a solid reference sample was prepared by mixing the measured amount of the barium carbonate powder with boric acid and pressing the resultant mixture at 15 tons per sq. inch. The resultant pellet was sprayed with transparent lacquer known to contain no barium. Immediately the counting on the solution was completed, another count was carried out on the reference standard, $BaL_{\alpha_{RS}}$. The correction for the background was made by counting the intensity of the scattered radiation at 87.13° (2 θ) from distilled water containing the same amount of hydrochloric acid as the samples. This method allows some time saving because the counting on the unknown, the reference standard and the distilled water can be carried out at the same angular position without re-setting of the goniometer. The intensity ratios $BaL_{\alpha_u}/BaL_{\alpha_{RS}}$, where BaL_{α_u} is the net intensity from the solution, were plotted against the percentage of barium w/w. The resultant straight line was used as a calibration graph for the analysis of unknowns. This graph was found to pass through the origin, indicating a satisfactory estimation of the background intensity.



Fig. 1. Effect of the target on the intensity of the barium L_{α_1} line in aqueous solutions. Operating conditions are as given in Table I

RESULTS AND DISCUSSION

The results obtained for both tungsten and chromium tubes are plotted in Fig. 1. The range of concentrations studied extended to 0.5 per cent. w/w of barium; only part of these results are plotted in Fig. 1. A setting of 44 kV and 22 mA was selected as giving a high intensity, and at the same time being within the permissible loading for the tubes. The runs carried out at 40 kV and 20 mA resulted in slightly reduced P/B ratios. The graph indicates that the chromium tube is more efficient than the tungsten tube.

The fact that the chromium tube gave the more satisfactory results is not unexpected. The chromium tube was especially developed for the analysis of elements lighter than chromium $(K_{\alpha_1} = 2 \cdot 290 \text{ Å})$. The increased intensities of the analytical lines of these elements are achieved, partly because of the location of the characteristic lines in respect to the absorption edges of these elements, but mainly because the combined energy reaching the sample is higher than, for example, that of the tungsten tube in this wavelength region. This is a consequence of the chromium tube having a thin window whose absorption is lower than that of the tungsten tube.

It therefore seemed likely that the chromium tube would be at least as efficient as tungsten for the excitation of the L spectrum of elements 38 to 57 in the periodic table, with $L_{\rm III}$ absorption edges extending from 6.39Å for strontium, to 2.26Å for lanthanum. It must be noted that some of the angles involved are very large and beyond the normal instrument range at present. The work reported here applies these ideas to the analysis for barium, and shows them to be valid.

Of the targets tested, the chromium gave the lowest background intensity as this originates mostly from the continuum, and is therefore dependent on the atomic number of the target material. The use of a pulse height discriminator to improve the P/B ratio was found to be more effective for the tungsten tube. However, the final results obtained with the tungsten and the chromium tubes at the same operating conditions indicate that the chromium tube is superior because the net intensity of the BaL_{α_1} line is increased by a factor of 3, and the P/B ratio by a factor of 2, in comparison with the tungsten tube. An attempt was made to use an asymmetrical setting of the channel height, as described by Dowling, Hendee, Kohlet and Parrish⁵; however, this did not improve the P/B ratio, indicating that the remaining wavelengths are close to the BaL_{α_1} radiation.

Several definitions of the practical limit of detectability are available. For example, Friedman and Birks⁶ indicate that it is inadvisable to attempt to detect a line intensity of less than one-tenth of the background, that is, setting the limit of detectability as one-tenth of the background intensity. However, from the practical point of view, the definition given by Birks⁷ is more satisfactory. He defines the practical limit of sensitivity as the intensity of the line which exceeds the background by at least three standard deviations of the background. In terms of the latter definition, the following sensitivities were obtained—

Chromium tube operated at 44 kV and 22 mA-0.002 per cent. w/w of barium. Tungsten tube operated at 44 kV and 22 mA-0.004 per cent. w/w of barium.

The use of a chromium tube in a given instrumental arrangement therefore doubled the sensitivity obtainable with a tungsten tube. It is not clear why the sensitivity obtained with a tungsten tube was not as high as that obtained under apparently similar conditions by Toussaint and Vos.⁴

When a more complicated matrix is encountered and interference from other elements is expected, resort may be made to the internal standard method which is well described by Adler and Alexrod.⁸ For barium, several investigators^{2,4} found lanthanum to be a satisfactory internal standard.

CONCLUSION

It has been established that, for the analysis of barium in solution, the use of the L_{α_1} line results in a much higher sensitivity than the use of the K_{α} line. The advantage of using the L_{α_1} line was further enhanced by exciting the specimen with a chromium-target tube rather than a tungsten-target tube. A sensitivity of 0.002 per cent. w/w of barium was achieved in standard X-ray spectrographic equipment. Changing the X-ray tube as a method of increasing the sensitivity is more convenient than, for example, the use of a helium atmosphere.

PROKOPOVICH AND MCCARTNEY

References

- Davis, E. N., and Van Nordstrand, R. A., Analyt. Chem., 1954, 26, 973.
 Lewis, G. J., jun., and Goldberg, E. D., Ibid., 1956, 28, 1282.
 Gulbransen, L. B., Ibid., 1955, 27, 1181.
 Toussaint, C. J. G., and Vos, G., Philips Serv. Sci. Ind., 1964, 11, (6), 2.
 Dowling, P. H., Hendee, C. F., Kohler, T. R., and Parrish, W., Philips Tech. Rev., 1956/1957, 18, (9), 262.
 Fridman H. and Birke, L. S. Day Scient Intervent 1040, 10, 202
- 6.
- Friedman, H., and Birks, L. S., *Rev. Scient. Instrum.*, 1948, 19, 323. Birks, L. S., "X-ray Spectrochemical Analysis," Interscience Publishers Inc., New York, 1959, 7. p. 54.
- 8. Adler, I., and Alexrod, J. M., Spectrochim. Acta, 1955, 7, 91.

Received May 23rd, 1966

The Loss of Elements during the Decomposition of Biological Materials with Special Reference to Arsenic, Sodium, Strontium and Zinc

BY E. I. HAMILTON, MISS M. J. MINSKI AND J. J. CLEARY

(Radiological Protection Service, Clifton Avenue, Belmont, Sutton, Surrey)

The problems encountered during dry ashing of biological materials are discussed, and an attempt has been made to show the variability of results quoted in the literature. Special reference has been made to sodium, arsenic, zinc and strontium, which have been incorporated into rat tissue by injection. These are representative of the various groups of elements when considering their stability towards heat. It is concluded that each biological sample must be treated individually when considering losses of elements during dry ashing.

It is accepted that, unless the appropriate precautions are taken, many elements are partially or totally lost during the decomposition of biological tissues. Although this subject has been studied in considerable detail, the results are inconclusive for losses incurred as a result of using dry-ashing procedures. In most instances negligible losses occur during wet ashing and this technique will not be discussed in this paper. The losses of elements when using dry-ashing procedures occur as a result of the following factors.

MATRIX EFFECTS-

In many instances the matrix of a sample influences the volatility of the various elements that are present in a variety of chemical forms. Gorsuch¹ used an inorganic matrix to which lead nitrate was added; the volatility of lead was enhanced by the presence of chloride ions, if converted to hydrogen chloride, but depressed by sodium phosphate. The influences of varying concentrations of chloride and phosphate ions are undoubtedly responsible for the differences in lead losses, as shown in Table I, for blood and bone. These pose the problems of losses from intermediate tissues such as connective tissue and cartilage, or from young bone, in which calcification is incomplete.

TABLE I

LOSSES OF LEAD AT DIFFERENT TEMPERATURES AS FOUND BY VARIOUS WORKERS

Author	Matrix	Ashing temperature, °C	Losses
Petrov and Cover ²	Human bone Animal bone	550 to 600	Losses for temperatures $> 600^{\circ}\mathrm{C}$
Holtzman ³	Human bone	900	None
Hursh ⁴	Human bone	900	None
Hasson and Cherry ⁵	Human blood	100	50 per cent.
Hasson and Cherry ⁵	Human blood	600	90 per cent.

The addition of a carrier-free radioactive tracer is a method commonly used to determine chemical yields. For this method to be valid, the tracer must be mixed completely with the stable element at the start of the experiment, and both must be present in the same chemical form. For biological tissues, it is further required that the tracer is incorporated into the same structural position as the stable element. A comprehensive study by Gorsuch^{1,6,7} was made on a matrix of cocoa. In our limited study we have injected sodium-22, zinc-65, arsenic-74 and strontium-85 into live rats so that, before sampling various organs, the radiotracer has become incorporated into the organic tissue matrix; this is considered to be closely related to true biological conditions. After ashing, the losses of these elements were compared with the losses of the same tracers that had been added to dry ox blood. Measurements were made by determining the total γ -activity by scintillation counting of the dish before and after the ashing. The results are given in Table II, in which losses are divided into two types: those occurring as a result of the retention of the radionuclide to the inner walls of the silica dishes during the ashing, and which could not be removed by washing with 6 M hydrochloric acid; and those caused by volatilisation that occurred during the ashing.



Fig. 1. Relationship between temperature and position in a furnace as determined with standard sentinels

ASHING TEMPERATURE-

A general survey of the literature^{1,6,7,8} would indicate a maximum temperature of 450° C to produce negligible losses for the majority of the elements, exceptions being compounds of arsenic, mercury and the halogens. The point that is not emphasised is that in a muffle furnace, with a thermocouple projecting 4 inches from the back of the oven, there is usually a considerable temperature gradient, as shown in Fig. 1, and although the thermocouple may indicate 450° C, there could be a deviation of 50° C from the actual temperature at this setting. Some samples could, therefore, be at 500° C and losses would thus be increased. This problem has been investigated in this laboratory by using standard melting-point sentinels for five different melting-points between 420° and 900° C. At high temperatures the range becomes more pronounced, and at 900° C a difference of $\pm 200°$ C in some parts of the furnace is possible.

TABLE	Π

Losses of various elements from different matrixes ashed at various temperatures

		Tem-	Lo By vola-	ss, per cer By	nt.	Com- pound	Radio-	
Element	Condi- tions* t	pera- ture, °C	tilisa- tion	reten- tion	Total	used for test	nuclide used	Matrix
Strontium Sodium Arsenic Zinc	Blood spiked externally with radio- nuclide	450 450 550 850 450 550 850 850 850 450	9 Slight 28 29 35 0 0 0 0 0	Slight Slight 0 Slight 8 Slight 5 45 Slight	9 Slight 28 29 43 Slight 5 45 —	SrCl ₂ Na ₂ SO ₄ Na ₃ AsO ₄ ZnCl ₂	Strontium-85 Sodium-22 Arsenic-74 Zinc-65	Dry ox blood Dry ox blood Dry ox blood Dry ox blood Dry ox blood Dry ox blood Dry ox blood Human blood
Strontium]	Rats	45 0	Slight 16 5	0 7 Slight	Slight 23 5	SrCl ₂	Strontium-85	Rat-Bone Blood Kidney
Arsenic	injected with radio-	450	44 86 82	5 0 Slight	49 86 82	Na ₃ AsO ₄	Arsenic-74	Rat—Bone Blood Kidney
Sodium	nuclides	450	0 Slight Slight	0 8 0	0 8 0	Na_2SO_4	Sodium-22	Rat—Bone Blood Kidney
	* Th	e sampl	es were	ashed for	16 hour	rs in Vitre	osil dishes.	

All results are to within ± 5 per cent.

April. 1967] DURING THE DECOMPOSITION OF BIOLOGICAL MATERIALS

MATERIAL OF VESSELS USED FOR ASHING-

If chemical or physical reaction is likely to occur between the sample and the material of the vessel during various stages of decomposition, then losses of some elements are to be expected. Magnesium, copper and zinc are lost to the walls of porcelain or silica dishes as a result of chemical reaction at the surface, while gold and lead can be readily deposited or absorbed on to platinum surfaces.^{1,8} The age and previous use of a dish has to be considered; a new silica dish tends to retain some elements (e.g., zinc) more readily than a well used dish.^{1,8}

LITHIUM TETRABORATE FUSION METHOD-

In X-ray fluorescence analysis, matrix problems can often be reduced by the distribution of a small aliquot of the sample into a large volume of material with a homogeneous matrix. Lithium tetraborate⁹ is commonly used, and as the technique requires at least two periods of heating to about 1100° C, it is conceivable that some elements will be at least partially lost by volatilisation from the borate melt. Losses occurring as a result of volatilisation and retention by the dish were determined as before by using sodium, zinc, arsenic and barium radioactive tracers. The results given in Table III show that the losses of the selected elements are surprisingly small.

TABLE III

LOSSES OF RADIONUCLIDES ON FUSION WITH LITHIUM TETRABORATE

			Volatilisation losses		Retention losses			
Radionuclides			Mean, per cent.	Range	Mean, per cent.	Range	Total losses, per cent.	
Arsenic-74			6	4 to 7	9	3 to 16	15	
Barium-133		••	9	5 to 17	0		9	
Sodium-22			1	1 to 5	0		Slight	
Zinc-65			2	2 to 3	0		Slight	

LOW TEMPERATURE ASHERS-

A low temperature asher,¹⁰ such as that supplied by Tracerlab, produces a gaseous plasma by applying radio-frequency voltage to a copper coil surrounding a vacuum chamber in which the sample is placed in an atmosphere of oxygen. Oxygen at low pressures is produced in highly excited states and reacts with the sample, and oxidises at low temperatures of about 100° C. Although low and consistent volatilisation losses have been reported for some seventeen elements, the studies have been limited to a matrix of dry ox blood.

From this brief survey of problems encountered when dry ashing biological samples, it is obviously essential to treat each type of sample individually. It is not advisable to accept losses for a particular element that have been obtained on a significantly different matrix.

