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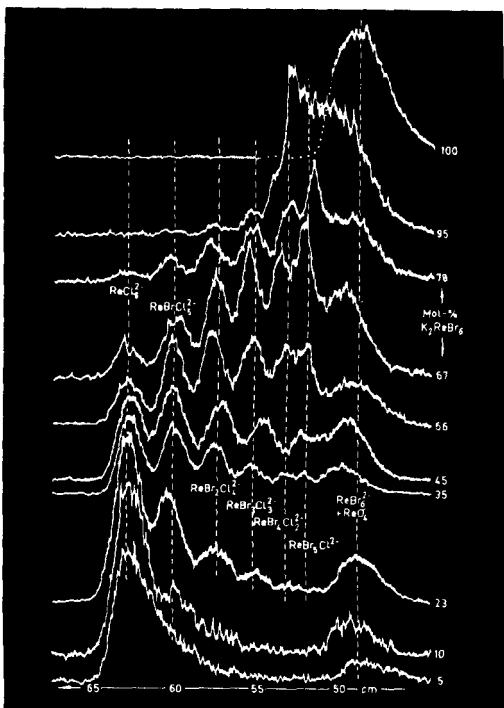
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Established as a medium for the rapid publication of papers dealing with all aspects of analytical chemistry, *Talanta* is the natural vehicle for the international communication of progress in this field. As an international journal, its papers are expected to be of a very high standard and to make definite contributions to the subject: they must be new publications. Papers may be written in English, French, or German; all papers have abstracts in these three languages and also in Russian. Special importance is attached to work dealing with the principles of analytical chemistry in which experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields or of hitherto widely scattered material are considered for publication, but should be critical. Original papers, short communications and reviews are refereed in the normal manner. Preliminary communications are refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemists is welcomed by the Editor-in-Chief, at whose discretion it is published. A new feature is Annotations, which are critical commentaries on some aspect of analytical chemistry and deal with topics such as sources of error, or the scope and limitations of methods and techniques; these commentaries are refereed.

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Talanta

An International Journal of Analytical Chemistry



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Established as a medium for the rapid publication of papers dealing with all aspects of analytical chemistry, *Talanta* is the natural vehicle for the international communication of progress in this field. As an international journal, its papers are expected to be of a very high standard and to make definite contributions to the subject: they must be new publications. Papers may be written in English, French, or German; all papers have abstracts in these three languages and also in Russian. Special importance is attached to work dealing with the principles of analytical chemistry in which experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields or of hitherto widely scattered material are considered for publication, but should be critical. Original papers, short communications and reviews are refereed in the normal manner. Preliminary communications are refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemists is welcomed by the Editor-in Chief, at whose discretion it is published. A new feature is Annotations, which are critical commentaries on some aspect of analytical chemistry and deal with topics such as sources of error, or the scope and limitations of methods and techniques; these commentaries are refereed.

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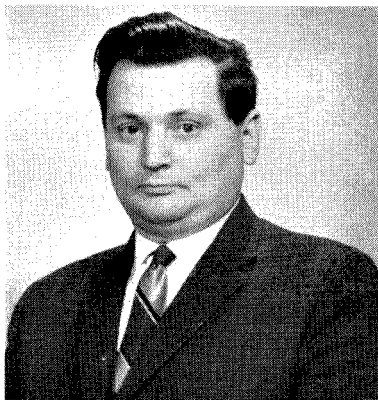
G. SVEHLA

Also, they would like to record their sincere thanks for the help given by

R. E. WAINERDI

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Dr. G. SVEHLA, Reader in Analytical Chemistry, Queen's University, Belfast, was born in Hungary in 1929. He graduated from the Technical University of Budapest in 1951 and took his Ph.D. in 1959. After working at the Technical University of Budapest and spending one year as Research Fellow in Aberdeen, Scotland, he joined Queen's University in 1966. He is a Fellow of the Royal Institute of Chemistry and recently became co-editor of Wilson and Wilson's *Comprehensive Analytical Chemistry*. His publications are on ascorbinometric titrations, catalytic analysis, flame photometry and on problems of error calculation. With his research team in the Department of Analytical Chemistry at Queen's University, Dr. Svehla works on the application of Landolt reactions in analytical chemistry, radiofrequency titrations in non-aqueous media, the use of displacement reactions in flame photometry and on polarography.



COMPARATIVE DISTRIBUTION COEFFICIENTS AND CATION-EXCHANGE BEHAVIOUR OF THE ALKALINE EARTH ELEMENTS WITH VARIOUS COMPLEXING AGENTS

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Summary—Equilibrium distribution coefficients are presented for the alkaline earth metals Be(II), Mg(II), Ca(II), Sr(II) and Ba(II) with the complexing agents acetate, formate, lactate, citrate, tartrate, α -hydroxyisobutyrate, malonate, malate, acetylacetonate, EDTA, EGTA and DCTA, and the AG50W-X8 cation-exchange resin. Coefficients in HCl, HNO₃, HClO₄ and NH₄Cl are included for the sake of completeness. The merits of the various complexing agents for the separation of adjacent element pairs are discussed and experimental elution curves are presented for selected separations. Separation factors for adjacent elements are calculated at eluting agent concentrations corresponding to a distribution coefficient of 10 for the less strongly absorbed element and are presented together with the eluting agent concentrations to form a basis for comparison.

SEPARATION factors for cation-exchange chromatography of the alkaline earth elements in aqueous hydrochloric or other non-complexing acids are rather small.¹⁻⁴ Many complexing agents such as acetate,^{5,6} formate,⁷ citrate,^{8,9} lactate,¹⁰ malonate,² α -hydroxyisobutyrate,^{11,12} EDTA,¹³ DCTA,^{14,15} EGTA,¹⁶ 2,6-pyridinedicarboxylate¹⁷ and acetylacetonate therefore have been suggested for improved separation. In almost all cases the suggested methods seem to have been developed empirically by trying out a few eluting concentrations in a column procedure and settling for the best one. Distribution coefficient data from which the most favourable eluent concentration could be obtained directly, and which also would make possible an evaluation and comparison of the merits of the various eluting agents, do not seem to be available. Therefore, a systematic investigation of the cation-exchange distribution coefficients of the alkaline earth elements, Be, Mg, Ca, Sr and Ba, in various complexing solutions was carried out in this laboratory. Included were the following complexing agents: acetate, formate, lactate, citrate, tartrate, α -hydroxyisobutyrate, malonate, malate, acetylacetonate, EDTA, EGTA and DCTA. The results, their application, and discussion are presented in this paper. The malonate system has been investigated before,² but the coefficients are included for comparative purposes. Coefficients in hydrochloric, nitric and perchloric acids and ammonium chloride solutions are also given for the sake of completeness.

EXPERIMENTAL

Reagents

Chemicals of analytical-reagent grade purity were used throughout with the exception of malonic and DL-malic acid which were obtained as 99% pure reagents and were further purified by an ion-exchange method.²

The resin used was the AG50W-X8 sulphonated polystyrene marketed by Bio-Rad Laboratories, Richmond, California. Resin of 100–200-mesh particle size was used for equilibrium and of 200–400 mesh for column experiments.

Apparatus

Borosilicate glass tubes of 20 mm inner diameter with fused-in sintered glass plates of No. 2 porosity and a burette tap at the bottom, were used as columns.

A Perkin–Elmer 303 atomic absorption spectrometer was employed for determinations of low concentration of alkaline earth metals (elution curves).

Procedures

Distribution coefficients. Coefficients were determined by equilibrating for 24 hr in a mechanical shaking apparatus 2.718 g of dry AG50W-X8 resin in the ammonium form (equivalent to 2.500 g of resin in the hydrogen form) with 250 ml of a solution containing 1 mmole of the required element and the required concentration of the organic complexing agent as the ammonium salt. Only 0.1 mmole of magnesium(II) was used for equilibria with ammonium α -hydroxyisobutyrate because of its limited solubility with this reagent. The pH was kept at 7.0 throughout except for the equilibration of beryllium in ammonium chloride, acetate and formate where a pH of 5.0 was used to prevent hydroxide precipitation in the external solution, and the equilibration of all elements in acetylacetonate, where a pH of 9.0 was used. Coefficients in EDTA, EGTA and DCTA were determined at starting pH values ranging from 5 to 9 at intervals of 1.0, and at concentrations of 0.02M and 0.10M for EDTA and 0.02M for EGTA and DCTA. One series of coefficients was measured in the presence of 0.30M ammonium acetate as buffer, another series was measured in the absence of the buffer.

After equilibration the resin was separated from the aqueous phase by filtration and the pH of the filtrate was measured with a pH meter in the cases of EDTA, EGTA and DCTA. The amounts of the elements in the resin phase (after ashing) and in the water phase were determined by suitable analytical methods.² From the results the equilibrium distribution coefficients,

$$D = \frac{\text{amount of element in resin phase}}{\text{amount of element in water phase}} \times \frac{\text{ml of solution}}{\text{g of resin (dry weight in H}^+\text{ form)}}$$

were calculated. For EDTA, EGTA and DCTA, curves of D against pH after equilibration were plotted and the coefficients at the required pH values were read from these curves. The results are presented in Tables I and II. Coefficients in perchloric acid were also determined. Their values and those of the coefficients in hydrochloric and nitric acids, for 1 mmole of the element and 2.5 g of resin are included in the Tables. Coefficients for 2.5 mmole have been published before,^{1, 19} but the coefficients for lower loading are included for the sake of completeness.

Separation factors. For comparison of the merits of the various eluting agents the values of the separation factors for element pairs at a distribution coefficient of 10 for the less strongly adsorbed element were obtained from plots of coefficients against eluent concentration or pH value (for EDTA, EGTA and DCTA). Table III presents a summary of these separation factors and the corresponding eluent concentration.

Elution curves. Satisfactory column kinetics are required in addition to a favourable separation factor to obtain a good chromatographic separation. The excellence of the separations possible for adjacent group IIA elements when working under near optimum conditions are demonstrated by some elution curves.

Figure 1 shows an elution curve for the 2 mmole of beryllium, 1 mmole of magnesium and 0.10N ammonium malate of pH 7.5 as eluting agent. The column had an inner diameter of 15 mm and contained 15 ml (5 g) of AG50W-X8 resin of 200–400-mesh particle size in the ammonium form. The flow rate was kept at 2.0 ± 0.2 ml/min.

Figure 2 shows an elution curve for the magnesium(II)–calcium(II) pair with a similar column, but 0.20M ammonium acetylacetonate of pH 9.0 as eluting agent; the same column and 2.0M ammonium acetylacetonate of pH 9.0 as eluting agent were used for the calcium(II)–strontium(II) pair as shown in Fig. 3. The eluting agent was prepared by neutralizing a mixture of acetylacetonate and water with aqueous ammonia to a pH of 9, with vigorous stirring. The solution was left standing for 15–20 min before elution was started. When a 30-ml (10-g) column was used the calcium was eluted quantitatively with 300 ml of the eluting agent while no strontium appeared in the first 1000 ml of eluate when 1 mmole of each element was present.

Figures 4–6 show elution curves for the calcium(II)–strontium(II) pair with 0.70N ammonium α -hydroxyisobutyrate of pH 7.0, 0.20N ammonium citrate of pH 7.5, 0.10M EDTA of pH 5.0 containing 0.30M ammonium acetate, and 0.10M EDTA of pH 5.0 and 5.5 in the absence of ammonium acetate, as eluents. The columns contained 60 ml (20 g) of AG50W-X8 resin of 200–400-mesh

TABLE I.—DISTRIBUTION COEFFICIENTS

Eluent	Be	Mg	Ca	Sr	Ba
0.10N HClO ₄	834	1340	2980	4510	>10 ⁴
HNO ₃	763	1180	2310	4350	6800
HCl	334	1320	4570	6500	>10 ⁴
NH ₄ Cl	1530	816	2390	4300	13800
NH ₄ acetate	1900	915	2060	3900	10900
NH ₄ formate	1870	804	2060	3500	10000
NH ₄ lactate	770	331	473	881	1320
NH ₄ malate	3.5	311	502	1070	2815
NH ₄ α-hydroxyisobutyrate	440	811	1360	4060	20000
NH ₄ tartrate	38.6	476	52	952	2460
NH ₄ acetylacetonate	5.7	48.0	12300	16600	>10 ⁴
NH ₄ malonate	7.8	205	910	1760	4500
NH ₄ citrate	<0.5	27.9	48.0	172	565
0.20N HClO ₄	283	418	871	1290	3370
HNO ₃	244	393	719	1150	2330
HCl	158	387	1160	1590	4450
NH ₄ Cl	440	254	631	944	2480
NH ₄ acetate	805	214	481	817	3460
NH ₄ formate	140	219	475	774	2480
NH ₄ lactate	79	100	142	283	498
NH ₄ malate	1.8	86	118	284	766
NH ₄ α-hydroxyisobutyrate	51	142	285	678	2280
NH ₄ tartrate	5.6	124	30	226	503
NH ₄ acetylacetonate	<1.0	8.0	2640	9900	>10 ⁴
NH ₄ malonate	5.1	49.3	290	460	990
NH ₄ citrate	<0.5	7.8	10.8	43.3	144
0.50N HClO ₄	65	98	198	268	645
HNO ₃	63	93	150	196	309
HCl	51	88	188	278	746
NH ₄ Cl	106	51	124	170	379
NH ₄ acetate	30.1	33.5	73	132	323
NH ₄ formate	8.7	32.0	74	125	288
NH ₄ lactate	2.1	13.2	23.5	61	123
NH ₄ malate	1.0	11.7	15.2	42.3	114
NH ₄ α-hydroxyisobutyrate	1.8	12.1	24.3	91	280
NH ₄ tartrate	1.8	19.3	7.4	26.7	68
NH ₄ acetylacetonate	<1.0	2.2	377	2500	>10 ⁴
NH ₄ malonate	3.3	6.1	33.7	71	160
NH ₄ citrate	<0.5	1.5	2.5	7.6	22.2
1.00N HCl	18.7	26.9	60	88	173
HNO ₃	16.1	24.6	38.1	43.1	88
HCl	14.4	21.8	43.8	73	168
NH ₄ Cl	29.2	15.2	39.2	52	116
NH ₄ acetate	4.2	8.6	18.3	35.3	85
NH ₄ formate	2.7	7.7	18.4	35.1	76
NH ₄ lactate	<1.0	2.9	4.8	14.2	38.6
NH ₄ malate	<1.0	3.7	3.0	9.4	26.7
NH ₄ α-hydroxyisobutyrate	1.2	4.2	5.9	18.4	61
NH ₄ tartrate	1.2	5.1	2.1	5.8	14.3
NH ₄ acetylacetonate	<1.0	1.2	115	1170	>10 ⁴
NH ₄ malonate	<1.0	3.2	7.3	17.3	40.5
NH ₄ citrate	<0.5	0.7	0.7	2.0	5.6

TABLE I. (Contd.)

Eluent	Be	Mg	Ca	Sr	Ba
2.00N HClO ₄	4.7	8.5	18.9	25.2	53
HNO ₃	8.5	9.7	10.5	11.2	13.1
HCl	5.4	6.4	13.2	19.2	38.9
NH ₄ Cl	8.9	5.7	12.5	17.9	37.1
NH ₄ acetate	2.3	2.5	4.5	9.4	22.7
NH ₄ formate	1.5	2.7	4.8	8.5	19.9
NH ₄ lactate	<1.0	1.6	2.2	3.3	10.3
NH ₄ malate	<1.0	1.7	0.9	1.7	6.9
NH ₄ α-hydroxyisobutyrate	<1.0	1.7	2.5	6.3	17.9
NH ₄ tartrate	<1.0	1.8	0.9	2.1	2.9
NH ₄ acetylacetonate	<1.0	1.0	78	838	6800
NH ₄ malonate	<1.0	1.6	1.8	3.8	13.3
NH ₄ citrate	<0.5	0.4	0.2	0.6	1.7
3.00N HClO ₄	2.2	4.2	11.0	14.4	27.3
HNO ₃	4.5	5.8	4.8	6.2	4.7
HCl	3.3	4.3	7.1	10.6	20.0
NH ₄ Cl	7.5	3.4	7.7	10.0	19.5
NH ₄ acetate	1.6	1.4	2.5	4.7	11.4
NH ₄ formate	1.0	1.9	3.2	4.4	9.6
NH ₄ lactate	<1.0	1.4	1.4	2.0	5.8
NH ₄ α-hydroxyisobutyrate	<1.0	1.0	1.7	3.6	10.6
NH ₄ tartrate	<1.0	1.3	0.8	1.2	1.5
NH ₄ acetylacetonate					
NH ₄ malonate	<1.0	0.8	0.9	2.0	11.1
NH ₄ citrate	<0.5	0.2	<0.2	0.3	0.9
4.00N HClO ₄	1.7	2.9	7.9	10.9	20.2
HNO ₃	2.8	4.1	2.8	4.7	3.2
HCl	2.4	3.0	5.8	7.6	12.4
NH ₄ Cl	6.4	2.2	5.2	7.5	13.5
NH ₄ acetate	1.1	1.1	2.0	3.9	7.1
NH ₄ formate	<1.0	1.7	3.0	3.7	5.9
NH ₄ lactate	<1.0	1.3	1.2	1.7	4.8
NH ₄ α-hydroxyisobutyrate	<1.0	<1.0	1.4	2.7	7.5
NH ₄ tartrate	<1.0	1.0	0.5	0.9	1.1
NH ₄ malonate	<1.0	0.5	0.6	1.3	9.7
NH ₄ citrate	<0.5	<0.2	<0.2	0.2	0.6

TABLE II.—DISTRIBUTION COEFFICIENTS WITH 0.02M COMPLEXONES
CONTAINING 0.30M NH₄ ACETATE

Eluting agent	pH	Mg(II)	Ca(II)	Sr(II)	Ba(II)
EDTA	4.5	101 (2250)	33.1 (128)	396 (8300)	1210 (>10 ⁴)
	5.0	53 (401)	3.9 (26.8)	292 (1220)	784 (10 ⁴)
	6.0	3.1 (15.3)	0.2 (2.1)	16.3 (54)	104 (535)
	7.0	0.8 (1.2)	<0.2 (<0.2)	2.4 (5.7)	7.5 (33.5)
	8.0	<0.5 (<0.5)	<0.2 (<0.2)	0.8 (1.1)	1.2 (3.7)
	9.0	<0.5 (0.5)	<0.2 (<0.2)	<0.5 (<0.5)	0.5 (1.0)
DCTA	4.5	42.5 (958)	19.4 (305)	394 (10 ⁴)	865 (>10 ⁴)
	5.0	8.3 (130)	2.6 (36.5)	274 (3400)	504 (6500)
	6.0	0.5 (2.7)	<0.2 (2.1)	37.8 (183)	202 (1460)
	7.0	<0.5 (<0.5)	<0.2 (<0.2)	5.6 (8.2)	65 (356)
	8.0	<0.5 (<0.5)	<0.2 (<0.2)	0.9 (<0.5)	13.6 (80)
	9.0	<0.5 (<0.5)	<0.2 (<0.2)	<0.5 (<0.5)	1.9 (18.4)

TABLE II. (Contd.)

EGTA	4.5	91 (765)	60 (1540)	161 (2980)	740 (4500)
	5.0	88 (765)	32.6 (865)	157 (2830)	715 (3700)
	6.0	75 (665)	1.6 (19.8)	87 (1590)	345 (1820)
	7.0	48.0 (322)	<0.2 (4.5)	5.9 (50)	28 (69)
	8.0	11.4 (67)	<0.2 (1.9)	<0.5 (4.1)	2.8 (5.0)
	9.0	2.6 (12.0)	<0.2 (1.3)	<0.5 (<1.0)	<1.0 (<1.0)
EDTA (0.10M)	4.5	(120)	(9.8)	(26.7)	(1030)
	5.0	(20.4)	(2.7)	(70)	(315)
	6.0	(1.2)	(<0.5)	(3.9)	(30.5)
	7.0	(<0.5)	(<0.5)	(<0.5)	(2.4)
	8.0	(<0.5)	(<0.5)	(<0.5)	(<0.5)
	9.0	(<0.5)	(<0.5)	(<0.5)	(<0.5)

Coefficients in brackets were determined in absence of NH_4 acetate (0.133M acetate present in the case of EGTA).

particle size in the ammonium form and had an inner diameter of 22 mm. The flow-rate was kept at 3.0 ± 0.3 ml/min, and 1 mmole of each element was used.

Figures 7 and 8 present elution curves for the strontium(II)-barium(II) pair with 0.020M DCTA of pH 7.0 containing 0.30M ammonium acetate and with 1.20N α -hydroxyisobutyrate of pH 7.0, respectively. Resin, column dimensions and flow-rate were the same as those for Figs. 4-6. No

TABLE III.—SEPARATION FACTORS

Eluting agent	Mg/Be		Ca/Mg		Sr/Ca		Ba/Sr	
	Conc., <i>N</i>	Factor	Conc., <i>N</i>	Factor	Conc., <i>N</i>	Factor	Conc., <i>N</i>	Factor
Acetylacetate	0.08	>10	0.18	~320	~2.0*	~15*	—	—
Citrate	0.06	~50	0.18	1.3	0.20	4.3	0.44	2.9
α -hydroxyisobutyrate	0.30	4.0	0.55	1.9	0.74	3.8	1.40	3.2
Lactate	0.33	3.1	0.53	2.0	0.72	3.0	1.17	2.8
Malate	0.07	~100	0.54	1.3	0.60	2.9	0.97	2.8
Malonate	0.08	~30	0.45	4.3	0.87	2.4	1.27	2.7
Formate	0.48	3.4	0.87	2.4	1.33	1.9	1.82	2.3
Acetate	0.67	1.9	0.92	2.2	1.34	2.0	1.92	2.5
Tartrate	0.15	28	0.41	0.40	0.41	3.7	0.75	2.7
NH_4Cl	1.85	0.6	1.32	2.4	2.32	1.4	3.00	2.0
HCl	1.25	1.4	1.50	2.1	2.55	1.4	3.00	1.9
HClO_4	1.32	1.6	1.75	2.1	3.10	1.3	4.20	1.9
HNO_3	1.33	1.5	1.85	1.1	2.03	1.1	2.10	1.2

Eluting agent	Ca/Mg		Sr/Ca		Ba/Sr	
	pH	Factor	pH	Factor	pH	Factor
0.02M EDTA + B	4.77	1/7.4	4.77	34	6.21	5.5
0.02M EDTA	5.43	1/11	5.43	28	6.68	7.1
0.10M EDTA	4.48	1/12	4.48	27	5.65	6.8
0.02M DCTA	5.33	1/3.6	5.33	148	6.92	38
0.02M DCTA + B	4.65	1/2.8	4.65	34	6.72	9.1
0.02M EGTA	6.36	1/54	6.36	66	7.59	1.2
0.02M EGTA + B	5.40	1/8.2	5.40	15	6.85	4.3

* From elution curves.

B = buffer of 0.30M NH_4 acetate.

barium appeared in the first 1000 ml of eluate on elution with 0.020M DCTA, but the strontium peak was very wide for larger amounts of strontium. When the DCTA concentration was increased to 0.10M and the pH was decreased to 6.0 or 6.5, the separation factor α_{Sr}^{Ba} decreased considerably and a slight overlapping of the barium and strontium occurred when 1 mmole of each element was present in a column run.

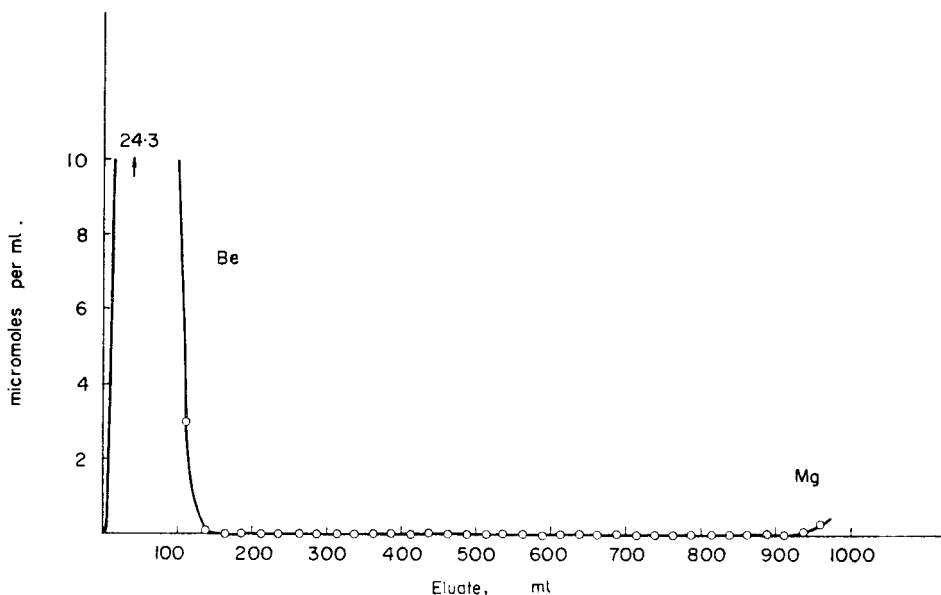


FIG. 1.—Elution curve for Be(II)-Mg(II) with 0.10N NH_4 malate of pH 7.0. Column, 15 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+ -form. Diameter 15 mm. Flow-rate 2.0 ± 0.2 ml/min.

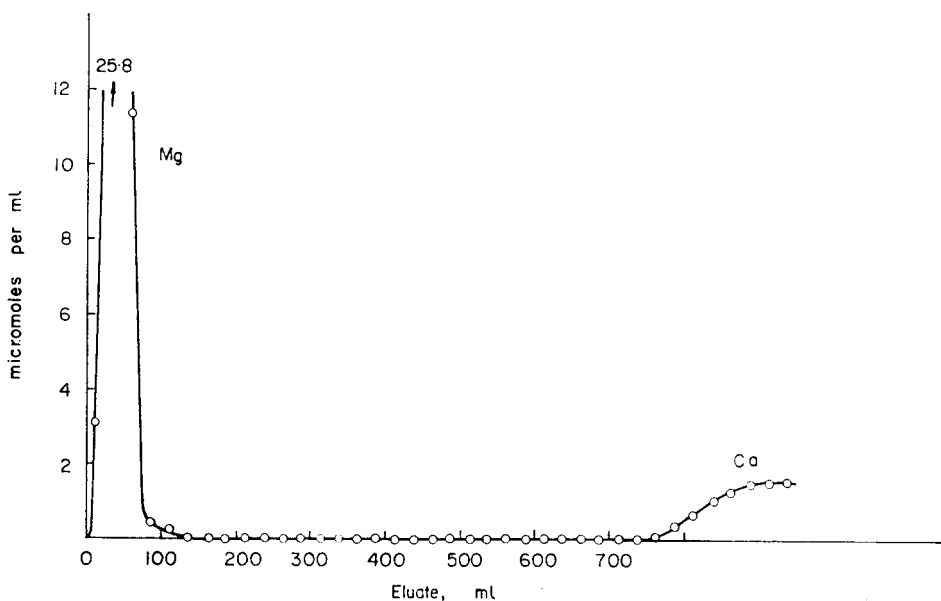


FIG. 2.—Elution curve for Mg(II)-Ca(II) with 0.20M NH_4 acetylacetonate of pH 9.0. Column, 15 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+ -form. Diameter 15 mm. Flow-rate 2.0 ± 0.2 ml/min.

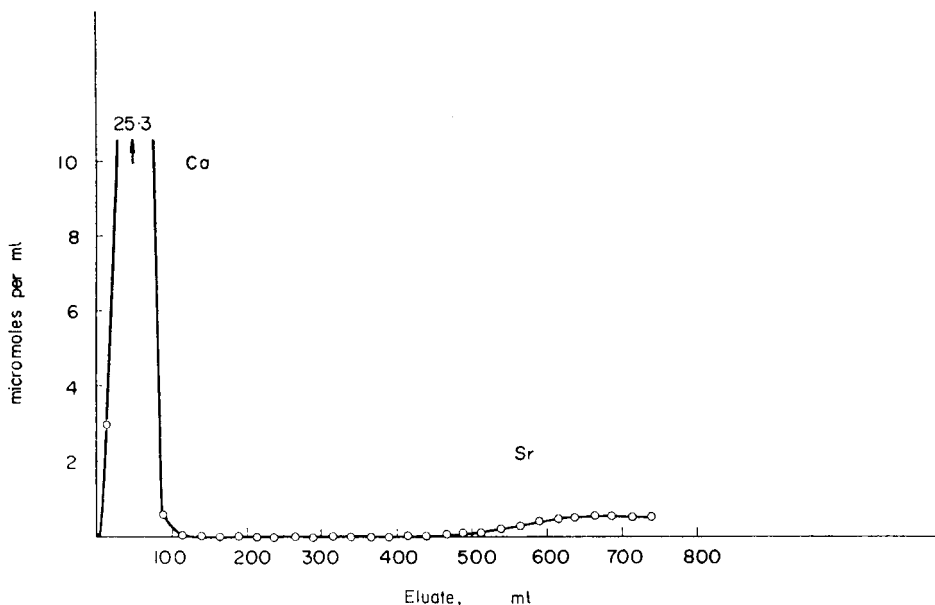


FIG. 3.—Elution curve for Ca(II)-Sr(II) with 2.0M NH_4 acetylacetonate of pH 9.0. Column, 15 ml of AG50W-X8 resin, 200–400-mesh NH_4^+ -form. Diameter 15 mm. Flow-rate 2.0 ± 0.2 ml/min.

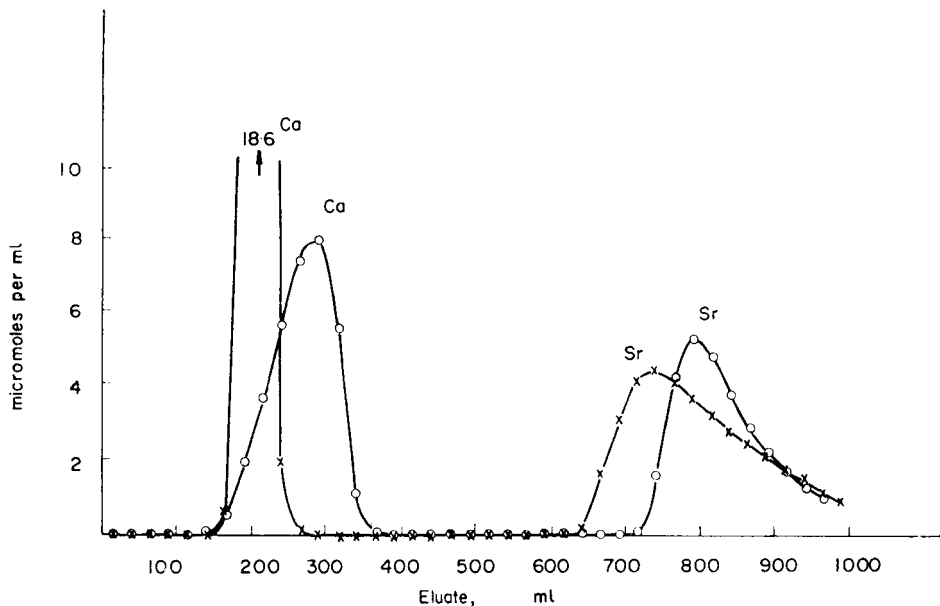


FIG. 4.—Elution curves for Ca(II)-Sr(II) with
 $\times - \times - \times$ 0.70N NH_4 α -hydroxyisobutyrate of pH 7.0.
 $\circ - \circ - \circ$ 0.20N NH_4 citrate of pH 7.5.
 Column, 60 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+ -form.
 Diameter 21 mm. Flow-rate 3.0 ± 0.3 ml/min.