REFERENCES

- Gorsuch, T. T., Analyst, 1959, 84, 135. 1.
- 2. Petrov, H. G., and Cover, A., Analyt. Chem., 1965, 37 (13), 1659.
- Holtzman, R., Hlth Phys., 1965, 11 (6), 477. 3.
- 4.
- Hursh, J., Science, 1960, **132**, 1666. Hasson, V., and Cherry, R. D., Nature, 1966, **210** (5036), 591. Gorsuch, T. T., Analyst, 1960, **85**, 225. 5.
- 6.
- 7. -, Ibid., 1962, 87, 112.
- , in Kolthoff, I. M., and Elving, P. J., Editors, "Treatise on Analytical Chemistry," Interscience 8. Publishers, New York and London, 1965, Volume 12, Part II, p. 295.
- 9. Glaisse, F., Quebec Department of Mines, P.R. 327, 1956.
- 10. Gleit, C. E., and Holland, W. E., Analyt. Chem., 1962, 34, 1454.

Received September 8th, 1966

Determination of Arsenic by the Uranyl Salt Method

Part II.* The Radiometric Determination of Microgram Amounts of Arsenic by a Filter-spot Technique

By A. D. WILSON AND D. T. LEWIS

(Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.1)

A development of the uranyl salt method for the gravimetric determination of arsenic is described. Gravimetric manipulations are conducted on a filter-paper base and the arsenic content of the ammonium uranyl arsenate precipitate is determined indirectly by measuring the alpha countrate of the associated uranium.

The method has been demonstrated to be applicable in the range I to $8 \mu g$ of arsenic.

THE use of uranyl salt as a precipitant for arsenic(V) has been reported by Pullar,¹ and Lewis and Davies.² As the ammonium uranyl arsenate precipitate is bulky and gelatinous, rendering filtration difficult, Wilson and Lewis³ prefer precipitation from homogeneous solution, which yields a compact coarsely crystalline material. Following the collection of arsenic from solution as ammonium uranyl arsenate the determination may be completed by a titrimetric or gravimetric procedure. The weighing forms of the precipitate on ignition have been discussed by Wilson and Lewis,³ who have established that the method is capable of a high degree of accuracy.

In applying this method to the quantitative determination of microgram amounts of arsenic by spot analysis on filter-paper, an alternative finish based on the radioactive properties of uranium is now proposed. Arsenite must initially be oxidised to arsenate with bromine. Precipitation is carried out at the centre of a filter-paper and excess of uranyl salt reagent is removed to a peripheral zone by washing, an operation conveniently carried out by the use of a Weiss ring oven. After removal of the filter-paper by ignition, the uranium content of the precipitate is determined by alpha counting and will be proportional to the countrate, provided the material is dispersed in a thin layer so that no self-absorption occurs. As the chemical composition of the precipitate may be represented by the formula, $NH_4.UO_2.AsO_4.nH_2O$, so that arsenic is equivalent to uranium, the arsenic content of the precipitate can be calculated. Such a calculation is independent of the subsequent thermal history of the precipitate, for, provided uranium is not lost the exact composition is of no consequence.

Because the relationship between the alpha count-rate and the uranium content of the precipitate is dependent on the specific disintegration rate of the uranium source used, it follows that the sensitivity of the method is a function of isotopic composition. The specific disintegration rates of various uranium sources differ considerably; natural uranium containing the alpha-emitting radioisotopes uranium-238, uranium-235 and uranium-234, exhibits a rate of $2 \cdot 504 \times 10^4$ disintegrations per second per gram. As the corresponding figure for pure uranium-235, $7 \cdot 89 \times 10^4$, is $3 \cdot 15$ times greater, the use of a uranium source enriched with this isotope will increase the sensitivity of the method up to this limit.

However, such sources are not generally available; most commercially available uranium salts are derived from the residues of isotopic separation plants and are of diminished activity compared with natural uranium. In the present work the uranium source used had a specific disintegration rate of 2.326×10^4 disintegrations per second per gram, *i.e.*, 0.930 of that of natural uranium. The sensitivity of the method is also dependent on the efficiency of the counter, but it is not necessary to determine experimentally either this factor or the specific disintegration rate of the particular uranium source used. Provided a pre-calibration is made of the alpha count-rate associated with a given amount of arsenic by using known

* For details of Part I of this series, see reference list, p. 263.

WILSON AND LEWIS

equivalent amounts of uranium, any subsequent analysis for arsenic may be interpolated within these values. The uranium used must, of course, be derived from the identical source with that used in the preparation of the precipitant; other experimental conditions must also remain unchanged. This procedure was adopted in the work now described.

The method rests on the basic assumption that the activity of the uranium source remains unchanged over the experimental period and this is clearly so when natural uranium is used. The method is also valid for any isotopic mixture of uranium-238, uranium-235 and uranium-234 as these are all long-lived, and although they yield radioactive decay products, the first alpha-emitting daughter in each chain is also long-lived and will therefore not grow to significant proportions for a century or so.

METHOD

REAGENTS---

Uranyl salt precipitant (1)—Prepare a solution of 2 g of uranyl acetate, 2 g of ammonium acetate and 2 ml of acetic acid in 100 ml of water.

Uranyl salt precipitant (2)—Prepare a solution of 8 g of uranyl acetate, 8 g of ammonium acetate and 8 ml of acetic acid in 100 ml of water.

Wash solution (A)—Prepare a solution of 0.5 g of ammonium acetate and 0.5 ml of acetic acid in 100 ml of water.

Wash solution (B)—Prepare a solution of 0.5 ml of acetic acid in 100 ml of water.

Standard uranium solution for alpha counter calibration—Dissolve 0.1873 g of tri-uranium octoxide (derived from the uranyl acetate used in preparing the precipitating reagent) in a little nitric acid and remove the excess of acid by gentle evaporation to dryness. Dissolve the residue in water and dilute to 50 ml exactly.

 $1 \mu l$ of solution $\equiv 3.746 \mu g$ of tri-uranium octoxide ($\equiv 1.0 \mu g$ of arsenic).

PROCEDURE-

Preparation of a calibration graph—By using a Hamilton pipette (0 to 10μ l) transfer measured amounts of the standard uranium solution, in the range 0 to 8μ l, to separate 1.4-cm diameter circles of Schleicher and Schüll 589² filter-paper. Allow to dry and add about equivalent amounts of arsenic(III) solution. (This addition is made to simulate those counting conditions that will exist during an actual determination of arsenic by this method, and to correct for any minor differences in count-rate that the presence of arsenic may induce.) Allow the filter-paper to dry over bromine water vapour and expose to ammonia fumes. Place the paper disc at the centre of an aluminium 2-inch alpha counting



Fig. 1. Calibration of an alpha counter with uranium reagent

planchet. Ignite at 600° C and carefully remove it from the furnace. Cool, moisten with 1 drop of 0.1 per cent. Teepol and spread the ignited material around the centre of the planchet with a glass rod to ensure that the precipitate is dispersed evenly in a thin layer so as to avoid self-absorption. Wash down the rod with one or two drops of water. Evaporate to dryness and re-ignite. Transfer to an alpha counter. From the known weights of uranium applied to each disc, and by using the relationship of uranium equivalent to arsenic, calculate the theoretical concentration of arsenic. Plot these values against the alpha count-rate, less the background. A linear calibration graph should be obtained, as shown in Fig. 1.

Determination—By using a Hamilton pipette (0 to $10 \ \mu$ l) transfer not more than $2 \ \mu$ l of solution to the centre of a Schleicher and Schüll No. 589² filter-paper, 5.5 cm in diameter. Allow the spot to dry over bromine water vapour. Add 5 μ l of precipitant solution; for amounts of arsenic not exceeding 4 μ g, use solution (1), and for amounts in the range 4 to 8 μ g, use solution (2). Place the filter-paper in a Weiss ring oven and wash the precipitate four times with wash solution (A) and four times with wash solution (B), by using 0.02 to 0.03 ml of wash solution each time. Punch out the centre of the filter-paper containing the washed precipitate with a cork borer (diameter 1.4 cm). Place this disc at the centre of an aluminium 2-inch alpha counting planchet and ignite at 600° C. Cool it and moisten the residue with 1 drop of 0.1 per cent. Teepol; spread the ignited material evenly around the centre of the planchet with a glass rod and wash down the rod with one or two drops of water. Evaporate to dryness and re-ignite. Cool, transfer the planchet to an alpha counter and estimate the alpha count-rate. For routine determinations a convenient period is 10⁴ seconds. Read the arsenic content from the calibration graph and subtract from this value that of the blank obtained by using reagents only in the procedure.

RESULTS AND DISCUSSION

An automatic alpha counter (supplied by Isotopic Development Limited) of about 30 per cent. efficiency was used throughout this work and calibrated with known amounts of uranium derived from the same source as the uranyl salt used in the precipitant solution. Values obtained over the entire working range of 0 to $30.0 \ \mu g$ of tri-uranium octoxide (equivalent to 0 to $8.0 \ \mu g$ of arsenic) were represented graphically after subtraction of the background

TABLE I

DETERMINATION OF ARSENIC BY THE PROPOSED METHOD

Alpha count

			<u> </u>			
Arsenic added,		Total count	Time,	Count per	Arsenic found,	
μg	Precipitant	(observed)	10 ⁴ seconds	10 ⁴ seconds	μg	Error
8.0	(2)	5080	4	1270	8.2	+0.2
8.0	(2)	5260	4	1315	8.5	+0.5
8.0	(2)	1279	1	1279	8.2	+0.2
4.0	(1)	2364	4	591	3.8	0.2
4.0	(2)	4478	7	640	3.9	-0.1
4.0	(2)	1218	2	609	3.7	-0.3
2.0	(1)	304	1	304	1.9	-0.1
$2 \cdot 0$	(1)	1373	4	343	$2 \cdot 1$	+0.1
2.0	(2)	2229	6	371	$2 \cdot 1$	+0.1
2.0	(1)	644	2	322	2.0	0.0
2.0	(1)	1310	4	327	2.0	0.0
2.0	(1)	1499	6	250	1.5	-0.5
1.0	(1)	645	4	161	0.9	-0.1
1.0	(1)	769	4	192	1.1	+0.1
0.2	(1)	506	7	72	0.3	+0.1
0.2	(1)	181	3	60	0.2	+0.0
0.0	(1)	85	3	28	Ded. 1	
0.0	(1)	227	6	38 > 32	Background	_
0.0	(1)	30	1	30	for precipitant (1)	
0.0	(2)	177	3	59 โ		
0.0	(2)	618	7	67		
0.0	(2)	180	3	60	Destaural	
0.0	(2)	298	3	100 > 68	background	
0.0	(2)	109	2	55	for precipitant (2)	
0.0	(2)	108	2	54		
0.0	(2)	158	2	79		

April, 1967]

count. The best straight line was drawn through the plotted points (Fig. 1) and a factor of 1.00 μg of arsenic (equivalent to 147 alpha counts per 10⁴ seconds) was obtained. To confirm that there was no possibility of self-absorption within this working range, the calibration was checked at a point well above it (equivalent to 50 μ g of arsenic). A factor of 1.00 μg of arsenic (equivalent to 150 alpha counts per 10⁴ seconds) was obtained, the agreement between these two factors confirming the linearity of the calibration graph.

The behaviour of the method with solutions containing known amounts of arsenic is illustrated by the results presented in Table I. Inspection of this table reveals that the method has been demonstrated to be applicable in the range 1 to $8 \mu g$ of arsenic, as at lower levels (0.2 μg of arsenic) relative error is considerable. The total analytical error associated with a determination by the proposed method is composed of manipulative error and the random error inherent in the statistics of alpha-particle counting. At an arsenic level of $0.2 \,\mu g$ of arsenic the count-rate is low and, in addition, only about twice that caused by the reagent blank. As the variance of counting errors is the sum of sample and blank variances. the counting error is considerable. The method can only be expected to be approximate at the low level (0.2 μ g of arsenic).

Gutzeit's well known chemical method is usually used in the range 5 to 10 μ g of arsenic, with an estimated error of 10 per cent.⁴

References

- Pullar, R. E. O., Z. analyt. Chem., 1871, 10, 72.
 Lewis, D. T., and Davies, V. E., J. Chem. Soc., 1939, 284.
 *Wilson, A. D., and Lewis, D. T., Analyst, 1963, 88, 510.
 Kodama, K., "Methods of Quantitative Inorganic Analysis," Interscience Publishers, a division of John Wiley and Sons Inc., New York and London, 1963, p. 194.

Received May 9th, 1966

* The paper referred to may be taken as Part I of this series.

Direct Injection Enthalpimetry in the Routine Determination of the Hydroxyl Value of Alkylphenols

BY F. L. SNELSON, W. R. ELLIS AND J. VILKAULS

(Shell Chemicals U.K. Ltd., Laboratory Department, Stanlow Refinery, Ellesmere Port, Wirral, Cheshire)

A thermometric method in which the heat of reaction is used as a quantitative measure of the hydroxyl value of alkylphenols is in routine use. This method has replaced a lengthy acetylation procedure that necessitated measuring the difference between two titrations.

By catalysing the acetylation reaction with perchloric acid and then measuring the temperature rise resulting from the heat of reaction, a method has been developed that takes less than 5 minutes to carry out. Standardisation of reagents is unnecessary and only one volumetric measurement is important to the result. The advantages of this method are simplicity and speed, and also a repeatability equal to that of time consuming conventional titration techniques.

In the manufacture of alkylphenols the measurement of the hydroxyl value is an important control analysis which is required at various times during the 24 hours of the day. It is, therefore, desirable to have a simple and fast method of analysis that can be used on the plant by plant-operating personnel.

The laboratory method in use was based on the acetylation of the hydroxyl group with an excess of acetic anhydride and the subsequent hydration of the excess with water. The acetic acid produced was then titrated with standardised sodium hydroxide. A blank determination carried out without sample gave the total amount of acetic anhydride available for the reaction, and the difference between the blank and sample titrations was proportional to the hydroxyl value of the sample.

This whole procedure took 2 to $2\frac{1}{2}$ hours (elapsed time) and required a certain amount of analytical skill for good precision to be achieved.

Recently, Wasilewski, Pei and Jordan¹ showed that various analyses, *i.e.*, EDTA titrations, acid - alkali titrations and anionic - cationic detergent titrations, could be carried out by using direct injection enthalpimetry. This same principle has been applied to the hydroxy-acetylation reaction.

EXPERIMENTAL

The heat produced by a chemical process is a quantitative property proportional to the number of molecules of product formed by the reaction. Under conditions of constant heat capacity this heat of reaction can be measured as a change in temperature, ΔT . If the reaction is rapid and stoicheiometric, and if the amount of one of the reactants is constant and in excess, the measured temperature change, on adding a standard amount of one reactant, is proportional to the concentration of the second reactant.

APPARATUS-

To establish the principle of the method, a simple apparatus was made from readily available components. As previously mentioned, ΔT should be measured under conditions of constant heat capacity, and in the laboratory this condition was most readily achieved by standardising the reaction vessel and stirring conditions by using fixed volumes of reagent and sample, and insulating the reaction vessel effectively from its surroundings.

The change in temperature, ΔT , was detected by a thermistor sensing element situated in the reaction vessel and connected as one arm of a Wheatstone bridge. Out-of-balance signals across the bridge were measured by a standard Sunvic, potentiometric, strip chart recorder with a sensitivity of 50-mV full-scale deflection. Fig. 1 shows the reaction cell, and a schematic wiring diagram of the simple circuit is illustrated in Fig. 2.



Fig. 1. Direct injection enthalpimetric reaction cell

The resistance of the thermistor (a Stantel F2311/30C) was about 2000 ohms at ambient temperature, and its rate of change with temperature was 43 ohms per °C. Hence, with a 3-volt supply to the bridge, a 1° C change in temperature produced an out-of-balance signal of about 20 mV (equivalent to 40 per cent. of the recorder response or 100-mm deflection).

The routine plant instrument was designed for simplicity of operation and to minimise operator variability. The reagent is introduced by a "Zipette" manually operated dispenser, and the sample is injected into the magnetically stirred reaction cell with a Struer automatic dispenser (obtainable from H. Struers Chemiske Laboratorium, Copenhagen, Denmark). The cell is emptied by suction through a water-pump operated probe. In laboratory models of the instrument the reagent may be dispensed with pipettes and the sample by a hand-operated 1-ml hypodermic syringe.

The application of direct injection enthalpimetry to the determination of hydroxyl VALUE-

For direct injection enthalpimetry to be applied successfully to the determination of hydroxyl value, it was necessary to accelerate the reaction so that it became almost instantaneous. The use of perchloric $acid^2$ as a catalyst for the acetylation produced a reaction that was both rapid and stoicheiometric.



Battery = Two Mallory cells RM-42, each 1.35 volt



265



Fig. 3. Enthalpimetric determination of hydroxyl values

To test the validity of the method, the temperature rise caused by the acylation, as indicated by the recorder deflection in millimetres (equivalent to ΔT), was measured for a variety of commercially available alcohols and phenols. A regression curve of the results is shown in Fig. 3 where millimetres deflection per gram of sample is plotted against hydroxyl value. The results show a significant correlation between hydroxyl values and ΔT measurements, although individual calibration would be necessary for different compounds.

Because pure alkylphenols of high molecular weight were not available as calibration standards for the particular analysis which it was desired to standardise, it was decided to calibrate the apparatus by using actual samples for which average hydroxyl values had been determined by repeated analyses with traditional methods. The resultant calibration graph covering the range of hydroxyl values of 1.5 to 2.4 milli-equivalents per gram was linear with respect to recorder response.



Fig. 4. Typical enthalpigram

PROCEDURE-

It can be seen from the enthalpigram shown in Fig. 4 that the recorder deflection is measured from the injection point to the point of intersection of the main rise and the extrapolation of the steady-state temperature line. The peak that occurs above this intersection is caused by a transient heating of the thermistor probe as a result of a brief period of incomplete mixing. The method, which has been in routine use on the plant for 12 months, is briefly outlined as follows.

Rinse the reaction vessel with acetylating reagent, empty it and transfer into it 20 ml of the acetylating reagent. Balance the bridge with the variable potentiometer. Inject 1 ml of the sample into the reaction vessel, and measure the deflection of the recorder in millimetres. Read from the calibration graph the hydroxyl value corresponding to this deflection.

(Measurement of the deflection and the calibration reading can be combined by calibrating a ruler in hydroxyl values.)

The acetylating reagent is made up by mixing together 720 ml of ethyl acetate, 120 ml of acetic anhydride and 4 ml of perchloric acid (sp.gr. 1.70). The mixture should be allowed to stand for 24 hours before use.

RESULTS

The repeatability of the method (2 standard deviations) was determined (see Table I) and was found to be 0.07 absolute or 3.6 per cent. relative, which is better than that achieved when using the traditional method.

TABLE I

COMPARISON OF REPEATABILITY

	Sample B
Sample A	Direct injection
Traditional method	enthalpimetric method
1.82	1.92
1.80	1.93
1.83	1.94
1.81	1.91
1.73	1.93
1.88	1.92
1.92	1.88
1.84	1.92
1.90	1.89
1.88	1.90
1.82	1.89
1.81	1.89
1.79	1.93
1.77	1.93
1.78	1.93
1.81	1.92
1.78	2.00
1.77	1.98
1.75	1.99
1.79	1-99
Mean value 1.82	Mean value 1.93
Repeatability	Repeatability
2 standard deviations 0.10	2 standard deviations 0.07

DISCUSSION

Direct injection enthalpimetry has simplified the analysis as follows.

The acetylating reagent is present in considerable excess and therefore does not require standardisation. An approximate but consistent strength is all that is required.

Only reasonable care is required in the measurement of the 20 ml of reagent, to achieve the constant heat capacity conditions necessary for the ΔT measurement.

The only volumetric measurement critical to the analysis is the 1 ml of sample. This was achieved by using an automatic dispenser or a 1-ml hypodermic syringe used with care.

A permanent record of the ΔT deflection is obtained on a recorder chart, and this can be measured easily with a ruler calibrated in millimetres or, if desired, in hydroxyl values.

The reaction vessel does not require cleaning between tests. A suction probe connected to a water pump is adequate to remove the reactants after each analysis. The reaction vessel is rinsed with reagent and sucked dry immediately before an analysis.

The analysis is completed in less than 5 minutes.

References

- 1. Wasilewski, J. C., Pei, P. T. S., and Jordan, J., Analyt. Chem., 1964, 36, 2131.
- 2. Stelzler, R. S., and Smullin, C. F., Ibid., 1962, 34, 194.

A Note on the Determination of Vapour - Liquid Equilibrium for Multi-component Systems

By K. A. PIKE

(Imperial Smelting Co. Ltd., Avonmouth)

AND D. C. FRESHWATER

(Loughborough University of Technology, Loughborough, Leicestershire)

The use of a gas chromatograph connected to a data-logging system is described for analysing samples taken in the determination of ternary vapour - liquid equilibria.

Data are produced in a form that is ready for processing by digital computer, and therefore their accuracy may be determined within a short time of sampling. There is a distinct improvement in the accuracy of the method over more traditional methods for ternary system analysis.

ONE of the major hindrances to experimental investigation of the vapour - liquid equilibrium of multi-component systems is the time-consuming and usually tedious analysis of experimental samples. Many of these difficulties disappear if gas - liquid chromatography is used, but by itself this is still a lengthy technique for the many samples that have to be examined. However, we have developed a method that not only reduces the time of operation to a minimum but also gives the actual composition results directly from the detector output. These results can also be produced in a one-step operation from sample injection, in a form suitable for immediate processing by digital computer. The method has been developed for a three-component system which was of particular interest for other purposes.¹

The method can be easily adapted to analyse four or more components.

ANALYSIS PROCEDURE

The main components of the equipment used are shown in the form of a flow-chart (Fig. 1). The data-logging system is multi-purpose and is used for recording experimental results in the Chemical Engineering Laboratories of Loughborough University of Technology.



Fig. 1. Flow-chart of analytical equipment

The gas-liquid chromatograph used was a Shandon universal model with a flame thermocouple detector. The chromatograph column (20 feet $\times \frac{1}{4}$ inch, external diameter) was packed with Celite, and diglycerol was used as the stationary liquid phase. This column was maintained at 100° C. The detector output was fed simultaneously to a chart recorder and also the data-logging system. At the conditions chosen, samples of the system, acetone - methanol - isopropyl alcohol, which were to be analysed, gave three well separated peaks on the recorder chart.

The areas of these peaks were measured by recording several peak height values, read at regular time intervals and then performing an integration to obtain the area. A transmitting potentiometer was incorporated in the chart recorder, which enabled the alterations in the thermocouple output to be read and then recorded by the data-logging system.

The peak height was recorded at precise 1-second intervals by the data-logging system. Each peak had a duration of about 100 seconds, and considerably more readings for each peak were obtained to ensure that the whole peak was sampled.

Peak areas were obtained by integrating the precisely recorded peak heights by using a form of Simpson's rule—

$$f(x) dx = \frac{h}{3}(y_0 + 4y_1 + y_2) + \frac{h}{3}(y_2 + 4y_3 + y_4) + \frac{h}{3}(y_4 + 4y_5 + y_6) + \text{error function} \quad (1)$$

(where h = increment 1 second, and y = peak height above base-line), which gives—

$$f(x) dx = \frac{h}{3}(y_0 + 4y_1 + 2y_2 + 4y_3 + 2y_4) + \text{error function} \quad .. \quad (2).$$

By sampling the peak height above a base-line, which is calculated for each peak in turn, the method allows for the slight drift of base-line that can occur when using an amplifier over an extended period. For the type of peak obtained with the signal voltage equal to the base-line voltage immediately before and after a peak, the first and last terms of equation (2) tended to zero and were neglected. The error function was also negligible for the size of increment being considered. The peak areas so obtained were normalised by using heats of combustion, with methanol being considered as the basic component. The normalised peak areas were then converted into mole fractions of the components present.

All of the computations necessary to produce an analysis result were carried out by a digital computer programme compiled in Fortran for the I.B.M. 1620 data processing system. Other functions of the programme were to compare an analysis result with previously defined accuracy limits. If the results were of the required accuracy a data tape was compiled for use in other programmes. Data of insufficient accuracy were simply printed out and not punched out as a data-source tape.

When operating the analysis procedure for the systems composed of acetone - methanolisopropyl alcohol, it was necessary to accumulate a number of vapour - liquid equilibrium samples that required analysing to make optimum use of the system. The peak height information was then accumulated as a continuous reel of paper tape that could be stored until processing time was available on the digital computer. The processing time for the longest reel of data containing some thirty ternary analyses was about 20 minutes. The same programme as that used for ternary samples was also used for binary samples. This was possible because the programme would integrate the signal voltage *less* the base-line voltage for a period where a peak should have occurred and obtain an area of zero, as during this period the base-line voltage was equal to the signal voltage.

ACCURACY OF THE METHOD-

Besides the distinct advantage of the convenience of the method over more traditional techniques, there are significant improvements in other directions. With the physical property measurement technique for a ternary system, Jones² has quoted an accuracy of analysis of ± 0.2 per cent., while the procedure outlined here has an accuracy of better than ± 0.1 mole per cent. This is a small but significant improvement when considering vapour - liquid equilibrium results. The gas - liquid chromatograph was calibrated with standard samples made up by weight to the fourth decimal place, the total weight of a sample being about 10 g.

In the event of a contaminant entering the system, which is unlikely in a vapour - liquid equilibrium study where very high purity components are required, the digital computer programme would identify the whole analysis result as being of insufficient accuracy for further processing. Again in a vapour - liquid equilibrium study this would not be too serious as the experimental point could be repeated.

OTHER APPLICATIONS-

In addition to its use for analysing complex multi-component mixtures, gas - liquid chromatography can be used to obtain, by direct measurement, activity coefficients under conditions tending towards infinite dilution. The method depends upon obtaining retention volume data, which, in turn, require the determination of retention times. Retention times are variously defined as being the time taken from actual sample injection to the emergence of the maximum peak height, or as the time between emergence of an inert-gas peak and the emergence of the maximum peak height. A feature of the analysis procedure described in this paper is that the emergence of peaks can be accurately recorded to small time intervals. Thus the timing operation for retention volume determination can be carried out automatically and to a high degree of accuracy.

The technique could also be used advantageously linked to an equilibrium still along the lines of the suggestion by Wichterle and Hálà.³ Besides providing analyses of a high accuracy, the continuous analysis of the mixture could be used to ensure that equilibrium between liquid and vapour phases was being achieved.

References

1. Pike, K. A., Ph.D. Thesis, Loughborough University of Technology, 1965.

2. Jones, T. H., Ph.D. Thesis, University of Birmingham, 1962.

3. Wichterle, I., and Hálà, E., Ind. Engng Chem. Fundamentals, 1963, 2, 155.

Received August 1st, 1966

The Preparation of Analysis Samples of Hard Materials with a Boron Carbide Mortar

BY J. F. BOULTON AND R. P. EARDLEY

(British Ceramic Research Association, Queens Road, Penkhull, Stoke-on-Trent)

Boron carbide has advantages as a grinding medium for hard ceramic materials. Owing to its hardness the contamination is slight and does not interfere with the normal chemical analysis.

Contamination that occurs when grinding fused alumina, sillimanite, silicon carbide and magnesite has been determined by a spectrometric method. The degree of contamination introduced by the boron carbide appears to be an order of magnitude lower than when a 95 per cent. alumina mortar is used.