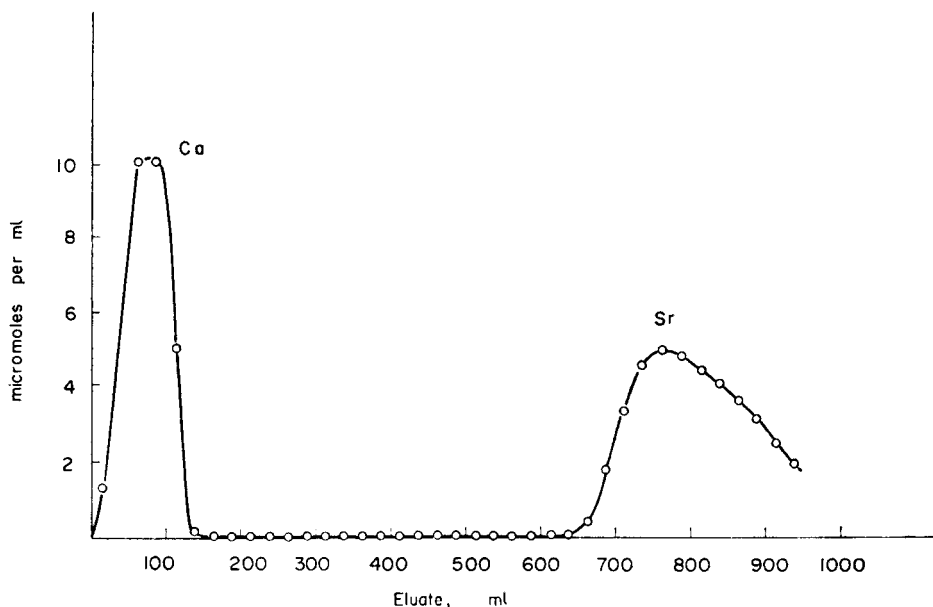


FIG. 5.—Elution curve for Ca(II)-Sr(II) with 0.10M EDTA of pH 5.0 containing 0.30M NH_4 acetate. Column, 60 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+ -form. Diameter 22 mm. Flow-rate 3.0 ± 0.3 ml/min.

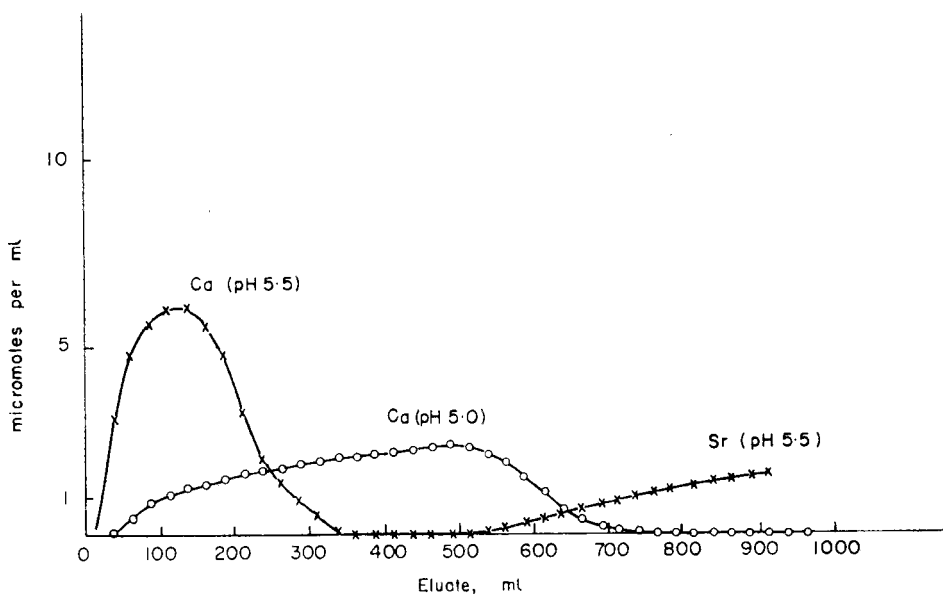


FIG. 6.—Elution curves for Ca(II)-Sr(II) with 0.10M EDTA of pH 5.0 and 5.5. Column, 60 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+ -form. Diameter 22 mm. Flow-rate 3.0 ± 0.3 ml/min.

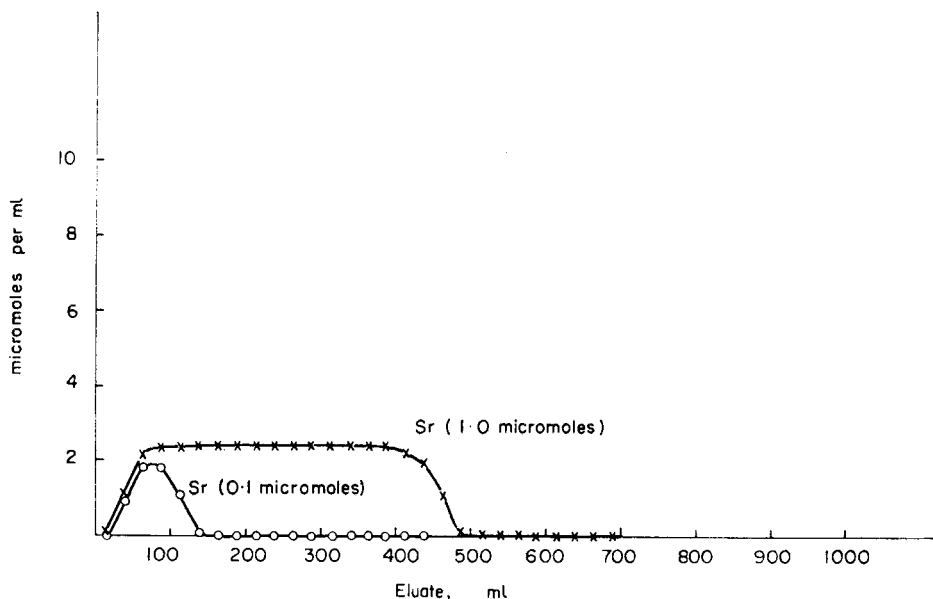


FIG. 7.—Elution curves for Sr(II)-Ba(II) with 0.020M DCTA of pH 7.0 containing 0.30M NH_4 acetate. Column, 60 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+ -form. Diameter 21 mm. Flow-rate 3.0 ± 0.3 ml/min. No Ba(II) detectable in first 1000 ml.

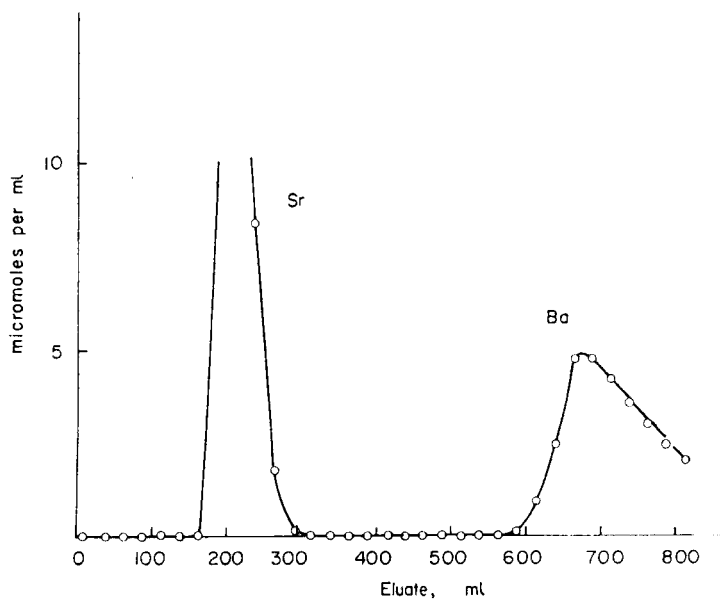


FIG. 8.—Elution curve for Sr(II)-Ba(II) with 1.20N NH_4 α -hydroxyisobutyrate of pH 7.0. Column, 60 ml of AG50W-X8 resin, 200–400-mesh, NH_4^+ -form. Diameter 21 mm. Flow-rate 3.0 ± 0.3 ml/min.

DISCUSSION

The analytical errors for the coefficients presented are about $\pm 1\%$ or better in the range of values from 20 to 100 and are greater for higher or lower values. This does not apply to the coefficients in EDTA, EGTA, DCTA and acetylacetonate. These coefficients are strongly pH-dependent with the first three reagents and therefore less accurate because of uncertain pH-values (not better than ± 0.03 pH), while coefficients in acetylacetonate depend on the history of the eluting agent and are very much less reproducible than those in acetate, malonate *etc.* The values given can be considered only as approximate. Furthermore, calcium, strontium and barium are eluted with acetylacetonate at much lower eluent concentration than predicted by the distribution coefficient. Apparently the reagent undergoes a slow reaction in ammoniacal aqueous solution which changes its ion-exchange properties, and no correlation between coefficients and elution curves can be obtained.

Be(II)–Mg(II). The largest separation factor ($\alpha_{\text{Be}}^{\text{Mg}} \sim 90$) and excellent separations are obtained with 0.10*N* ammonium malate of pH 7.0 as eluting agent (Fig. 1). This seems to be the largest separation factor known for this pair. The 0.10*N* ammonium citrate and malonate of pH 7.0 and 0.20*N* ammonium tartrate of pH 7.0 also give a large separation factor and good separations. The 0.20*N* ammonium malonate containing 0.1*N* malonic acid is a good eluting agent for practical purposes. Beryllium(II) is eluted with a small volume of eluting agent, the separation factor is still reasonably large ($\alpha_{\text{Be}}^{\text{Mg}} \sim 10$) and the reagent can be destroyed very easily.² The 0.10*M* ammonium acetylacetonate of pH 9 also gives a large separation factor, but actual separations are less satisfactory, because magnesium appears in the eluate sooner than predicted by the distribution coefficients.

Ca(II)–Mg(II). The most effective separation of this pair is obtained with 0.20*M* ammonium acetylacetonate of pH 9, with the very large separation factor of $\alpha_{\text{Mg}}^{\text{Ca}} \sim 200$ (Fig. 2). A good separation is also obtained by using 0.40 or 0.45*N* ammonium malonate as eluting agent.² The separation factor is not very large ($\alpha_{\text{Mg}}^{\text{Ca}} = 4.3$), but exchange kinetics are good and the reagent can be destroyed easily. The 0.10*M* EGTA of pH 6.0 containing 0.3*M* sodium acetate–acetic acid buffer also gives a large separation factor, but calcium is eluted first. The separation factor with EGTA is considerably reduced by the presence of ammonium acetate (Table III) as has been observed by Povondra and Přibil¹⁶ previously. A fairly good separation is also obtained with 0.10*M* EDTA of pH 4.5 containing 0.20*M* sodium acetate–acetic acid buffer, but with DCTA separation is not satisfactory. With both eluents calcium is again eluted first. Lactate,¹⁰ formate,⁷ acetate,^{5,6} α -hydroxyisobutyrate^{11,12} and ammonium chloride have separation factors not much different from those with aqueous hydrochloric acid and therefore do not present any advantage over this reagent. More attractive for practical purposes than any of the reagents above seems to be 3.00*M* hydrochloric acid containing 60% of ethanol.³ The separation factor is still reasonably large $\alpha_{\text{Mg}}^{\text{Ca}} \sim 6$ (~ 8 for small amounts), separations are excellent, and the eluting agent can be removed most easily.

Sr(II)–Ca(II). The 0.10*M* DCTA of pH 4.7 containing 0.30*M* ammonium acetate provides the best separation of strontium from calcium (Fig. 5), and 0.10*M* EDTA under similar conditions is almost as good, with about 5 fraction volumes less between the peaks when a 60-ml resin column and 1 mmole of each element are used. At pH 5.0 the calcium peaks are even sharper for both reagents, while strontium is still

retained strongly enough for an excellent separation. While batch separation factors are as high as, or higher in the absence of ammonium acetate buffer than in its presence, actual column separations are considerably improved by the presence of the buffer (Figs. 5 and 6). An even more effective separation is obtained with 2.0*M* ammonium acetylacetonate of pH 9.0 as eluent ($\alpha_{\text{Ca}}^{\text{Sr}} \sim 15$ according to column work), and 1-mmole amounts can easily be separated even on a 15-ml (5-g) resin column (Fig. 3), but the removal of the reagent is much more troublesome than that of EDTA. The 0.10*M* EGTA of pH 5.8 containing 0.30*M* ammonium acetate also provides an excellent separation of calcium and strontium. Citrate ($\alpha_{\text{Ca}}^{\text{Sr}} = 4.3$) and α -hydroxyisobutyrate ($\alpha_{\text{Ca}}^{\text{Sr}} = 3.8$), both of pH 7, have somewhat lower separation factors than the above reagents, but they still provide very good separations, as shown in Fig. 4. It is remarkable that despite a lower separation factor the α -hydroxyisobutyrate separation is as good as the separation with citrate. The somewhat sharper elution peak of calcium with α -hydroxyisobutyrate seems to indicate that this reagent has better column kinetics which make up for the larger separation factor with citrate. Citrate nevertheless is quite attractive because good separation can be obtained at low eluting agent concentration (0.20*N*). This facilitates removal of the eluting agent. After addition of hydrochloric acid to reduce the pH to below 3, the eluate can be passed directly onto a small second cation-exchange column in the hydrogen-ion form which will absorb the calcium while the citrate passes through. Figure 4 seems to contradict the work of Milton and Grummit⁸ who came to the conclusion that cation-exchange in citrate is unsatisfactory for the separation of calcium from strontium. The reason for this is that their elutions were carried out with 5% citrate of pH 5. Our own investigations showed that distribution coefficients are considerably higher and separation factors distinctly lower at pH 5 than at pH 7. This is caused by the dissociation of the second and third hydrogen ions of citric acid between pH 5 and pH 7. Apparently complexes of Ca with L^{3-} are somewhat more stable than complexes with HL^{2-} ($\text{L}^{3-} = \text{citrate}$).²⁰ From pH 7 to 9 distribution coefficients and separation factors remain practically constant. Ammonium lactate and malate are less effective eluting agents than α -hydroxyisobutyrate, but are still quite satisfactory, while even malonate is superior to acetate and formate, which again are better than hydrochloric acid. Tsubota²¹ has suggested 1*M* ammonium formate containing 50% of acetone and 1*M* ammonium acetate containing 50% of methanol as eluting agents for the improved separation of calcium from strontium. The separation factor has values of about 5–6, but the elution curves do not show much improvement as compared with the aqueous reagents, apparently because the increased separation factors are accompanied by less favourable column kinetics caused by the partly organic solvent. Separations appear to be less effective than those with citrate or α -hydroxyisobutyrate.

Ba(II)–Sr(II). The highest separation factor for this pair is obtained in 0.02*M* DCTA of pH 7.0 containing 0.30*M* ammonium acetate. Unfortunately the separation factor decreases with increasing concentration of DCTA and decreasing pH values. Separations with 0.10*M* DCTA are therefore not satisfactory. For this reason 1.20*N* ammonium α -hydroxyisobutyrate of pH 7.0 (Fig. 8) is preferred for the separation of large amounts of strontium from small amounts of barium, but DCTA has definite advantages for the separation of small amounts of strontium from large amounts of barium. Reasonable separations can also be obtained with 1.0*N* ammonium lactate, 0.85*N* ammonium malate or 1.1*M* ammonium malonate of pH 7.0 or with 0.10*M*

EDTA of pH 6.0 in the presence of 0.30M ammonium acetate. More attractive than any of these eluting agents for practical purposes is 3.0N hydrochloric acid containing 20% of ethanol.⁴

Zusammenfassung—Die Gleichgewichts-Verteilungskoeffizienten der Erdalkalimetalle Be(II), Mg(II), Ca(II), Sr(II) und Ba(II) zwischen den Komplexbildnern Acetat, Formiat, Lactat, Citrat, Tartrat, α -Hydroxyisobutyrat, Malonat, Malat, Acetylacetonat, EDTA, EGTA sowie DCTA und dem Kationenaustauschharz AG50W-X8 werden angegeben. Der Vollständigkeit halber werden die Koeffizienten in HCl, HNO₃, HClO₄ und NH₄Cl beigelegt. Die Vorteile der verschiedenen Komplexbildner zur Trennung von Paaren benachbarter Elemente werden diskutiert und experimentelle Elutionskurven ausgewählter Trennungen wiedergegeben. Trennfaktoren für benachbarte Elemente werden berechnet für Konzentrationen des Elutionsmittels, die einem Verteilungskoeffizienten von 10 für das schwächer adsorbierte Element entsprechen. Sie werden zusammen mit den Konzentrationen an Elutionsmittel als Vergleichsbasis angegeben.

Résumé—On présente les coefficients de partage à l'équilibre pour les métaux alcalins-terreux Be(II), Mg(II), Ca(II), Sr(II) et Ba(II) avec les agents complexants acétate, formiate, lactate, citrate, tartrate, α -hydroxyisobutyrate, malonate, malate, acétylacétonate, EDTA, EGTA et DCTA, et la résine échangeuse de cations AG 50W-X8. On inclut les coefficients en HCl, HNO₃, HClO₄ et NH₄Cl pour être complet. On discute des mérites des divers agents complexants pour la séparation de paires d'éléments adjacents et présente des courbes d'éluion expérimentales pour des séparations choisies. On calcule les facteurs de séparation pour les éléments adjacents à des concentrations d'agent éluant correspondant à un coefficient de partage de 10 pour l'élément le moins fortement absorbé, et les présente en même temps que les concentrations d'agent éluant pour former une base de comparaison.

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ANALYTICAL APPLICATIONS OF TERNARY COMPLEXES—VIII*

AN IMPROVED REAGENT SYSTEM FOR THE SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM

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Summary—Aluminium ions form a ternary complex with Catechol Violet (CV) and cetyltrimethylammonium bromide (CTAB) in which an $Al^{3+}:CV:CTAB$ ratio of 1:2:5 is observed. The sensitivity of the binary complex between aluminium and Catechol Violet $\epsilon_{615nm} = 1.50 \times 10^3 \text{ l. mole}^{-1} \cdot \text{mm}^{-1}$ is enhanced on ternary complex formation to $\epsilon_{670nm} = 5.30 \times 10^3 \text{ l. mole}^{-1} \cdot \text{mm}^{-1}$. The colour is formed instantaneously, stabilizes within 20 min, and may be used for the detection of aluminium in the range 0.27–54 μm in the presence of EDTA which prevents the interference of most ions. A benzoate extraction procedure for aluminium is used to prevent interference from hundred-fold amounts of Cr(VI), Fe(II), Fe(III), Hg(II), Sb(III), Ti(IV) and acetate, but Be, Cr(III), rare earths, V(V), Zr and tartrate must be absent, as must high concentrations of phosphate and fluoride ions.

CATECHOL VIOLET was proposed as a reagent for the absorptiometric determination of aluminium by Anton¹ in 1960. Subsequently, Tanaka and Yamayoshi² reported extremely high sensitivities with the same reagent for tin and aluminium (molar absorptivity for Al = $6.8 \times 10^3 \text{ l. mole}^{-1} \cdot \text{mm}^{-1}$). In common with other workers^{3,4} we have been unable to obtain such high values for tin in this laboratory⁵ and have only been able to approach the sensitivity for aluminium by ternary complex formation.

During our studies on the sensitizing effect of cetyltrimethylammonium bromide (CTAB) on the reaction of Catechol Violet with various metal ions,^{3,6,7} it was established that the addition of CTAB to the binary aluminium–Catechol Violet complex produced a marked bathochromic shift in wavelength of absorption from 615 to 670 nm. In addition, the molar absorptivity increased from 1.50×10^3 to $5.30 \times 10^3 \text{ l. mole}^{-1} \cdot \text{mm}^{-1}$. This communication describes the spectrophotometric determination of aluminium by means of this ternary complex, which is of comparable or greater sensitivity than methods previously described utilizing Chromazurol,^{8–10} Eriochrome Cyanine,¹¹ Aluminon^{12,13} or 8-hydroxyquinoline.^{12–15} We have found this colour reaction to be more reproducible and less prone to variations in reagent composition than the binary complex.

EXPERIMENTAL

Reagents

All are of analytical grade unless stated otherwise.

Benzoic acid (GPR), 5% solution in ethyl acetate.

Ammonium benzoate, 10% aqueous solution.

Ammonium acetate, 50% aqueous solution.

1,10-Phenanthroline, 2% aqueous solution.

Hydroxylammonium chloride, 10% aqueous solution.

Ascorbic acid, 5% aqueous solution. Prepared fresh every 2 days.

* Part VII—Talanta, 1968, 15, 1359.

EDTA, ca. 0.1M. Dissolve 7.5 g of EDTA (GPR free acid) in ca. 200 ml of water by addition of the minimum volume of conc. ammonia solution. Adjust the pH to 9.5 and dilute to 250 ml with distilled water.

Buffer, pH 10.2. Dilute 50 ml of conc. ammonia solution to 350 ml with distilled water and adjust the pH to 10.2 with conc. hydrochloric acid. Dilute to 400 ml with distilled water.

Aluminium solution. Dissolve 0.2267 g of ammonium alum $[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ in 500 ml of distilled water. (More dilute solutions may be prepared from this stock solution.) Store in polythene or glassware treated with a silicone water-repellent such as "Repelcote" (Hopkin and Williams).

Reagent solution. Catechol Violet $2 \times 10^{-4}M$ and CTAB $2 \times 10^{-3}M$. Dissolve 0.1546 g of Catechol Violet in 500 ml of distilled water, add 1.458 g of CTAB and stir to dissolve until there is no turbidity (the solution may need gentle warming). Dilute to 2 l. with distilled water.

Procedure

To prepare the calibration curve transfer by pipette 1–10 ml portions of $10^{-4}M$ aluminium solution into 100-ml volumetric flasks. Add 25 ml of the reagent solution, 5 ml of 5% ascorbic acid solution and 5 ml of the pH 10.2 buffer solution. After 20 min, add 5 ml of 0.1M EDTA, make up to volume and measure the absorbance at 670 nm against a reagent blank. The curve is a straight line passing through the origin.

Proceed similarly for test samples, but modify the procedure as follows for both test samples and calibration if interfering species are present. Transfer an appropriate aliquot (1–10 ml) of the ca. $10^{-4}M$ aluminium test solution into a 100-ml separating-funnel. Add 2 ml of 50% ammonium acetate solution, 2 ml of 2% 1,10-phenanthroline solution, 1 ml of 10% hydroxylammonium chloride solution and 5 ml of 10% ammonium benzoate solution. If necessary, adjust the pH to 7.5–9. Add 10 ml of 5% benzoic acid solution in ethyl acetate and shake vigorously. Separate and discard the lower (aqueous) layer and back-extract the organic phase with two 10-ml portions of 1M hydrochloric acid. Combine these extracts in a 100-ml flask containing 25 ml of the reagent solution and 5 ml of ascorbic acid. Add conc. ammonia solution dropwise until the colour of the solution changes from orange to green. Then add 5 ml of the pH 10.2 buffer solution and, after 20 min, 5 ml of 0.1M EDTA solution, make up to volume and measure the absorbance at 670 nm against a reagent blank. The coloured complex tends to adhere strongly to glassware so it is necessary to wash all vessels which have come in contact with it, concentrated hydrochloric acid being used for this purpose; this procedure must also be used for cleaning the cuvettes between each measurement.

RESULTS AND DISCUSSION

Spectral characteristics

The absorption spectra of the reagent solution (Catechol Violet and CTAB) and the ternary complex with aluminium at pH 10.2 are shown in Fig. 1. Included, for comparison, are the spectra of Catechol Violet and the binary complex obtained with aluminium at the same pH value. The ternary complex shows a pronounced absorption at ca. 670 nm whereas the binary aluminium complex gives a less well-defined absorption (compared with the reagent alone) with a peak at 615 nm. The absorption of Catechol Violet at 615 nm is reduced appreciably by the addition of CTAB.

Optimum conditions for colour development

The optimum pH for complex formation was found to lie in the range 9.7–10.2 (Fig. 2). Values of pH greater than about 10.5 could not be achieved without very rapid oxidation of the mixed reagent solution. Oxidation of Catechol Violet was in fact found to occur in alkaline solutions at pH values less than 10.5 unless an anti-oxidant such as ascorbate or hydroxylammonium chloride was present. These were ineffective above pH 10.5.

Maximum colour formation was found to occur with slightly greater than a 2-fold molar excess of Catechol Violet and a 5-fold molar excess of CTAB over aluminium. A greater molar excess of Catechol Violet than about 2-fold produced a slightly

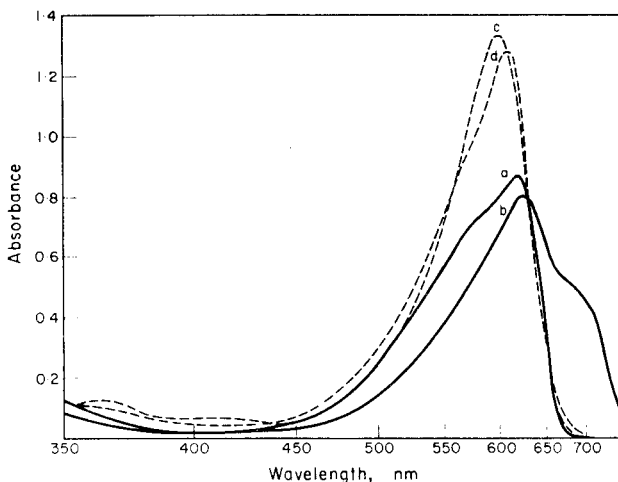


FIG. 1.—Absorption spectra.

(a) 5 ml of $10^{-3}M$ Catechol Violet and 5 ml of $10^{-2}M$ CTAB diluted to 100 ml with distilled water; (b) as (a) plus 1 ml of $10^{-3}M$ aluminium; (c) 5 ml of $10^{-3}M$ Catechol Violet diluted to 100 ml with distilled water; (d) as (c) plus 1 ml of $10^{-3}M$ aluminium. All solutions adjusted to pH 10.2.

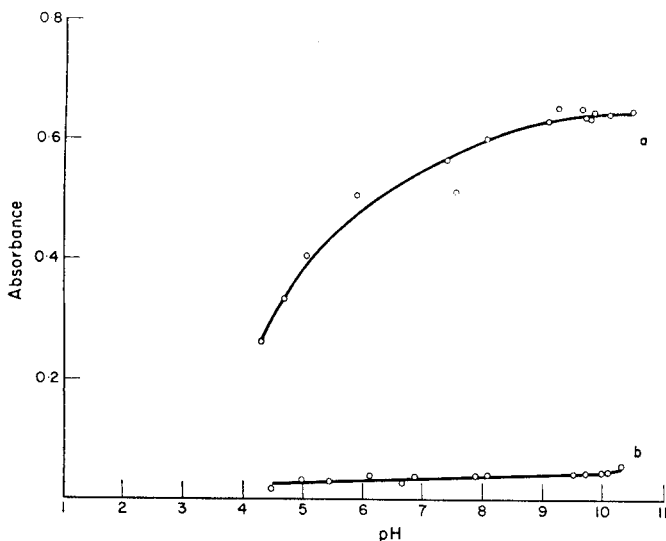


FIG. 2.—Optimum pH for colour formation.

(a) 5 ml of $10^{-3}M$ Catechol Violet, 5 ml of $10^{-2}M$ CTAB and 1 ml of $10^{-3}M$ aluminium solution diluted to 100 ml with distilled water. (b) as (a) but with no aluminium.

diminished sensitivity. It was, however, found necessary to use a 25–50-fold molar excess of CTAB over aluminium in order to stabilize the colour and prevent a rapid decrease in absorbance owing to precipitation of the complex. This necessitated special treatment of the mixed reagent solution to secure the maximum colour formation and prevent the reagent solution from precipitating. When the temperature of the mixed reagent solution fell below *ca.* 20° for any length of time, the reagent solution

deposited a flocculent precipitate of CTAB. This deposition could be postponed almost indefinitely by constant low-speed stirring or reversed by warming the solution to *ca.* 30°.

When these precautions were not observed and the mixed reagent solution was allowed to become even faintly turbid, the blank absorbance value increased without a corresponding increase in the complex absorbance. This behaviour prevented an absolute value being ascribed to the molar absorptivity of the complex, although a series of solutions prepared at the same time from the same mixed reagent solution obeyed Beer's Law.

Colour development in alkaline solution was found to be instantaneous but this was followed immediately by a rapid decrease for some 20 min. After this time, the rate of decrease in absorbance was found to have slowed so that there was only a further 15% decrease over the next 24 hr. Measurement of a series of solutions allowed to age for 20 min was found to give consistent absorbance values. The decrease in absorbance in the first 20 min was measured as 30% of the initial absorbance value; this decrease could not be prevented.

With the optimum conditions described above, a linear calibration curve was obtained for the direct method over the range 0.27–54 ppm aluminium, the effective molar absorptivity being $5.30 \times 10^3 \text{ l.mole}^{-1}.\text{mm}^{-1}$ ($\pm 4\%$). The solvent extraction procedure which was subsequently developed to avoid certain interferences was found to give a linear calibration curve over the range 2.7–27 ppm aluminium, the molar absorptivity coefficient remaining the same.

Nature of complex

The Catechol Violet:aluminium ratio was determined by the method of continuous variation to be 2:1. No other complexes were observed. Potentiometric titrations indicated the formation of the $\text{Al}(\text{Catechol Violet})_2(\text{CTAB})_5$ complex. Figure 3 shows a possible form of it, which is supported by the observed partial extraction of a blue species into chloroform. This extract was not studied further because it was not found possible to separate completely the emulsion formed when CTAB-containing solutions were shaken with chloroform. The ternary complex is insoluble in water. Salts of the cetyltrimethylammonium ion with bulky anions such as perchlorate or iodide are also insoluble.³

In the light of these observations and the known requirement for the presence of micelles for complex formation,^{6,7} it is postulated that the complex formed with aluminium is present as finely dispersed particles protected within the CTAB micelles in solution. This is supported by the observed initial rapid drop in absorbance of the complex, corresponding to aggregation of these particles.

The bathochromic shift is thought to be due to further deprotonation of the hydroxyl groups on the dye molecule with formation of the ion shown in Fig. 3. Potentiometric titrations indicated the release of eight equivalents of protons per equivalent of ternary complex which is in agreement with the results obtained by Malát and Zelinka.¹⁶ It also demonstrated that the nature of the cationic surfactant plays at most a minor role in the colour change, in that when cetylpyridinium bromide was substituted for CTAB, the absorption spectra obtained for the respective ternary complexes were nearly identical. Thus, the colour change is not thought to be a charge-transfer phenomenon. Further support is lent to this view by the formation of

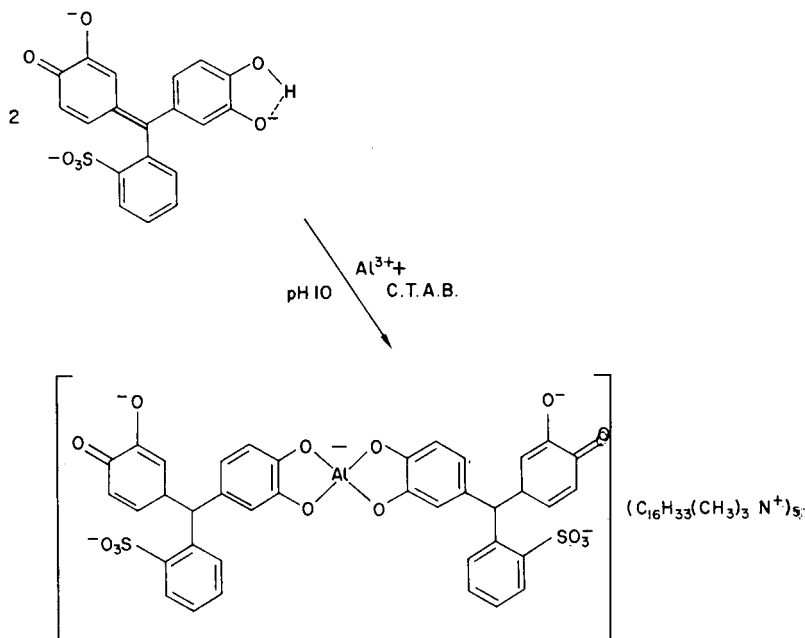


FIG. 3.—Formation of complex.

a ternary molybdenum(VI)/carminic acid/CTAB complex together with a bathochromic shift and increased absorbance. The binary molybdenum(VI)/carminic acid complex possesses a number of hydroxyl groups which would be expected to deprotonate readily.