THE analysis of harder ceramic materials is usually complicated by the problem of preparing a pure powdered sample, as severe contamination must be experienced if the sample is ground in agate (as much as 5 per cent. of silicon dioxide for a sample of corundum). The usual technique is to prepare two samples, one ground in alumina and the other in iron. The analysis is carried out on the iron-ground sample, the true iron content being determined on the alumina-ground sample. With the purer and harder materials this correction is not usually sufficiently stringent, as the alloy content of the iron and the minor constituents of the alumina become significant, and therefore two full analyses are required. Even then the analyst has to accept the assumption that the minimum content of impurity determined is that of the pure sample.

Boron carbide mortars have been available for some time from American sources, but prototype production in this country led to the experiments to be described. Boron carbide is extremely pure, and contributes to the material two elements that are not usually determined in the analysis, do not interfere with the normal analytical method, and are easily determined.

EXPERIMENTAL

Samples of 0.5 g of the materials of interest were ground in a boron carbide mortar of 2 inches diameter for varying periods of time from 5 to 30 minutes. The samples obtained were analysed by using a direct-reading spectrometric powder technique with dilutions of boron carbide in the base material as standards. When the original material was too coarse to allow adequate mixing of the standards, the latter were ground in an alumina mortar and the degree of contamination evaluated.

The materials examined and the results obtained are shown in Table I.

To aid comparison with other methods of grinding, some samples were ground in an alumina mortar known to have contents of about 0.8 per cent. of chromium trioxide and 4 per cent. of silicon dioxide. The chromium was a useful monitor for determining the contamination of the coarse alumina grain by this mortar, and the results obtained are shown in the fourth column. The result for magnesite was determined directly, and that for the sillimanite could easily be in error owing to the high (0.03 per cent.) content of chromium trioxide of this material. Comparative results were not attempted for silicon carbide because of the risk of serious damage to the mortar, and because it was not thought that this would be attempted in practice.

It should be noted that the results for a 30-minute grinding are really only of theoretical interest, as all of the samples were reduced to a satisfactory degree of fineness after grinding for 10 to 15 minutes As this grinding was accomplished with a pestle roughly fashioned from a piece of stock rod, it is fair to conclude that this period could be reduced by the use of a pestle of profile matched with that of the mortar. A larger mortar would have been useful in that it would allow the preparation of sample increments larger than 0.5 g. It was found that boron carbide powder was readily decomposed by the fluxes used in routine analysis, such as sodium carbonate and the mixture with boric acid. The use of sorbitol or glycerol

BOULTON AND EARDLEY

as a complexing agent should remove risk of interference with the silicon determination. The extent of contamination should be easily determined, if not by direct-reading spectrometry, then either by emission spectrography or colorimetric methods.

TABLE I

CONTAMINATION INTRODUCED BY GRINDING IN BORON CARBIDE

Material ground	G	rinding time, minutes	Boron carbide introduced, per cent.	Alumina produced by grinding in an alumina mortar (for comparison), per cent.
Alumina powder, less than 80 B.S. mesh		5	0.13	—
-		10	0.10	_
		15	0.18	_
		30	0.16	
Alumina grain, about $\frac{1}{16}$ inch diameter	••	15	0.18	5
Silicon carbide, less than 80 B.S. mesh		5	0.45	
		10	0.65	_
		15	0.70	_
		30	0.85	
Sillimanite, about $\frac{1}{8}$ inch diameter		5	0.03	about 0.25
		15	0.04	_
		30	0.02	
Magnesite, dead-burnt, less than 80 B.S. m	iesh	15	<0.01	0.4
•		30	0.01	-

CONCLUSION

Boron carbide is a useful mortar material for the preparation of hard ceramic samples. The degree of contamination is low, easy to determine, and should have little effect on the normal analysis.

Increase in the capacity of the mortar should make it more generally useful, and improvement in the profile of the pestle should make it more efficient.

The authors thank the Carborundum Co. Ltd. for making the prototype mortar available for these experiments, and the Director of Research, Dr. N. F. Astbury, for permission to publish this work.

Received October 3rd, 1966

Book Reviews

KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY. Volume 9. FERRO-ELECTRICS TO FOAMS. Edited by HERMAN F. MARK, JOHN J. MCKETTA, jun., DONALD F. OTHMER and ANTHONY STANDEN. Second Edition. Pp. xvi + 901. New York, London and Sydney: John Wiley & Sons Inc. 1966. Price £16 18s.; price per volume for subscribers to the complete set of 18 volumes £13.

This, the ninth volume of this series, corresponds with the half-way point in its publication (see *Analyst*, 1963, 88, 899 *et seq*.). Statistically, this means about 8200 pages, and almost six letters of the alphabet in three years. It is interesting to note that the subject matter of chemical technology falls chiefly in the first quarter of the alphabetical sequence.

Over one-third of the present volume, *i.e.*, 341 pages, is taken up with the treatment of fluorine the element, inorganic fluorine compounds and organic fluorine compounds, under these three separate headings. Of this total, 159 pages deal with inorganic fluorine compounds, which in itself is a significant reflection of the importance of this element in modern chemical technology. Substances dealt with in some detail include aluminium trifluoride, which is used in the electrolytic process for refining aluminium; cryolite, which can be a natural or synthetic product these days. and in this connection it is important to note that different methods of analysis apply accordingly; boron trifluoride, which is a catalyst, and whose manufacture and analytical methods are described: and fluoroborates (used as a flux, for grinding and in electroplating), which also present certain analytical problems, but can be precipitated quantitatively as nitron fluoroborate. Another interesting analytical problem is raised by chlorine trifluoride, which reacts violently and inconsistently with water. This precludes the classical chemical methods for determining chlorine, but physical methods depending on freezing-point depression, infrared absorption or gas chromatography have been suggested with more satisfactory results. As might be expected there are sections dealing with the toxicity of the various fluorine compounds, and also with the often specialised and difficult problems of handling and transport.

The class of organic fluorine compounds (described collectively as "fluorochemicals") is regarded as of sufficient importance to justify an historical introduction, which is followed by a detailed treatment of the surface chemistry of these compounds. This leads to a theory of adhesive action, which is also invoked to explain adhesion, *i.e.*, release properties. This part of the subject is treated on a theoretical basis, and will be of value to those interested in adhesives as distinct from fluorine compounds as such. The numerous other usual and unusual technological applications of organic fluorine compounds include the surface treatment of textiles, the separation of olefins by preferential reaction, the eradication of lampreys from lakes, uses in inhalant anaesthetics, and (for the inert compounds) in gaseous dielectrics. In addition there is, of course, the wide range of polymers based, for instance, on polytetrafluoroethylene; and the manufacture of a wide range of solvents. It is not difficult, therefore, to justify the large proportion of this volume devoted to this element of many derivatives and applications, and indeed the monograph is probably unique in its coverage.

Many of the other monographs in this volume, although shorter, are of equal importance although in a more restricted sense. Perhaps the most outstanding are those dealing with man-made fibres (20 pages) and vegetable fibres (15 pages). Closely allied to the latter subject, and conveniently near it alphabetically, is the monograph on film materials (24 pages); and this in turn links up with the monograph on film deposition techniques, a short but informative account of the more important methods now being employed. The monograph on vegetable fibres has as its author D. Himmelfarb, of the Boston Naval Shipyard, and its contents may be described as of a textbook nature supplemented by some statistical data. As is to be expected, the bias of the monograph is towards uses as cordage and textiles rather than for other purposes, such as papermaking pulp. There is a useful table of properties, but it is remarkable that a monograph on this subject should make no reference, either in the text or pictorially, to appearance under the microscope.

The monograph on man-made fibres is by H. F. Mark (of the Polytechnic Institute of Brooklyn) and S. M. Atlas. The first part is also descriptive and of a textbook nature, but Professor Mark's views (well known to his colleagues in this field) on the future of such fibres are set out in the second half of the monograph, and make interesting and stimulating reading. The production of conjugate fibres (which is based on the principle of the use of two polymers having sufficiently similar characteristics to make spinning them into bi-component fibres a possibility) is an example.

The monograph finishes with a section on research possibilities in connection with the fully synthetic fibres, *e.g.*, polyesters; this continues the theme of future developments. There is nothing of analytical interest in this monograph, but it will serve nevertheless as a valuable contribution to the general knowledge of any chemist on this subject.

The monograph on films (described as a flat section of thermoplastic resin or regenerated cellulose material) deals with a wide variety of familiar (and some unfamiliar) materials, including the fluorochemicals already mentioned. In this connection the term "Cellophane" is used in such a way as to give the impression that it is a generic description of regenerated cellulose of the rayon type, and not the product of a particular company. It is also stated that it burns at a rate similar to that of newsprint, which may be accurate in theory in view of its cellulosic composition, but is hardly so in practice because of the presence of additives such as plasticisers.

Another important monograph is that on fertilisers (126 pages). As its author points out, this industry is in a phase of rapid change. It is no longer an industry concerned primarily with the mixing and handling of materials, but is a major division of the chemical industry and it is becoming more and more based on chemical engineering technology. The increasing world-wide pressure of population and the necessity to find food to sustain it will undoubtedly accentuate this trend. The monograph deals with the various types of fertilisers and methods of winning, handling and processing them both from a practical and an economic point of view. There is also a section on evaluation, although the subject is dealt with more from the point of view of the chemical constituents than that of chemical analysis. Individual fertilisers are then discussed, and there is a special and interesting reference to micro-nutrients, the term used to describe certain inorganic compounds that sometimes have spectacular effects on the efficiency of fertilisers containing them. It is interesting to note that the greatest consumption of any one micro-nutrient in the United States in 1962 to 1963, was that of zinc sulphate, and this totalled only about 6000 tons; so that the use of the prefix "micro" in this connection is fully justified. Another monograph of special interest to analysts is perhaps that on flavour characterisation (11 pages). As it happens, this is followed by the monograph on flavours and spices. The former difficult subject is dealt with from the point of view of isolating the volatile flavouring compounds from certain solid foods, followed by their fractionation and chemical identification. Gas chromatography, infrared spectrophotometry and mass spectrometry all play an important part in this work, which can be applied to fruits of all kinds, beverages, meats, dairy products, spices, fats, oils, vegetables and starch products. The procedure, therefore, is quite distinct from organoleptic evaluation, although the two methods should be used together rather than independently; and there is a cross-reference to a monograph to come on organoleptic testing.

The remainder of the monographs in this volume likely to be of interest to the analyst can be mentioned only by name. They include fire-resistant textiles, fish, filtration, flotation and foams; for the more mechanically minded there are fluid mechanics, fluidisation and ferro-electrics.

It will be seen that the half-way milestone in the publication of this work fully maintains the high standard of its predecessors. Julius Grant

HANDBUCH FÜR DAS EISENHÜTTENLABORATORIUM. BAND 2. DIE UNTERSUCHUNG DER METAL-LISCHEN STOFFE. Edited by CHEMIKERAUSCHUSS DES VEREINS DEUTSCHER EISENHÜTTEL-LEUTE. Pp. xxiv + 441. Verlag Stahleisen mbH: Dusseldorf. 1966. Price DM 88.

This is the second edition of Volume II, Analysis of Metallic Materials, of the comprehensive "Handbook for the Iron and Steel Works Laboratory" issued by the V.d. E-h (the other volumes being I—Analysis of Non-metallic Materials, III—Sampling, and IV—Referee Methods). The first edition appeared in 1941 after a delay due, said the editors with remarkable restraint, "to the political developments of the last two years." Difficulties of the post-war years have likewise delayed the second edition, but the delay has made it possible to include recent developments such as the application of X-ray fluorescence to the analysis of steel and ferro-alloys.

After a general introduction and a section on reagents, a chapter is devoted to methods for removing large amounts of iron, chromium and other elements from solution; this includes a useful account of the application of mercury-cathode electrolysis.

The longest section (150 pages) is on the determination of alloying elements and residuals, including gases, in iron and steel. Although anyone who wants to determine beryllium, thorium or uranium will have to refer to the first edition, it is hard to think of anything else even rarely added to steel which is not covered here. For most elements alternative methods are given.

The next hundred pages on the analysis of ferro-alloys provide the best treatment of the subject I have seen. Methods are given not only for the main elements in all of the most important ferroalloys (including some that are often omitted, such as ferro-phosphorus), but also for impurities that are of increasing interest to the steel maker today. Under ferro-tungsten, for example, we have methods for determining C, Si, Mn, P, S, Al, As, Cr, Cu, Mo, Ni and Sn. Ferro-niobium - tantalum is fully dealt with, although sulphurous hydrolysis as a method of obtaining mixed oxides should now be scrapped. Anyone interested in the analysis of tungsten metal will want to know more than the iron and oxygen contents. There is a brief section on the analysis of hard metals.

Perhaps no other technique offers quite the same combination of benefits and headaches as X-ray fluorescence. This must be the first work of its kind to devote more space (39 pages) to X-ray fluorescence than to emission spectrography; the possibilities are indicated, and 119 references are given to papers on the subject.

Sections on micro-chemical analysis and identification of structural constituents follow, and a full treatment of the analysis of metal coatings is given.

There is a detailed list of contents and a full index. The book is excellently printed on high quality paper and strongly bound, and is worth $\frac{1}{8}$ to anyone who can make full use of it.

G. M. HOLMES

QUALITATIVE ORGANIC ANALYSIS. Second Edition. By B. HAYNES. London, Melbourne and Toronto: Macmillan, incorporating Cleaver-Hume Press. 1966. Price 25s.

As long as examining bodies continue to rely on the identification of organic compounds as a basis for assessing ability in practical organic chemistry, there will remain a need for books of this kind. Much care and thought has been given to the writing of this manual, which can be thoroughly recommended.

The importance of a thorough preliminary examination and the necessity for a logical collation of all the observations are well stressed. The student who uses this book intelligently will soon realise that functional tests, valuable as they are, cannot be regarded as the organic chemist's equivalent of the inorganic group tables. In this way, he will avoid the pitfalls that frequently arise from hasty or haphazard use of functional or specific tests, or even through a cursory scanning of a table of melting-points.