A notable physical property of the ternary complex with aluminium was its adsorbability onto the walls of glass vessels, even after treatment with a silicone water-repellent. An adhering film was found to build up slowly and continuously over a period of days until the original solution became noticeably decolorized. The film could be removed by washing with acetone or concentrated hydrochloric acid which destroys the complex. Washing with water had little effect.

Interferences

A number of possible interfering species likely to be present in a sample for analysis were investigated. No interference was found from the alkalis, boron (as borate), molybdenum(VI), selenium(IV), fluoride or phosphate when present in concentrations less than $10^{-3}M$ (*i.e.*, less than about 100-fold molar excess over aluminium). The addition of EDTA after formation of the ternary aluminium complex (*i.e.*, after adjustment of pH to 10.2) prevented interference from a 100-fold molar excess over aluminium of magnesium, cobalt, nickel, zinc, copper(II), cadmium and lead. EDTA added *before* complex formation was also found to interfere.

The solvent extraction procedure developed was able to prevent interference from 100-fold molar excesses of iron(II), iron(III), chromium(VI), mercury(II), titanium(IV), antimony(III) and acetate. Interference was, however, still observed from zirconium, vanadate, beryllium, the rare earth elements, chromium(III) and tartrate. High concentrations of phosphate, ascorbate and fluoride (1000-fold molar excess

over aluminium) interfered by reducing the extraction efficiency. Ascorbate does not interfere with the formation of the ternary complex when it is subsequently added as a protective agent.

Solvent extraction of aluminium with benzoate

The solvent extraction procedure used for the separation of aluminium as its benzoate is based on the procedure described by Morrison and Freiser.¹⁷ It was found necessary to modify the procedure by using 5% benzoic acid in ethyl acetate in order to increase the recovery of aluminium from 75% to 100%. The addition of ammonium rather than sodium benzoate to the aqueous solution was effective in reducing the absorbance of the blank. It was found to be beneficial to form the extractable complex in an acid solution *ca.* pH 4 since the efficiency of extraction was improved, probably because of the formation of a basic benzoate at higher pH values. The presence of the ascorbic and tartaric acids in the extraction medium decreased the extraction efficiency by competing for the aluminium ions.

The anomalous interference of chromium(III) arose from the complete obscuration of the phase boundary by the bulky precipitate formed at the interface. Chromium(VI), reduced to chromium(III) *in situ* by the hydroxylamine, yielded less precipitate and although the phase boundary was still indistinct its precise location was rendered possible by the red colour imparted to the solution in the presence of iron by the tris-1,10-phenanthroline iron(II) ion. When iron was absent an addition of iron was made to chromium containing solutions to render the phase boundary visible.

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Zusammenfassung—Aluminiumionen bilden einen ternären Komplex mit Catechinviolett (CV) und Cetyltrimethylammoniumbromid (CTAB), in dem das Verhältnis $Al^{3+}:CV:CTAB = 1:2:5$ beobachtet wird. Die Empfindlichkeit des binären Komplexes zwischen Aluminium und Catechinviolett $\epsilon_{615nm} = 1,50 \cdot 10^3 \text{ l. mol}^{-1} \text{ mm}^{-1}$ wird durch Bildung des ternären Komplexes auf $\epsilon_{670nm} = 5,3 \cdot 10^3 \text{ l. mol}^{-1} \text{ mm}^{-1}$ gesteigert. Die Farbe bildet sich augenblicklich stabilisiert sich in 20 min und kann zur Bestimmung von Aluminium im Bereich 0,27–54 ppm verwendet werden. Zur Vermeidung von Störungen durch die meisten Ionen gibt man EDTA zu. Um Störung durch hundertfache Mengen Cr(VI), Fe(II), Fe(III), Hg(II), Sb(III), Ti(IV) und Acetat zu vermeiden, wird Aluminium mit Benzoat extrahiert. Be, Cr(III), seltene Erden, V(V), Zr und Tartrat dürfen nicht anwesend sein ebenso hohe Konzentrationen von Phosphat- und Fluoridionen.

Résumé—Les ions aluminium forment un complexe ternaire avec le Violet de Catéchol (CV) et le bromure de cetyltriméthylammonium (CTAB) dans lequel on observe un rapport $Al^{3+}:CV:CTAB$ de 1:2:5. La sensibilité du complexe binaire entre l'aluminium et le Violet de Catechol, $\epsilon_{615nm} = 1,50 \times 10^3 \text{ l. mole}^{-1} \cdot \text{mm}^{-1}$ est exaltée par formation du complexe ternaire à $\epsilon_{670nm} = 5,30 \times 10^3 \text{ l. mole}^{-1} \cdot \text{mm}^{-1}$. La coloration se forme instantanément, se stabilise en 20 min, et peut être utilisée pour la détection de l'aluminium dans le domaine 0,27–54 ppm en la présence d'EDTA qui évite l'interférence de la plupart des ions. On utilise une technique d'extraction au benzoate pour l'aluminium pour éviter l'interférence de quantités cent fois plus élevées de Cr(VI), Fe(II), Fe(III), Hg(II), Sb(III), Ti(IV) et acétate, mais Be, Cr(III), les terres rares, V(V), Zr et tartrate doivent être absents, ainsi que des concentrations élevées d'ions phosphate et fluorure.

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THE PERFORMANCE-CHARACTERISTICS OF ANALYTICAL METHODS—I

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Summary—The ever-increasing volume of analytical literature makes it important to be able to compare unambiguously the advantages and disadvantages of analytical methods. To this end, a set of consistent definitions and methods for determining quantitative performance-characteristics (*e.g.*, precision, sensitivity, bias) is needed. The aim of this series of papers is to review the definition and determination of such parameters, and to suggest criteria for general use. This first paper discusses the general problem, considers those general aspects of analytical methods that are important, and establishes the performance-characteristics to be considered in detail.

KIRKBRIGHT¹ has pointed out the difficulties experienced by analysts when attempting to determine from the literature the most suitable spectrophotometric method or reagent for a particular purpose. These difficulties arise for two main reasons: (a) the nature and extent of investigation vary markedly from one paper to another; (b) authors use different approaches in defining, determining and expressing the quantitative characteristics of their methods. Kirkbright's paper is timely for, as he says, when new or modified methods are being presented in the literature at an ever-increasing rate, confusion and ambiguity are likely to increase so long as (a) and (b) persist. Conversely and desirably, greater uniformity will lead to more certain and efficient utilization of the vast amount of information appearing.

In an attempt to eliminate or reduce these problems, Kirkbright made a number of suggestions concerning the minimum amount of quantitative data that should be included in any publications describing new or modified reagents and methods. He dealt mainly with important experimental parameters in spectrophotometry but also recommended that data should be quoted for precision, sensitivity, selectivity, *etc.* Such parameters are of fundamental importance in defining the usefulness of all analytical methods. Garton *et al*² have used the term "performance-characteristics" to describe parameters of this nature. This term seems admirable, and is used throughout this series of papers.

Many authors, *e.g.*, refs. 2 and 3, have stressed the importance of uniformity in the definition and determination of performance-characteristics; otherwise, unambiguous comparison of analytical methods is either impossible or severely hindered. Nevertheless, analytical literature is notable for the multiplicity of methods used to describe performance-characteristics. This lack of uniformity is probably due to many factors among which may be included the following.

(a) Surprisingly, there appear to be no generally accepted definitions of several basic concepts such as "analytical method," "precision" and "interference."

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(b) A unified treatment of performance-characteristics is either absent, superficial or not comprehensive in the standard analytical texts, or in the journals. The most complete discussion known to the author is in Gottschalk's book,⁴ which is in German, and tends to emphasize the statistical rather than the analytical aspects. Published papers generally present the views of their authors rather than attempt a critical review, and any suggestions made are often expressed in terms of a particular technique rather than in terms capable of general application.

(c) Statistical concepts must be used in consideration of many performance-characteristics. Many analysts seem unfamiliar with, or partially averse to, the use of such techniques, particularly when the topic is approached from the statistical rather than the analytical viewpoint.

For these reasons alone, it is not surprising that wide variations occur in the definition and determination of performance-characteristics. This series of papers has the following aims: (a) to discuss the characterization of analytical methods and propose performance-characteristics of general importance; (b) to consider the various definitions that have been suggested for these characteristics and to recommend definitions thought most suitable for general use; (c) to suggest suitable experimental techniques for determining these characteristics. These proposals are unlikely to meet with general agreement, but the author will be well satisfied if these papers provoke comment and discussion and perhaps help to lead to the general agreement that is so desirable and must ultimately be obtained. It should be emphasized that few of the individual ideas in this series are original; most if not all are to be found in the literature. The aim was not to provide a series of new observations but rather to attempt to weld existing concepts into a consistent whole.

The first part deals with several aspects that must be considered before individual performance-characteristics are discussed in detail. Throughout, only quantitative methods for analysing discrete samples are considered. Qualitative and continuous analysis are excluded; the former because quantitative treatment on the lines intended seems unnecessary and inappropriate, and the latter because a different type of treatment is preferable for some of the performance-characteristics.

DEFINITION OF ANALYTICAL METHOD

First it is essential to be clear on the meaning of the term "analytical method." The general concept seems clear at first sight but its very familiarity may conceal important differences in interpretation.

Analytical methods are of interest principally because they are, or may be, used in the production of analytical results. However, several other components are also involved in producing results. Thus, in addition to a description of the procedure to be used, an analyst, apparatus, reagents, laboratory and sample are all generally required. The question immediately arises—which combination of all or some of these components constitutes the analytical method? If none of the last five components affected analytical results, the question would be trivial. However, experience shows indisputably that each may markedly affect, for example, the precision and/or bias of analytical results. Thus, if any of these components were included with the procedure in a definition of "analytical method," it would follow that the method could change each time that a different analyst, apparatus, reagent, laboratory or sample

was involved; such an ambiguous situation is to be avoided. It is concluded, therefore, that an unambiguous and useful definition can be framed only in terms of the procedure. A suggested definition is given below, and is recommended for general adoption.

Definition. An analytical method is to be regarded as the set of written instructions completely defining the procedure to be adopted by the analyst in order to obtain the required analytical result.

Surprisingly, only two definitions of the term "analytical method" have been found in the literature. Essentially the same definition as that proposed above has been given by the American Society for Testing and Materials (A.S.T.M.).⁵ Kaiser and Specker³ have suggested a different definition for "methods of measurement" and state that "analytical methods" are to be regarded as a special class of such methods. Their definition is "A method of measurement (Messverfahren) is embodied in the measuring arrangements and conditions (Messanordnung) and the specified procedure (Messvorschrift) which determines in every detail the operations (Messvorgang) to be carried out." The exact meaning of the term "Messanordnung" was not explicitly defined, and Kaiser⁶ later emphasized that all details capable of affecting analytical results must be stated before the method can be considered to have been defined. This definition therefore leads to such detailed specification that the method would change each time the analyst, the laboratory, the reagents or the apparatus changed. Such a concept appears to the writer to be of little or no practical value, and, in addition, logically prevents consideration of one of the most important features of analytical methods, *i.e.*, their ability to allow good results to be obtained under a wide variety of experimental conditions. Sandell⁷ and Maurice⁸ have both mentioned the problem of defining the term "analytical method." Although neither gave a definition, they suggested that certain factors such as analysts and laboratories should be excluded from any definition. Their views thus support the definition proposed in this paper.

The definition proposed has two important consequences: (a) a distinction must be made between the errors of analytical methods and results; (b) great emphasis must be placed on accurate and complete specification of methods.

DISTINGUISHING BETWEEN ANALYTICAL METHODS AND RESULTS

Papers often contain such statements as "the precision (or other performance-characteristic) of the method is . . ." Such statements would be incorrect if the proposed definition were adopted, because the concept of precision could not be applied to printed paper. The correct form would be "when the method was followed, analytical results were obtained with a precision of . . ." or more simply, "the precision of analytical results was . . ." Thus emphasis is immediately placed on the quality of results; this can only help to stimulate more critical appraisal by analysts of the validity of their results. The shift of emphasis from methods to results should also encourage more searching investigations of the effects of the other five components involved in producing results.

It may be argued that any method has an associated limiting precision which cannot be bettered. In the author's opinion, such a concept is debatable but the question need not be laboured. In characterization of an analytical method, the precision obtained experimentally is crucial because it states what is known about

the actual results rather than results relating to hypothetical conditions. Limiting precisions, if they exist, can easily be calculated for any set of hypothetical conditions. If experience with a particular method shows that the precision of results is essentially constant with time and in different laboratories, it may then be argued that the method rather than the results can be correctly associated with the experimentally determined precision.⁹ Such an approach is considered undesirable because even extensive experience cannot guarantee universal applicability (as many analysts must know to their discomfort), though it is useful to think of such a method as a good one.

It is of interest that the A.S.T.M. propose the association of performance-characteristics such as precision and bias neither with methods nor with analytical results but with "measurement procedures." Such a procedure is defined⁵ as "a method of measurement together with a system of causes." This "system of causes" represents a set of specified values for all the factors affecting performance-characteristics. This definition therefore leads logically to the same difficulties as Kaiser and Specker's proposed definition of "analytical method."³ However, the term "error of an analytical method" retains a useful meaning in association with the definition proposed here, signifying an omission, ambiguity or mistake in the written procedure.

SPECIFICATION OF ANALYTICAL METHODS

It is vital that methods contain *all* experimental details of importance in achieving results of the quality obtained by the authors. This obvious but frequently neglected point has been emphasized by Kaiser⁶ and often and eloquently by Youden.^{9,10} Otherwise, different laboratories will use, in effect, different methods although each will state that the same method is employed. Analysts are well aware of the large effects that may be caused by apparently minor procedural variations. Such variations could easily lead to confusion concerning the quality of results obtainable, and hence to falsely severe judgment on the procedure or its description, and to further experimental investigations in a number of laboratories. If both consequences arise from inadequate description, it is correct to regard the method as unsuitable. Authors should therefore gladly accept the responsibility of attempting to specify their methods unambiguously. Youden,⁹ in discussing interlaboratory comparative analyses, has stated "Unless and until a procedure has been adequately described, so that nearly all the laboratories show acceptable agreement for their averages, the question of agreement with a true value is hardly meaningful. If laboratories disagree, the procedure needs more careful specification." This view of an authority on the subject indicates the importance of satisfactory description of analytical procedures, and introduces the concept of "the true value."

Several authors (*e.g.*, Eisenhart¹¹) have argued that a true value can be defined only in terms of the result of a measuring process—a further strong reason for unambiguous and complete description of analytical procedures. Such description meets two main difficulties.

First, many experimental and environmental factors may affect analytical results, and authors have the problem of deciding which factors should be specified in the method. Although it is not impossible to specify all the conditions, it is usually impracticable and often unnecessary. For example, it will usually be unimportant and unnecessarily restrictive to state in which direction the laboratory windows faced or which type of separating-funnel was used. It is customary not to specify such

factors in analytical methods; they are left to the discretion of the analyst using the method. Nevertheless, the complete description of an analytical procedure ideally requires that the author should establish all those experimental conditions that may affect analytical results. This information can, in general, be obtained only by experimental study, and as this study is made more searching, so can the method be better defined.

Even if a full investigation is not possible, it is often of value to publish the method, but lack of knowledge should not then be taken as an excuse for an ambiguous analytical method. When the effects of certain factors are not known, authors should be even more careful to state exactly the procedures they have used. For example, if the effects of the intervals between reagent additions have not been determined, the author should state the range of intervals used during his work. Methods abound with common, basic procedures such as weighing and use of volumetric apparatus, of which complete details need not be given, because they are adequately described elsewhere. All procedural details peculiar to a particular method or not commonly known should be described in full. A related point has been emphasized by Youden:⁹ he strongly condemns instructions such as “shake vigorously” and “clean thoroughly.” Such wording is open to large differences in interpretation, and should always be expressed less ambiguously. All these points may appear so obvious as not to require stating, but so many published methods pay so little regard to them as to warrant their repetition. Editors could stimulate the improvement of analytical methods by striving still more keenly for unambiguous descriptions in published papers.

The second problem arises when authors have to specify the numerical values for experimental parameters such as weight, volume, time and temperature. In the writer's view, these numerical values should aim to define not only the optimum values but also the deviations from them that can be tolerated without causing more than a stated deterioration in the quality of results, thus ensuring a close enough approach to optimum values without waste of time, effort and money on unnecessarily fine control. As an example, consider the instruction “add 5 ml of reagent;” one analyst may painstakingly use a bulb pipette and add 5 ± 0.002 ml while another may use a graduated cylinder and add 5 ± 0.5 ml. The latter may be perfectly adequate (to achieve a stated precision) and in that case the instruction “add 5 ml (± 0.5 ml)” is far more informative in indicating the degree of control required, but does not preclude the use of a pipette. Similarly, “add 5 ml (± 0.002 ml)” immediately indicates that strict control is required, and that a graduated cylinder should not be used. The quantities in brackets may be called tolerances, and besides aiding choice of technique, serve as a guide to the critical factors of a method, so helping to prevent the false assessment of importance of factors that is sometimes made by analysts presented with an unfamiliar method or technique. Analytical methods should always quote tolerances for each such parameter; the additional space required is a small price to pay for the extra information. Sometimes “add 5 ml” is taken to mean addition of 5 ± 1 ml or 5 ± 0.5 ml and “add 5.0 ml” to mean addition of 5.0 ± 0.1 ml or 5.0 ± 0.05 ml, and so on. However, there appears to be no universal agreement to this system, which is also much less flexible in defining tolerances, and it seems better to specify the tolerance.

Every method quoting tolerances should define the criteria used in deciding their values, *e.g.*, that the results were not affected by more than a certain amount by

variations within the stated range; no strong reason appears for attempting more precise definition of tolerances. Tolerances should not be regarded as an excuse for careless or slipshod work; the aim should be to achieve the specified (optimum) value of the parameter; the tolerance indicates the necessary technique and degree of control required.

Tolerances should ideally be determined experimentally but the choice of values may not always be straightforward, and whenever there is any doubt as to the values to be specified or no investigations have been made, the best plan would be to quote the values observed during the development of the procedure. If an author gave falsely large tolerances there would be a tendency for results by other analysts to be of poorer quality (*e.g.*, less precise, more biased). Conversely, specification of too many extremely fine tolerances would tend to lead to rejection of a method. Thus, analysts would favour use of methods for which the tolerances had been reasonably chosen, a situation likely to encourage a more critical approach to the choice of tolerances and consequent improvement of analysis and analytical methods.

Consistent general application of this approach to definition and specification of analytical methods could be of great and increasing value to all analysts. General adoption of these suggestions is therefore recommended. Gottschalk¹² has argued for a standardized format for analytical methods and gives two examples. In the writer's opinion, his suggestions represent unnecessary standardization but indicate a possible line of development.

PERFORMANCE-CHARACTERISTICS

A primary aim of a new analytical method should be to improve the quality and/or efficiency with which samples (for which the method is relevant) can be analysed, and it is essential for authors to publish information giving the maximum possible assistance in deciding whether the method is likely to be of value for their purposes. Obvious examples are the bias and precision of the results. Such parameters may be called "performance-characteristics."

From what has been said above on analytical methods, it follows that performance-characteristics are not, in general, invariant properties of a method, and only show the performance obtained under a given set of experimental conditions. For that reason, it is essential to define these conditions closely, as emphasized by Garton *et al.*² and recommended by a British Standard¹³ on the presentation of experimental results. Factors such as laboratory temperature, skill and experience of the analyst, and whether the work was carried out under research or routine conditions, may be important but are often omitted in papers, so that it becomes quite possible for different values for the one characteristic to be obtained when the same method is used by different workers. This possibility appears to be considered undesirable by many analysts, who seem to favour the concept of invariant performance-characteristics. It is worth briefly examining whether this concept has any advantages, as it is contrary to the approach recommended in this paper.

The practising analyst faces two main situations relevant to the point: (*a*) choosing a method for a particular sample, and (*b*) publishing a method or the results obtained by use of a published method. In (*a*), the analyst chooses that method apparently most suitable (on the basis of published performance-characteristics) for his particular problem. However, he would usually be ill-advised to assume that he will inevitably

obtain the same values for all characteristics as those quoted in the method. In practice, he would always seek to obtain an estimate of some, at least, of the characteristics relevant to his own conditions, and this procedure in no way requires the concept of invariant performance-characteristics; indeed, it is clearly based on the contrary concept. If the performance with the chosen method is found to be satisfactory, the matter is at an end. If the performance turns out to be unsatisfactory, the analyst has either to select another method or attempt to locate the reasons why the performance under his conditions is not as good as that reported by others, and neither course of action is facilitated by the concept of invariant performance-characteristics. In (b), the analyst has merely, in effect, to quote experimental results. Clearly, he is then concerned solely with his observed performance-characteristics, and it is immaterial whether they are considered invariant or not. Different values for the performance-characteristics associated with a method may therefore be reported, which simply provide additional information for analysts facing situation (a) and present problems only if one tries to maintain a concept of invariant performance-characteristics; such a concept therefore appears to have no important advantages. In contrast, the concept of variable characteristics proposed in this paper should favour their more critical evaluation because the emphasis is placed on experimental estimation of performance rather than prediction.

On this basis, the following definition of performance-characteristics is proposed.

Definition. The performance-characteristics of an analytical method used under a given set of experimental conditions are a set of quantitative and experimentally-determined values for parameters of fundamental importance in assessing the suitability of the method for any given purpose.

Although this definition includes all the elements required from the previous discussion, it has been deliberately put in very general terms. In this way, the same definition can be used if parameters other than those suggested in these papers are later considered to require inclusion.

There are, of course, several factors that are not included by the proposed definition, e.g., the equipment and/or experience available in a particular laboratory, the care with which experimental operations need to be carried out, the ease or difficulty of making reagents and/or calibrating the analytical system. Quantitative expression of such factors is often impossible and in any case may be of little or no value to another analyst working under different conditions. Further, a well written method should itself allow any analyst to make an adequate assessment of such points without the need for any particular performance-characteristics. Performance-characteristics need, and should, refer only to the quality of the results obtained and the time required to make the analyses.

The literature dealing with analytical methods in general contains little discussion of the characteristics that should be quoted. Morrison and Skogerboe¹⁴ state that sensitivity, accuracy, precision and selectivity are of primary importance in choosing a method. They mention that other factors such as scope, sampling and standards requirements, cost of equipment and time of analysis are also of great practical significance. Gottschalk¹² suggests eight factors required in evaluating a method, viz., range, selectivity, errors, limit of determination, difficulty, apparatus required,

cost and time of analysis. Kaiser and Specker³ have proposed range, calibration function, systematic errors, precision, limit of detection, cost and time of analysis. These different suggestions can be summarized, once the factors excluded by the proposed definition have been omitted, by stating that information is required on the errors of analytical results, on the calibration curve, and on the time of analysis.

Analytical results are always affected by random errors, and systematic errors (*e.g.*, interferences) may also occur. Thus, performance-characteristics must aim to define the magnitude of both types of error. Random errors (precision) and the related concept of "limit of detection" will be considered in detail in Parts II and III of this series. Systematic errors (bias) and, in particular, the phenomenon of interference will be considered in detail in Part IV.

Mathematical expression of the calibration curve shows the relationship between the analytical measurement and the concentration (or amount) of the determinand.* This information is of value in revealing the range of concentrations covered by the method, the ease of calibration and the rate at which the magnitude of the analytical measurement changes with concentration. The last feature is of importance because it allows a check on unrealistic claims for precision. These aspects together with some comments on time of analysis and other miscellaneous factors will be dealt with in Part V, which also gives some detailed examples of a technique proposed for reporting performance-characteristics.

Acknowledgements—I should like to acknowledge the stimulating discussions with many of my colleagues and, in particular, Mr. I. R. Morrison.

Zusammenfassung—Der immer größer werdende Umfang der analytischen Literatur läßt es immer wichtiger erscheinen, Vor- und Nachteile analytischer Methoden zweifelsfrei gegeneinander abwägen zu können. Zu diesem Zweck braucht man einen Satz konsistenter Definitionen und Methoden, um quantitativ Gütekenneichen (z.B. Genauigkeit, Empfindlichkeit, systematischer Fehler) ermitteln zu können. Das Ziel dieser Reihe von Publikationen ist es, einen Überblick über Definition und Bestimmung solcher Parameter zu geben und allgemein verwendbare Unterscheidungsmerkmale vorzuschlagen. Diese erste Arbeit diskutiert das Problem im allgemeinen, erörtert die allgemeinen Aspekte analytischer Methoden, die für dieses Problem wichtig sind, und gibt die Gütekenneichen an, die im einzelnen betrachtet werden sollen.

Résumé—Le volume toujours croissant de la littérature analytique rend importante la possibilité de comparer sans ambiguïté les avantages et désavantages de méthodes analytiques. A cette fin, il est besoin d'un ensemble de définitions et de méthodes logiques pour la détermination de caractéristiques de performances quantitatives (par ex., précision, sensibilité, influences). Le but de cette série de mémoires est de passer en revue la définition et la détermination de tels paramètres, et de suggérer des critères d'emploi général. Ce premier mémoire discute du problème général, considère tels aspects généraux de méthodes analytiques qui sont importants, et établit les caractéristiques de performances que l'on doit considérer en détail.

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THE PERFORMANCE-CHARACTERISTICS OF ANALYTICAL METHODS—II*

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Summary—Statements on the errors of analytical results are an important aspect of characterizing the performance of analytical methods. The general nature of random and systematic errors is briefly discussed, and methods of numerically defining the former are considered. It is suggested that the standard deviation of analytical results be used exclusively as the quantitative measure of precision within the context of performance-characteristics. Techniques for, and precautions to be observed in, estimating standard deviation are critically discussed. On this basis, general principles are proposed that should be observed whenever possible in experimental tests to estimate standard deviation.

IN PART I¹ it was concluded that among the performance-characteristics of analytical methods should be included statements on the errors of analytical results. Although it seems that all analysts are in agreement on this, many different methods are used to determine and express analytical errors so that it is often difficult and sometimes impossible to interpret reported results quantitatively and/or unambiguously. Occasionally, the experiments reported do not allow even an estimate of the errors, despite the firm conclusions drawn. It seems most desirable to attempt to obtain greater uniformity in the determination and expression of errors.

NATURE OF ERRORS

Eisenhart² has given a particularly clear and illuminating discussion of this topic, and the brief outline below essentially follows his approach.

Consider the analysis of a stable, homogeneous sample for a substance with true concentration τ . When a number of identical portions of this sample are analysed, it is a matter of experience that the results $(x_1 x_2 \dots x_n)$ [‡] differ§ among themselves and in general from the true concentration. The error, E_i , of a result, x_i , is universally defined as the difference between the result and the true concentration, *i.e.*, $E_i = x_i - \tau$. The concept of a "true value" is of great importance, and will be discussed in more detail in Part IV. For the present, it suffices to think of the term in its literal sense.

There is experimental and mathematical² justification for the postulate that the mean of n analytical results approaches a definite value, μ , as the number of results is increased indefinitely provided that the analytical measurements are in "a state of statistical control" (*i.e.*, that all the causes of errors remain the same). That is to say, an analyst's results are meaningful estimates of the concentration to be determined. When the limiting mean concentration μ differs from the true concentration, results are said to be subject to bias or systematic error of magnitude B where $B = \mu - \tau$.

* Part I—*Talanta*, 1970, 17, 21.

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‡ § See page 32.

The terms "bias" and "systematic error" are usually used synonymously, though Murphy⁶ states that some regard systematic error as the cause of bias—a distinction that seems unimportant in the present context. The several sources of bias will be considered in Part IV; one familiar example is the effect of an interfering substance.

In the IUPAC recommendations¹ for presentation of results of chemical analysis, bias is defined as the difference between the mean of a series of results and the true value, *i.e.*, the experimental results define the bias exactly. Experimental results defined as in this paper provide only an estimate of the bias. For a given set of results, both definitions lead to the same numerical value for bias, but it seems inconsistent that IUPAC should imply that this experimental value has no uncertainty when this is quite contrary to the statistical approach. For example, according to the IUPAC definition the bias would, in general, vary with the number of results. Accordingly, the IUPAC definition is not followed in this series. *Analytical Chemistry*⁷ recommends the term "mean error," defined in the same way as the IUPAC definition of bias. The use of mean error in this sense avoids the problem caused by the definition of bias in two different ways. Mean error is no more than a statement of experimental observation, and can be used as an estimate of bias in the sense used in this paper. It is unfortunate that the IUPAC and *Analytical Chemistry* definitions lead to two different terms for the identical concept. The IUPAC definition should be changed so that either bias is defined in the sense used in this paper or the term "bias" is replaced by "mean error."||

The magnitudes and signs of the deviations of individual results from their mean are found to vary randomly because of the inevitable variations in experimental conditions, such as slightly different amounts of reagents, differing reaction-times, temperatures, *etc.* These random variations are always present even if systematic errors are absent, and thus form a second source of error of profound importance.

Several different words are used to express this concept of the variability of results among themselves, *e.g.*, precision, reproducibility, repeatability. There seems to be little to choose etymologically between these terms. Precision has been recommended by IUPAC,³ *Analytical Chemistry*⁷ and ASTM.⁸ A British Standard⁹ favours reproducibility but recognizes that precision may ultimately be preferable. Usage in journals varies. It is desirable that one term be used consistently to avoid confusion.

‡ In this series the term "analytical result" means the value obtained for the concentration (or amount) of the determinand when the procedure described in the analytical method is followed. It does not signify a primary "measured value" such as a weight, an electric current or voltage, a time. This usage follows the recommendations of IUPAC.³ As Kaiser^{4,5} points out, it is important to distinguish between a result obtained as described in a method and the mean result of replicate determinations. For example, a method may state that two portions of a sample must be analysed and the mean of the two determinations used to calculate an analytical result; the variability which characterizes the performance is then the variability of the means of duplicate determinations. Similarly, if a method specifies a single determination for each sample, variability should not be calculated for the means of a number of determinations.

§ Strictly, this statement is true only when one attempts to minimize any discrepancy between results and true values. Otherwise, identical results may be obtained if the analytical system is of such coarse discrimination that differences are concealed. In such cases, the excellent concordance of results is misleading because real differences between the concentration of samples will also pass undetected.

|| EDITORIAL NOTE: Unfortunately, the term "mean error" is ambiguous, since it could be interpreted as the average error; what is really meant is the error of the average, *i.e.*, the difference between the average and the true result, and the term "error of the mean" would be more correct.