The various types of compounds are grouped into eight sections, with the corresponding generic tests for the different types in the relevant chapters. A table giving the characteristic ultraviolet and infrared absorption frequencies of the principal organic functional groups (*e.g.*, carbonyl, ethylenic) could well have been included in this part of the book. The preparation of appropriate derivatives is dealt with in a separate chapter, which is followed by a comprehensive table of melting- (or boiling) points of compounds and their derivatives. The instructions for carrying out the tests are clear and unambiguous, while the hazards involved in certain laboratory manipulations are duly emphasised.

Finally, as is most desirable in a laboratory manual, the book is clearly printed on high quality paper, and is very good value for money. F. G. ANGELL

PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY. By WALTER E. HARRIS and HENRY W. HABGOOD. Pp. xvi + 305. New York, London and Sydney: John Wiley and Sons Inc. 1966. Price 83s.

Gas chromatography must rank as one of the most significant developments that has ever occurred in analytical science, and in the course of its widespread application to the problems of chemical manufacture it has inevitably encountered mixtures of components with a wide range of boiling-points. Columns operating at a fixed temperature cannot deal conveniently with mixtures of this kind, and the device of raising the column temperature during separation, so as to speed up the higher boiling components, was an obvious step. Programmed temperature gas chromatography, as this is called, has been used empirically on many occasions, and so successful has it been that freedom to vary column temperature is now a most important factor in comparing the merits of commercial instruments.

Walter E. Harris, Professor of Analytical Chemisty in the University of Alberta, and Henry W. Habgood, Chief of the Fuels Branch of the Research Council of Alberta, have collaborated since 1958 in developing the theoretical treatment of programmed temperature gas chromatography, and in the book that they have published jointly they have attempted to give a unified and
consistent presentation of the theoretical equations that have been produced, both by themselves and by other workers in the same field.

Retention temperature is presented as the most important parameter in programmed temperature gas chromatography, and the first four chapters of the book contain a detailed and mathematical treatment of the theory of retention, leading to the development of characteristic equations from which the retention temperature can be calculated for any component of a mixture, provided that one knows the isothermal retention volumes of that component over a range of temperatures on a column containing the same stationary phase; the fifth chapter deals with the factors affecting resolution of components having similar retention temperature, and the sixth with the use of retention indices as a method of identifying unknown components.

In the last three chapters, the authors turn to the practical application of these theoretical equations and to the apparatus required for programmed temperature gas chromatography, and they conclude with a section on preparative and pyrolysis gas - liquid chromatography carried out under programmed temperature conditions.

The book is not, therefore, an exclusively theoretical treatise, and the later chapters on practical aspects will undoubtedly be of value to everyone concerned with the use of programmed temperature gas chromatography: nevertheless, it must be recognised that the real challenge is presented by the mathematical treatment given in the first part, and it is the challenge of the theoretical approach compared with the instinctive, experimental approach to a problem that is adopted by most commercial analysts. While countless problems have been solved by the empirical method, a fundamental understanding of the separation process must be beneficial, and may well become the preferred method of attack in the future.

Many will find this book rather tough going, but those who do are recommended, in the preface, to read the easy parts first and come back to the more difficult ones later. This, one feels, is good advice, and if it is heeded it should enable all concerned in the field of gas - liquid chromatography, expert and novice alike, to benefit from the painstaking labour of these two authors.

The book is clearly printed, well bound and apparently free from typographical mistakes; each chapter is neatly summarised, and both subject and authors indexes are included.

H. E. STAGG

POLAROGRAPHY 1964. PROCEEDINGS OF THE THIRD INTERNATIONAL CONGRESS, SOUTHAMPTON.
Volumes 1 and 2. Edited by GRAHAM J. HILLS, Ph.D., D.Sc., F.R.I.C. Pp. xxviii + 685 (Volume 1); xxviii + 687-1164 (Volume 2). London and Melbourne: Macmillan. 1966. Price £15 15s. per set.

These two volumes are a record of the Third International Congress of Polarography held in Southampton, under the auspices of the Polarographic Society.

The 89 papers presented were grouped into five main categories: Theory, Methods and Instrumentation; the Analysis of Inorganic Systems; the Analysis of Organic Systems; the Analysis of Biological Systems; and the Study of Non-aqueous Systems.

Six principal lectures were given. Professor Kolthoff gave a classical account of the fundamentals of organic polarography in inert organic solvents, and a lucid picture of the current trends in organic polarography was provided by Dr. Zuman. Electrochemical methods for determining the kinetics of fast electrode processes was the subject of Fleischman's paper, while Barker described the study of fast electrode processes by non-linear relaxation techniques. A brave attempt to introduce a new and confusing electrochemical terminology was made by Milazzo with his paper "Temperature Coefficients of the Electrode Tension of Individual Electrodes." In the final introductory lecture, Breyer described some practical applications of a.c. polarography.

A large proportion of the papers either describe or have some bearing on analytical methods. In view, however, of the increasing application of polarographic methods, particularly in the field of rapid automated analysis, many of the more theoretical contributions, especially those dealing with the rôle of the various factors that influence the electrode process, also have some practical importance. Although it is invidious to pick out a single contribution, the excellent paper by Fisher, Belew and Kelley, in which recent advances in d.c. polarography are described, is a very valuable and readable treatment of the subject.

It is evident that these proceedings cover the whole spectrum of polarographic and related techniques. This fact, together with the large number of references quoted, makes it a valuable reference book. Although the price is rather high, the book can be recommended to all those wishing to keep abreast of developments in this field. B. FLEET

276

April, 1967]

ADVANCES IN X-RAY ANALYSIS. Volume 9. Edited by GAVIN R. MALLETT, MARIE FAY and WILLIAM M. MUELLER. Proceedings of the Fourteenth Annual Conference on Applications of X-Ray Analysis. August 25–27, 1965. Pp. x + 544. New York: Plenum Press. 1966. Price \$22.50.

This volume contains 46 of the papers presented at the Denver Conference on the Applications of X-Ray Analysis, held in August, 1965, and they are arranged in the now familiar format.

Aspects of a wide range of subjects are considered, including electron-probe microanalysis, uses of soft X-rays in emission analysis, X-ray diffraction and fluorescence analysis. Several papers on X-ray diffraction topograpy are included.

A group of 8 papers on the effects of chemical combination on X-ray spectra and on X-ray absorption fine structure, together with a record of an open discussion at the Conference on the first of these topics, will be of special interest to chemists. These papers show clearly that, in addition to its use in determining the elemental composition of a sample, X-ray spectrochemical analysis can be used to investigate bonding. Significant effects are detected in K and L spectra of elements of low atomic number arising from changes in the state of bonding, and results are reported for silicon, boron, carbon, nitrogen, chlorine and sulphur.

Reviving interest in high intensity, rotating-anode X-ray tubes is reflected in a paper describing a de-mountable tube dissipating $7\frac{1}{2}$ kW.

The publishers have maintained their good standard of production and the time that has elapsed between conference presentation and publication is again relatively short. The work is recommended for those whose interests lie in X-ray analysis. E. A. KELLETT

ELECTRONIC ELECTROCHEMICAL MEASURING INSTRUMENTS. By D. DOBOS. Translated by T. DAMOKOS and Z. ERDÖKÜRTY. Pp. 449. Budapest: Akadémiai Kiadó. 1966. Price 105s.

This is an English edition of a work first published in Hungary. It is intended primarily for those who use electronic instruments in the chemical field. There must be many who require a book on basic electronic principles with the emphasis on electrochemistry rather than communications, and in the choice and arrangement of the subject matter this book should be well suited to fill that need.

It starts with sections on the construction and properties of the various components used, and proceeds to basic circuit configurations: amplifiers, stabilisers, oscillators, etc., followed by sections on the principles of electrochemical measurements.

Unfortunately, it falls far short of the standard of clarity and orderly presentation of information that is so essential in an introductory work. It seems likely that this is due largely to inadequate translation; much of the English is clumsy, explanations are often devious where they should be concise and clear, and various words and phrases appear which are certainly not in common use. Difficulties of this sort are bound to arise when translating into a foreign language, but much of it could have been avoided had the proof been checked by an Englishman with even a superficial knowledge of the subject. He might also have noticed some of the printing errors, which are quite numerous, and corrected the author's few mistakes, such as the parallel connection of stabilisers in Fig. 160, which is quite impracticable. It is a pity that the publishers who have produced a very attractive volume in layout, printing and illustrations do not seem to have taken this step.

There is a large section occupying nearly half the book in which commercially available instruments are described in detail. The instruments are selected from many European countries, including a fair proportion from Britain. The information appears to be drawn mainly from manufacturers' instruction manuals which are usually only available to purchasers, rather than from sales literature. In some cases it is quoted in extreme detail, including full circuit diagrams, component schedules, operating instructions and fault finding procedure. All of the instruments are illustrated.

Including nearly 60 pH meters and titrators, also 14 conductance meters and instruments for high frequency measurements, polarography and coulometry, this section provides the reader with an opportunity to compare instruments from many countries on the basis of much more detailed information than he could hope to acquire himself. In this lies the chief value of the book; the reader seeking instruction in basic electronics would do better to look elsewhere.

Continental symbols are used in circuit diagrams throughout the book.

There is an extensive international bibliography classified by subject. G. Ross TAYLOR

PROGRESS IN NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. Volume I. Edited by J. W. EMSLEY, J. FEENEY and L. H. SUTCLIFFE. Pp. viii + 386. Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris and Braunschweig: Pergamon Press. 1966. Price 105s.

Should nuclear magnetic resonance be new to any reader of this journal, it is best stated early that n.m.r. is predominantly a technique for the analytical chemist. I use the word technique carefully, for the progress reported in this volume is largely progress in techniques.

This is the first of two volumes. The editors point out on the dust jacket that the first volume is concerned with basic theory and spectral analysis, and the second with the correlation of spectral parameters with molecular structure. It is also noted that the two volumes have been written as a single entity, with extensive cross-referencing.

Volume 1 of this new series contains four chapters and is best judged, initially, by considering them separately.

Dr. Haworth and Professor Richard's chapter on the use of modulation in magnetic resonance gives a clear understanding of this technique and is applicable to both nuclear magnetic and electron paramagnetic resonance. The theory of modulation is considered in some detail, and this chapter will be of interest and of practical use to all radio-frequency and microwave spectroscopists. In order not to mislead the reader, I should point out that this chapter forms only a very small part of the book, although its size in no way detracts from its quality.

Chapter 2 is concerned with high resolution nuclear magnetic double and multiple resonance and explains how these techniques lead to more powerful methods of obtaining additional information in the interpretation of the single resonance spectrum. Many practical examples of double resonance experiments are given, and instrumentation is dealt with very clearly. Other sections cover the theory and applications of the technique. The glossary, appendices and references are extremely comprehensive.

The third chapter deals with computer techniques in the analysis of n.m.r. spectra. Since the acceptance of computer techniques to facilitate identification of spectra there has been a need for a review which could fully explain and exploit this, and which is also understandable to the non-computer expert. This review achieves many of these requirements. The approach is clear and systematic, and the references are good. The four appendices are particularly useful, and include problems dealt with by various computer programmes, a complete sample problem, and, particularly useful to the non-specialist, a good explanation of computer terminology.

Chapter 4 deals with the progress achieved in the n.m.r. field on phosphorus compounds with special emphasis on organic compounds. A comprehensive account is given of the information derived from the resonance spectra of proton, fluorine and other nuclei, with the exception of phosphorus-31. From an exhaustive literature survey, all of the significant features have been well tabulated and a complete formula index is given. Besides providing bibliographical information to those concerned with the structural chemistry of phosphorus, a rationalisation of available data is also given, in relation to molecular features.

This book will be very useful to n.m.r. specialists, and comes at a time when there is need for full coverage of this rapidly expanding branch of chemistry. This particular volume, I might venture to add, by the nature of its contents relating to techniques, is equally applicable to those concerned with the sister subject to n.m.r., namely, electron spin resonance.

The complete volume has a good index, is extremely well bound, has clear print and is easy to read. Typographical errors are at a minimum. The price of this book is ± 5 5s., which I think is rather a high price to pay to keep abreast of new developments. This should not stop readers from buying a copy. H. M. ASSENHEIM

Errata

DECEMBER (1966) ISSUE, p. 790, caption to figure. For "Fig. 1. Chromatogram of a Scotch allmalt whisky on polyethylene glycol 200" read "Fig. 1. Chromatogram of a cognac brandy on diethyl tartate."

IBID., p. 792, caption to figure. For "Fig. 2. Chromatogram of a cognac brandy on diethyl tartate" read "Fig. 2. Chromatogram of a Scotch all-malt whisky on polyethylene glycol 200."
IBID., p. 794, reference 2. For "1965, 26" read "1964, 27."

FEBRUARY (1967) ISSUE, p. 108, 7th line. For "Potassium permanganate, N" read "Potassium permanganate, 0.1 N."

IBID., p. 141, 7th line from the bottom. For "hexane ozonide" /read "hexene ozonide."

278

Summaries of Papers in this Issue

Heterocyclic Azo Dyestuffs in Analytical Chemistry A Review

SUMMARY OF CONTENTS

General introduction and scope

1-(2-Pyridylazo)-2-naphthol

General properties

Applications as a complexometric indicator Applications as a spectrophotometric reagent Other applications in analytical chemistry

4-(2-Pyridylazo)-resorcinol

General properties Applications as a complexometric indicator Applications as a spectrophotometric reagent Other applications in analytical chemistry

Other pyridylazo dyestuffs and related compounds

Thiazolylazo and benzothiazolylazo dyestuffs

Miscellaneous heterocyclic azo dyestuffs

General

Azo derivatives of 8-hydroxyquinoline

Conclusions

R. G. ANDERSON and G. NICKLESS

School of Chemistry, The University, Bristol 8.