Precision appears to be the most widely recommended and used, and is therefore used in this series and recommended for general adoption.

Thus, the terms bias and precision refer to the two types of error. Neither alone is capable of defining the total error of an analytical result, and it is useful to have a term connoting total error. There is concurrence on the use of the term "accuracy" for this purpose^{3,7-9} This usage is followed in this series, and is recommended for general adoption. Eisenhart² has discussed the relative importance of bias and precision when methods of measurement are chosen.

Quantitative statement of precision

Random variations have the effect that the deviation of an analytical result from the limiting mean cannot be known exactly. Thus, each result must be regarded as an estimate to which attaches some uncertainty. Limits must be set on this uncertainty; otherwise the analytical result is worthless. For this purpose, statistical techniques are required. Of course, when an analyst's experience with a particular method shows that random variations have never been larger than r , and he is concerned only with detecting differences (between samples) that are very much larger than r , he is justified in not using formal statistical techniques. However, this approach is in essence the same as that required by statistics, and is a justifiable approximation. The basis of the statistical techniques has been covered in several books written especially for chemists and analysts.¹⁰⁻¹³ The statistical approach requires calculation of an estimate of the variability of the results, and use of this estimate to calculate the likely maximum deviation of a result from the limiting mean.

To obtain a quantitative measure of precision corresponding to a given method and set of conditions, several parameters can be used, *e.g.*, the range of the results, the mean deviation from the mean, the standard deviation. The aim is to determine, from a finite number of results, the variability that would be observed in an infinite number of results, *i.e.*, an estimate is made of the true variability. The parameter used should therefore have as good precision and bias as possible, and the best parameter is variance. For a homogeneous set of n results, the estimate, V , of the true variance is given by the equation:

$$V = \frac{\sum_1^n (x_i - \bar{x})^2}{n - 1}$$

where \bar{x} is the mean result.

The square root of the variance gives an estimate, s , of the true standard deviation, σ , which is used to calculate the likely deviation of a result from the limiting mean. The key role played by standard deviation in the characterization of precision has been generally recognized by analysts who have increasingly quoted it rather than other measures of precision such as range and mean deviation. There may however, be occasions when other parameters than s may allow better estimates of σ , *e.g.*, the mean deviation when results contain occasional gross deviations that are not representative of the normal precision.¹² Such possibilities do not alter the basic aim of obtaining as good an estimate as possible of the true standard deviation.

With an estimate of the true standard deviation *and* knowledge of the distribution* of the results, it is possible to calculate the range round the analytical result within

* See page 34.

which the limiting mean is likely to lie. For a normal distribution, 68% of results will, on average, lie in the range $\mu \pm \sigma$, and $\sim 95\%$ and 99.7% in the ranges $\mu \pm 2\sigma$ and $\pm 3\sigma$, respectively. These facts and an analytical result x then allow such statements as "the limiting mean lies in the range $x \pm 2\sigma$ " (95% confidence).† The confidence level of 95% implies that, on average, such statements will be correct on 95 occasions in every 100. If a greater or smaller degree of confidence is required for a particular application, the value of the factor used to multiply σ is changed accordingly. There is no reason why one confidence level should be suitable for all analytical work; indeed, quite the opposite is true. Thus, the confidence level must be chosen for each application and should not be fixed for the method. The confidence level is not a property of a set of results although their standard deviation is. For these reasons, it is undesirable to define a precision index as a fixed multiple of standard deviation as suggested in British Standard 4237:1967. The ASTM⁸ has suggested that various indices of precision may be used provided that their bases are clearly indicated by added statements such as "2s limits," etc, but this may lead to misinterpretation. The best approach seems to be that recommended by IUPAC,³ i.e., to quote the experimentally estimated standard deviation. This estimate may then be interpreted appropriately for any particular problem.

Eisenhart² points out that s is really a measure of imprecision, for it increases with decreasing precision. He states that this was recognized by Gauss who remarked in 1809 that the parameter $1/(\sqrt{2} \cdot \sigma)$ was more properly a measure of precision. Kaiser and Specker,¹⁴ also recognizing this fact, tentatively suggested a parameter $\Gamma = \bar{x}/\sigma$ as an index of precision, and this was later repeated more definitely by Kaiser.⁴ Murphy⁶ and the ASTM⁸ have discussed this and conclude that the normal usage is so entrenched that changes in nomenclature and usage are not justified. Further, it is highly desirable for numerical statements on precision to be in units directly of interest to the analyst, so definition of precision as an inverse function of s seems undesirable.

It is often of interest to quote s as a fraction of the mean of the results from which it was estimated. The term "coefficient of variation" has often been used but *Analytical Chemistry*⁷ and IUPAC³ recommend the term "relative standard deviation" be used.

* "Distribution" denotes the relationship between the value of an analytical result and the probability of obtaining such a value; hence it is a fundamental indication of the variability of analytical results and is the best index of precision. Because the distribution usually cannot be estimated precisely from experimental results (and it is impracticable to quote all these) it is customary to postulate a given distribution (until evidence to the contrary is obtained) and to quote the experimental estimates of the parameters defining it. The normal (Gaussian) distribution is most frequently assumed. The distribution of experimental results often approximates to it, as expected from theory.¹⁰ It is defined by the standard deviation, which thus becomes an index of precision and a convenient performance-characteristic. Nalimov¹⁰ has discussed factors leading to non-normal distributions. Apparent non-normality may arise from the nature of the experimental design and interpretation of results, but the design proposed here should minimize this risk. Even when other distributions occur, they often approximate to the normal distribution, which therefore can usually be assumed. If some other distribution is postulated, experimental and/or theoretical grounds for doing so should be clearly stated, and its nature included with any statement of precision.

† The true standard deviation σ can never be known, and only the estimate s will be available. The uncertainty of this estimate means that broader confidence limits for an analytical result must be used, given by $\pm ts/n$ where t is the appropriate value of the parameter "Student's- t " (given in statistical tables), and n is the number of independent determinations on which the analytical result is based.

The former defines this parameter as $100 s/\bar{x}$ while the latter recommends s/\bar{x} so as to avoid confusion that might arise when analytical results are themselves expressed in per cent. On balance, the definition proposed in *Analytical Chemistry* seems preferable because it is in very common use, and the type of confusion postulated by IUPAC should be avoided so long as the word "relative" is placed before "standard deviation" whenever appropriate.

The term "precision," then, should be used when speaking generally of the degree of agreement among repeated results. For numerical definition of this degree of agreement, the parameters standard deviation or relative standard deviation should be used exclusively.

Factors affecting precision

Often, so little description of the experimental design and statistical interpretation of the results is given in published papers that it is impossible to assess the true significance of the reported precision. This section considers certain aspects of experimental design on the basis of performance-characteristics, and proposes a set of principles to be used whenever possible in experimental designs for estimating precision as a performance-characteristic. These principles are not intended to apply to the estimation of precision for other purposes which are likely to require individual consideration and other experimental designs.

Definition of analytical method. There is little point in quantifying precision if the analytical method is ill-defined. Therefore, as emphasised in Part I,¹ the analytical method must be complete and unambiguous before experimental estimation of precision is attempted.

Choice of experimental conditions. The magnitude of the random variations should be kept as constant as possible during the tests, which should be so designed that the results do not fall into groups between which systematic differences are likely; the effect of such grouping would be to give falsely large estimates of the standard deviation. If such grouping cannot be avoided or is of interest, the experimental design and the interpretation of results should be planned so that the standard deviations corresponding to variations within and between groups can be estimated independently.

First, the degree of control to be exercised over procedural details (reagent volumes, times, temperatures, voltages, *etc.*) must be decided and adhered to throughout. There is generally no need to seek extreme fineness of control; so long as the degree of control is specified when results are reported, s is a measure of the precision obtained with that degree of control.

Secondly, experience shows that analysts, apparatus and laboratories may all cause marked systematic deviations in both bias and precision so the basic unit for precision tests should be one analyst using one set of apparatus in one laboratory. The definition of performance-characteristics proposed in Part I¹ took account of this by associating the characteristics with a given set of experimental conditions. Of course, tests of precision may usefully be designed to involve several analysts, *etc.*, but then the standard deviation associated with each combination should be estimated independently.

Even analytical results obtained solely by the basic combination (as defined above) may fall into groups. For example, in spectrographic analysis different photographic

plates may cause systematic differences in results, and many other such grouping effects exist. Some confusion in published work is then possible unless the experimental design and statistical interpretation are clearly defined. For example, tests made on one plate would tend to give better precision than tests made on a number of plates—which of the two precisions is of interest for performance-characteristics? It is of value to know both, and their estimation is considered below.

Duration and number of tests. When the general experimental conditions have been decided, the number and duration of tests must be fixed. The latter factor is closely connected with the grouping effect just mentioned. Experience shows that the precision of results often worsens as the time period within which they were obtained increases. Aging of various components (*e.g.*, reagents, apparatus) of the analytical system may affect results, but increasing time periods will also usually give increasing chance of grouping effects. The analytical results may be regarded² as produced in batches which have essentially the same within-batch true standard deviation σ_w and a between-batch standard deviation σ_b , operating independently. In this model, the true standard deviation σ_t for any result in any batch is then given by:

$$\sigma_t = \sqrt{(\sigma_w^2 + \sigma_b^2)}.$$

Several points arise in connection with the validity of this model. First, the true standard deviation within a batch may vary from batch to batch. However, attention to the points mentioned earlier should normally ensure that such variations are unimportant. Minor variations will also tend to be averaged if the standard deviation is estimated from the variability within several batches. It is therefore reasonable to assume constancy of σ_w until evidence is obtained to the contrary. If such evidence were obtained, it would be better to seek and eliminate the source of variation than to employ the more complex statistical model that would be required.

Secondly, the differences between batches have been postulated as random, and though this is normally justifiable, the variations could be largely systematic, *e.g.*, if the ambient temperature increased from the first to last batch of results, and caused a systematic change in the results. This effect, however, would not call for any changes in the statistical model, but rather for elimination of the systematic effect, recalculation of s_b for the corrected results, and specification of the effect in the published method.

Thirdly, the between-batch standard deviation may not be constant. Again using the example of photographic plates, there may be systematic differences not only between plates from the same production batch but also between different production batches. This situation could be dealt with statistically, but in practice the problem is usually eliminated by recalibration of the analytical system.

Granted the model, it follows that σ_w represents the best precision achievable with the given experimental conditions, and is of interest when the analyst is concerned with the smallest concentration difference detectable between two samples, *e.g.*, in considerations of the limit of detection (see Part III) and the effects of other substances (see Part IV). The value of σ_t is of interest to analysts concerned with the regular analysis of samples of a particular type in order to detect changes in concentration. The value for σ_b is a measure of the between-batch variations occurring in the calibration curve for the method. Since it is preferable for the calibration curve to be constant, σ_b is also of interest.

On this basis, experimental designs for estimating precision should be chosen so that estimates, s_w and s_b , of the true standard deviations are obtained whenever

possible, *i.e.*, designs in which n portions of a sample are analysed in each of m batches. The term "batch" requires amplification. The approach adopted implicitly defines a batch as that time during which the calibration curve remains constant. Such a definition is not practically useful, and a more pragmatic one is needed. The batches should be arranged so that there is likely to be reasonable correspondence between the between-batch variations in the precision tests and those that would be found in the regular analysis of samples of a given type. Often this will simply mean that a batch corresponds to the analysis of a number of samples more or less in parallel. No more rigorous definition of batch is considered necessary since the description of the experimental design ought to make clear the precise meaning in each particular case. Some analytical methods may allow the analysis of only one sample at a time; in that case all results obtained within one day might be regarded as a batch, but it would be more revealing to speak of within- and between-days standard deviations. Ambiguity can be avoided by clear description of the design and of the interpretation of results. It is important to ensure that any factors considered likely to have between-batch variations that may affect analytical results, are allowed to show these variations in the precision tests. Most often, these precautions in "batching" will lead to no more complication than the design already suggested, the analysis of n portions of the sample in each of m "batches."

Given this design m and n must be decided. Statistical considerations indicate that the larger m and n the better. However, it seems reasonable to obtain estimates of σ_w and σ_b with approximately the same numbers of degrees of freedom, and this is ensured by choosing $n = 2$. Then s_w and s_b will have m and $(m - 1)$ degrees of freedom, respectively. In choosing m , a compromise must be made between the uncertainty of the estimates and the time and effort available for the tests. A choice of $m = 10$ seems generally reasonable. For example, for normally-distributed results and at the 95% confidence level, the true within-batch standard deviation would lie in the range $0.7-1.8 s_w$; it would also be possible to detect a statistically-significant between-batch variation such that $s_b = s_w$.

More detailed knowledge of likely sources of error can, of course, be used with advantage in choosing values for m and n . In trace analysis, contamination is often the dominant random error and may be unlikely to vary in general magnitude from one batch to another. In this situation, it would be more efficient in estimating σ_w to use the values $n = 5$ and $m = 4$ since the estimate s_w would then have 16 degrees of freedom as against 10 when $n = 2$ and $m = 10$. In general, it is suggested that the product nm should never be less than 10 and preferably not less than 20.

The final parameter to be fixed is the duration of the tests. Many arrangements are possible but, in general, it is considered reasonable to analyse one batch every 1-2 days. In this way, the design will usually give more opportunity for sources of between-batch variation to exert their effects than if all the tests had been completed in a much shorter period.

Choice of samples

It is important that the samples used be sufficiently stable and homogeneous for differences in the concentration of the determinand in the portions analysed not to cause any variations in results that are appreciable relative to analytical errors.

A further point of importance is the possible dependence of s on the concentration of the determinand, C . Numerous examples have been reported, and Nalimov¹⁰ has

suggested a general equation of the form:

$$s = aC + b$$

where a and b are constants for given experimental conditions.

The true functional relationship between s and C is unimportant in the present context; the prime point is that the precision cannot be characterized by estimating the standard deviation for only one concentration of the determinand, and at least two concentrations should be used. Concentrations at the extremes of the calibration curve are best if only two values are used, since interpolation rather than extrapolation can be used to estimate standard deviations for other concentrations. More information is obtained if several concentrations are used, and the linearity of the calibration curve can then be checked with good precision, but as with many other design parameters, there must be a compromise between information obtained and time and effort expended.

Samples for the tests must be homogeneous, stable, and available in sufficient amount and range of concentrations of the determinand; these requirements are usually best met by standards prepared by the analyst to contain accurately-known concentrations of the determinand. For certain techniques, *e.g.*, direct spectrography of metals and alloys, standards in the appropriate form can usually be more easily obtained commercially than prepared in the laboratory.

Usually, standards cannot be prepared with exactly the same physical form and chemical composition as the samples for which the method is intended. Differences in these factors may possibly affect precision so that the estimates obtained with standards do not apply to samples, and the extent to which standards are made to correspond with samples must be decided in each particular case. This point is less important if the precision for samples is also estimated as a check on the relevance of the estimates for standards. This check can be made with the same design as for standards if sufficient amounts of adequately stable samples are available. However, useful checks may be made even without such samples because it is not essential to estimate both s_w and s_b for samples. The latter (s_b) reflects between-batch variations in the calibration curve and these are validly estimated from standards. Thus, for samples it is mainly necessary to estimate s_w . For this, it suffices to make duplicate analyses on a sample in each batch. Different samples may be used in each batch but they should all contain approximately the same concentration of the determinand in case s_w varies with concentration. Two or more series of such samples may be used to check the dependence of s_w on concentration.

It is most desirable to include in each batch duplicate determinations on a sample or standard containing essentially none of the determinand (blank determination). It will be seen in Part III that the precision of such determinations is of great interest in connection with the smallest detectable concentration of the determinand.

Need to obtain independent analytical results

The analytical results used for estimating standard deviation should be statistically independent. This requirement involves two further aspects of experimental design both of which are apparently often ignored in the literature.

First, many methods call for a blank* determination, the result from which is used to correct the result obtained from a sample. Thus, the precision of both blank and

* See page 39.

sample determinations affects the precision of analytical results. When the blank is subtracted from the sample result, the standard deviation of analytical results σ_R is given by:

$$\sigma_R = \sqrt{(\sigma_S^2 + \sigma_B^2)}$$

where σ_S and σ_B are the standard deviations (in units of concentration) for sample and blank results. Thus, an analytical result is derived from a pair of determinations, and independent determinations of such pairs should be made. For this experimental design, if n portions of d samples and standards are analysed in each of m batches, each batch must also contain n blank determinations; otherwise the estimated standard deviation will be falsely low by an amount depending on the values of σ_S and σ_B (e.g., this bias will be approximately $-0.4\sigma_S$ when $\sigma_B = \sigma_S$).

Secondly "randomization" must be used to ensure that unsuspected sources of variation during the tests in each batch do not cause bias in the statistical estimates. Suppose that some factor (e.g., temperature) and hence the slope of the calibration curve varies systematically during a batch; then if samples were analysed in order of increasing concentration, the results might indicate a non-linear calibration curve, and the variability of the n replicate determinations of each sample would be smaller than if they had not been made one after the other. The first effect is clearly undesirable and the second leads, in general, to falsely optimistic estimates of the within-batch standard deviation. Both effects can be eliminated by analysing the samples, standards and blanks in a random order chosen from tables of random numbers, a new order for each batch. Other factors may also cause systematic effects, e.g., one piece of apparatus may cause more contamination than another, or "memory" effects may exist leading to biased estimates for the slope of the calibration curve and to falsely optimistic estimates of precision. Therefore, the assignment of determinations in each batch to particular pieces of apparatus should also be randomized.

Conversion of measured values into concentrations

The standard deviations and analytical results are expressed in terms of the concentration (or amount) of the determinand. A calibration curve (or a factor) is required to convert the measured values into concentrations. For estimating precision, it is not generally necessary to establish the calibration with the best possible accuracy because errors as large as 10% in the standard deviations will usually be unimportant compared to the statistical uncertainties of the estimates. The results of the precision tests will establish the calibration sufficiently well except when few concentrations have been used and the calibration curve is markedly non-linear, in which case additional tests may be required for sufficiently accurate conversion.

In normal analysis the imprecision of results will lead, in general, to bias in the calibration curve used, but this error does not affect the precision of results, and can be made as small as desired by replication of the calibration determinations. Accordingly, if the analytical method specifies use of a fixed calibration curve (or factor), the error of the latter need not be considered further when quoting precision numerically. If, however, a fresh calibration is specified for each batch of analyses, the

* Discussed in detail in Part III. For the present it suffices that the term "blank" be defined by the procedure called for by a method. This approach ensures a valid estimate of precision achieved when the method is used, although some approaches to blank determination lead to possibilities of bias in analytical results.

within-batch variations of the standards will cause the bias of the calibration to vary from batch to batch. The between-batch standard deviation for samples will then be greater than the true value for between-batch sources of variability; the difference is not considered important, and can be estimated from an estimate of the within-batch standard deviation for the standard. Accordingly, for methods involving within-batch calibration, it is considered adequate to obtain only one estimate for the calibration in each batch. Alternatively, this tendency to create apparent between-batch variability from within-batch variations can be avoided by making n independent estimates of the calibration in each batch, and analysing the analytical results so that s_w for samples includes the within-batch contribution from the calibration.

The relative values of s_w and s_b and their dependence on concentration are of basic importance in deciding whether or not a fixed calibration or a batch calibration should be used in normal analysis.

Precision of analytical and measurement systems

Many analytical methods proceed in two stages: (1) the sample is treated so that the determinand is brought into the required physical and/or chemical form in the required chemical environment (e.g., dissolution of an alloy and separation of the determinand from other constituents): (2) the concentration or amount of the determinand in the treated sample is measured. The errors associated with each stage are often of interest, and though not strictly required for characterizing the precision obtained with the method, are often easily estimated. If s_A and s_M are the standard deviations associated with stages 1 and 2, respectively, and s is the overall standard deviation from the precision tests, then

$$s_A = \sqrt{(s^2 - s_M^2)}$$

The value of s_M can be obtained by applying the design principles already discussed to suitable standards or samples which are subjected only to stage 2 of the complete analytical procedure; s_A is then calculated from the equation above. As an example for spectrophotometric methods in which the coloured product is stable, duplicate measurement of the final solutions will give an estimate of s_M . Alternatively, if the colour is not stable, stable standard solutions with similar absorption spectra may be used.

Summary of suggested principles of experimental designs

The following set of principles is proposed for use in characterizing the precision achieved when a given method is used.

1. The analytical method should be complete and unambiguous.
2. Before any tests are made to estimate precision, the degree of control to be exercised over experimental factors should be decided, and adhered to throughout the tests.
3. Estimates of precision should be based on the results obtained by one analyst in one laboratory, using one set of apparatus.
4. The basic experimental design should allow estimates of within-batch and between-batch precision to be obtained. In general therefore, the tests should consist of the analysis of n portions of d samples and/or standards in each of m batches. Values of $n = 2$ and $m = 10$ are generally useful but other values may sometimes be more appropriate; d should be at least 2, and the samples and standards should always include two corresponding to the extremes of the calibration curve.

5. If standards are used so that the nature of the calibration curve and the variation of precision with concentration can both be estimated, the precision of analysing samples should be estimated for at least one concentration level.

6. Whenever the method calls for a blank determination, n such determinations should be made in each batch.

7. The order of analysis of samples, standards and blanks, and their assignment to particular pieces of apparatus, should be randomized in each batch.

8. The experimental design and methods of calculating statistical parameters must be described explicitly in published papers.

EXAMPLE OF STATISTICAL CALCULATIONS

The calculations may be made on the measured parameters (weight, absorbance, *etc.*) or the final results (concentration or amount). The former is usually more convenient and has been used in the following example. There are several methods of calculation but the method given here is suitable for any values of m and n .

In the example, duplicate portions of 4 solutions were analysed spectrophotometrically in each of five batches, so $n = 2$ and $m = 5$. The results are first tabulated in logical order (assuming that the order of tests had been randomized), and then the blank correction is applied, Table I.

TABLE I.—EXPERIMENTAL RESULTS (AS ABSORBANCES) FOR ESTIMATING PRECISION

Concentration	1st Batch		2nd Batch		3rd Batch		4th Batch		5th Batch	
	Uncorrected	Corrected*	Uncorrected	Corrected*	Uncorrected	Corrected*	Uncorrected	Corrected*	Uncorrected	Corrected*
0 (blank)	0.004	—	0.011	—	0.005	—	0.004	—	0.006	—
	0.002	—	0.005	—	0.004	—	0.005	—	0.006	—
C	0.211	0.207	0.211	0.200	0.213	0.208	0.210	0.206	0.211	0.205
	0.212	0.210	0.212	0.207	0.215	0.211	0.213	0.208	0.213	0.207
2C	0.416	0.412	0.414	0.403	0.412	0.407	0.416	0.412	0.413	0.407
	0.415	0.413	0.413	0.408	0.414	0.410	0.416	0.411	0.414	0.408
4C	0.820	0.816	0.821	0.810	0.821	0.816	0.819	0.815	0.818	0.812
	0.819	0.817	0.819	0.814	0.822	0.818	0.820	0.815	0.819	0.813

* In each batch, the first blank to be measured is assigned to the first portion measured of each of the other solutions; similarly for the second measurements of blank and other solutions, and for other measurements when $n > 2$.

The corrected results for each of the three solutions containing the determinand are now analysed as illustrated for the solution of concentration 2C. To simplify the arithmetic, it is convenient to transform the corrected results, x , to give a set of simpler numbers, X by using the equation $X = 1000(x - 0.408)$, Table II.

TABLE II.—TRANSFORMED RESULTS FOR ESTIMATING PRECISION

	Batch					Sum	
	1	2	3	4	5		
Test 1	4	-5	-1	4	-1	1	$\Sigma X^2 = 97$ $\Sigma B^2/n = 78.5$
Test 2	5	0	2	3	0	10	
Sum (= B)	9	-5	1	7	-1	11	$(\Sigma B)^2/mn = 12.1$
B^2	81	25	1	49	1	157	

If more than 2 tests are made on each sample in each batch the additional corrected and transformed results are included in the appropriate batch columns of Table II and the summations carried out on all the results. In addition to these summations, the sum of the squares of the individual results

(ΣX^2) in Table II must also be calculated. An analysis of variance table is next drawn up for each solution, *e.g.*, Table III. For the results in Table II, the values of M_1 and M_0 are 16.6 ($N_1 = 4$) and 3.7 ($N_0 = 5$), respectively.

In these analysis of variance tables, $M_0 = s_w^2$ and $M_1 = ns_b^2 + s_w^2$, where s_w and s_b are the estimates of the within-batch and between-batch standard deviations. However, it is first necessary to test whether M_1 is statistically greater than M_0 . For this purpose, the standard variance-ratio test (or Snedecor F -test) is used.

TABLE III—ANALYSIS OF VARIANCE OF TRANSFORMED RESULTS

Source of variability	Sums of squares (S_i)	Degrees of freedom	Mean squares
Between batches	$S_1 = \Sigma B^2/n - (\Sigma B)^2/mn$	$N_1 = m - 1$	$M_1 = S_1/N_1$
Within batches	$S_0 = \Sigma X^2 - \Sigma B^2/n$	$N_0 = m(n - 1)$	$M_0 = S_0/N_0$
Total	$S_t = \Sigma X^2 - (\Sigma B)^2/mn$	$N_t = mn - 1$	—

If M_1 is significantly greater (at the chosen probability level) than M_0 , this is evidence of between-batch variations and then

$$ns_b^2 = M_1 - M_0$$

and

$$s_t^2 = s_w^2 + s_b^2.$$

If M_1 is not significantly greater than M_0 , the evidence is too weak to assert that between-batch variations have been detected, and it is best to record s_b as non-significant (but not zero), and to calculate s_t^2 from

$$s_t^2 = [M_1 + (n - 1) M_0]/n$$

If M_1 is significantly smaller than M_0 , the procedure and technique should be examined for abnormal sources of error since such a conclusion is inconsistent with the model used as a basis for the experimental design and calculations.

If M_1 is not significantly smaller than M_0 , the best estimate for s_b is zero, and it is prudent to regard M_0 as the best estimate not only of s_w^2 but also of s_t^2 .

These calculations and significances tests applied to the results in Table I lead to the conclusion shown in Table IV (after transformation of the results back to absorbance units).

TABLE IV—ESTIMATED STANDARD DEVIATIONS

Concentration	Standard deviation (absorbance units)			Average absorbance
	Within-batch	Between-batch	Total	
0	0.0020	—	—	0.005 ₂
C	0.0027	NS	0.0030	0.206 ₉
2C	0.0019	NS	0.0032	0.409 ₁
4C	0.0015	NS	0.0025	0.814 ₆

NS = not significant but not zero.

These standard deviations are then converted into concentration units to yield the final estimated standard deviations of analytical results. The figures in the first and last columns provide the conversion factor.

No estimates have been calculated for s_b and s_t for the blank determinations. This is because it has been assumed that a blank determination would be made with each batch of sample analysis, and therefore batch-to-batch variations of the blank should not affect analytical results. If a blank is not carried out with each batch of normal sample analyses, its between-batch variations are then of interest and s_b and s_t can be calculated by applying the same analysis of variance technique to the blank results.

REPORTING RESULTS OF PRECISION TESTS

If the experimental design used for precision tests is that proposed in this paper, Table IV illustrates a suitable method for summarizing the statistical results. To complete the table, it is necessary only to add a footnote stating the various numbers of

degrees of freedom. The description of the experimental design will make it clear how many determinations were involved and how they were arranged in batches.

It is also useful to summarize concisely the main performance-characteristics. Table IV does this but a briefer statement giving concentration, s_w and s_t would indicate whether the method was worth consideration by a potential user. The concise statement of performance-characteristics will be dealt with in Part V.

CONCLUSIONS

Determination, reporting and discussion of the errors of analytical results are of great importance to all analysts, and it is clearly desirable that all analysts should use the same basic terminology in this field. The first part of this paper reviews some of the definitions proposed for the terms precision, bias and accuracy, and shows that differences existed between some of these definitions. These differences are both undesirable and easily avoidable. The definitions proposed by the American Society for Testing and Materials are very suitable, and it would be beneficial if they were used by all analysts.

Although there is general agreement that the term precision be used to denote the variability of analytical results, various suggestions have been made for the parameters to be used as quantitative indices of precision. There are two main aims for such quantification: (1) to characterize the precision achieved when a given method was used, and (2) to set confidence limits on particular analytical results; only the first is of interest in the context of performance-characteristics for which the best parameter for quantifying precision is the standard deviation.

The second part of this paper discusses factors that may affect precision, and proposes a set of principles for experimental designs of tests for estimating precision as a performance-characteristic. The aim has been to express these principles in such a way that they are applicable to all analytical methods. General adoption of these suggestions would help analysts in several ways: (1) by reducing problems arising in interpreting published data; (2) by facilitating comparison of the performances obtained with different methods, and (3) by encouraging a critical approach to experimental designs for precision tests.

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Zusammenfassung—Angaben über die Fehler analytischer Ergebnisse sind ein wichtiger Teil der Kennzeichnung analytischer Methoden. Die allgemeinen Eigenschaften zufälliger und systematischer Fehler werden kurz diskutiert und Methoden betrachtet, die zufälligen Fehler numerisch zu definieren. Es wird vorgeschlagen, die Standardabweichung analytischer Ergebnisse ausschließlich als quantitatives Genauigkeitsmaß im Rahmen der Gütekennzeichnung zu verwenden. Verfahren zur Ermittlung der Standardabweichung und dabei zu beobachtende Vorsichtsmaßregeln werden kritisch diskutiert. Auf dieser Grundlage werden allgemeine Regeln vorgeschlagen, die man bei Experimenten zur Ermittlung der Standardabweichung, wenn irgendetwas möglich, beobachten sollte.

Résumé—Les rapports sur les erreurs de résultats analytiques sont un aspect important de la caractérisation des performances de méthodes analytiques. On discute brièvement de la nature générale des erreurs de hasard et systématiques, et considère des méthodes de définition numérique des premières. On suggère que l'écart-type de résultats analytiques soit utilisé exclusivement comme la mesure quantitative

de la précision à l'intérieur du contexte de caractéristiques de performances. On discute de manière critique des techniques pour l'estimation de l'écart-type et des précautions à observer en ce domaine. Sur cette base, on propose des principes généraux que l'on devrait observer chaque fois que possible dans les essais expérimentaux pour estimer l'écart-type.

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N-ACETYLSALICYLOYL-*N*-PHENYLHYDROXYLAMINE AS AN ANALYTICAL REAGENT

DETERMINATION OF NIOBIUM AND TANTALUM IN THE PRESENCE OF EACH OTHER

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Summary—*N*-Acetylsalicyloyl-*N*-phenylhydroxylamine is proposed for the separation of niobium(V) and tantalum(V) and their gravimetric determination. Niobium is precipitated at pH 5.5–6.5 by the reagent and the complex is weighed directly. Tantalum is precipitated from 1–2*M* hydrochloric acid solutions and the complex is ignited to tantalum pentoxide. The method is fairly selective. In the presence of thiocyanate the reagent forms an extractable complex with niobium. The reaction forms the basis of a selective and sensitive spectrophotometric determination of niobium.

SOME of the derivatives of hydroxamic acid have proved most useful for the determination of niobium and tantalum in the presence of each other. Thus, *N*-benzoyl-*N*-phenylhydroxylamine has been used for the spectrophotometric determination of niobium, in the absence of titanium and tantalum,¹ for the separation of niobium from tantalum by precipitation² and for the gravimetric determination of tantalum. Improvements in selectivity might be brought about by the introduction of suitable substituents into *N*-benzoyl-*N*-phenylhydroxylamine. *N*-Benzoyl-*N*-*o*-tolylhydroxylamine³ has been used for the separation of niobium from tantalum, and in this paper we show that *N*-acetylsalicyloyl-*N*-phenylhydroxylamine can be used for the separation and gravimetric determination of niobium and tantalum in presence of a number of other associated ions.