Analyst, 1967, 92, 207-238.

REPRINTS of this Review paper will soon be available from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1, at 5s. per copy, post free.

A remittance for the correct amount, made out to The Society for Analytical Chemistry, MUST accompany every order; these reprints are not available through Trade Agents.

The Determination of Plutonium in Refractory Materials by Electrometric Methods after Dissolution by Fusion with Ammonium Hydrogen Sulphate

A fusion with ammonium hydrogen sulphate at 400° C has been developed for the dissolution of refractory materials containing plutonium dioxide. On cooling, each melt is leached with sulphuric acid to produce a solution suitable for analysis for plutonium by electrometric methods. Plutonium concentrations (about 2 mg per ml) are determined either by a potentiometric titration based on the reduction of plutonium(VI) to plutonium(IV), or by a controlled-potential coulometric method, the Pu^{3+} - Pu^{4+} couple being used. Both techniques are suitable for the accurate determination of plutonium with a precision of better than 0.20 per cent. (coefficient of variation) for about 5-mg amounts or less. The behaviour of many other elements in these methods has been studied in some detail.

The fusion technique has been found to be suitable for the dissolution of several refractory materials, including samples of $PuO_2 - UO_2$ fired at 1550°C, and also samples of $PuO_2 - ThO_2$ produced by the ignition at 900°C of the carbides of these elements coated with pyrolytic graphite. The determination of the plutonium contents of these samples was then completed directly by the electrometric methods.

G. W. C. MILNER, A. J. WOOD, G. WELDRICK and G. PHILLIPS

Analytical Sciences Division, Atomic Energy Research Establishment, Harwell, Didcot, Berks.

Analyst, 1967, 92, 239-246.

THE SOCIETY FOR ANALYTICAL CHEMISTRY

"ANALYTICAL ABSTRACTS" DECENNIAL INDEX

1954 to 1963

This cumulative Index for Volumes 1 to 10 is in two parts, the Author section (1033 pages) and the Subject section (680 pages). It contains over 100,000 subject entries, and covers all the fields of analytical chemistry for the years 1954 to 1963.

Price: To members of the Society, £20 (\$56)

To subscribers, £25 (\$70)

Orders (with remittance) should be sent to— W. Heffer & Sons, Ltd. Cambridge England

The Spectrophotometric Determination of Ampicillin

A method is described for the determination of Ampicillin (α -aminobenzyl penicillin) based on the spectrophotometric measurement at 320 m μ of a compound formed by acid degradation of the penicillin at 75° C in the presence of buffer solution at pH 5·2 and a trace of a copper salt. Results obtained on samples of Ampicillin, Ampicillin Trihydrate and Ampicillin Sodium show good agreement with those recorded by the cup-plate microbiological method.

J. W. G. SMITH, G. E. de GREY and V. J. PATEL

Beecham Research Laboratorics, Clarendon Road, Worthing, Sussex.

Analyst. 1967, 92, 247-252.

An X-ray Spectrographic Method for Determining Barium

An X-ray spectrographic method is described in which a Philips 50-kV universal X-ray spectrograph with a chromium tube is used for the quantitative trace analysis of barium in aqueous solutions. The method involves the use of the barium $L\alpha_1$ line, and is suitable for concentrations of up to at least 0.5 per cent. w/w of barium. A limit of detection of 0.002 per cent. w/w of barium is achieved. The extension of the method to the neighbouring elements in the periodic table is suggested.

S. A. PROKOPOVICH and E. R. McCARTNEY

Department of Ceramic Engineering, School of Chemical Technology, The University of New South Wales, Kensington, N.S.W., Australia.

Analyst, 1967, 92, 253-256.

The Loss of Elements during the Decomposition of Biological Materials with Special Reference to Arsenic, Sodium, Strontium and Zinc

The problems encountered during dry ashing of biological materials are discussed, and an attempt has been made to show the variability of results quoted in the literature. Special reference has been made to sodium, arsenic, zinc and strontium, which have been incorporated into rat tissue by injection. These are representative of the various groups of elements when considering their stability towards heat. It is concluded that each biological sample must be treated individually when considering losses of elements during dry ashing.

E. I. HAMILTON, Miss M. J. MINSKI and J. J. CLEARY

Radiological Protection Service, Clifton Avenue, Belmont, Sutton, Surrey. Analyst, 1967, 92, 257-259.

Determination of Arsenic by the Uranyl Salt Method Part II. The Radiometric Determination of Microgram Amounts of Arsenic by a Filter-spot Technique

A development of the uranyl salt method for the gravimetric determination of arsenic is described. Gravimetric manipulations are conducted on a filter-paper base and the arsenic content of the ammonium uranyl arsenate precipitate is determined indirectly by measuring the alpha countrate of the associated uranium.

The method has been demonstrated to be applicable in the range 1 to $8 \mu g$ of arsenic.

A. D. WILSON and D. T. LEWIS

Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.1.

Analyst, 1967, 92, 260-263.



The Elliott installation at Atomic Energy Research Establishment Harwell

Elliott *integrated* activation analysis systems feature sealed tube



Elliott integrated activation analysis systems save space, reduce shielding costs, and offer automatic routine operation in the factory or laboratory. Elliott sealed neutron tubes provide constant output up to 10¹⁰ neutrons per second and carry a 100 hour warranty.

ELLIOTT ELECTRONIC TUBES LIMITED

Neutron Division, Elstree Way, Borehamwood, Hertfordshire, England Tel: Elstree 2040, Ext 459

In the USA: Baird-Atomic Inc., 33 University Road, Cambridge 38, Mass. Tel: University 4-7420



A Member of the Elliott-Automation Group

Direct Injection Enthalpimetry in the Routine Determination of the Hydroxyl Value of Alkylphenols

A thermometric method in which the heat of reaction is used as a quantitative measure of the hydroxyl value of alkylphenols is in routine use. This method has replaced a lengthy acetylation procedure that necessitated measuring the difference between two titrations.

By catalysing the acetylation reaction with perchloric acid and then measuring the temperature rise resulting from the heat of reaction, a method has been developed that takes less than 5 minutes to carry out. Standardisation of reagents is unnecessary and only one volumetric measurement is important to the result. The advantages of this method are simplicity and speed, and also a repeatability equal to that of time consuming conventional titration techniques.

F. L. SNELSON, W. R. ELLIS and J. VILKAULS

Shell Chemicals U.K. Ltd., Laboratory Department, Stanlow Refinery, Ellesmere Port, Wirral, Cheshire.

Analyst, 1967, 92, 264-267.

A Note on the Determination of Vapour - Liquid Equilibrium for Multi-component Systems

The use of a gas chromatograph connected to a data-logging system is described for analysing samples taken in the determination of ternary vapour - liquid equilibria.

Data are produced in a form that is ready for processing by digital computer, and therefore their accuracy may be determined within a short time of sampling. There is a distinct improvement in the accuracy of the method over more traditional methods for ternary system analysis.

K. A. PIKE

Imperial Smelting Co. Ltd., Avonmouth. and D. C. FRESHWATER Loughborough University of Technology, Loughborough, Leicestershire. Analyst, 1967, 92, 268-270.

The Preparation of Analysis Samples of Hard Materials with a Boron Carbide Mortar

Boron carbide has advantages as a grinding medium for hard ceramic materials. Owing to its hardness the contamination is slight and does not interfere with the normal chemical analysis.

Contamination that occurs when grinding fused alumina, sillimanite, silicon carbide and magnesite has been determined by a spectrometric method. The degree of contamination introduced by the boron carbide appears to be an order of magnitude lower than when a 95 per cent. alumina mortar is used.

J. F. BOULTON and R. P. EARDLEY

British Ceramic Research Association, Queens Road, Penkhull, Stoke-on-Trent. Analyst, 1967, 92, 271–272.



Transmission constant down to wavelengths less than 200n.m.



Spectrosil cells have high and constant transmissions at all wavelengths from the far ultra-violet to near infra-red, enabling accurate absorption measurements to be made throughout this spectral region.

All dimensions within B.S. 3875 specification.
 Cells with Spectrosil windows automatically match within B.S. limits for U.V. cells - at no extra charge.

or 0.v. cens — at no extra charge. PTFE Stoppers or glass lids supplied with cells. Spectrosil windows are virtually free from fluorescence. All cells are of completely fused construction. Standard 10 mm. rectangular cells with Spectrosil windows available from stock.

We supply a complete range of cells in Spectrosil, I.R. Vitreosil and Optical Glass for absorption and fluorescence measurements — please send details of your requirements.

THERMAL SYNDICATE LIMITED

P.O. Box No. 6, WALLSEND, NORTHUMBERLAND. Tel. Wallsend 625311 (8 lines) Telex 53614 9, BERKELEY STREET, LONDON, W.1. Tel. HYDe Park 1711 Telex 263945

SILICA INDUSTRIAL WARE • LABORATORY WARE • OPTICAL COMPONENTS ● HIGH TEMPERATURE OXIDE CERAMICS

THE ANALYST

REPORTS OF THE ANALYTICAL METHODS COMMITTEE OBTAINABLE FROM THE SECRETARY

The Reports of the Analytical Methods Committee listed below may be obtained direct from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1 (not through Trade Agents), at the price of 1s. 6d. to members of the Society and 2s. 6d. to non-members. Remittances must accompany orders and be made payable to "Society for Analytical Chemistry."

Certain Reports published before 1946 have been omitted from this list, but are still available.

Additives in Animal Feeding Stuffs Sub-Committee:

Report of the Antibiotics Panel: The Determination of Penicillin, Chlortetracycline and Oxytetracycline in Diet Supplements and Compound Feeding Stuffs.

Report of the Hormones Panel: The Determination of Stilboestrol and Hexoestrol in Compound Feeding Stuffs.

Report of the Prophylactics Panel: The Determination of Nitrofurazone in Compound Feeding Stuffs.

Report of the Vitamins (Water-soluble) Panel: The Determination of Water-soluble Vitamins in Compound Feeding Stuffs.

Report of the Vitamins (Fat-soluble) Panel: The Determination of Fat-soluble Vitamins in Diet Supplements and Compound Feeding-Stuffs.

Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Amprolium in Animal Feeding Stuffs.

Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Sulphaquinoxaline. Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Acinitrazole.

Analytical Standards Sub-Committee:

Sodium Carbonate as a Primary Standard in Acid - Base Titrimetry.

Chlorine in Organic Compounds Sub-Committee:

The Semi-micro-determination of Chlorine in Agricultural Technical Organic Chemicals and their Formulations.

Essential Oils Sub-Committee:

Report No. 14. Solubility Test for Ceylon Citronella Oil. (Gratis.) Report No. 15. Determination of Linalol in Essential Oils.

Fiore Method for Determining Linalol: Amendment. (Gratis.)

Application of Gas - Liquid Chromatography to Essential-oil Analysis: Interim Report on the Determination of Citronellol in Admixture with Geraniol.

Spectral Characteristics of Eugenol.

Fish Products Sub-Committee:

Nitrogen Factor for Cod Flesh.

Meat Products Sub-Committee (formerly Meat Extract Sub-Committee):

Analysis of Meat Extract.

Determination of Gelatin in Meat Extract and Meat Stocks: Interim Report.

Nitrogen Factors for Pork and Nitrogen Content of Rusk Filler (as one reprint).

Nitrogen Factors for Beef.

Nitrogen Factors for Chicken.

Nitrogen Factors for Liver.

Nitrogen Factor for Veal.

Nitrogen Factors for Turkey

Nitrogen Content of Rusk Filler.

Nitrogen Factor for Kidney.

Metallic Impurities in Foodstuffs Sub-Committee:

Report No. 4. Determination of Zinc.

Determination of Lead in Foodstuffs: Tentative Method.

Metallic Impurities in Organic Matter Sub-Committee:

Methods for the Destruction of Organic Matter.

Notes on Perchloric Acid and its Handling in Analytical Work.

The Determination of Lead.

The Determination of Small Amounts of Arsenic in Organic Matter.

The Determination of Small Amounts of Copper in Organic Matter.

The Determination of Small Amounts of Mercury in Organic Matter.

Sub-Committee on Vitamin Estimations:

Report on the Microbiological Assay of Riboflavine and Nicotinic Acid.

The Determination of Carotene in Green-Leaf Material. Part 1. Fresh Grass. The Determination of Carotene in Green-Leaf Material. Part 2. Green-Leaf Materials other than Grass. (Gratis.)

The Chemical Assay of Aneurine (Thiamine) in Foodstuffs. The Microbiological Determination of Thiamine.

The Estimation of Vitamin B₁₂.

Vitamin-E Panel:

The Determination of Tocopherols in Oils, Foods and Feeding Stuffs.

Pesticides Residues in Foodstuffs Sub-Committee:

Determination of Small Amounts of Total Organic Chlorine in Solvent Extracts of Vegetable Material



'Volucon'* volumetric concentrates for the rapid, accurate and convenient preparation of standard solutions.

'Volucon' concentrates, supplied in plastic or glass ampoules, each make one litre of the stated normality. Other normalities can be obtained by varying the dilution rate.

Further information will gladly be supplied on request.

May & Baker Ltd Dagenham Essex

Telephone 01–592 3060 Extensions: 320 and 316. M&B brand products

xi

LA963/100



OERTLING 'V'swill be your next balances

-it's as simple as that!

The new Oertling V10 and V20 are contemporaries of the very successful R series balances. They offer the same thoroughly sensible design, with built-in preweighing and fast easy readout. You'll also be pleased to hear that the price of the new model has gone DOWN — not up! Your next balances will probably be Oertling 'V's — it's as simple as that. Prove it to yourself by arranging a demonstration now!