EXPERIMENTAL

Reagents

***N*-Acetylsalicyloyl-*N*-phenylhydroxylamine.** The reagent is prepared by condensing acetylsalicyloyl chloride and phenylhydroxylamine in the presence of sodium hydrogen carbonate, by the method of Bamberger,⁴ modified by Lutwick and Ryan,⁵ the acetylsalicyloyl chloride being prepared by the method of Riegel and Wittcoff.⁶ The white needle-shaped crystals of the reagent (recrystallized from ethanol–water) melt at 128°. Found: C, 66.9%; H, 4.8%; N, 5.1%; calculated for C₁₅H₁₃O₄N: C, 66.42%; H, 4.79%; N, 5.16%.

A 0.3% w/v solution of the reagent in purified chloroform is used for spectrophotometric work. For gravimetric experiments a 4% solution of the reagent in ethanol is prepared.

Ammonium thiocyanate, 4*M*. Prepared just before use.

Chloroform for spectrophotometric work. Purified by washing several times with half its volume of distilled water and finally distilled.

Solutions of metal ions. Standard niobium and tantalum solutions are prepared by fusing about 1 g of the appropriate pentoxide with about 10 g of potassium hydrogen sulphate in a silica crucible and extracting the cooled melt with 500 ml of 1*M* tartaric acid solution. The metal ion content is determined gravimetrically with cupferron.

Ammonium acetate, 1*M*.

Procedures

Separation and gravimetric determination of niobium. Take an aliquot of a tartrate solution of niobium(V) containing 10–20 mg of the metal and up to 16 times as much tantalum(V). Neutralize the solution to Methyl Red with 1M ammonia. Dilute the solution to about 100 ml and adjust the pH to 5.5–6.5 with 0.1M ammonia or 0.1M hydrochloric acid, then add 25 ml of 1M ammonium acetate as buffering agent. Precipitate niobium in the cold by slow addition of the alcoholic solution of the reagent. The dull white precipitate coagulates quickly. Stir for a few minutes, then filter off on Whatman No. 42 paper. Wash several times with water containing 0.2% reagent and 5% ammonium acetate. Dissolve the precipitate in the minimum quantity of 1M ammonia and dilute to about 150 ml with water. Acidify to 0.1–0.5M with hydrochloric acid. Heat to 70–80° and add 2–3 times the theoretical quantity of the 4% alcoholic solution of the reagent, with stirring. Immediate precipitation of niobium as a yellow granular complex results. Boil for 1 min and allow to settle for 2 hr at room temperature. Filter off on a porosity 4 sintered-glass crucible with decantation. Wash several times with cold water containing 0.1% reagent and dry to constant weight at 105–115°. Calculate the niobium content, using the conversion factor 0.1011.

Gravimetric determination of tantalum. Evaporate the filtrate from separation of niobium until the metal concentration is about 1 mg/ml. Acidify to 1–2N with either hydrochloric acid or sulphuric acid. Heat to 70–80° and add the reagent in alcohol in the proportion of 7–8 mg reagent per mg of tantalum. Boil the solution for a few minutes and then allow it to stand at room temperature for 2 hr. Filter off on Whatman No. 42 paper and wash with cold water. Dry the precipitate in the filter for 1 hr at 110° and ignite in a silica crucible at above 900° to constant weight. Weigh as Ta₂O₅.

Spectrophotometric determination of niobium. Take an aliquot of tartrate solution of niobium, containing 0.0125–0.875 mg of the metal, in a separatory funnel and add 2–3 ml of freshly prepared 4M ammonium thiocyanate followed by enough hydrochloric acid to make the solution 5–9M with respect to the acid. Add 2–3 ml of 0.3% w/v solution of the reagent in chloroform and equilibrate gently for 2 min with two 5-ml portions of chloroform. Dry the combined extracts with sodium sulphate and dilute to 25 ml with dry chloroform. Measure the absorbance at 400 nm against a reagent blank.

RESULTS AND DISCUSSION

Gravimetric procedures

Conditions. For quantitative separation of niobium, the pH should be kept in the range 5.5–6.5. At low pH tantalum is also precipitated and at higher pH the precipitation of niobium is not quantitative. Table I shows the effect of pH on the precipitation of 15 mg of niobium in the presence of 150 mg of tantalum. For the final precipitation of niobium at 70–90°, the acid strength should be 0.1–0.5M with respect to hydrochloric acid. The precipitate formed in sulphuric acid media is charred on drying. It is found that for quantitative precipitation of tantalum, the medium should be 1–2N hydrochloric or sulphuric acid.

TABLE I.—PRECIPITATION OF 15 mg OF Nb IN PRESENCE OF 150 mg OF Ta

pH	Nb found, mg	Error mg	pH	Nb found, mg	Error mg
1.2	23.28	+8.28	6.0	15.00	0.00
2.5	18.86	+3.86	6.5	14.99	–0.01
3.0	17.62	+2.62	7.0	14.60	–0.40
4.0	16.84	+1.84	8.0	10.80	–4.20
5.0	15.86	+0.86	9.0	2.28	–12.72
5.5	15.00	0.00	9.5	0.00	–15.00

When the temperature is raised above 35° the precipitate of niobium formed at pH 5.5–6.5 disintegrates and passes through the filter. Therefore it is always necessary to keep the temperature below 35° for the separation of niobium. However, for the final precipitation of niobium, the temperature should be above 70° because the yellow complex formed at 60° and below is partially melted on drying. The precipitation of tantalum is slow at low temperatures. Therefore it is always advantageous to conduct the precipitation at 70–80° with vigorous stirring.

For the separation of niobium about 15–20 mg of the reagent per mg of the metal is enough. The optimum concentration of the reagent in the final precipitation is 2–3 times the theoretical quantity. A large excess should be avoided because the reagent is soluble in water at 30° only to the extent of 0.25%. A large excess of the reagent may be used for the precipitation of tantalum. But about 7–8 mg of the reagent per mg of tantalum is enough to effect quantitative precipitation.

Effect of foreign ions. Separation of niobium is quantitative in the presence of almost all the cations examined except titanium(IV). Up to a 16-fold amount of tantalum(V) can be tolerated, and zirconium, iron(III) and cerium(IV) can be masked by EDTA. The effect of various foreign ions in the determination of 15 mg of niobium is given in Table II.

TABLE II.—INTERFERENCE OF FOREIGN IONS IN DETERMINATION OF 15 mg OF Nb

Ion, mg	Niobium			Ion, mg	Niobium		
	found, mg	Error, mg			found, mg	Error, mg	
Fe(II)	200	15.0	0.00	Ce(IV)	100	14.99	−0.01
Cu(II)	200	15.02	+0.02	V(IV)	100	14.98	−0.02
Co(II)	200	15.01	+0.01	Th	100	15.00	0.00
Ni	200	15.00	0.00	Ti(IV)	15	15.04	+0.04
Be	200	14.99	−0.01	Mo(VI)	50	15.01	+0.01
Zn	200	15.01	+0.01	W(VI)	50	15.00	0.00
Al	250	14.98	−0.02	Citrate	250	15.00	0.00
Cr(III)	200	14.98	−0.02	Oxalate	100	14.90	−0.10
Fe(III)	300	15.03	+0.03	EDTA	500	15.01	+0.01
Zr	100	15.04	+0.04	Fluoride	50	14.28	interferes

To eliminate the interference of small amounts of titanium(IV), niobium is precipitated in the presence of 2–3 ml of 20-vol hydrogen peroxide. The precipitate of niobium is then dissolved in ammonia and reprecipitated in the presence of 1 ml of hydrogen peroxide. An equal amount of titanium can then be tolerated.

Most of the ions examined are without effect in the determination of tantalum, but tungsten(VI) and molybdenum(VI) interfere seriously. Zirconium and cerium(IV) can be complexed by EDTA and vanadium(V) by thiocyanate. Titanium(IV) can be masked (up to 50-fold amount) by fluoride. Other cations such as Mn(II), Cu(II), Co(II), Fe(II), Fe(III), Al, Cr(III), Th, V(IV) and U(VI) will not interfere even in 50-fold amount even in the absence of complexing agents. Complexing agents such as oxalate, fluoride, citrate and EDTA are tolerated in still larger quantities.

The complex formed between niobium(V) and the reagent in 0.1–0.5M hydrochloric acid solutions was determined by analysis to be $\text{NbO}(\text{C}_{15}\text{H}_{12}\text{O}_4\text{N})_3$ (found: N, 4.9%; Nb, 10.1%; required N, 4.56%; Nb, 10.10%). The conversion factor is 0.1011.

Spectrophotometric determination. The complex shows no absorption maximum in the range 370–560 nm, but 400 nm is chosen as the wavelength for photometric measurements because the absorbance of the reagent is then negligible (Fig. 1).

For maximum colour development 5–9M hydrochloric acid medium is required. In sulphuric acid medium of the same acidity, the intensity of the colour is considerably less. For maximum colour development 2.5 ml of 4M ammonium thiocyanate is required. Lower amounts cause decreased sensitivity and stability, whereas no change is noticed with larger concentration of thiocyanate. The optimum concentration of the reagent is found to be 2–3 ml of 0.3% w/v solution of the reagent in

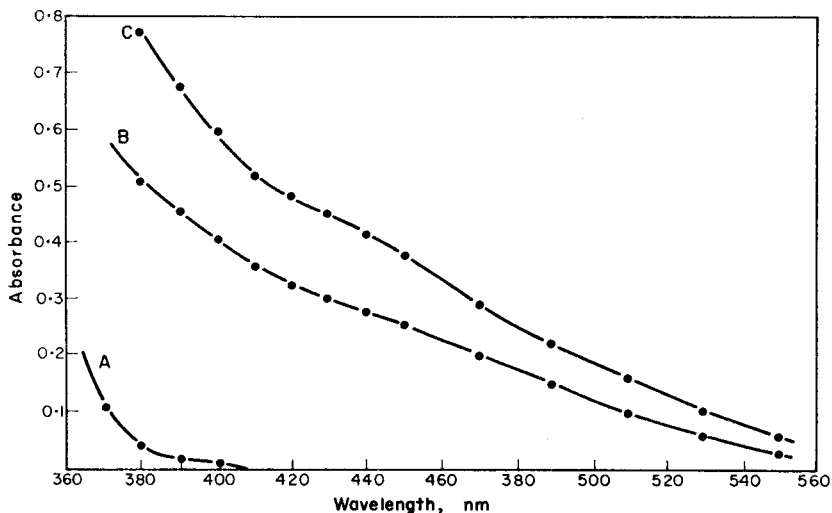


FIG. 1.—Absorption spectra.

- A. 2 ml of 0.5% w/v reagent in 25 ml against chloroform blank
 B. 2 ppm niobium against reagent blank
 C. 3 ppm niobium against reagent blank.

chloroform. In all experiments, the blanks should contain the same amount of reagent as in the test solution.

The complex is stable at room temperature for 18 hr and afterwards the absorbance increases slightly and a turbidity results. Variation in temperature from 15 to 50° has no marked effect if the volume change of the solution with temperature is allowed for.

The system obeys Beer's law from 0.25–4 ppm of niobium at 400 nm. The optimum concentration range according to Ringbom's method⁷ is from 0.5–3.5 ppm, the relative analytical error per 1% absolute photometric error calculated from Ayres's equation⁸ being 2.3%. The molar absorptivity of the complex is $17.7 \times 10^3 \text{ l.mole}^{-1} \cdot \text{mm}^{-1}$.

The complex is highly unstable and insensitive in the absence of a very large excess of thiocyanate, so that methods for the determination of composition in solution with respect to thiocyanate failed. Therefore Job's method⁹ and the molar ratio method¹⁰ were applied with equimolar solutions of the reagent and niobium, a constant excess of thiocyanate being kept. These methods indicate (Figs. 2 and 3) that the ratio of metal to reagent is 1:2.

The solid complex formed between niobium, reagent and thiocyanate in hydrochloric acid medium was isolated and analysed (found: N, 6.0%; S, 4.5%; Nb, 13.1%; $\text{NbO}(\text{C}_{15}\text{H}_{12}\text{O}_4\text{N})_2\text{SCN}$ requires N, 5.94%; S, 4.53%; Nb, 13.14%).

Interferences. It was found during this study that 25 μg of Nb can be determined in the presence of 25 mg each of Tl(I), Hg(II), Cd, Ni, Co(II), Fe(II), Ca, Ba, Sr, Be, Mg, Zn, Fe(III), Cr(III), Al, Sb(III), As(III), Bi, La, V(IV), Zr, Ce(IV), Th, V(V), W(VI), Mo(VI), U(VI) and Os(VIII). Copper(II) present in up to a 1000-fold amount can be masked by EDTA. Tantalum(V) forms a colourless complex which is not extractable with chloroform and a 200-fold amount can be tolerated. Only titanium(IV) causes a serious interference, and it is best to eliminate titanium, by prior removal with the reagent. Of the various anions, oxalate and fluoride cause serious interference. Citrate, tartrate, borate and EDTA are tolerable in 1000-fold amounts.

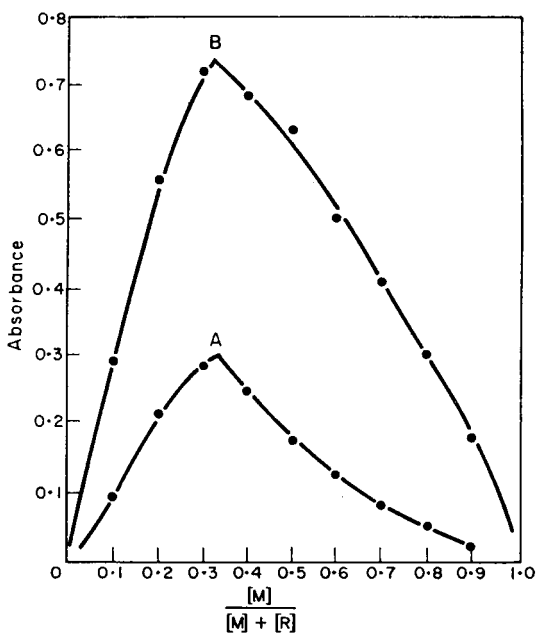


FIG. 2.—Job's method for composition.
 A. Niobium = Reagent = $0.25 \times 10^{-3}M$
 B. Niobium = Reagent = $0.5 \times 10^{-3}M$

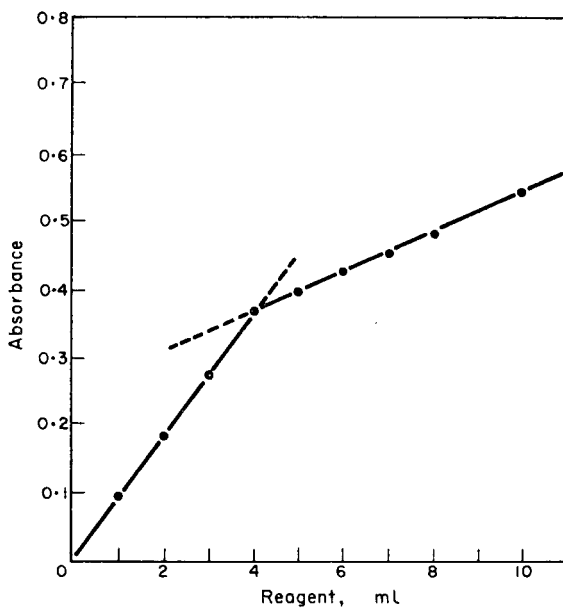


FIG. 3.—Molar ratio method for composition.
 Niobium = Reagent = $0.5 \times 10^{-3}M$; 2 ml of niobium solution taken.

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Zusammenfassung—*N*-Acetylsalicyloyl-*N*-phenylhydroxylamin wird zur Trennung von Niob(V) und Tantal(V) und deren gravimetrischer Bestimmung vorgeschlagen. Niob wird durch das Reagens bei pH 5,5–6,5 gefällt und der Komplex direkt gewogen. Tantal wird aus 1–2*M* salzsauren Lösungen gefällt und der Komplex zu Tantalpentoxid verglüht. Die Methode ist vergleichsweise selektiv. In Gegenwart von Rhodanid bildet das Reagens mit Niob einen extrahierbaren Komplex. Die Reaktion bildet die Grundlage für eine selektive und empfindliche spektrophotometrische Bestimmung von Niob.

Résumé—On propose la *N*-acétylsalicyloyl *N*-phénylhydroxylamine pour la séparation de niobium(V) et tantale(V) et leur détermination gravimétrique. On précipite le niobium par le réactif à pH 5,5–6,5 et pèse directement le complexe. On précipite le tantale de solutions en acide chlorhydrique 1–2*M* et calcine le complexe en pentoxyde de tantale. La méthode est moyennement sélective. En la présence de thiocyanate, le réactif forme un complexe extractible avec le niobium. La réaction forme la base d'une détermination spectrophotométrique sélective et sensible du niobium.

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DETERMINATION OF DEUTERIUM IN HEAVY WATER BY SECONDARY DEUTERON ACTIVATION

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Summary—The deuterium concentration of heavy water was determined by utilizing recoiling deuterium nuclei from n - d collisions to induce the reaction $^{16}\text{O}(d, n)^{17}\text{F}$. The internal ratio of 66-sec fluorine-17 to 7.35-sec nitrogen-16 activity, formed by the reaction $^{16}\text{O}(n, p)^{16}\text{N}$, was found to vary linearly with deuterium concentration. When such an internal ratio of activities is measured, the neutron flux and sample weight need not be known. Deuterium was determined over the range from 2.6 to 94.5 atom %, with a relative standard deviation of 2.8%. The effect of sample size was investigated and it was found that the relative amount of fluorine-17 activity formed became less as sample size decreased, due to the loss of recoiling deuterons from the sample. A simple relationship to account for this effect was obtained.

MANY of the lighter elements and their isotopes cannot readily be determined by neutron activation.^{1,2} These nuclides do, however, yield suitable measurable activities during charged particle activation, and several investigators³⁻⁹ having access to nuclear reactors but not to charged particle accelerators have consequently explored the possibility of using secondary nuclear reactions for charged particle activation. Tritons and alpha particles have been produced in reactors by utilizing the $^6\text{Li}(n, \alpha)t$ reaction, whereas protons and deuterons have been obtained for n - p and n - d "knock-on" reactions induced by epi-cadmium neutrons. These secondary charged particles have been successfully used for the determination of deuterium,³ lithium-6,^{4,5} oxygen-16^{6,7,8} and oxygen-18.⁹ Although the charged particle flux obtained by these methods is much smaller than fluxes obtained from accelerators, the technique does have the advantage that relatively large samples can be irradiated uniformly. Furthermore, target preparation and heating, which can be serious problems in charged particle activation, are almost totally eliminated.

Amiel and Peisach³ have determined the deuterium concentration in heavy water by the reaction $^{16}\text{O}(d, n)^{17}\text{F}$ utilizing knock-on deuterons produced by reactor fast neutrons. In the present work the feasibility of using 14-MeV neutrons from a neutron generator has been investigated.

When a water sample containing D_2O is irradiated with 14-MeV neutrons the following reactions take place.

- (i) $^2\text{H}(n, d)n$
- (ii) $^{16}\text{O}(d, n)^{17}\text{F}$
- (iii) $^{16}\text{O}(n, p)^{16}\text{N}$

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The amount of fluorine-17 ($t_{1/2} = 66$ sec) and nitrogen-16 ($t_{1/2} = 7.35$ sec) activity formed is given by:

$$A_{17F} = N_0 \sigma_2 \phi_d (1 - e^{-\lambda_2 t}) \quad (1)$$

$$A_{16N} = N_0 \sigma_3 \phi_n (1 - e^{-\lambda_3 t}) \quad (2)$$

where the indices refer to the specific nuclear reactions, and

A = activity produced, disintegrations/sec

N = number of atoms

σ = cross-section, mm²

ϕ = flux, particles/mm² . sec

λ = decay constant

t = irradiation time, sec.

If the neutron flux stays constant during the irradiation, the ratio of activities formed (R_A) can be expressed as

$$R_A = \frac{A_{17F}}{A_{16N}} = C_1 \frac{\phi_d}{\phi_n} \quad (3)$$

where C_1 is a constant.

From reaction (1) we have that the number of prompt deuterons per sec (P_d) can be written as:

$$P_d = N_d \sigma_1 \phi_n. \quad (4)$$

The number of deuterons per unit volume of the sample (N_d/V_s) is directly proportional to the deuterium concentration (a) of the sample expressed in atom % (atom % deuterium is here defined as the percentage of hydrogen atoms in the sample which have mass = 2). This assumption is true, because the change in volume caused by replacing the hydrogen atoms of water molecules with deuterium atoms is negligible [the difference between the ratio of the density of D₂O to that of water (1.107) and the ratio of their molecular weights (1.111) is negligible in comparison to the relative standard deviation of 2.8% for the method (Table II)]. Thus

$$\phi_d = C_2 \frac{P_d}{V_s} = C_3 a \sigma_1 \phi_n \quad (5)$$

where C_2 and C_3 are constants. By substituting for ϕ_d in equation (3) the following expression is obtained:

$$R_A = \frac{A_{17F}}{A_{16N}} = C_4 a. \quad (6)$$

It can thus be seen that the ratio of fluorine-17 and nitrogen-16 activities is directly proportional to the deuterium concentration of the sample expressed in atom %. It should be noted that this ratio is independent of sample size and neutron flux (if the neutron flux stays constant during irradiation).

Some of the usual methods for determining deuterium in water are mass spectrometry, interferometry, and optical and density measurements.¹⁰ The only methods currently available utilizing nuclear properties, other than the 'knock-on' technique, are those based on photoneutron emission^{11,12} and prompt neutron detection during irradiation with deuterons.¹³

EXPERIMENTAL

Samples weighing approximately 1 g were prepared by mixing known weights of heavy water, containing 94.5 atom % deuterium, with natural water. The deuterium concentration of the prepared samples ranged from 2.6 to 94.5 atom % deuterium. The samples were contained in cylindrical polyethylene vials which were heat-sealed before use. Natural water samples similarly prepared were used as blanks.

Irradiations were carried out with a 150-keV Cockcroft-Walton accelerator (Texas Nuclear Corporation) producing 14-MeV neutrons by bombarding a tritiated titanium target with a deuteron beam of 150–500 μ A. A neutron flux of approximately 10^{16} n. mm⁻². sec⁻¹ was obtained. The neutron output was monitored by a proton recoil detector connected to a ratemeter. The beam current of the neutron generator was varied when necessary during irradiation in an effort to maintain a constant neutron flux. All samples and standards were irradiated for 2 min.

The samples were transferred to and from the irradiation terminal through a polyethylene pneumatic tube by means of compressed air. The gamma-rays from the radioisotopes produced were detected by two matched 75 \times 75 mm NaI(Tl) crystals positioned 25 mm apart. The detectors were connected to a 400-channel pulse-height analyser operated in the multiscaler mode. Counting was started 30 sec after the end of each irradiation in order to allow the 7.35-sec nitrogen-16 activity to cool sufficiently, thereby minimizing dead-time effects.

RESULTS AND DISCUSSION

The decay of the activity produced in a sample containing 58.0 atom % deuterium is shown in Fig. 1, from which the relative contribution of 7.35-sec nitrogen-16, 66-sec fluorine-17 and 9.96-min nitrogen-13 can be seen; prolonged counting reveals the presence of 110-min fluorine-18 as well. The stripping of all the decay curves was done by computer, using the CLSQ program of Cumming.¹⁴ The possible origin of the activities found is given in Table I.

TABLE I.—REACTIONS LEADING TO ACTIVITIES FOUND IN FAST NEUTRON IRRADIATED HEAVY WATER SAMPLES

Source	Reaction	Q-value, MeV	Half-life
Sample	$^{16}\text{O}(\text{n}, \text{p})^{16}\text{N}$	-9.639	7.35 sec
	$^{18}\text{O}(\text{d}, \text{n})^{17}\text{F}$	-1.631	66 sec
	$^{16}\text{O}(\text{p}, \gamma)^{17}\text{F}$	0.596	
	$^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$	-5.208	9.96 min
	$^{16}\text{O}(\text{d}, \gamma)^{18}\text{F}$	7.538	110 min
	$^{18}\text{O}(\text{p}, \text{n})^{18}\text{F}$	-2.450	
Container	$^{12}\text{C}(\text{p}, \gamma)^{13}\text{N}$	1.941	9.96 min
	$^{12}\text{C}(\text{d}, \text{n})^{13}\text{N}$	-0.286	
	$^{13}\text{C}(\text{p}, \text{n})^{13}\text{N}$	-3.005	

The activity ratio (R_A) of fluorine-17 to nitrogen-16 at the end of the irradiation was found to change linearly with deuterium concentration, as expected from equation (6), and to go through the origin of the calibration curve so that one standard sample is sufficient to fix the calibration. The activity ratio per atom % deuterium was 8.47×10^{-5} . The linearity of the calibration curve over the concentration range studied indicates that fluorine-17 is predominantly formed by the $^{16}\text{O}(\text{d}, \text{n})^{17}\text{F}$ reaction. The contribution of fluorine-17, formed by knock-on protons (see Table I), is negligibly small even at low deuterium concentrations. Other reactions induced in pure water samples are unlikely to yield fluorine-17. Amiel and Peisach³ found that their calibration curve started to deviate from proportionality for deuterium concentrations below about 7 atom %. That such a deviation was not observed in this work can be ascribed to the fact that most of the epi-cadmium neutrons used in

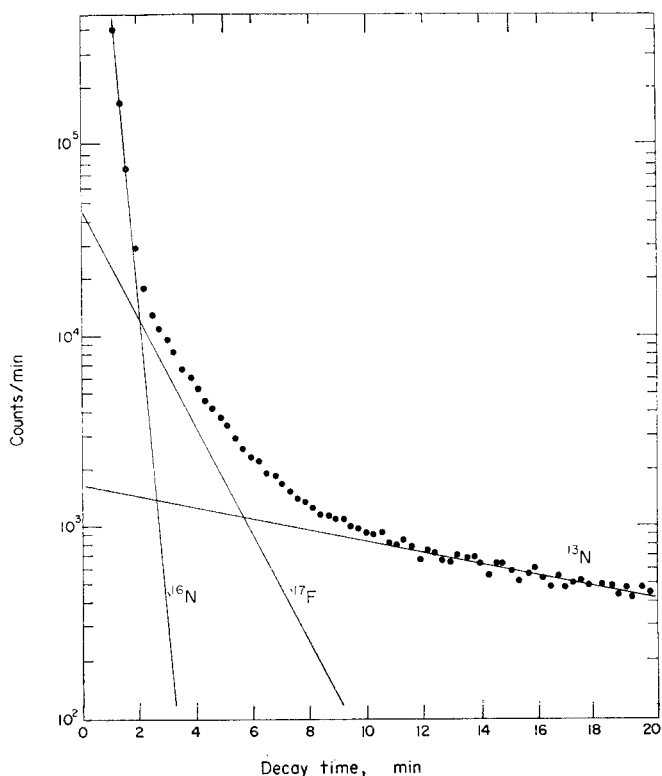


FIG. 1.—Decay of a sample containing 58.0 atom % deuterium, showing the relative amounts of 7.35-sec nitrogen-16, 66-sec fluorine-17 and 9.96-min nitrogen-13 formed.

their investigation have energies considerably below 14 MeV. Higher energy neutrons would thus favour the formation of fluorine-17 by the $^{16}\text{O}(d, n)^{17}\text{F}$ reaction rather than the $^{16}\text{O}(p, \gamma)^{17}\text{F}$ reaction, as the threshold for the former reaction is much higher (see Table I).

The results of some determinations of deuterium are shown in Table II, showing an average relative standard deviation of 2.8% over the concentration range studied. The error distribution (Table II) indicated the absence of bias. The mean value of the activity ratio per atom % deuterium was 8.50×10^{-5} , which is in agreement with the calibration value within the precision of the measurements. The deuterium concentration expressed as w/w% D_2O can be obtained from the concentration in atom % (a) by the relationship:

$$\text{w/w}\% \text{D}_2\text{O} = \frac{20a}{18 + 0.02a} \quad (7)$$

The precision of the method is not affected by the reproducibility of sample position at the irradiation terminal, because the activity ratio (R_A) is independent of flux. A variation of neutron flux does however affect the precision, owing to the large difference in half-lives of the two activities determined. This is thought to be the main source of error of the method, as the relative standard deviation due to statistical errors is about 0.8% (for a sample having a deuterium content of 50

TABLE II.—DETERMINATIONS OF DEUTERIUM

Known deuterium concentration, atom %	^{19}F zero activity, cpm	^{16}N zero activity, cpm	Activity ratio	Activity ratio per atom %	Deuterium concentration found, atom %	Error, atom %	Relative error, %
2.60	2237	9.440	0.237	9.12	2.79	+0.19	7.3
4.34	2980	8.514	0.350	8.07	4.13	-0.21	4.8
5.77	4642	9.375	0.495	8.58	5.84	+0.07	1.2
8.07	6163	9.171	0.672	8.33	7.93	-0.14	1.7
14.12	10880	9.179	1.185	8.39	13.99	-0.13	0.9
15.43	12288	9.380	1.310	8.49	15.47	+0.04	0.3
18.3	16230	10.187	1.593	8.70	18.8	+0.5	2.7
24.4	16810	8.288	2.03	8.32	24.0	-0.4	1.6
34.9	22742	7.536	3.02	8.65	35.6	+0.7	2.0
49.2	36051	8.549	4.22	8.58	49.8	+0.6	1.2
58.0	44684	9.351	4.78	8.24	56.4	-1.6	2.8
67.5	47530	8.168	5.82	8.62	68.8	+1.3	1.9
76.6	51067	7.962	6.41	8.37	75.7	-0.9	1.2
89.9	51831	6.870	7.55	8.40	89.1	-0.8	0.9
94.5	57318	7.054	8.13	8.60	96.0	+1.5	1.6

Mean value of activity ratio per atom % deuterium = 8.50×10^{-5} .

Relative standard deviation = 2.8%.

atom %) as compared to a value of 2.8% found. Even though the half-lives of nitrogen-16 and nitrogen-13 differ greatly from that of fluorine-17 (see Table I), their formation introduces a source of error in the determination of the fluorine-17 activity, which becomes appreciable in samples of very low deuterium content, (below about 2 atom %) and may be considered a limiting factor of the method. It is estimated that samples with a deuterium concentration of about 1 atom % can only be analysed with a relative standard deviation of approximately 20%. The sensitivity of the method, based on the criterion that the net measured fluorine-17 activity should be twice the standard deviation of the background, is about 0.6 atom % deuterium.