L. OERTLING LIMITED Cray Valley Works, St. Mary Cray, Orpington, Kent. Orpington 25771

TAS/OR.461



Specially designed by ULVAC as a device for the studies on surface structures and surface phenomena and crystallography. Observation over scattering angle 0° to 160° ; unobstructed diffraction patterns are possible from the back of the fluorescent screen through the glass envelope.

For full technical information please write





MARUBENI-IIDA CO., LTD. 164, Clapham Park Road, London, S.W.4. Telephone: 720-1911 (10 lines) Telex: 28735.



This white, flux-calcined diatomaceous earth is sizegraded by a process which also removes the 'fines' resulting in

- more reproducible packing characteristics,
- lower pressure drop across the column,
- increased resolution and efficiency.

As a result of its low bulk density 'Supasorb' is economical in use—a packed column will require about 25% less weight of material than of similar supports of equivalent mesh size. Three grades are available, each in five mesh sizes.



THE BRITISH DRUG HOUSES LTD. BDH LABORATORY CHEMICALS DIVISION POOLE DORSET



PHILIPS OFFER NEW, UNEQUALLED FLEXIBILITY IN GAS CHROMATOGRAPHY

PV4000 Series of modular units ensures a Chromatograph that always meets your needs precisely

Start with a basic routine Chromatograph – any of 20 different types – and you can economically add or interchange units to suit different or more sophisticated analyses as needs arise.

With the PV4000 series you get an oven/ analyser-top, an ionisation amplifier or katharometer supply and a choice of ...

Detectors – flame ionisation, electron capture, cross section (any two of which can be used simultaneously for dual or balanced detection), and katharometer. Injection Systems – and optional ionisation detector heaters.

Temperature Controllers – isothermal or programmed with two adjustable isothermal periods linked by 79 heating rates, and optional temperature read-out facilities.

Columns – a full range of metal and glass types to meet every requirement

 $\dots and a wide variety of ancillaries and accessories.\\$

Reliable too – solid state circuitry, high quality components and Philips engineering experience and know-how see to that.

It's worth analysing the benefits of the New PV4000 Series. Start by sampling the brochure 'A Complete Range of Routine Chromatographs'.

PHILIPS CHROMATOGRAPHY



A division of THE M.E.L. EQUIPMENT COMPANY LTD · MANOR ROYAL · CRAWLEY · SUSSEX · ENGLAND · CRAWLEY 28787

The SP600 and 335 m μ



The SP600 is now an even better investment. A new prism material plus a few mechanical changes and the low wavelength limit can be guaranteed at 335 mµ. All this has been accomplished without change in accuracy, stability or price. Thousands of SP600 visible spectrophotometers are in regular use all over the world. Thousands of users will be happy to confirm all our claims regarding the rugged construction, reliability and performance of this extraordinary instrument. There will be one near you. Send for full details of the latest SP600 spectrophotometer today.

UNICAM

Precision Spectrophotometers



Unicam Instruments Limited York Street Cambridge England Telephone Cambridge 61631 Telex 81215

CLASSIFIED ADVERTISEMENTS

The rate for classified advertisements is 7s. a line (or space equivalent of a line), with an extra charge of 2s. for the use of a Box Number. Semi-displayed classified advertisements are 80s. for single-column inch.

Copy required not later than the 20th of the month preceding date of publication which is on the 16th of each month. Advertisements should be addressed to The Analyst, 47 Gresham Street, London, E.C.2. Tel.: MONarch 7644.

GREEN'S PURE FILTER PAPERS

for all kinds of filtration

Write for descriptive catalogue 43/G.65 J. BARCHAM GREEN LTD., HAYLE MILL, MAIDSTONE, KENT

ANALYST

Elgar Research Laboratories, a subsidiary of Thorn Electrical Industries Ltd., require a qualified Analyst, male or female, for interesting and varied work on fluorescent materials for the lighting industry. Previous industrial experience essential. Good salary, modern laboratories.

Apply: Personnel Manager, Thorn Electrical Industries Ltd., Great Cambridge Road, Enfield.

CORPORATION OF THE CITY OF GLASGOW CORPORATION CHEMIST AND CITY ANALYST

Applications are invited for appointment to the above post as from 1st August, 1967, from persons qualified in terms of the Public Analysts (Scotland) Regulations, 1956, with regard to the chemistry of food, drugs and water. In addition to the duties of the post under the Food and Drugs (Scotland) Act 1956, applicants should be experienced in the analytical control of sewage purification processes and the analytical control of the sewage service and the second service given to applicants who are Members or Associate-Members of the Institute of Water Pollution Control. Other duties include the analyses of stores, building, and road surfacing materials, and analyses required under the Road Traffic Act, 1962.

The salary applicable to the post is $\pounds 3155 \times \pounds 104-\pounds 3675.$ The appointment is superannuable, subject to medical examination.

Applications stating age and full particulars of qualifications and experience, accompanied by the names of two referees, should be lodged with me in an envelope marked "Corporation Chemist and City Analyst" not later than March 27th, 1967.

City Chambers, Glasgow, C.2. J. F. FALCONER, Town Clerk.

"ANALOID" COMPRESSED CHEMICAL REAGENTS

for metallurgical analysis

Now widely used in industrial analytical laboratories.

A range of over fifty chemicals includes a wide variety of oxidizing and reducing agents, reagents for colorimetric analysis and indicators for certain volumetric titrations.

> For full particulars send for List No. 420 to

RIDSDALE & CO. LTD.

Newham Hall, Newby, Middlesbrough

Telephone: Middlesbrough 37216 Telegrams: "Standards Middlesbrough" B.F.M.I.R.A.

FOOD ANALYST

A Vacancy occurs in the Laboratories of the British Food Manufacturing Industries Research Association for an Analyst. Applicants should be under 30 and have a degree in Chemistry or H.N.C. or similar qualifications, and a few years' experience of food analysis. The successful candidate must be interested in new developments and the instrumentation of analytical techniques and would be encouraged to study for the Branch E Diploma of the R.I.C.

The appointment in the first place would be in a grade carrying a salary between $\pounds 926$ and $\pounds 1,734$ p.a.

The work is interesting and varied, with a pension fund and good prospects of promotion.

Application to the Director, British Food Manufacturing Industries Research Association, Randalls Road, Leatherhead, Surrey.

U7

Upjohn

Medicine designed for health produced with care

MICROBIOLOGICAL ASSAY

This rapidly expanding organisation requires a suitably qualified graduate for the microbiological and pharmacological assay sections of its Quality Control Division. The post is suitable for a bacteriologist, a pharmacist, or chemist who has experience of microbiological assay, or who wishes to start his career in pharmaceutical analysis.

Promotion and salary prospects are excellent and the Company operates a forward-looking Pension and Life Assurance Scheme.

Removal expenses will be met by the Company and every assistance will be given in obtaining accommodation.

Applicants are invited to apply, in confidence, to:---

The Personnel Officer, Upjohn Limited, Fleming Way, Crawley, Sussex



April, 1967]

an important new book from ILIFFE!

Chemical Analysis of Radioactive Materials

A. K. Laurukhina T. V. Malysheva F. I. Pavlotskaya

In this book the authors have summarised and generalised the known facts of the subject drawing on 15 years of personal experience in this field.

The first two chapters are devoted to the theoretical aspects of the field covering the state and behaviour of radioelements in solution and the theoretical bases of radiochemical analysis. The third chapter of isotopes and the concluding chapters provide a detailed description of specific procedures including the isolation and concentration of the radioelements and methods of isolating individual elements in the radioactively pure state.

386 pages, including 86 diagrams 50s net available from leading booksellers

ILIFFE BOOKS LTD. Dorset House, Stamford Street, London, S.E.1

QUALITY CONTROL

over the radioactive sources, radiopharmaceuticals and other radiochemicals produced at the Centre is being reinforced. The following are examples of the posts to be filled in this Department.

- 1. Scientific Officer for development work on the control of radiochemicals and radiopharmaceuticals. Preferably an organic chemist with at least a good second-class honours degree.
- 2. Assistant Experimental Officer or Experimental Officer to study the preparation and control of pure radioisotopes for absolute standards of activity. Higher National Certificate or above preferred with emphasis on physical or inorganic chemistry.

Salaries will be assessed within the following scales:---

Scientific Officer $\pounds 995$ to $\pounds 1,685$ a year. Experimental Officer $\pounds 1,465$ to $\pounds 1,860$ a year—(must be at least aged 26).

Assistant Experimental Officer $\pounds 800$ (at age 21) to $\pounds 1,335$ a year.

- 3. Experimental Officer with experience in fine chemical or pharmaceutical industry for organisational work connected with quality control. Preferably a pass degree or H.N.C. in an appropriate subject.
- 4. Assistant Experimental Officer and Experimental Officers for control work on organic labelled compounds using isotope dilution analysis, gas liquid, paper and thin layer chromatography and spectrometric methods. Higher National Certificate or above preferred with emphasis on organic chemistry.

Send a postcard quoting ref. S10658 to

The Personnel Officer

THE RADIOCHEMICAL CENTRE

Amersham

Bucks



BINDING

Have your back numbers of *The Analyst* bound in the standard binding case.

Send the parts together with a remittance for £1 3s. 3d.

To-

W. HEFFER & SONS LTD HILLS ROAD CAMBRIDGE



Accurate production control analysis at the touch of a button with the new Philips PW 1250 automatic simultaneous spectrometer

The new Philips PW 1250 Automatic Simultaneous X-ray Spectrometer performs fast, accurate analyses for routine production control of such materials as cement, glass, steel, oil and non-ferrous materials. Once the machine has been set up, it performs multi-element analysis automatically at the touch of a button.

- Up to 7 elements above atomic number 11 for analysis in each sample.
- Three programmes may be

preset, for different types of substances.

- Allows choice of measuring method: absolute, ratio or monitor.
- Manual or automatic specimen changing of up to 9 or 160 samples at a time - vacuum airlock allows the next sample to be loaded and brought into vacuum while the previous one is under analysis.
- Facilities for computer operation

 either with an integral data processor or separate computer

so that analytical results can be presented as concentrations, intensities, or both. With data processing, accurate analyses may be accomplished in 20-30 seconds.

• Air, vacuum or helium path.

With the PW 1250, extreme stability exists for high voltage and tube current. Maximum power is 3 kW. Use of printed circuit boards ensures easy servicing and rugged dust-proof design facilitates efficient operation in industrial environments.



Further information. A 16-page brochure gives comprehensive details; copies of it are available on request.

N.V. Philips' Gloeilampenfabrieken, Scientific and Analytical Equipment Department, Eindhoven, The Netherlands.





• Scientific and technical papers which give original research findings in qualitative and quantitative analysis and instrumentation, both theoretical and applied. Contributions are from analytical chemists throughout the world.

- Special Reports
- · Book Reviews
- Editorial Comments

 Information on: Meetings and technical courses Interesting laboratories Trends in instrumentation Commercially available instruments, chemicals and laboratory equipment

SUBSCRIBE NOW 12 regular issues

1967 ANALYTICAL REVIEWS

The Analytical Reviews are published as a separate issue in April. In 1967 the review issue will cover significant developments in analytical applications over the past two years. The subjects reviewed are listed below. Critical and selective, rather than all-inclusive, the reviews are supported by detailed bibliographies.

Air Pollution Clinical Chemistry Coatings Essential Oils Fertilizers Food Metallurgy Pesticide Residues Petroleum Pharmaceuticals Rubber Solid and Gaseous Fuels Water Analysis

Plus

The LABORATORY GUIDE, separately bound and mailed in July. This publication contains information on laboratory equipment and services, chemicals and services including research chemicals not yet commercialized, and their manufacturers and suppliers. One year of ANALYTICAL CHEMISTRY, including 12 monthly issues, the Analytical Reviews, and the Laboratory Guide, costs only \$18.50 including postage—or only \$7.50 for American Chemical Society members. Slightly lower postage applies for the Pan-American Union, Canada, and Spain.

Send your order to **AMERICAN CHEMICAL SOCIETY** 1155 Sixteenth Street, N.W. Washington, D.C. 20036, U.S.A.

or

W. HEFFER & SONS LIMITED Booksellers, Cambridge, England

Your analytical accuracy depends on the standards you use...

... but by relying on JMC spectrographic materials you can be sure of highest accuracy from your analytical techniques- every time In spectrographic analysis, as in many other techniques, the reliability of the results you get rests on the standards you use for comparison. And the best way for you to be sure that the standards you use are fully reliable is to specify JMC spectrographically standardised materials.

You will find in the JMC range ultra-high purity metals and Specpure[®] chemicals representing 70 elements. These substances are employed as reference standards in qualitative spectrography and in making standard mixtures containing known amounts of certain elements for quantitative work.

Individual supplies of each substance are accompanied by an analytical report giving the level, in parts per million, of each impurity detected in the batch.

Write for information and price list today!





Spectrographically Standardised Substances

JOHNSON MATTHEY CHEMICALS LIMITED 74 Hatton Garden, London, E.C.1 Telephone: 01-405 6989 Telex: 21465

Eine neue Schriftenreihe

Reinstostoffprobleme

Herausgegeben von Prof. ERNST REXER

Deutsche Akademie der Wissenschaften zu Berlin Institut für Metallphysik und Reinstmetalle, Dresden

> Zunächst erscheint ein Bericht über das 2 Internationale Symposium "Reinststaffe in Wissenschaft und Techeik" vom 28, September bis 2. Oktober 1965 in Dresden, veranstaltet von der Chemischen Gesellschaft in der Deutscher Demakratischen Republik, der Gesellschaft Deutscher Berg- und Hüttenleute und der Physikalischen Gesellschaft in der Deutschen Demokratischen Republik.

> In 174 Vorträgen des Symposiums, an dem etwa 850 Fachleute aus 22 Ländern teilnahmen, wurden aktuelle Probleme aus allen Gebieten der Reinststofforschung behandelt. Wegen der Fülle des dargebotenen Stoffes erscheint der Tagungsbericht in drei selbständigen Teilbänden

- I. Reinststoffdarstellung
- II. Reinststoffanalytik
- III. Realstruktur und Eigenschaften von Reinststoffen.