The effect of sample size was investigated and it was found that the activity ratio (R_A) became smaller as sample size decreased, because the relative amount of fluorine-17 activity formed decreased owing to the loss of recoiling deuterons from the sample. To a first approximation the loss of recoiling deuterons from the sample is directly proportional to the area (A) of the sample; therefore the fluorine-17 activity formed in a sample with weight W is given by

$$A_{17F} = k_1(W - k_2A) \quad (8)$$

where k_1 and k_2 are constants. The relationship between the area (A) and weight (W) of a sample (expressed in mm^2 and g respectively) contained in a cylindrical container with a radius of r mm is given by the expression

$$A = 2\pi r^2 + 2W/rD$$

where D is the density of the sample, in g/mm^3 . By substitution for A in equation (8) and from the fact that the activity ratio (R_A) is proportional to the fluorine-17 activity per unit weight of sample, the relationship between R_A and sample weight can be found.

$$R_A = C_1 - C_2/W. \quad (9)$$

The values of the constants C_1 and C_2 were obtained by measuring the activity ratios (R_A) for different size samples and were found to be 8.68×10^{-5} and 0.368×10^{-5} respectively for the conditions of this experiment, which differed slightly from those prevailing during the actual analyses. Therefore

$$R_A = \left(8.68 - \frac{0.368}{W} \right) \times 10^{-5} \quad (10)$$

The maximum energy attained by knock-on deuterons during 14-MeV neutron irradiation can be determined from momentum considerations, and is about 12.5 MeV. The range of such deuterons in water is approximately 1.2 mm.¹⁵ Equation (10) is not applicable in cases where any of the linear dimensions of the sample are less than twice the range of the maximum energy of the knock-on deuterons. This corresponds to sample weights less than approximately 0.16 g, for the sample holders used in this experiment.

The effect of sample size on activity ratio (R_A) is shown in Fig. 2. The smooth curve was calculated from equation (10) and the points were measured for sample sizes between 0.18 and 1.1 g. It can be seen that as sample size increases the activity ratio per atom% increases asymptotically to the maximum value of 8.68×10^{-5} . It is also clear that small variations in sample size below about 0.5 g (see Fig. 2) will

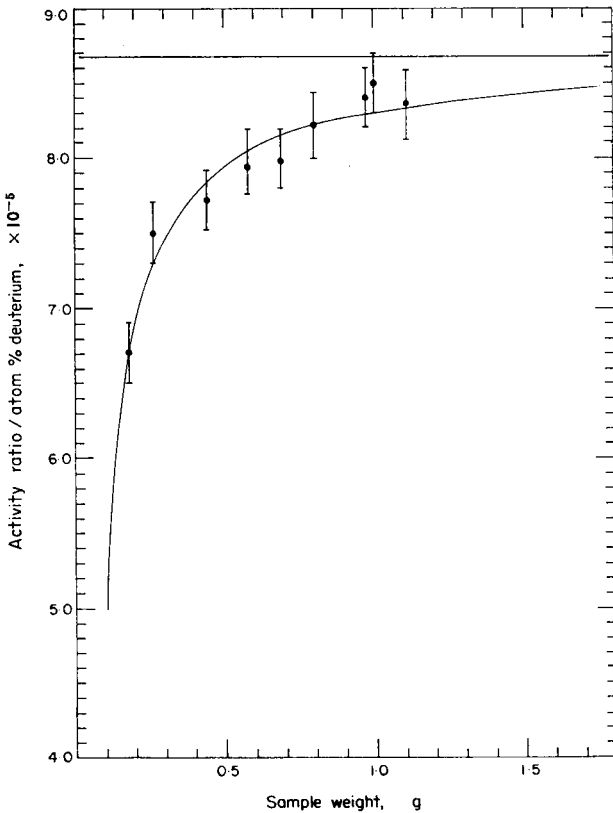


FIG. 2.—The effect of sample size on the activity ratio ($^{17}\text{F}/^{16}\text{N}$) measured, for a sample containing 94.5 atom % deuterium.

considerably affect the precision of the method, owing to the loss of recoiling deuterons from the sample. Variation of sample size between samples and standards weighing more than 0.5 g will, however, not appreciably add to the errors of the method.

The flux obtainable from neutron generators is about four orders of magnitude smaller than the epi-cadmium flux of a reactor. This is somewhat compensated for by the fact that all the neutrons from a 14-MeV generator can contribute to the formation of fluorine-17, whereas a large majority of epi-cadmium neutrons have energies lower than that necessary to produce knock-on deuterons with energies above the threshold of the $^{18}\text{O}(\text{d}, \text{n})^{17}\text{F}$ reaction. From the yield of fluorine-17 activity per atom % deuterium, obtained during reactor irradiation³ and in this work, it is estimated that the effective cross-section for the production of fluorine-17 by 14-MeV neutrons is approximately 200 times larger than that for reactor epi-cadmium neutrons. Furthermore, reactor thermal neutrons which do not contribute to knock-on activation products, do form serious interfering activities, owing to activation of impurities either in the sample or sample vial. This necessitates enclosing the samples in cadmium covers during irradiation. Care must also be taken to prevent cross-contamination from the cadmium covers. Although the cross-sections of many common impurities for 14-MeV neutrons can be appreciable, the activities produced are usually not positron emitters and can be discriminated against

if necessary by coincidence counting of annihilation gammas in the case of fluorine-17. The nitrogen-16 activity formed in the sample can also be measured very specifically by suitable energy discrimination, as this nuclide emits very high energy gamma-rays.

The present method provides a simple and rapid non-destructive method for determining heavy water concentrations. Furthermore, irradiation flux and sample weight need not be determined, as use is made of an internal ratio of activities. The relative amounts of deuterium and oxygen in the sample are measured directly; impurities which do not form interfering activities but which may affect other methods of heavy water determination (such as density measurements) do not present any problem when this method is used.

Recent developments¹⁶ in 14-MeV neutron generator technology have made it possible to obtain fluxes of up to 10^9 n.mm⁻².sec⁻¹. The availability of such a generator would greatly improve the sensitivity of the analysis described here and would in general greatly increase the scope and applicability of secondary charged particle activation analysis. Furthermore, the low cost of neutron generators as compared to nuclear reactors makes them more readily available to smaller analytical laboratories.

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Zusammenfassung—Die Deuteriumkonzentration in schwerem Wasser wurde bestimmt; dabei wurden Rückstoß-Deuteriumkerne aus n-d-Stößen zu der Reaktion $^{16}\text{O}(\text{d}, \text{n})^{17}\text{F}$ verwendet. Das innere Verhältnis der Aktivitäten von Fluor-17 (66 sec) und Stickstoff-16 (7,35 sec) der sich durch die Reaktion $^{16}\text{O}(\text{n}, \text{p})^{16}\text{N}$ bildet, änderte sich linear mit der Deuteriumkonzentration. Mißt man ein solches inneres Aktivitätsverhältnis, dann braucht man weder Neutronenfluß noch Probengewicht zu kennen. Deuterium wurde im Bereich 2,6–94,5 Atom-% mit einer relativen Standardabweichung von 2,8% bestimmt. Der Einfluß der Probengröße wurde untersucht; mit fallender Probengröße wurde die relative Fluor-17-Aktivität kleiner, da Rückstoßdeuteronen aus der Probe verloren gingen. Zur Berücksichtigung dieses Effekts wurde ein einfacher Ausdruck gefunden.

Résumé—On a déterminé la concentration en deutérium de l'eau lourde en utilisant les noyaux deutérium de recul des collisions n-d pour induire la réaction $^{16}\text{O}(\text{d}, \text{n})^{17}\text{F}$. On a trouvé que le rapport interne de l'activité du fluor-17 66 s à celle de l'azote-16 7,35 s, formé par la réaction $^{16}\text{O}(\text{n}, \text{p})^{16}\text{N}$, varie linéairement avec la concentration en deutérium. Lorsqu'un tel rapport interne d'activités est mesuré, le flux de neutrons et le poids d'échantillon n'ont pas besoin d'être connus. On a déterminé le deutérium dans le domaine allant de 2,6 à 94,5 atomes %, avec un écart-type relatif de 2,8%. On a étudié l'influence de la dimension de l'échantillon et l'on a trouvé que l'importance relative de l'activité du fluor-17 formé devenait moindre quand la dimension de l'échantillon décroissait, par suite de la perte de deutérons de recul de l'échantillon. On a obtenu une relation simple pour rendre compte de cette influence.

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RAPID SPECTROPHOTOMETRIC DETERMINATION OF BORON IN STEEL*

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Summary—A rapid spectrophotometric method is presented for the determination of boron in steel by use of the fluoborate–Methylene Blue complex. The method is in principle similar to that of Rosotte, but modifications simplify the operation, obviate contamination and avoid problems with emulsion formation. Up to 20% Cr, 10% Ni, and 1% each of V, Mo and W present either individually or collectively do not interfere in the determination, making it applicable to alloy steels. The determination limit of the method has been lowered from 5 to 0.2 ppm boron. Samples are dissolved at room temperature in polythene bottles, solubilizing all forms of boron including boron nitride, and avoiding loss of relatively volatile boron compounds. The precision of the method is good. Six samples can be analysed in less than 2 hr.

SEVERAL reagents have been used for the photometric determination of boron in steel. Amongst the most frequent are 1,1-dianthrimide, quinalizarin and curcumin. A critical evaluation of these reagents has been made by the B.I.S.R.A. Methods of Analysis Committee,¹ who adopted the reagent 1,1-dianthrimide for use after a preliminary separation of iron by cation-exchange. However, the conditions established for the colour development are critical and so less useful for routine work. The present ASTM method² involves a prior distillation of methyl borate in an expensive all-quartz apparatus, and there is a great possibility of contamination from the relatively large quantities of reagents required in the procedure.

Takeuchi³ and co-workers described a method for determining boron in steel by pyrohydrolysis and constant-current coulometry. This approach was unsuccessful in our laboratory; even with pure synthetic solutions containing microgram amounts of boron, the yields were erratic. Harrison and Cobb⁴ used the boron–curcumin complex in an acetic anhydride medium. The dissolution at 80° in 20% sulphuric acid, recommended in the procedure, required excessive time. Further, the blanks were high, and calibration was inconsistent. Very recently Tolk *et al.*⁶ also used curcumin for determining boron. The method appears to be time-consuming in the sample dissolution step and requires an additional 3 hr for subsequent treatment and colour development. Further the authors reported a serious limitation of the method in that no oxidizing agents could be used, which leaves uncertain the treatment of the carbides *etc* inherent in iron and steel. No alternative is offered.

The triple complex of Methylene Blue, fluorine and boron in dichloroethane medium has been proposed by many workers^{6–9} for the determination of boron in steel. Rosotte⁹ successfully dissolved steel directly in a fluorine-containing medium, with the obvious advantage of reducing the amount of reagents capable of affecting the blank. Ammonium hydrogen fluoride, hydrofluoric acid *etc* were used to achieve

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both the rapid dissolution and the conversion of boron into BF_4^- (the active species) at room temperature.

However the extraction technique recommended by her, involving a pneumatic separator, was found far from satisfactory in our laboratory. Polyethylene separatory funnels proved to be successful both in providing a quick separation of the two phases and in equilibrating the excess of reagents into the aqueous phase without emulsion formation. As will be illustrated the method presented here is suitable down to 0.2 ppm of boron, with satisfactory precision.

EXPERIMENTAL

Apparatus

Nalgene 4-oz (125-ml) narrow-mouth bottles with polypropylene screw closures (Canlab, Cat. 5-803 or equivalent). Nalgene 60-ml bottles with dropper assembly and polypropylene closures (Canlab, Cat. 6-251 or equivalent). Nalgene Squibb pear-shape separatory-funnels (polypropylene, Teflon plug, polyethylene stopper, capacity 125 ml (Canlab, Cat. 37-287 or equivalent)). These bottles and funnels should be kept filled with demineralized distilled water until just before use, and refilled after use and washing. Polyethylene measuring cylinders, funnels and beakers. Mohr pipette graduated to 0.01 ml.

Reagents

Use demineralized distilled water throughout, and chemically pure reagents. Prepare reagents in plastic or polyethylene ware and transfer immediately to polyethylene containers with screw closures.

Hydrofluoric acid, 5%. Carefully add 10 ml of 50% HF (27M) to 90 ml of water in a polyethylene beaker.

Boron stock solution, 50 $\mu\text{g}/\text{ml}$. Dissolve 0.287 g of boric acid in water and dilute to a litre in a volumetric flask.

Standard BF_4^- solution A, 1 μg of boron/ml. Transfer 5 ml of boron stock solution into a 125-ml polyethylene bottle, add 20 ml of water and 2.5 ml of 5% hydrofluoric acid. Mix, let stand for 24 hr and dilute to 250 ml in a volumetric flask. This solution is stable for 6 months.

Standard BF_4^- solution B, 0.1 μg of boron/ml. Transfer 10 ml of solution A into a polyethylene beaker. Add 1 ml of 5% hydrofluoric acid followed by 80 ml of water. Mix, transfer, and dilute to 100 ml in a volumetric flask with water. Prepare this solution fresh as needed.

Ammonium hydrogen fluoride, 8M. Dissolve 91 g of $\text{NH}_4\text{F}\cdot\text{HF}$ in 150 ml of boiling water. Filter.

Phosphoric acid (3 + 2). Dilute 3 parts of phosphoric acid (sp. gr. 1.69) with 2 parts of water.

Hydrogen peroxide, 100-vol.

Hexamethylenetetramine solution, 40%. Dissolve 40 g of hexamethylenetetramine in water by slight warming. Filter and dilute to 100 ml with water. Prepare fresh as needed.

Methylene Blue solution, 0.01M. Dissolve 0.8 g of "medicinal Methylene Blue" in 200 ml of water. Filter through a glass filter (fine porosity) and dilute to 250 ml with water.

1,2-Dichloroethane. Distilled.

Pure iron chips, boron-free. NBS 55e is suitable.

The ammonium hydrogen fluoride, phosphoric acid, hydrogen peroxide, Methylene Blue and conc. hydrofluoric acid solutions should be kept in bottles fitted with droppers to facilitate transfer. Volumes can be measured by counting drops or graduating the droppers.

Procedure

Calibration. Weigh 0.100 g of pure iron or NBS 55e chips into a series of 6 polyethylene bottles (narrow mouth) and add in the following order (making sure the sample remains in contact with the reagents): 1 ml of ammonium hydrogen fluoride solution, 1 ml of phosphoric acid (3 + 2), 0.5 ml of concentrated hydrofluoric acid, and 2.0 ml of 100-vol hydrogen peroxide. Cap the bottle immediately after the addition of hydrogen peroxide and tap gently to bring the sample in contact with the reagents. It takes 5–10 min for complete dissolution. Let stand for an additional 15 min. Transfer the contents to separatory-funnels, using 10, 9.5, 9, 8, 7 and 6 ml of water for rinsing. Add (by pipette) 0, 0.5, 1.0, 2.0, 3.0 and 4.0 of standard boron solution A to the respective separatory-funnels (to give the same total volume in each) and mix (this covers the range 5–40 ppm boron; to cover the range lower than 5 ppm use standard solution B). Add 5 ml of hexamine solution and mix, then add 1 ml of Methylene Blue solution and mix. Add 15.0 ml of dichloroethane (from a burette). Stopper and manipulate the separatory-funnels so that no aqueous phase is trapped under the organic layer. Clamp the funnels in a mechanical wrist-action shaker and shake for 5 min. Let settle for 2–4 min. Tap the funnels, if necessary, to ensure complete separation of the two phases.

Transfer the (lower) organic phase into another separatory-funnel, add 10 ml of water, stopper the funnel, mix very gently for 30 sec to extract the excess of Methylene Blue into the aqueous phase (excessive shaking may produce an emulsion; this must be avoided). A clear separation is achieved. Let settle for about 5 min, drain off about 1 ml to flush the stem and then transfer the organic layer through a 70-mm fast filter paper (*e.g.*, Whatman No. 541) supported on a dry 50-ml beaker, leaving about 1 ml of it in the separatory-funnel.

Transfer an appropriate aliquot of the extract into a dry 25-ml volumetric flask and dilute to the mark with dichloroethane. In the range 0.2–1.0 ppm boron no dilution with dichloroethane is needed. Measure the absorbance in a 10-mm cuvette, with dichloroethane as reference, at 650 nm, using a red-sensitive phototube. Obtain the net absorbance by subtracting the blank (0 μg boron). Plot absorbance *vs.* μg of boron or calculate a conversion factor.

Samples. Weigh sample and add boron-free iron as follows.

Boron, ppm	Sample wt., g	Boron-free iron, g	Final extract aliquot, ml
Blank	nil	0.1000	As in example
0.2–1	0.1000	nil	No dilution
1–5	0.1000	nil	10
5–40	0.1000	nil	5
40–70	0.0500	0.0500	5
70–100	0.0300	0.0700	5

Carry out the procedure as described (including blank) under calibration except for the addition of boron standard solution; instead use 10 ml of water for rinsing.

RESULTS AND DISCUSSION

Interferences

Residual elements in steel such as Cu, Cr, Ni, V, Mo and W did not present any problem in the boron determination, but their effect was investigated to ensure that the method would be applicable to alloy steels. Table I shows the interference study with British Chemical Standards steel 273 containing 25 ppm boron, which was used to provide the steel matrix. Potassium dichromate and nickel ammonium sulphate were used to provide 20 mg of Cr and 10 mg of Ni, and ammonium vanadate, ammonium molybdate and sodium tungstate were used to provide 1 mg each of V, Mo and W, added to a 0.1 g sample.

TABLE I.—INTERFERENCE STUDY WITH BCS STEEL STANDARD, CERTIFIED 25 ppm BORON

Element added	Boron found, ppm
nil	23
nil	25
20% Cr	24
10% Ni	22
1% V	24
1% Mo	25
1% W	23
20% Cr + 10% Ni + 1% V + 1% Mo + 1% W	24

Evidently 20% Cr, 10% Ni, and 1% each of V, Mo and W added either individually or collectively do not interfere in the boron determination.

Range of application

Extension of the lower limit of the method from 5 ppm down to 0.2 ppm of boron by use of a bigger sample weight did not give encouraging results. The alternative—use

of a larger proportion of the Methylene Blue extract—proved satisfactory, as shown in Table II. The blanks were similarly carried out with a 10-ml aliquot.

TABLE II.—RECOVERY TESTS

Boron, ppm			Boron, ppm		
Present	Found*	Range	Present	Found†	Range
1.0	1.1	0.8–1.1	0.2	0.3	0.25–0.3
2.0	2.4	2.0–2.5	0.5	0.5	0.3–0.55
3.0	2.8	2.6–3.1	0.8	0.8	0.7–0.9
4.0	3.9	3.5–4.0	1.0	1.0	0.9–1.1
5.0	5.1	4.7–5.2			

* 10 ml of extract diluted to 25 ml for absorbance measurement.

† Absorbance of undiluted extract measured.

The procedure described was applied to a number of British Chemical Standard steels. The results are recorded in Table III. The wide spread in the range of values listed in the certificates prevents knowledge of the “true” content but the precision of the present method is good throughout.

TABLE III.—BORON IN BCS STEEL STANDARDS

BCS No.	Certificate		Boron found, ppm	Standard deviation, ppm	No. of detns.
	Value, ppm	Range, ppm			
272	40	30–40	30	1.1	5
273	25	15–30	23	1.8	5
275	10	10–25	11	1.1	5
326	10	10	6	1.3	8
327	30	25–40	38	1.7	5
328	40	35–50	44	0.8	6
329	80	70–80	65	1.4	4
330	70	70–80	71	2.0	7

Conclusions

In the determination of boron as described under the procedure the active species is BF_4^- , which forms the ion-association complex with Methylene Blue. Normally it takes about 18 hr to convert boron into BF_4^- . However, iron catalyses this reaction, which is completed in 5–10 min, the time needed to dissolve the steel. The incorporation of phosphoric acid prevents the formation of anionic complex iron fluorides capable of entering into extractable combination with Methylene Blue. Attack with ammonium hydrogen fluoride destroys boron nitride, solubilizing the boron; hence total boron is obtained.⁹ Addition of hydrogen peroxide speeds up the dissolution and oxidizes the iron. The dissolution at room temperature avoids risk of loss of boron compounds volatile at higher temperatures (*e.g.*, $\sim 70^\circ$).

The partition coefficient of the ion-association complex is such that the volume of both the aqueous and organic phases must be precise, as indicated in the method, otherwise variable errors will occur.

It is advisable to clean the polyethylene ware initially with a mixture of ammonia solution (1 part) and dichloroethane (2 parts) and to rinse with water. It is of the

utmost importance subsequently to keep the apparatus clean and filled with water between tests. It has been reported that some batches of dichloroethane, usually with a slight yellowish tinge, interfere with the extraction of the fluoborate-Methylene Blue complex. Strizovic and Caldwell⁸ purified the dichloroethane by treating it with small portions of sodium hydroxide until colourless. Excess of alkali was removed by washing with dilute sulphuric acid and then water.

Up to 20% Cr, 10% Ni, 1% each of V, Mo and W present either individually or collectively do not interfere in the boron determination, showing the feasibility of applying the method to alloy steels. The method can also be applied to determine trace amounts of boron in fertilizers containing phosphate, or in glass, but it is then necessary to use boron-free iron, as indicated in the method, to catalyse the BF_4^- formation. The lower limit of the method is 0.2 ppm of boron. Sample dissolution is carried out at room temperature, solubilizing all forms of boron including boron nitride. This avoids loss of relatively volatile boron compounds. The precision of the method is good and six samples can be analysed in less than 2 hr. The method has been in use in our laboratory for the last 2 years.

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Zusammenfassung—Ein schnelles spektrophotometrisches Verfahren zur Bestimmung von Bor in Stahl mit Hilfe des Fluoborat-Methylenblau-Komplexes wird angegeben. Es ähnelt im Prinzip der Methode von Rosotte, aber Änderungen vereinfachen die Handlung und vermeiden Verunreinigung und Probleme der Emulsionsbildung. Bis 20% Cr, 10% Ni und je 1% V, Mo und W stören einzeln oder gemeinsam bei der Bestimmung nicht; dadurch wird das Verfahren auf legierte Stähle anwendbar. Die Nachweisgrenze wurde von 5 auf 0,2 ppm Bor gesenkt. Die Proben werden bei Raumtemperatur in Polythene-Flaschen aufgeschlossen, wobei alle Formen von Bor auch Bornitrid, in Lösung gehen und der Verlust von relativ flüchtigen Borverbindungen vermieden wird. Die Genauigkeit des Verfahrens ist gut. Sechs Proben können in weniger als zwei Stunden analysiert werden.

Résumé—On présente une méthode spectrophotométrique rapide pour la détermination du bore dans l'acier par l'emploi du complexe fluoborate-bleu de méthylène. La méthode est en principe similaire à celle de Rosotte, mais des modifications simplifient l'opération, évitent la contamination et écartent les problèmes de formation d'émulsion. Des quantités allant jusqu'à 20% Cr, 10% Ni et 1% de chacun des métaux V, Mo et W présents soit individuellement, soit collectivement, n'interfèrent pas dans le dosage, le rendant applicable aux aciers alliés. La limite de dosage de la méthode a été abaissée de 5 à 0,2 ppm de bore. Les échantillons sont dissous à température ordinaire dans des bouteilles en polythène, solubilisant toutes les formes du bore y compris l'azoture de bore, et évitant la perte de composés du bore relativement volatils. La précision de la méthode est bonne. On peut analyser six échantillons en moins de 2 h.

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ANION-EXCHANGE SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN SILICATE ROCKS

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Summary—A combined ion-exchange spectrophotometric method has been developed for the determination of molybdenum and tungsten in silicate rocks. After the decomposition of samples with a mixture of sulphuric, nitric and hydrofluoric acids, traces of molybdenum and tungsten are separated from other elements by anion-exchange in acid sulphate media containing hydrogen peroxide. The adsorbed molybdenum and tungsten can easily be stripped from the column by elution with sodium hydroxide-sodium chloride solution. The adsorption and desorption steps provide selective concentration of molybdenum and tungsten, allowing the simultaneous spectrophotometric determination of the two metals with dithiol. Results on the quantitative determination of molybdenum and tungsten in the U.S. Geological Survey standard samples are included.

MOLYBDENUM is quite frequently reported in the routine spectrochemical analysis of common types of rocks, although its concentration often borders on the spectrochemical detection limits. Unlike molybdenum, the abundance of tungsten in most rocks and sediments is below the limits of detection by direct spectrochemical methods. A number of photometric methods have been described for the determination of molybdenum in silicate rocks. Recent progress in concentration and the subsequent photometric determination of molybdenum in rocks has been reviewed by Chan and Riley.¹ The colorimetric method developed by Stanton and Hardwick² for molybdenum in soils, sediments and rocks is primarily intended to provide a rapid procedure for field work, involving fusion of samples with potassium hydrogen sulphate.

There are fewer photometric methods for tungsten in silicate rocks. For photometric determination with the tin(II) chloride-thiocyanate method, Sandell³ first removed iron and titanium by a double precipitation, and molybdenum by hydrogen sulphide precipitation, using antimony(V) sulphide as a carrier. Jeffery⁴ concentrated molybdenum and tungsten by extraction with α -benzoinoxime into chloroform after alkali fusion of silicates, the two metals being determined simultaneously with dithiol. Chan and Riley⁵ co-precipitated tungsten with manganese dioxide from a perchloric acid solution of rocks, purified it by cation-exchange, and finally determined it spectrophotometrically with dithiol. Since the carrier, co-precipitating agent or organic extracting agent has generally to be removed before tungsten can be determined spectrophotometrically, the procedures are tedious and time-consuming.

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It has been demonstrated that comparatively few metal ions, including molybdenum and tungsten, adsorb on a strongly basic anion-exchange resin in the sulphate form from sulphuric acid or sulphate media.^{6,7,8} This behaviour of molybdenum and tungsten may offer a good basis for separating them from many other metals in silicate rocks before photometric determination. However, we found that even though the distribution coefficients of both metals are sufficiently high in sulphuric acid or sulphate media, a considerable portion of the two metals appears in the effluent from the sample solution, probably because of hydrolysis and the slow kinetics of the exchange reactions involved.

This difficulty can be overcome by allowing the two metals to adsorb on the resin from sulphuric acid or sulphate media containing a small amount of hydrogen peroxide. Thus, selective anion-exchange in sulphuric acid media coupled with simultaneous determination with dithiol allows the development of a simple, rapid, and highly selective method for the determination of molybdenum and tungsten in a variety of silicate rocks.

EXPERIMENTAL

Reagents and apparatus

Stock solutions. Molybdenum(VI): an appropriate amount of ammonium molybdate was dissolved in water to give *ca.* 10 mg of Mo/ml. The solution was standardized against EDTA. Tungsten(VI): an appropriate amount of sodium tungstate was dissolved in water to give *ca.* 10 mg of W/ml. The solution was standardized gravimetrically. From these stock solutions, standard solutions were freshly prepared by dilution with water.

Ion-exchange resin. A strong base anion-exchange resin, Dowex I-X8, SO₄-form, 100–200 mesh, was used. An appropriate amount of resin (Cl-form) was purified by placing it in a large column and backwashing with water to remove fine particles. Then it was washed with 3*M* sulphuric acid (to convert it into the sulphate form) until the effluent gave a negative test with silver nitrate. Finally the resin was washed thoroughly with water until the effluent gave a negative test with barium chloride. After drying at 60° for several hours the resin was stored in a desiccator containing a saturated potassium bromide solution.

Dithiol solution. An appropriate amount of toluene-3,4-dithiol was dissolved in 0.25*M* sodium hydroxide to yield a *ca.* 0.1% solution, and a few drops of thioglycolic acid were added. This solution was freshly prepared, when needed.

Column. Dried resin (5 g) was slurred with water and poured into a conventional glass column, 15 mm bore, drawn to a tip and with a plug of glass wool at the outlet. The resulting resin bed was about 50 mm long.

Equilibrium study

The distribution coefficient, K_d , for molybdenum(VI) and tungsten(VI) was determined by a batch method.⁹ Portions of dried resin (1 g each) were weighed and placed in glass stoppered conical flasks, to which 41-ml portions of ammonium sulphate solution were added. The solution was previously adjusted to 0.025*M* in sulphuric acid and contained varying amounts of ammonium sulphate and 1.03 mg of molybdenum(VI) or 1.04 mg of tungsten(VI). After mechanical shaking for 20 hr at room temperature, the two phases were separated by filtration. An aliquot of the filtrate was analysed colorimetrically for the respective element with dithiol. The K_d was calculated from the formula

$$K_d = \frac{\text{amount of ion in resin phase/g of resin}}{\text{amount of ion in solution phase/ml of solution}}$$

The K_d values for molybdenum(VI) and tungsten(VI) on the resin as a function of concentration of sulphuric acid were determined in the same manner. The K_d values were also determined in the presence of hydrogen peroxide at selected concentrations of sulphuric acid.

Procedure

Weigh out about 2 g of powdered sample in a platinum dish. Add 10 ml of 5*M* sulphuric acid, 4 ml of nitric acid and 10 ml of hydrofluoric acid. Heat on a hot-plate and evaporate to dryness. Continue the heating until no further fumes of sulphuric acid are evolved. Repeat the fuming with a

further 2 ml of sulphuric acid and 20 ml of water in order to remove all traces of fluoride. Add a further 2 ml of sulphuric acid and 20 ml of water and digest at slightly below the boiling point for 30 min while stirring at intervals. Dilute to about 150 ml and boil gently until a clear solution results. After cooling, add 4 ml of 30% hydrogen peroxide and dilute to 200 ml with water. Pass the solution through the resin column at a flow-rate of 1–2 ml/min. After washing the column with 50 ml of 1M ammonium sulphate–0.025M sulphuric acid solution, strip the molybdenum and tungsten by elution with 50 ml of 0.5M sodium hydroxide–0.5M sodium chloride solution at a flow-rate of 0.5 ml/min. Discard the first 20-ml fraction of the effluent and collect the subsequent 25-ml fraction for the determination of both elements.

Transfer the fraction containing molybdenum and tungsten into a Kjeldahl flask. Add 2 ml of sulphuric acid and heat until dense white fumes of sulphuric acid are evolved. After cooling add a few drops of 30% hydrogen peroxide and heat again until white fumes evolve. Add a few ml of water and three drops of 85% phosphoric acid, make alkaline with ammonia and expel the excess of ammonia by boiling. Add 1 ml of 5M sulphuric acid to the resulting solution and dilute to about 18 ml with water. Add 3 ml of the dithiol solution and warm on a steam-bath for 30 min. After cooling, extract the dithiol complexes of molybdenum and tungsten with 5 ml of n-butyl acetate and filter into a 10-mm cell. Measure the absorbance of the extract at 630 and 670 nm against the blank solution. Calculate the amounts of molybdenum and tungsten from the following equations

$$Mo = A_{670} \cdot a_W^{630} - A_{630} \cdot a_W^{670} / a_{Mo}^{670} \cdot a_W^{630} - a_{Mo}^{630} \cdot a_W^{670}$$

$$W = A_{630} \cdot a_{Mo}^{670} - A_{670} \cdot a_{Mo}^{630} / a_{Mo}^{670} \cdot a_W^{630} - a_{Mo}^{630} \cdot a_W^{670}$$

where A_{630} and A_{670} are the absorbances at 630 and 670 nm, respectively, a_W^{630} , a_W^{670} , a_{Mo}^{630} and a_{Mo}^{670} are constants which are determined experimentally with standard solutions, and the result is expressed in μg .

RESULTS AND DISCUSSION

Adsorption on Dowex I ion-exchange resin

K_d values for molybdenum(VI) and tungsten(VI) in acid sulphate media on Dowex I are tabulated in Table I as a function of the sulphate concentration. K_d values for

TABLE I.—DISTRIBUTION COEFFICIENTS OF Mo(VI) AND W(VI) AS A FUNCTION OF CONCENTRATION OF AMMONIUM SULPHATE (Free acid concentration kept constant at 0.025M H_2SO_4)

$(\text{NH}_4)_2\text{SO}_4$, M	0.050	0.10	0.25	0.50	1.00
K_d Mo(VI)	4.0×10^3	2.5×10^3	2.0×10^3	1.2×10^3	0.8×10^3
W(VI)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$

the two metals in sulphuric acid media of varying concentration are listed in Table II. The values in parentheses indicate the K_d values for molybdenum and tungsten in the presence of 0.8% hydrogen peroxide. The K_d values for molybdenum and tungsten generally decrease monotonically with increasing sulphate or sulphuric acid concentration in the range covered. It can be seen that the K_d values for molybdenum and tungsten in slightly acidic sulphate media are much higher than the respective values in sulphuric acid media. The presence of hydrogen peroxide makes molybdenum favour the resin phase to a greater extent, but lowers the K_d values for tungsten in sulphuric acid media.