Sie enthalten alle auf dem Symposium gehaltenen Plenar-, Hauptund Kurzorträge sowie die wichtigsten Diskussionen. Die Vorträge erschinen in derjenigen Konferenzsprache (deutsch, russisch, englisch oder französish), in der sie vorgetragen wurden. Den russishen Texten wurde eine deutsche Übersetzung beigegeben. Jedem Vortrag ist eine dreisgrachige Zusammenfassung vorangestelit.

Die Bände sind im Offsetverfahren gedruckt und in Ganzleinen gebunden. (Format 16,7 \times 24 cm)

- Bd I 1266. XIV, 602 Seiten 246 Abbildungen, dav. 65 auf 35 Tafein 62 Tabellen Ganzleinen MDN 55,-
- Bd II 1966. XI, 709 Seiten 238 Abbildungen, davan 39 auf 24 Tafein 99 Tobellen — Ganzleinen MDN 55,-
- Bd III 1967. Ca 1068 Seiten 594 Abbildungen, 49 Tabellen 135 Tafein— Ganzleinen ca MDN 116,-

Jeder Band ist in sich abgeschlossen, enthält ein Autorenverzeichnis und ist auch einzeln käuflich.

Bestellungen druch eine Buchhandlung erbeten

Ausführlichen Prospekt erhalten Sie auf Wunsch direkt vom

AKADEMIE · VERLAG · BERLIN



New Digital in-line reading makes weighing easier than ever

This new CL4D balance gives 4th place weighing by direct reading. All 7 relevant digits are in line and no vernier or micrometer "interpretation" is called for. 100% accuracy is thus obtainable even by inexperienced assistants, and time and fatigue are further reduced. The CL4D also has all the advantages of the ergonomically designed CL range — all hand-movements within a 10" x 5" ellipse, all controls used with hands in the "rest" position, large pan-chamber giving 180° accessibility, indicating lights for full and partial release.

Full details from Stanton Instruments Ltd Copper Mill Lane London SW17 Telephone: Wimbledon 7731





THE ANALYST

THE *COMPLETE* FLAME SPECTROPHOTOMETER

choice of burners — Meker or blowtorch. all burners burn organic solvents. t metre grating monochromator — linear in wavelength. digital wavelength readout. built in scanning motor — flame spectra in under 10 minutes with high speed recorder. recorder outlet. electronic integration, 2 to 20 seconds — unique measuring method gives absolutely stable readings. automatic correction for background emission

gives greatly improved resolution. atomic absorption attachment for non-emitting elements. combines high precision, sensitivity, stability and resolution in a compact, aesthetically pleasing unit. SOUTHERN ANALYTICAL offer you the ultimate in flame photometry with the present state of knowledge. Demonstrations on your samples. Telephone Camberley 3401.

A1730 Interference filter version also available.

SOUTHERN ANALYTICAL LIMITED

FRIMLEY ROAD, CAMBERLEY, SURREY Tel. Camberley 3401. Telex 85249.



NEW AUTOMATIC INSTRUMENT FOR THE DETERMINATION OF VISCOSITY

The most obvious virtue of the Auto- 1) automatic measuring of efflux time Viscometer is its complete automation which does away with the tedious and 2) time stability of 2 parts in 10^6 per time-consuming routine of manual methods of capillary viscometry.

Even more important in the scientific sense is the ability of the Auto-Viscometer to make viscosity determinations with a precision of 0,005%.

This is a significant advance to the scientist whose ultimate concern is the determination of viscosity-average molecular weight.

A number of instrument characteristics are responsible for the Auto-Viscometers' precision:

- within 0.01 second
- week
- 3) digital readout of efflux time
- 4) uniform temperature control within ± 0,005 C°

In addition the Auto-Viscometer will accomodate most commercially available glass viscometers.

Hewlett-Packard S.A., 54 Route des Acacias, Geneva, Switzerland.



xxviii

[April, 1967





U.S. and other National Standards

NO CREVICES—NO BLIND SPOTS—

PROJECTOR SELECTED WIRE CLOTHS

Unsurpassable for the separation of powder and aggregates, particle analysis, and micro sieving problems. Recovering Service.



LOMBARD ROAD - MORDEN FACTORY ESTATE - LONDON SW19 PHONE LIBerty 8121/2/3-GRAMS ENDTESIV LONDON SW19

The Determination of Sterols

Society for Analytical Chemistry Monograph No. 2

This Monograph contains six papers on various aspects of the determination of sterols by colorimetric and chromatographic methods applicable in many fields



Available ONLY from The Editor, "The Analyst," 14 Belgrave Square, London, S.W.1 (Not through Trade Agents)

Price 15s. or U.S. \$2.00 Post free

A remittance made out to "Society for Analytical Chemistry" should accompany every order. Members of the Society may purchase copies at the special price of 5s., post free. April, 1967]

THE ANALYST

Nuclear Magnetic Resonance Abstract Service

- B. L. Shapiro, Editor Illinois Institute of Technology
- S. Forsén Royal Institute of Technology, Stockholm, Sweden
- R. Harris
- University of East Anglia, Norwich, England J. Jonáš

Czechoslovak Academy of Sciences, Prague, Czechoslovakia

P. C. Lauterbur State University of New York at Stony Brook

- G. F. G. Mavel
- Institut National de Recherche Chimique Appliquée Paris, France

- W. von Philipsborn Organisch-Chemisches Institut der Universität Zürich, Zürich, Switzerland
- W. M. Ritchey The Standard Oil Company (Ohio)
- S. Sternhell University of Sydney Sydney, Australia
- J. B. Stothers University of Western Ontario London, Ontario, Canada
- C. W. Wilson III Union Carbide Chemicals Company

This service provides in one place and in a form to facilitate retrieval, the total world literature on all aspects of nuclear magnetic resonance (NMR). Articles, books, patents, government reports, etc., which contribute to the state of any aspect of the NMR art are abstracted, as are papers which make extensive or novel use of existing techniques. This includes both theoretical and applied papers in both the high resolution and broad line areas, techniques, apparatus, etc. Coverage is comprehensive—abstracting is done by professional chemists and physicists active in the field. The Abstracts—all in English—are supplied from the literature of all countries, in any language.

Between 150 and 200 Abstract cards are currently being issued per month, in two batches. These cards also include the full references to those papers found which, while they do not contribute to the state of NMR (or its use) enough to warrant abstracting, contain small amounts of data or information which may be of use to specific readers.

Abstracts are supplied on 5 in. \times 8 in. double row punched cards. A system of classification has been developed to facilitate searching. Sufficient holes are left unused to permit the individual user to adapt and expand the classification system to his particular needs.

A sample set of abstracts will be sent to those requesting it. Write to Preston Technical Abstracts Company.

Published by:

PRESTON TECHNICAL ABSTRACTS CO.

909 PITNER AVENUE • EVANSTON, ILLINOIS 60202, U.S.A.

THE SOCIETY FOR ANALYTICAL CHEMISTRY

Founded 1874. Incorporated 1907.

THE objects of the Society are to encourage, assist and extend the knowledge and study of analytical chemistry and of all questions relating to the analysis, nature and composition of natural and manufactured materials by promoting lectures, demonstrations, discussions and conferences and by publishing journals, reports and books.

The Society includes members of the following classes:—(a) Ordinary Members who are persons of not less than 21 years of age and who are or have been engaged in analytical, consulting or professional chemistry; (b) Junior Members who are persons between the ages of 18 and 27 years and who are or have been engaged in analytical, consulting or professional chemistry or *bona fide* full-time or part-time students of chemistry. Each candidate for election must be proposed by three Ordinary Members of the Society. If the Council in their discretion think fit, such sponsorship may be dispensed with in the case of a candidate not residing in the United Kingdom. Every application is placed before the Council and the Council have the power in their absolute discretion to elect candidates or to suspend or reject any application. Subject to the approval of Council, any Junior Member above the age of 21 may become an Ordinary Member if he so wishes. A member ceases to be a Junior Member on the 31st day of December in the year in which he attains the age of 27 years. Junior Members may attend all meetings, but are not entitled to vote.

The Entrance Fee for Ordinary Members is $\pounds 1$ Is. and the Annual Subscription is $\pounds 4$ for Ordinary Members taking *The Analyst* and *Proceedings of the Society for Analytical Chemistry* only, or $\pounds 9$ for Ordinary Members taking *Analytical Abstracts* in addition to *The Analyst* and *Proceedings*. Junior Members are not required to pay an Entrance Fee and their Annual Subscription is $\pounds 1$ Is. No Entrance Fee is payable by a Junior Member on transferring to Ordinary Membership. The Entrance Fee (where applicable) and first year's Subscription must accompany the completed Form of Application for Membership. Subscriptions are due on January 1st of each year.

Scientific Meetings of the Society are usually held in October, November, December, February, April and May, in London, but from time to time meetings are arranged in other parts of the country. Notices of all meetings are sent to members by post.

All members of the Society have the privilege of using the Library of The Chemical Society. Full details about this facility can be obtained from the Librarian, The Chemical Society, Burlington House, Piccadilly, London, W.1.

The Analyst, the Journal of the Society, which contains original and review papers, information about analytical methods and reviews of books, and has a world-wide distribution, and Proceedings of the Society for Analytical Chemistry, in which are reported the day-to-day activities of the Society, are issued monthly to all Ordinary and Junior Members. In addition, any Ordinary Member may receive Analytical Abstracts, providing a reliable index to the analytical literature of the world, on payment of higher Annual Subscription.

Forms of application for membership of the Society may be obtained from the Secretary. The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1.

LOCAL SECTIONS AND SUBJECT GROUPS

THE North of England, Scottish, Western, Midlands and North East Sections were formed to promote the aims and interests of the Society among the members in those areas.

Specialised Groups within the Society are concerned with the study of various branches of analytical chemistry of specialised or topical interest. Groups dealing with such topics as Microchemical Methods, Biological Methods, Thin-Layer Chromatography, Atomic-Absorption Spectroscopy, Thermal Analysis, Automatic Methods, Particle Size Analysis, Radiochemical Methods and a Special Techniques Group, covering very new developments and specialised physical methods, are at present active—and further Groups are formed from time to time as the need arises.

Non-members of the Society may participate in the activities of a Group.

The Sections and Groups hold their own meetings from time to time in different places. Members of the Society pay no extra for membership of a Section or Group. Application for registration as a member should be made to the Secretary of the Society.



This JMM dish has seen 10 years of regular use...

... how long does your platinum apparatus last?

You can always ensure the longest life potential for your apparatus simply by specifying that it should be JMM. All JMM products are of the finest platinum and platinum alloys and are fabricated by precision methods to give you the very best quality.

But the actual life of your apparatus depends on how you treat it! Study the section on "Care and Maintenance" in your copy of our catalogue on Platinum Laboratory Apparatus. Treat your JMM apparatus right, and you'll benefit from years and years of extra service.

If you haven't a copy of Platinum Laboratory Apparatus ask for one today.

JMM Platinum Laboratory Apparatus

JOHNSON MATTHEY METALS LIMITED, 81 (Hatton Garden, London, E.C.1 Telephone: 01-405 6989 Telex: 21465

Vittoria Street, Birmingham, 1

Telephone: 021-236 8004

04 75-79 Eyre Street, Sheffield, I

heffield, I Telephone: 23121

In the following countries contact: U.S.A. J. Bishop & Co., Platinum Works, Malvern, Pennsylvania

CANADA Johnson, Matthey & Mallory Limited, 110 Industry Street, Toronto 15 JAPAN Tanaka Kikinzoku Kogyo KK, 14, 2-Chome Kayabacko, Nihonbashi, Chuo-Ku, Tokyo. **REVIEW PAPER**

April, 1967

Page

THE ANALYST

THE JOURNAL OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

CONTENTS

Heterocyclic Azo Dyestuffs in Analytical Chemistry—R. G. Anderson and G. Nickl	ess 207
ORIGINAL PAPERS	
The Determination of Plutonium in Refractory Materials by Electromet	ric
Methods after Dissolution by Fusion with Ammonium Hydrogen Sulpha	ite
—G. W. C. Milner, A. J. Wood, G. Weldrick and G. Phillips	239
The Spectrophotometric Determination of Ampicillin—J. W. G. Smith, G. E.	de
Grey and V. J. Patel	247
An X-ray Spectrographic Method for Determining Barium—S. A. Prokopov	ich
and E. R. McCartney	253
The Loss of Elements during the Decomposition of Biological Materials w	i th
Special Reference to Arsenic, Sodium, Strontium and Zinc—E. I. Hamilt	on,
Miss M. J. Minski and J. J. Cleary	257
Determination of Arsenic by the Uranyl Salt Method. Part II. The Radiomet	ric
Determination of Microgram Amounts of Arsenic by a Filter-spot Technic	jue
—A. D. Wilson and D. T. Lewis	260
Direct Injection Enthalpimetry in the Routine Determination of the Hydro	xyl
Value of Alkylphenols—F. L. Snelson, W. R. Ellis and J. Vilkauls	264
A Note on the Determination of Vapour - Liquid Equilibrium for Multi-co	m-
ponent Systems—K. A. Pike and D. C. Freshwater	268
The Preparation of Analysis Samples of Hard Materials with a Boron Carb	ide
Mortar—J. F. Boulton and R. P. Eardley	271
Book Reviews	273
Errata	278
Summaries of Papers in this Issue	iv, vi, viii

Printed and Published for the Society for Analytical Chemistry by W. Heffer & Sons Ltd., Cambridge, England. Communications to be addressed to the Editor, J. B. Attrill, 14 Belgrave Square, London, S.W.I. Enquiries about advertisements should be addressed to Walter Judd Ltd., 47 Gresham Street, London, E.C.2.

Entered as Second Class at New York, U.S.A., Post Office.