TABLE II.—DISTRIBUTION COEFFICIENTS OF Mo(VI) AND W(VI) AS A FUNCTION OF CONCENTRATION OF SULPHURIC ACID

H_2SO_4 , M	0.050	0.25	0.50	0.75	1.00
K_d Mo(VI)	937	187(625)	52(227)	28	12(72)
W(VI)	2130	566(353)	229(153)	125	21(63)

Values in parentheses are the distribution coefficients in the presence of 0.8% H_2O_2 .

Over a wide range of sulphate or sulphuric acid concentration, the K_d values for molybdenum and tungsten should be sufficiently high to allow the two metals to adsorb on the column, but an attempt to adsorb molybdenum and tungsten quantitatively on the column failed with 200 ml of 0.5M ammonium sulphate-0.025M sulphuric acid solution containing 52 μg each of molybdenum and tungsten; a small fraction of both metals (3-4%), passed through. Similarly the uptake of molybdenum and tungsten from sulphuric acid solutions is only partial; when 200 ml of 0.45M sulphuric acid solution containing the two metals (52 μg each) is loaded onto the column, approximately 50% of molybdenum and 70% of tungsten pass through the column. The partial breakthrough of molybdenum and tungsten may be accounted for as due to the slow kinetics of the exchange reactions involving the hydrolysis products.

The partial breakthrough can be avoided by introducing a small amount of hydrogen peroxide into the sulphuric acid or sulphate solution containing the two metals. The concentration of hydrogen peroxide in sulphuric acid (pH 1) which is necessary to retain molybdenum and tungsten on the column covers a range from at least 0.3 to 6% peroxide in the final solution. However, a higher concentration of peroxide should be avoided, particularly if iron(III) is present, as this acts as a catalyst for deterioration of the resin.

Interferences

Adsorption of molybdenum and tungsten on the Dowex I column from sulphuric or sulphate media, and the subsequent elution with sodium hydroxide solution provides a selective removal of molybdenum and tungsten from a number of metals including alkali and alkaline earth metals, titanium, iron(II), iron(III), aluminium, beryllium, cadmium, cobalt, copper, gallium, germanium, nickel, vanadium and zinc.⁷ Uranium(VI), thorium, zirconium and scandium, which are retained strongly

TABLE III.—DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN 2-g SAMPLES OF SILICATE ROCKS

Sample (location collected)	Added, μg		Found, μg		Content in original sample, μg	
	Mo(VI)	W(VI)	Mo	W	Mo	W
Granite (Gunma)	—	—	1.54	1.32	1.54	1.32
	—	—	1.39	1.63	1.39	1.63
	—	—	1.56	1.54	1.56	1.54
	2.06	—	3.56	1.17	1.50	1.17
	—	2.08	1.39	3.46	1.39	1.38
				Av. 1.48 \pm 0.07	Av. 1.41 \pm 0.16	
Andesite (Gunma)	—	—	1.73	0.07	1.73	0.07
	—	—	1.74	0.08	1.74	0.08
	—	—	1.72	0.06	1.72	0.06
	2.06	—	3.62	0.10	1.56	0.10
	—	2.08	1.50	2.21	1.50	0.13
				Av. 1.65 \pm 0.10	Av. 0.09 \pm 0.01	
Basalt (Hiyogo)	—	—	1.17	0.95	1.17	0.95
	—	—	1.24	0.85	1.24	0.85
	—	—	1.24	0.85	1.24	0.85
	2.06	—	3.19	0.82	1.13	0.82
	—	2.08	1.22	2.89	1.22	0.81
				Av. 1.20 \pm 0.04	Av. 0.86 \pm 0.05	

TABLE IV.—DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN STANDARD ROCKS

MOLYBDENUM, ppm										
G-1 (Granite)	W-1 (Diabase)	G-2 (Granite)	GSP-1 (Granodiorite)	AGV-1 (Andesite)	PCC-1 (Peridotite)	DTS-1 (Dunite)	BCR-1 (Basalt)	Method	Author	
5.44, 5.45	0.52	0.15, 0.15	0.32, 0.28	1.68, 1.64	0.02, 0.04	0.02, 0.06	1.20, 1.21	Photometric	This work	
6.23*	0.5	1.9	2.6	4.6	0.2	1.3	2.9	Photometric	Fleischer ¹¹	
7		<0.1	0.2	1.7	<0.1	<0.1	1.2	Spectrochemical	Chan and Riley ¹³	
		1.4	1.5	5.5	6.5	8.2	6.5	Spectrochemical	LeRiche†	
		0.94	1.6	3.0	—	—	1.4	Spectrochemical	Kulbicki <i>et al.</i> †	
									Champ†	
TUNGSTEN, ppm										
1.21, 1.40	0.45	0.00, 0.00	0.29, 0.32	0.64, 0.62	0.06, 0.06	0.06, 0.03	0.53, 0.55	Photometric	This work	
0.51*	0.45								Fleischer ¹⁰	
0.4	—	0.4	0.5	1.1	0.2	0.2	0.7	Photometric	Fleischer ¹¹	
									Chan and Riley ¹³	

* Molybdenum and tungsten separated chromatographically with a DEAE column.¹⁴† Quoted by Flanagan.¹²

on the resin, may not be stripped from the column by elution with 0.5M sodium hydroxide-0.5M sodium chloride solution. It will not generally be necessary to purify the eluted fraction of molybdenum and tungsten, particularly if the two metals are determined spectrophotometrically with dithiol.

Precision and accuracy

Results of repeated determinations of molybdenum and tungsten in three types of rocks, which represent the igneous rocks, are given in Table III. A known amount of molybdenum or tungsten was added to each rock sample, and the overall recoveries were estimated. The results are also quoted in Table III. The averages and errors (expressed as the standard deviation) are based on all determinations including addition tests. In general, the overall precision is satisfactory, the relative standard deviations ranging from 6 to 11%.

To obtain information about the accuracy of the method, the U.S. Geological Survey standard rock samples were analysed by the proposed procedure, the results being quoted in Table IV. For comparison, recommended values for G-1 and W-1 given by Fleischer, and some recent literature values cited by Flanagan for the new series of rock samples are also listed in Table IV. With respect to W-1 our values for molybdenum and tungsten are in good agreement with recommended values. Since the molybdenum concentration in G-1 is unusually high, causing a high concentration ratio of molybdenum to tungsten, considerable uncertainty may be introduced into the simultaneous dithiol determination of molybdenum and tungsten.⁴ Our values obtained after the separation of molybdenum and tungsten are close to recommended values.

For the new series of standard rocks our values for molybdenum agree with spectrochemical results given by Le Riche. For tungsten the photometric values given by Chan and Riley are distinctly higher than our values, the disagreement being particularly marked for granite G-2 and two ultrabasic rocks PCC-1 and DTS-1.

Zusammenfassung—Ein kombiniertes spektrophotometrisches Ionenaustauschverfahren zur Bestimmung von Molybdän und Wolfram in Silikatgesteinen wurde entwickelt. Nach Aufschluß der Proben mit einem Gemisch von Schwefel-, Salpeter- und Elußsäure werden Molybdän- und Wolframspuren von anderen Elementen durch Anionenaustausch in saurem, Sulfat und Wasserstoffperoxid enthaltendem Medium getrennt. Das adsorbierte Molybdän und Wolfram kann durch Elution mit Natriumhydroxid-Natriumchloridlösung leicht von der Säule gelöst werden. Die Adsorptions- und Desorptionsschritte bewirken selektive Anreicherung von Molybdän und Wolfram; die gleichzeitige spektrophotometrische Bestimmung beider Metalle mit Dithiol wird möglich. Ergebnisse der quantitativen Bestimmung von Molybdän und Wolfram in Standardproben vom U.S. Geological Survey sind beigefügt.

Résumé—On a élaboré une méthode associée échange d'ions-spectrophotométrie pour la détermination du molybdène et du tungstène dans des roches aux silicates. Après la décomposition des échantillons avec un mélange d'acides sulfurique, nitrique et fluorhydrique, les traces de molybdène et de tungstène sont séparées des autres éléments par échange anionique dans des milieux de sulfate acide contenant de l'eau oxygénée. On peut aisément détacher de la colonne les molybdène et tungstène adsorbés par élution avec une solution de soude-chlorure de sodium. Les stades d'adsorption et de désorption fournissent une

concentration sélective du molybdène et du tungstène, permettant la détermination spectrophotométrique simultanée des deux métaux au dithiol. On inclut les résultats sur la détermination quantitative du molybdène et du tungstène dans des échantillons étalons du U.S. Geological Survey.

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USE OF 3-HYDROXY-1,3-DIPHENYLTRIAZINE IN THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER, PALLADIUM, IRON, COBALT, NICKEL, AND MOLYBDENUM

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Summary—3-Hydroxy-1,3-diphenyltriazine (HDPTA) forms brightly coloured complexes with copper, palladium, iron, cobalt and nickel ions, which are readily extractable in benzene. The deep yellow molybdenum complex is completely soluble in 60% ethanol. All the chelates have a definite absorption maximum between 398 and 422 nm, the reagent absorption being negligible above 415 nm. The molar composition of the chelates is ML_2 , except for iron and cobalt which form ML_3 complexes. Microquantities of these metals can be determined spectrophotometrically with HDPTA.

3-HYDROXY-1,3-DIPHENYLTRIAZINE (HDPTA) was suggested by Shome¹ as an analytical reagent in which the nitroso group of cupferron was replaced by the benzene-diazonium group. Later Sogani and Bhattacharya² used this reagent for the gravimetric determination of palladium, copper and nickel. The reagent was subsequently employed by Shome, Das and Das³ for the spectrophotometric determination of thallium. In the present study, HDPTA was used for the extraction and subsequent photometric determination of copper, palladium, iron, cobalt and nickel in benzene medium.

Molybdenum was determined previously by Kaimal⁴ and Shome by precipitation with HDPTA followed by ignition and weighing as oxide. The present investigation was carried out to examine the possibility of spectrophotometric determination of the metal in 60% ethanol, with HDPTA as the colour-forming reagent.

EXPERIMENTAL

Reagents

Solutions of the metals were prepared by dissolving their chlorides, nitrates or sulphates in water; acids were added wherever necessary and the metal contents were determined by the usual methods. Weighed amounts of ammonium or alkali metal salts of various anions were dissolved in water and made up to standard volumes. Sodium acetate, ammonia or hydrochloric acid solutions were used for the regulation of pH. All the reagents and chemicals used were analytical reagent grade.

HDPTA ($C_{12}H_{11}N_3O$) was crystallized twice from alcohol, and $\sim 0.01 M$ solutions of the compound were prepared in spectroscopic grade ethanol.

Dry benzene and spectroscopic grade ethanol were prepared and stored in the usual manner.

Extraction and spectrophotometric determination of copper, palladium, iron, cobalt and nickel in benzene

An aliquot of the metal solution was taken in a 100-ml separatory funnel, diluted, and adjusted to an optimum pH value (Table I); 2–5 ml of the ethanol solution of HDPTA were then introduced into the funnel and shaken thoroughly. The metal chelate was then extracted with 2 or 3 successive

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TABLE I.—PHOTOMETRIC DETERMINATION OF COPPER, PALLADIUM, IRON, COBALT, NICKEL AND MOLYBDENUM WITH HDPTA (TEMPERATURE 25°C)

Metal ion	λ , * nm	Time limit for colour stability hr.	Range for adherence to Beer's law, $\mu\text{g/ml}$	Molar absorptivity $\times 100$	Optimum concentration range, $\mu\text{g/ml}$	pH range
Cu ²⁺	415	24	1.0–10.2	50	2.5–9.3	3.8–5.4
Pd ²⁺	415	48	0.2–5.5	219	0.7–3.4	3.6–5.6
Fe ³⁺	418	24	0.5–3.9	98	1.15–4.0	4.0–5.7
Co ²⁺	420	36	0.45–3.25	148	0.6–2.8	6.8–8.3
Ni ²⁺	422	72	0.4–3.5	152	0.75–2.7	6.4–8.0
Mo ⁶⁺	420	6	1.0–15.0	51	3.6–13.0	2.0–4.0

* Appropriate wavelength for the determination.

5-ml portions of benzene. The combined organic extracts were then diluted to the mark with benzene in a 25-ml volumetric flask and dried with a pinch of anhydrous sodium sulphate. A corresponding blank solution was prepared and the absorbance of the complex was measured against the reagent blank at an appropriate wavelength (Table I).

Spectrophotometric determination of molybdenum in 60% ethanol

A measured volume of molybdenum solution was adjusted to pH 2.5–3.5, the reagent (2–5 ml) was added and the volume was made up with ethanol and water so that the final solution contained 60% of alcohol. The pH was checked and the absorbance was measured at room temperature against a reagent blank prepared under the same conditions.

RESULTS

Characteristics of the complexes

The molybdenum, nickel and palladium complexes are yellow, the copper and cobalt complexes brownish yellow, and the iron complex blue-violet. Each has a well defined absorption maximum in the visible region (Fig. 1).

Conformity to Beer's law was tested at the appropriate λ_{max} or at a longer wavelength. Longer wavelengths were preferred when the reagent interfered with measurements at λ_{max} because it also absorbed at that wavelength. The ranges of metal concentration for adherence to Beer's law and of optimum concentration for photometric determination⁵ are listed in Table I.

The metal complexes were extracted with benzene from solutions adjusted to different pH values, the other conditions remaining the same, and the pH ranges for complete extraction were determined from absorbance studies (Fig. 2). The colour of the molybdenum complex in 60% ethanol was found to be independent of the acidity in the pH range 2.0–4.0.

When a definite amount of $\sim 10^{-3}M$ metal solution was treated with varying amounts of $10^{-3}M$ ethanolic HDPTA solution and the complex was extracted into benzene, the absorbances of the extracts showed that extraction is quantitative only when at least a 5-fold excess of the reagent is used. Molar ratio studies⁶ indicated the composition of the chelates as ML_2 , except for the iron and cobalt complexes which were ML_3 (M = metal, L = ligand). For molybdenum a 60% ethanol medium was used for these studies, and the complex was found to be ML_2 .

The colour of the metal–HDPTA complexes was stable for at least 24 hr except for the molybdenum complex, the colour of which gradually decreased after 6 hr. Time limits for colour stability are given along with the molar absorptivities, in Table I.

Solvents such as chloroform, carbon tetrachloride, ether and ethyl acetate could

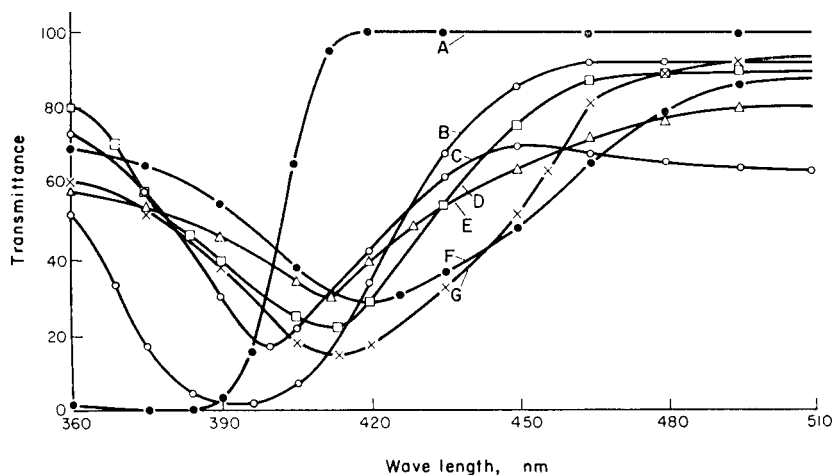


FIG. 1.—Transmittance curves of HDPTA complexes.
A— $10^{-2}M$ reagent; *B*—Cu, $10.2 \mu\text{g/ml}$; *C*—Fe, $2.61 \mu\text{g/ml}$; *D*—Mo, $10.3 \mu\text{g/ml}$;
E—Co, $1.36 \mu\text{g/ml}$; *F*—Ni, $2.0 \mu\text{g/ml}$; *G*—Pd, $3.7 \mu\text{g/ml}$; concentrations refer to metal ions.

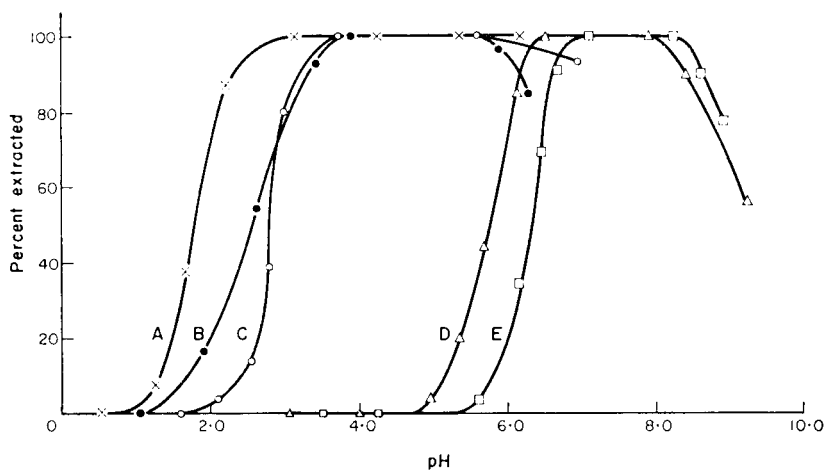


FIG. 2.—Extraction of HDPTA complexes as a function of pH.
A—Pd; *B*—Fe; *C*—Cu; *D*—Ni; *E*—Co.

not be used for the extraction of metal-HDPTA complexes, because the reagent was found to be unstable in these media. Toluene and xylene appeared to be usable. The molybdenum complex could be extracted with benzene, but the colour intensity was less than that in alcoholic medium. Moreover, the molybdenum-HDPTA chelate showed a tendency to decompose in benzene solution.

Interferences

The effect of a number of foreign ions on the spectrophotometric determination of the metals was studied; the procedure involved appropriate pH adjustments and use

TABLE II.—EFFECT OF DIVERSE IONS ON THE PHOTOMETRIC ANALYSIS OF METALS

Foreign ion	Amount tolerated (mg) in the determination of					
	Iron (Fe ³⁺ = 65.25 µg)	Cobalt (Co ²⁺ = 45.3 µg)	Nickel (Ni ²⁺ = 50.0 µg)	Copper (Cu ²⁺ = 127.5 µg)	Palladium (Pd ²⁺ = 57.5 µg)	Molybdenum (Mo ⁶⁺ = 193.5 µg)
Ni ²⁺	1.4†	—	—	1.4†	1.42	1.25
Zn ²⁺	1.25	0.18	0.26	1.45	1.55	1.5
Cd ²⁺	1.2	0.10	0.12	1.4	1.5	1.6
Hg ²⁺	2.0	2.0	2.0	2.0	2.0	1.2
Mn ²⁺	1.2	0.075*	0.18*	1.25	1.25	0.75
Co ²⁺	1.0†	—	—	1.5†	1.4	1.4
Cu ²⁺	Nil	0.50‡	0.50‡	—	Nil	0.20§
Pd ²⁺	Nil	0.75‡	0.75‡	Nil	—	0.25§
Pb ²⁺	0.75†	1.0†	1.0†	1.2†	1.25†	0.15
Bi ³⁺	0.50†	1.45†	1.7†	1.45†	1.7†	Nil
Al ³⁺	1.4	0.60*	0.80*	1.4	1.6	1.6
Ga ³⁺	0.23	—	—	—	—	0.35§
In ³⁺	0.60	—	—	1.1¶	1.1¶	0.60
Fe ³⁺	—	0.32*	0.60*	1.1¶	1.2¶	0.010
Th ⁴⁺	1.0	0.80*	1.25*	0.58	0.70	1.2
Ti ⁴⁺	0.025	1.0*	1.0*	0.90¶	0.90¶	0.80§
Sn ⁴⁺	—	0.25*	0.30*	0.75	0.30	0.40
V ⁵⁺	0.15†	0.25	0.25	0.30†	0.30	0.050 (V ⁴⁺)
Mo ⁶⁺	0.65†	0.95*	1.2*	0.90¶	0.90¶	—
W ⁶⁺	0.65	0.80	0.80	0.65	0.80†	1.4
U ⁶⁺	0.90	0.75	1.0	1.0	1.0	0.45
F ⁻	Nil	100	100	100	100	0.10
oxalate	0.10	10	10	100	10	Nil
tartrate	10	10	10	10	10	0.18
EDTA ⁴⁻	Nil	Nil	Nil	Nil	Nil	0.40

* Citrate-fluoride as masking agent.

† Tartrate as masking agent.

‡ Prior extraction of the foreign ions with HDPTA.

§ Filtration before measurement.

¶ Oxalate as masking agent.

|| Fluoride as masking agent.

of masking agents. In some cases, especially in the interference studies in the determination of molybdenum, the solutions were filtered before the absorbance measurements. The results are shown in Table II. A 2% error was considered tolerable.

Precision and accuracy

The precision and accuracy of determination of each of the metals with HDPTA according to the recommended procedures were obtained by employing a set of five solutions of a particular concentration for each, and the results are shown in Table III.

DISCUSSION

A great many organic reagents have been proposed for the colorimetric determination of copper, palladium, iron, cobalt, nickel and molybdenum. Most suffer from

TABLE III.—PRECISION AND ACCURACY

Metal ion	Concentration, <i>μg/ml</i>	Coefficient of variation, %	Mean relative error, %
Fe ³⁺	2.61	0.5	-0.3
Co ²⁺	1.36	0.8	-0.3
Ni ²⁺	1.52	0.1	-0.4
Cu ²⁺	2.55	0.1	-0.4
Pd ²⁺	1.47	0.8	-0.4
Mo ⁶⁺	5.16	0.9	-0.2

some drawback such as lack of specificity, selectivity, sensitivity, precision, and stability of complexes. HDPTA is superior to some of the commonly used reagents.

Although HDPTA was long ago introduced as an analytical reagent it has not previously been used successfully for the colorimetric determination of metals, owing mainly to the low solubility and the unstable nature of the reagent and its metal chelates in aqueous and many non-aqueous solvents. However, benzene has now been found an appropriate solvent for the purpose. The HDPTA-complexes of copper, palladium, iron, cobalt and nickel can be rapidly extracted into benzene and the colour of the extracted complexes is sufficiently stable to permit spectrophotometric determination of these metals. In some cases the reagent is selective, but difficulties arise in the determination of iron in the presence of copper and palladium, and in separation of copper and palladium, or cobalt and nickel.

Zusammenfassung—3-Hydroxy-1,3-diphenyltriazin (HDPTA) bildet kräftig gefärbte Komplexe mit Kupfer, Palladium, Eisen, Kobalt und Nickel, die sich leicht in Benzol extrahieren lassen. Der tiefgelbe Molybdänkomplex ist in 60% Athanol vollständig löslich. Alle Chelate haben ein deutliches Absorptionsmaximum zwischen 398 und 422 nm; die Absorption des Reagens ist über 415 nm zu vernachlässigen. Die Zusammensetzung der Chelate ist ML₂, außer bei Eisen und Kobalt, die ML₃-Komplexe bilden. Mikromengen dieser Metalle können mit HDPTA spektrophotometrisch bestimmt werden.

Résumé—La 3-hydroxy 1,3-diphényltriazine (HDPTA) forme des complexes vivement colorés avec les ions cuivre, palladium, fer, cobalt et nickel, qui sont aisément extractibles en benzène. Le complexe jaune foncé du molybdène est complètement soluble en éthanol à 60%. Tous les chélates ont un maximum d'absorption défini entre 398 et 422 nm, l'absorption du réactif étant négligeable au-dessus de 415 nm. La composition molaire des chélates est ML₂, à l'exception des complexes de fer et de cobalt qui forment des complexes ML₃. On peut déterminer spectrophotométriquement des microquantités de ces métaux avec le HDPTA.

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A SEPARATION SCHEME FOR THE ANALYSIS OF MULTICOMPONENT SAMPLES*

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Summary—A sequential separation scheme has been devised for the quantitative analytical separation of 27 different metal ions. Five different chromatographic and ion-exchange columns are used to separate the metal ions into groups. The metal ions of each group are eluted separately from each column by means of selective eluents. Following separation, the metal ions are determined by titrimetry, flame spectrometry or other appropriate analytical methods. The reliability of the proposed scheme has been demonstrated by extensive testing, including the analysis of U.S. National Bureau of Standards samples. The scheme can be used for macro or micro quantities.

ALTHOUGH efficient methods can usually be worked out for the analysis of large numbers of samples of similar chemical composition, the incidental analysis of samples of different types often presents a difficult problem. The selection of a plan for analysis of a multicomponent sample requires an experienced, trained chemist. Even then, the myriads of analytical methods in books and journals are often confusing, and selection of methods is apt to be a hit and miss proposition. All too often a method will not be successful the first time it is tried on a particular sample. Minor difficulties are often encountered and the method will work only after some modification. Therefore, the analysis of new or non-routine samples is frequently slow and costly. Each new type of sample often becomes a research project in itself.

A more systematic approach to the analysis of analytical samples, particularly those of a non-routine nature, is clearly called for. The aim of the present work is to provide at least a start in that direction. A systematic scheme for the separation of some 27 different metal ions by column chromatographic techniques is presented. Once each metal ion component of the sample has been separated, measurement by appropriate titrimetric, spectral or other method is easily accomplished. Sometimes the measurement method used will permit determination of two or more elements without mutual interference, thereby reducing the number of separations required and simplifying the analytical process. Extensive testing has shown that this separation scheme is dependable and provides quantitative separations for both macro and trace amounts of the various metal ions.

The classical hydrogen sulphide scheme is a somewhat systematic approach to chemical analysis, but the methods are often slow and subject to co-precipitation errors. More recently, several comprehensive separation schemes using solvent extraction, chromatography and ion-exchange have been described.¹⁻⁷ However, these are largely schemes for radiochemical separations and the separations are not always quantitative. Chalmers and co-workers^{8,9} have approached the analysis of

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metal ion mixtures systematically using solvent extraction with cupferron and other complexing reagents. Their method uses spectrophotometric and polarographic measurement of separated elements and is intended for 100 μg or less of each element.

EXPERIMENTAL

Reagents

Amberlyst XAD-2, an inert cross-linked polystyrene polymer, was obtained from Rohm & Haas as 20–50 mesh beads. The beads were ground in a Waring blender and sieved to obtain the proper mesh sizes. This product was washed successively with 6M hydrochloric acid and methanol, and air-dried.

Amberlyst A-26 macroreticular anion-exchange resin was obtained from the same source and was similarly ground and sieved. It was then washed with 2M perchloric acid, 1M hydrochloric acid, and then with water.

Dowex 50W-X8 cation-exchange resin, 100–200 mesh was purified by washing with 10% ammonium citrate solution, 3M hydrochloric acid, and finally with water.

Indicators were 0.5% w/v aqueous solutions of Xylenol Orange, 8-hydroxy-7-(6-sulpho-2-naphthylazo)-5-quinoline sulphonic acid (NAS) and Arsenazo I.

Isopropyl ether (IPE) and isobutyl methyl ketone (IBMK) were redistilled before use. Trioctylphosphine oxide (TOPO) was obtained from Eastman Organic Chemicals and used as received.

Column preparation

Conventional columns were used. The flow was controlled by a 1-mm bore stop-cock and the column support was held in place by a small plug of glass wool. Columns with Amberlyst XAD-2 as the inert support were all prepared by the same method. The requisite amount of XAD-2 slurried in methanol was added to the column and the methanol was allowed to drain rapidly just to the top of the support. A perforated Teflon disk was then placed on the top of the support to prevent disturbance of the column bed. Next the support was impregnated with the extractant by adding 3–5 column volumes of equilibrated IPE, IBMK or 0.5M TOPO in cyclohexane and allowing the extractant to displace the methanol by gravity flow. Then the interstitial organic liquid was removed with equilibrated 8M hydrochloric acid. This is best accomplished by using some air pressure and a rapid flow-rate (10–20 ml/min).

The stripping solvent used to remove sorbed metal ions from the IPE and IBMK columns is 0.1M hydrochloric acid in 98% methanol. After the metal ions have been stripped from the column, the support is in essentially the same condition as when the methanol slurry was first added to the column. Therefore it can be made-ready for the next sample by repetition of the procedure above.

Since elutions from the TOPO column are carried out with aqueous solutions, the column can be used a dozen times or more without reconditioning. When reconditioning is necessary it is sufficient to pass a few ml of 0.5M TOPO–cyclohexane through the column to replace any lost extractant and then displace the interstitial TOPO solution with 8M hydrochloric acid as described above.

Any three of the first four columns used in the separation scheme may be connected so that the effluent from one flows directly into the next. A flow-rate of approximately 1 ml/min was used for elutions requiring up to 20 ml per element. Elements requiring a larger volume were eluted at a flow-rate of approximately 2 ml/min.

Analytical procedures

Antimony was determined by an oxidation-reduction method. Add 10 ml of hydrochloric acid and 20 ml of 10% potassium bromide solution to a 30–50-ml sample containing antimony(V). If the solution contains tartrate, also add 4 ml of sulphuric acid. If an organic solvent is present, remove it by boiling. Add excess 8% sulphurous acid and boil for 10 min to reduce to antimony(III). Remove any excess of sulphur dioxide by bubbling air through the solution for 5 min. Cool and titrate with standard potassium bromate, using α -naphthoflavone indicator.

Most elements were titrated with 0.02M EDTA; solutions as dilute as 0.001M were used to titrate very small quantities of separated metal ions. Conditions for EDTA titrations are given in Table I. Ammonia–ammonium chloride buffers were used for pH 9–10 and pyridine for pH 6.

Chromium was determined by a standard oxidation-reduction method employing ammonium persulphate.¹⁰ To solutions also containing citrate, add 5 ml of sulphuric acid and evaporate until sulphur trioxide fumes appear and the sample becomes charred. Cool slightly, add 10 ml of nitric acid and again evaporate to sulphur trioxide fumes. Cool, wash down the beaker walls with distilled water and again evaporate to fumes. Dilute and determine the chromium by the persulphate oxidation procedure.

TABLE I.—SUMMARY OF EDTA TITRATION METHODS

Element	Method	pH	Indicator	Notes
Ga(III)	back-titn. Zn	6	NAS	
Fe(III)	back-titn. Th	2	Xylenol Orange	
Sn(IV)	back-titn. Cu	3.5	NAS	1
Cu(II)	direct	6	NAS	
Co(II)	direct	6	NAS	
Zn(II)	direct	6	NAS	
Cd(II)	back-titn. Cu	6	NAS	
Bi(III)	direct	2	Xylenol Orange	2
Ti(IV)	back-titn. Cu	4.5	NAS	3
Th(IV)	direct	2	Xylenol Orange	
Zr(IV)	back-titn. Th	2	Xylenol Orange	4
V(IV)	back-titn. Zn	6	NAS	5
Pb(II)	back-titn. Cu	6	NAS	
Mn(II)	direct	9	Arsenazo I	6
Al(III)	back-titn. Cu	6	NAS	7
Ni(II)	back-titn. Zn	6	NAS	8
Mg(II)	direct	10	Arsenazo I	Photometric end-point, 565 nm
Re(III)	direct	6	Arsenazo I	9
Ca(II), Sr(II), Ba(II)	direct	10	Arsenazo I	Photometric end-point, 565 nm

Notes 1. Acidify to pH 1 or below to prevent hydrolysis. Add 2 g of sodium chloride and a 50–100% excess of standard EDTA, and boil for 5 min. Cool, buffer with ammonium acetate to pH 3.5 and back-titrate.

2. If sulphate or chloride is present add excess of standard EDTA to solution at pH 2 and boil for 5 min. Cool, buffer to pH 6, back-titrate with standard copper(II), using NAS indicator.

3. Add excess of standard EDTA, buffer to pH 4.5 with ammonium acetate, add several drops of 30% hydrogen peroxide, and boil for 5 min. Cool and back-titrate.

4. Add 100% excess of standard EDTA to a pH 1 solution and boil for 10 min. Cool, adjust pH to 2.0 with ammonia and back-titrate.

5. If hydrogen peroxide is present, boil to remove. Then add a small amount of 8% sulphurous acid or ascorbic acid to reduce to V(IV). Then determine as indicated in the table.

6. Titrate with DCTA (1,2-diaminocyclohexanetetra-acetic acid) instead of EDTA. Add several drops of 8% sulphurous acid to ensure complete reduction to Mn(II). A spectrophotometric end-point (565 nm) is more accurate than the visual end-point.

7. Add 50–100% excess of standard DCTA, buffer to pH 6 with pyridine and ammonia, and boil for 5 min. Cool and back-titrate. If hydrofluoric acid is present, add 2–3 ml of sulphuric acid and evaporate to heavy fumes. Cool and redissolve the aluminium sulfate with water, heating if necessary.

8. For successive titration of nickel(II) and magnesium(II) in mixtures, first determine nickel(II) at pH 6 by zinc(II) back-titration, using a minimum amount of NAS indicator. Then adjust the pH to 10 with ammonia, add Arsenazo I indicator and titrate the magnesium(II). Best results are obtained by using a spectrophotometric end-point at 565 nm.

9. Total rare earths and alkaline earths in mixtures may be successively titrated, first the rare earths at pH 6, then the alkaline earths at pH 10. A spectrophotometric end-point is recommended for the latter titration.

Atomic-absorption methods were used to analyse for metals when a good microtitration method was not available or where more than one component was to be measured without further separation. A Perkin-Elmer model 290 atomic-absorption unit was used and the procedures followed were those recommended by the manufacturer. In general, standard solutions were prepared in the solvent used to elute the metal of interest from the chromatographic column.

SELECTION OF SYSTEMS

Among the various methods of separating metal ions from one another, ion-exchange and extraction chromatography (liquid-liquid partition chromatography)

are outstanding. Many separations have been reported, that use these two multistage techniques; the separations are quantitative and can usually be used with one element (or more) present in large excess over the others. Several systems have been studied extensively and the behaviour of a number of elements is well known. These systems include anion-exchange with aqueous hydrochloric acid,¹¹ hydrochloric acid in non-aqueous solvents,^{12,13} aqueous hydrofluoric acid,¹⁴ and cation-exchange with hydrochloric acid in acetone.^{15,16} In extraction chromatography aqueous hydrochloric acid-ketone systems,¹⁷ trioctylphosphine oxide (TOPO),^{18,19} bis(2-ethylhexyl)phosphoric acid²⁰⁻²² and others have been studied extensively. Any single system works well for certain elements but either fails or is not advantageous for separation of other elements. For example, anion-exchange with aqueous hydrochloric acid separates many elements very well but tin(IV) is difficult to remove quantitatively from the column. Iron(III) and uranium(VI) are difficult to separate from each other; if the hydrochloric acid concentration is too high manganese is retained, albeit weakly, and is difficult to elute quantitatively. A number of elements are not retained by an anion-exchange column from hydrochloric acid solutions.

Some general requirements of an efficient separation scheme may be listed.

1. The separations should be quantitative with each element being strongly retained by the chromatographic column or not retained at all.
2. The separations should be quick and the elution volumes small.
3. The eluting media should be easily volatilized and should keep all elements in solution. Any incompatible combinations of metal ions and eluting media should be avoided by a separation earlier in the scheme.
4. Sufficient information should be available for prediction of the behaviour of many elements under the conditions used.
5. The sequence of steps should be such that a minimum number of changes in eluent composition is required for group separations.

The separation scheme presented in the next section fits these requirements very well. The first four group separations are carried out on chromatographic and ion-exchange columns, each using 8*M* hydrochloric acid as the eluent. The columns are small to minimize elution volumes, and the flow-rates employed are reasonably fast. Following a single evaporation, the remaining elements are separated on a cation-exchange column.

The column support is an important consideration in any chromatographic separation. Special halogenated polyethylene supports have been successfully used in the past. However, we have found that Amberlyst XAD-2, a porous polystyrene, sorbs significantly larger quantities of organic solvents than polyfluoroethylene supports and yet is hard and mechanically strong. For this reason XAD-2 was used in the present work.

For anion-exchange separations, Amberlyst A-26 macroreticular resin was employed. This is similar to Amberlyst XAD-2 but has quaternary ammonium functional groups to provide sites for anion-exchange. The highly porous, rigid structure of the A-26 resin permits somewhat faster flow-rates and smaller elution volumes than the ordinary gel-type resins. Dowex 50W-X8 was selected as the cation-exchange resin for this study. It was found that some metal ions are more easily eluted from this resin than from a column of the macroreticular cation-exchange resin, Amberlyst 15.

SEPARATION SCHEME

A flow chart summarizing the separation of sample mixtures into groups and the column methods of separating the metal ions in the individual groups is given in Table II. Elements listed under each group are retained by that column and are later eluted by the eluents listed at the right. The elements not retained by a column are washed from the column with 8M hydrochloric acid (for columns 1-4). Several notes on various details concerning the group separations are given in footnotes in Table II.

Methods for measurement of individual metal ions (once they are separated) are outlined under *Experimental* above. However, several additional details regarding separation and determination of some of the metal ions should be mentioned.

1. No reliable method was found for separating antimony(V), iron(III) and gallium(III) on the IPE column. Antimony(V) can be separated from iron(III) and gallium(III) by passing an acidic solution containing excess of tartrate through a short Dowex-50 column. Antimony(V) passes through while iron(III) and gallium(III) are retained. After stripping from the column, iron and gallium may be separated from each other on an A-26 column, a small amount of ascorbic acid being used to reduce the iron to iron(II), and 0.45M hydrobromic acid in 90% methanol being the eluent.²³

2. When copper(II) and cobalt(II) (Group 3) are both present in the sample, the cobalt(II) will be sorbed onto the column above the copper(II) band. When the eluting solvent is changed to 0.5M hydrochloric acid in 65% ethanol, the order of elution is reversed and cobalt is eluted from the column ahead of the copper. Because copper(II) is also slowly eluted by this eluent, extra care must be taken to ensure use of a column of sufficient size to allow a clean separation.

3. The separation of copper(II) from uranium(VI) (Group 3) by elution with 2.5M hydrochloric acid is marginal.

4. Several good methods are available for separating zirconium and hafnium (Group 4) should it be desirable to separate these two elements.^{24,25}

5. When 0.6M hydrobromic acid is added to the column (Group 5), lead bromide is initially precipitated at the top of the column. If the amount of lead(II) is small this precipitate readily redissolves on continued elution. When larger amounts of lead are present, the dissolution of the precipitate may be hastened by using heated eluent or by using a hot water-jacket on the exchange column.

6. If aluminium(III) is eluted with 0.3M hydrofluoric acid, a column of Kel F (or another plastic) is used in place of a glass column.

7. A method for successive titration of nickel(II) and magnesium(II) in mixtures is outlined in Table I.

8. A method for successive titration of total rare earths and alkaline earths is outlined in Table 1.

The probable effect of several additional elements on the separation scheme was also considered.

Arsenic(III), germanium(IV). These elements should be retained by the IPE column. However, separation of arsenic and germanium from a large number of elements by extraction into benzene from 10-12M hydrochloric acid has been reported;²⁶ this separation has also been accomplished by using a column of benzene sorbed onto a porous solid support.²⁷

Niobium(V), tantalum(V), tungsten(VI). A separation scheme for these three

TABLE II.—FLOW CHART FOR SEPARATION SCHEME

Abbreviations: IPE = isopropyl ether, IBMK = isobutyl methyl ketone,
TOPO = trioctylphosphine oxide

Data in parentheses are recommended column bed volumes for trace (T) and macro (M) amounts of metal ions.

Sample in 8M HCl

↓

1. IPE on XAD-2 column* (T 5 ml; M 6 ml + 1 ml/additional 0.1 mmole)

Sb(V)	}	Strip with 0.1M HCl in MeOH
Ga(III)		
Fe(III)		

↓

2. IBMK on XAD-2 column (T 5–10 ml; M 15 ml + 2 ml/additional 0.1 mmole)

Mo(VI)	Elute with 1M HCl–3M H ₂ SO ₄
Sn(IV)	Strip with 0.1M HCl in MeOH

↓

3. Amberlyst A-26 column,† (T 4–5 ml; M 6ml + 1 ml/additional 0.1 mmole)

Co(II)	Elute with 0.5M HCl in 65% EtOH
Cu(II)‡	Elute with 2.5M HCl
U(VI)	Elute with 1.0M HCl
Zn(II)	Elute with 0.05M HBr
Cd(II)	Elute with 1.0M HNO ₃ –0.01M HBr
Bi(III)	Elute with 2.0M HClO ₄

↓

4. TOPO–cyclohexane on XAD-2 column§ (T 5–10 ml: M 15 ml + 2 ml/additional 0.1 mmole)

Ti(IV)	}	Elute with 5.0M HNO ₃
Sc(III)		
Th(IV)	Elute with 12M HCL	
Zr(IV)	}	Elute with 1.0M HCl
Hf(IV)		

↓

Evaporate to near dryness. Add HNO₃ and re-evaporate. Dissolve in 20 ml of H₂O.

↓

If Cr present add citrate, pH 4, boil, cool, adjust to pH 2.¶**

↓

5. Dowex 50W-X8 column (T 4 ml; M 6 ml + 1 ml/additional 0.1 mmole)

V(IV)	Elute with 1% H ₂ O ₂ –0.01M HClO ₄	
Pb(II)	Elute with 0.6M HBr	
Mn(II)	Elute with 1.0M HCl in 92% acetone	
Al(III)	Elute with 0.3M HF	
Ni(II)	}	Elute with 3.0M HCl in 60% EtOH
Mg(II)		
Ca(II)	}	Strip with 4.0M HNO ₃
Ba(II)		
Sr(II)		
RE(III)		

elements has been reported, that uses a hydrofluoric acid medium and a chromatographic column containing IBMK on a solid support.²⁸ These separations appear to be selective, but extensive testing would be needed to determine how well such a separation would fit into the present scheme.

Indium. Published extraction data²⁹ (and work by the present authors) indicated that indium(III) should be quantitatively retained by the IBMK column from 8M hydrochloric acid. However, experimentation showed that indium is only partly retained by this column; the remainder is sorbed by the A-26 column.

Gold(III). Gold is easily extracted from hydrochloric acid solution and will be retained by the IPE column. Platinum, rhodium, osmium and iridium have not been tested at all.

Mercury(II). Mercury passes through the IPE and IBMK columns, although a larger volume of 8M hydrochloric acid than normal is needed for complete elution.¹⁷ Mercury(II) is retained by the A-26 column.

Silver (I). Silver forms an anionic chloride complex that is reasonably soluble in 8M hydrochloric acid. Thus moderate amounts of silver will remain in solution and will pass quantitatively through the first four columns. Evaporation of the eluate from the TOPO column, followed by dilution with water, should permit quantitative gravimetric separation of silver from the remaining elements. Interference from lead can be avoided by repeated washing of the precipitated silver chloride with hot dilute nitric acid.³⁰

Alkali metals. These will pass quantitatively through the first four columns, but some of the alkali metals may be retained by the Dowex-50 column.

EVALUATION OF SEPARATION SCHEME

The reliability of any comprehensive analytical separation scheme can only be established by thorough testing. The likelihood of an actual sample containing macro amounts of all 27 elements is negligible. Most samples will contain only a few

Footnotes to Table II

* The best eluting solvent here is a 1:1 mixture of equilibrated 8M hydrochloric acid and non-equilibrated acid. Otherwise when the eluting solvent is first added to the column some of the dissolved IPE may be salted out of solution, causing streaking of the sorbed metal bands and bleeding of the extracting agent from the column.

† Manganese(II) and lead(II) are weakly extracted by the resin. The elution volume required for these two metals is greater than for the other metals considered. An elution volume equivalent to 8 column volumes is sufficient to elute these metals from the column.

‡ Copper(II), although retained by the resin, has a sufficiently low distribution coefficient for it to move slowly down the column. Therefore, when large amounts of copper(II) are present in the sample, care must be taken to ensure the column is of sufficient size to perform the desired separations.

§ If a larger than usual IPE or IBMK column is used, the effluent from the A-26 column should be heated for a few minutes to remove any dissolved organic solvent. This avoids the possibility of removal of any TOPO from the column by dissolved organic IPE or IBMK.

¶ Omit the citrate step if chromium is absent. A vanadium residue from the evaporation step may be redissolved by adding a few drops of hydrogen peroxide.

** A faster method may be used for separation of small amounts of chromium(III) (<1%), provided sulphate will not interfere with subsequent operations. After removing hydrochloric acid, add a small amount of sulphuric acid and evaporate to fumes. This converts the chromium(III) into an anionic sulphate complex. Cool, dilute with water to reduce the sulphuric acid concentration to 0.1-0.25M, then transfer to the Dowex-50 column that has been conditioned with 0.1M sulphuric acid. Elute the chromium(III) sulphate complex from the column with 0.1M sulphuric acid. This method will recover approximately 99% of the chromium present in the sample.

elements, but the variety of combinations is very large. The following testing programme was used to demonstrate the validity of the proposed separation scheme.

1. Each element was separated on an appropriate column from the elements immediately preceding and following it in the scheme. Spot tests (or other qualitative tests) were used to determine the point of complete elution of an element and to ascertain that breakthrough of the next element did not occur with a reasonable additional volume of eluent. This general procedure has proven to be a dependable test of separation efficiency and is much more reliable than using only batch distribution coefficients to predict actual column separations.

2. Several synthetic samples were separated and analysed quantitatively. The sample compositions were chosen to test the reliability of various portions of the separation scheme. Results, together with actual separation conditions, are summarized in Table III.

TABLE III.—SEPARATION AND ANALYSIS OF METAL ION MIXTURES
Approximately 0.1 mmole of each element is present. Flow-rate 1 ml/min if
element requires 20 ml or less; otherwise 2 ml/min.

Metal ion mixture	Column <i>mm, type</i>	Wash,* <i>ml</i>	Elution <i>ml, eluent</i>	Recovery, %
Gallium(III)	60 × 12, IPE	10	20, MeOH	100.3
Lead(II)	60 × 10, A-26		15, 8M HCl	100.3
Zinc(II)			25, H ₂ O	99.8
Nickel(II)	140 × 10, A-26	—	25, 8M HCl	100.4
Cobalt(II)			30, 0.5M HCl/65% EtOH	100.4
Copper(II)			20, 1M HCl	99.8
Zinc(II)			100, 0.5M HBr	100.0
Cadmium(II)			100, 1M HNO ₃ /0.01M HBr	100.4
Titanium(IV)	110 × 14, TOPO	30	20, 0.05M HCl	99.9
Vanadium(IV)	60 × 12, Dowex-50		20, 1% H ₂ O ₂	99.6
Aluminium(III)			25, 3M HCl	99.9
Nickel(II)	100 × 13, TOPO	—	20, 8M HCl	100.0
Titanium(IV)			50, 5M HNO ₃	99.4
Thorium(IV)			100, 0.2M HCl	99.6
Lanthanum(III)	130 × 12, TOPO	—	20, 8M HCl	100.2
Titanium(IV)			40, 5M HNO ₃	100.0
Thorium(IV)			50, 12M HCl	100.0
Zirconium(IV)			125, 1M HCl	100.4
Nickel(II)	70 × 12, Dowex-50	—	100, 3M HCl/60% EtOH	99.8
Magnesium(II)				100.2
Calcium(II)			40, 4M HNO ₃	100.2

* "Wash" is the volume of 8M HCl needed to wash elements of later groups (see Table II) from the column.

3. Several U.S. National Bureau of Standards samples were analysed by using the separation methods of the present scheme. Some of these samples contain many different elements and their analysis is ordinarily quite complicated. Results are given in Table IV.

A simple statistical evaluation of the results obtained for separation and analysis of all synthetic and NBS samples is summarized in Table V. The average recoveries

TABLE IV.—ANALYSIS OF U.S. NATIONAL BUREAU OF STANDARDS SAMPLES
Flow-rate 1 ml/min if element requires 20 ml or less; otherwise 2 ml/min

Sample number	Metal determined	Column mm, type	Wash,* ml	Elution ml, eluent	Certificate value %	Found,† %
54d	Sb	60 × 10, IPE	7	20, IPE	7.04	7.06
	Sn	120 × 14, IBMK	9	30, IBMK	88.57	88.4 ₁
	Cu	50 × 10, A-26	10	20, H ₂ O	3.62	3.61
124d	Pb			10, 8M HCl	0.62	0.61
	Fe	50 × 10, IPE	6	15, MeOH	0.18	0.19
	Sn	150 × 10, IBMK	10	30, MeOH	4.56	4.51
	Cu	130 × 12, A-26	50	30, 1M HCl	83.60	83.6 ₀
	Zn			50, H ₂ O	5.06	5.05
	Pb	30 × 10, Dowex-50		30, 0.6M HBr	5.20	5.22
173a	Ni			15, 3M HCl	0.99	1.00
	Fe	70 × 10, IPE	10	20, MeOH	0.15	0.15
	Ti	300 × 14, TOPO	30	50, 0.5M HCl	—	—
20f	V	60 × 12, Dowex-50		15, 1% H ₂ O ₂	4.06	4.04
	Al			20, 3M HCl	6.47	6.49
	Fe	100 × 13, IPE	15	—	—	—
	Mo	80 × 10, IBMK	10	—	—	—
	Cu	50 × 10, A-26	30	30, H ₂ O	0.239	0.24 ₈
101e	Mn	50 × 10, Dowex-50		30, 1M HCl/92% acetone	0.754	0.76 ₄
	Ni			50, 3M HCl/60% EtOH	0.243	0.25 ₈
	Cr‡			0.1M H ₂ SO ₄	0.097	0.097
	Fe	100 × 10, IPE	20	—	—	—
	Mo‡	80 × 10, IBMK	5	10, MeOH	0.43	0.40
	Co‡	50 × 10, A-26	30	20, 0.001M HCl	0.18	0.19
	Cu‡				0.36	0.36
	Mn	70 × 10, Dowex-50	20	50, 1M HCl/92% acetone	1.77	1.74
	Ni			25, 3M HCl	9.48	9.44
	Cr			20, H ₂ O	17.98	17.8 ₀
1a	Fe§	60 × 10, IPE	10	20, MeOH	1.63	1.60
	Ti§	80 × 10, TOPO	15	20, 0.5M HCl	0.16	0.17
	Al§	120 × 10, Dowex-50		60, 0.3M HF	4.16	4.12
	Mg§			100, 3M HCl/60% EtOH	2.19	2.27
	Ca¶			40, 4M HNO ₃	41.44	41.2 ₈

* The volume of 8M HCl needed to remove elements from later groups.

† Average of 3 determinations.

‡ Determined by atomic absorption.

§ Reported as the metal oxide.

¶ Calcium plus strontium, calculated as CaO.

Dissolution Methods

No. 54 d (tin-base alloy). Dissolve 250 mg in 10 ml of 8M HCl, 0.5 ml of HNO₃, 1 ml of 3% H₂O₂. Dilute to 25 ml with 8M HCl, take 4-ml aliquot (40 mg of sample).

No. 124d (copper-base alloy). Dissolve 250 mg in 10 ml of 8M HCl, 1 ml of 30% H₂O₂. Dilute to 25 ml with 8M HCl, take 4-ml. aliquot (40-mg sample).

No. 173a (titanium-base alloy). Dissolve 50 mg in 5 ml of 8M HCl (90°, 2 hr). Add 0.25 ml of 30% H₂O₂ to oxidize Ti to Ti(IV), boil to remove H₂O₂. Add 0.5 ml of 6% H₂SO₃ to reduce V to V(IV). Adjust sample volume to about 5 ml with 8M HCl.

No. 20f (steel). Dissolve 1 g in 10 ml of HCl, 1 ml of HNO₃. Evaporate almost to dryness. Dilute to 100 ml with 8M HCl, take 10 ml (100-mg sample).

No. 101e (alloy steel). Dissolve 500 mg in 10 ml of HCl, 1 ml of HNO₃. Evaporate almost to dryness. Dilute to 100 ml with 8M HCl, take 5 ml (25-mg sample).

No. 1a (limestone). Weigh 500-mg sample, ignite for 30 min at 1000°. Dissolve in 5 ml of H₂O, 4 ml of HClO₄, 5 ml of HF. Evaporate to HClO₄ fumes. Dilute to 25 ml with 8M HCl, take 5 ml (50-mg sample).

TABLE V.—SUMMARY OF ANALYTICAL DATA

Type of sample	Number of samples	Average recovery, %	Relative standard deviation, %
Synthetic samples	25	100.1	0.3
NBS samples, components greater than 2% of sample	14	99.7	0.4
NBS samples, components less than 2% of sample	14	101.0	3.5

and relative standard deviations for major sample components are considered quite good, especially since most samples were only 40 or 50 mg. The average recovery of minor components of NBS samples is a bit high, but again it should be remembered that emphasis was placed on using small samples, which makes the accurate determination of minor constituents more difficult.

A study of the samples analysed (Tables III and IV) shows that for any given sample the separation scheme can usually be shortened considerably. If the sample contains no elements of certain groups, the column separation for those groups can be dispensed with. Stripping of the last element in the A-26 column group with water (or dilute acid), in the TOPO column group with 0.5*M* hydrochloric acid, or in the Dowex-50 column group with 3–4*M* hydrochloric acid often permits a more rapid elution than indicated by the scheme in Table II. Often the method of analysis will not require the separation of each element from the others. For example the analysis of an aluminium alloy for traces of iron, copper, zinc and bismuth by a flame method might require only the isolation of the minor elements from the aluminium matrix by the IBMK and A-26 columns or by an A-26 column alone. Automation of the separation steps by suitable pumps, valves and timers would further improve the convenience of the separations.

The scheme is incomplete to the extent that it does not include *all* metallic elements and does not cover the separation of some closely related elements such as the individual rare earths. However, it is felt that the proposed scheme is a useful step towards a systematic approach to the analysis of samples containing metallic elements. The scheme appears to be reliable and the separations are convenient and reasonably quick to carry out.

Zusammenfassung—Ein Trennungsgang zur quantitativen analytischen Trennung von 27 verschiedenen Metallionen wurde entworfen. Fünf verschiedene chromatographische und Ionenaustauschsäulen dienen zur Auftrennung der Metallionen in Gruppen. Die Metallionen jeder Gruppe werden von jeder Säule durch selektive Elutionsmittel einzeln eluiert. Nach der Trennung werden die Metallionen durch Titration, Flammenphotometrie oder andere geeignete analytische Verfahren bestimmt. Die Zuverlässigkeit des vorgeschlagenen Trennungsganges wurde durch eingehende Erprobung demonstriert; auch Proben vom US National Bureau of Standards wurden analysiert. Der Trennungsgang kann für Makro- und Mikromengen verwendet werden.

Résumé—On a établi un schéma de séparation séquentielle pour la séparation analytique quantitative de 27 ions métalliques différents. On utilise cinq colonnes chromatographiques et échangeuses d'ions différentes pour séparer les ions métalliques en groupes. Les ions métalliques de chaque groupe sont élués séparément de chaque colonne

au moyen d'éluants sélectifs. A la suite de la séparation, les ions métalliques sont dosés par titrimétrie, spectrométrie de flamme ou d'autres méthodes analytiques appropriées. On a démontré l'exactitude du schéma proposé par un examen étendu, incluant l'analyse d'échantillons du U.S. National Bureau of Standards. On peut utiliser le schéma pour des macro- ou micro-quantités.

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METALLEXTRAKTIONEN MIT ALIPHATISCHEN ALKOHOLEN

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Zusammenfassung—Eine Reihe von Metallen wird mit den Alkoholen 2-Äthyl-1-butanol, 4-Methyl-2-pentanol und 1-Butoxy-2-propanol aus jodidhaltigen schwefelsauren Lösungen quantitativ, ein anderer Teil unvollständig und einige Elemente werden überhaupt nicht extrahiert. Die Durchführung der Extraktion wird beschrieben. Es ergeben sich eine Fülle von Trennungsmöglichkeiten; zwei davon, die Trennungen Zink-Cadmium und Indium-Gallium werden besprochen und an technischen Produkten erprobt. Am Beispiel des Quecksilbers wird mittels konduktometrischer Extraktionstitration die Zusammensetzung der extrahierten Metallkomplexe bewiesen.

IN LETZTER Zeit haben Verteilungsverfahren zur Anreicherung und Trennung von Elementen erhebliche Bedeutung erlangt. Die Flüssig-Flüssig-Extraktion zeichnet sich gegenüber Fällungsreaktionen durch einige Vorteile aus, die es gestatten, diese Arbeitsweise in der analytischen Praxis bevorzugt gegenüber anderen Methoden zu verwenden.

Wir haben eingehende Untersuchungen über die Extrahierbarkeit von Metallen mit den Alkoholen 2-Äthyl-1-butanol, 4-Methyl-2-pentanol und 1-Butoxy-2-propanol in jodidhaltigen schwefelsauren Lösungen durchgeführt. Diese Solventien sind nicht oder nur sehr wenig wasserlöslich und stellen sich preismäßig kaum höher als etwa Äthanol oder Methanol. Wie bekannt, werden hohe Verteilungskoeffizienten in jodidhaltigen Systemen schon bei geringeren Konzentrationen des komplexbildenden Halogenidions erreicht als in chlorid- und bromidhaltigen Lösungen.¹ Auch wirkt sich der Einfluß des Gegenkations (H^+ , Li^+ , Na^+ usw.) weniger aus als in chloridhaltigen Systemen. Neben den komplexbildenden Liganden haben aber das organische Solvens und die Acidität der Lösung einen entscheidenden Einfluß auf das Extraktionsvermögen. Hierfür geeignet sind alle organischen Lösungsmittel, deren Molekül ein Sauerstoffatom enthält und Oxoniumsalze bilden können.

Aliphatische Alkohole und Äther, die von sich aus keine mesomeren Oxoniumkationen bilden können, werden mit starken Säuren zu einer Protonenaddition gezwungen, wobei pro Molekül Alkohol, das als Base mit Schwefelsäure zu einem Oxoniumsalz reagiert, zwei Ionen gebildet werden. Die Metalle können dann aus wäßriger Phase über den Sauerstoff gebunden als undissoziiertes Molekül oder komplexe Metallsäure extrahiert werden. Bemerkenswert erscheint, daß einfach negativ geladene Komplexe allgemein gut extrahiert werden, gegenüber zwei- oder mehrfach negativ geladenen. Systematische Untersuchungen über das Extraktionsverhalten von mit Wasser nicht mischbaren aliphatischen Alkoholen bezüglich Metallen aus jodidhaltigen Medien wurden bisher nicht durchgeführt. Es war nun interessant zu erfahren, ob unsere Arbeiten Vorteile in der analytischen Praxis

bezüglich Extrahierbarkeit, Trennungsmöglichkeiten, Säurekonzentration usw. ergeben.

EXPERIMENTELLER TEIL

Durchführung der Extraktion

Die Untersuchungen wurden in zylindrischen Schütteltrichtern von 250 ml Inhalt bei Raumtemperatur vorgenommen. Da die meisten Elemente nach einmaliger Extraktion mit 20 ml Lösungsmittel nicht vollständig in die organische Phase überführt werden, verwendeten wir ein Lösungsmittelgemisch von 20 ml Alkohol und 25 ml Tetrachlorkohlenstoff. Durch die Beschwerung des organischen Extraktionsmittels war eine schnelle Phasentrennung gewährleistet, wobei sich die organische Phase im unteren Teil des Schütteltrichters sammelt. Das Extraktionsvermögen dieses Lösungsmittelgemisches wird dadurch zwar etwas verschlechtert, es ist jedoch auf diese Art eine 2-3 fache Ausschüttelung ohne größeren Arbeitsaufwand möglich.

Die Extraktion wurde durch 2 Minuten dauerndes Schütteln bewerkstelligt. Längeres Schütteln hatte auf den Extraktionseffekt keinerlei steigernden Einfluß. Nach vollständiger Phasentrennung wurde der organische Anteil zur weiteren Aufarbeitung abgetrennt. Die wäßrige Schicht kam nun in einen 250-ml-Titrierkolben, wobei der Restanteil des Lösungsmittels verkocht wird. Durch anschließenden Zusatz von 5 ml konz. Salpetersäure und Aufkochen der Lösung konnte das Jodid entfernt werden. Die Analysen wurden nach üblichen Verfahren durchgeführt.

Die Bestimmung der Metalle in der organischen Phase erfolgte nach zwei Methoden.

1. Die in ein Becherglas überführte organische Schicht wurde mit Wasser versetzt und auf dem Sandbad eingeeengt. Waren im Rückstand noch organische Anteile vorhanden, so wurde er mit 5 ml konz. Schwefelsäure und 5 ml konz. Salpetersäure aufgenommen und zum Sieden gebracht. In dieses Säuregemisch wurde solange tropfenweise Perhydrol zugesetzt, bis alle organischen Reste zerstört waren.

2. Die Methode der Rückextraktion des Metalls aus organischer Phase mit Natronlauge ist zeitsparend und gut reproduzierbar, wobei diese Phase in einem 250 ml-Schütteltrichter gesammelt und mit 20 ml 20% iger Natronlauge 1 Minute lang geschüttelt wurde. Zur besseren Schichttrennung wurden dann 50 ml Wasser zugesetzt und nochmals kurz geschüttelt. Nach dieser Extraktion befinden sich die Metalle quantitativ in wäßriger Phase. Diese wird nach Trennung in einem Titrierkolben gesammelt und Lösungsmittelreste durch Verkochen entfernt. Nach Erkalten der Lösung werden zur Entfernung des Jodids 20 ml konz. Salpetersäure zugegeben und zum Sieden erhitzt.

DISKUSSION DER ERGEBNISSE

Wie Abb. 1 zeigt, lassen sich die Elemente Indium, Thallium, Zinn, Antimon, Wismut, Tellur, Kupfer, Silber, Gold, Quecksilber, Cadmium, Palladium und Platin nach ein- oder höchstens dreimaliger Extraktion zu 98–100% in die organische Phase überführen. Blei, Arsen und Zink konnten trotz aller Variationsversuche, die Jodidkonzentration, Säuregrad und Extraktionsmittelgemisch betrafen, nur zu 80–90% extrahiert werden. Die Metalle Titan, Zirkonium, Hafnium, Vanadin, Niob und Molybdän waren nur zu einem geringen Prozentsatz, Aluminium, Gallium, Chrom, Mangan, Eisen, Kobalt, Nickel, Rhodium und Uran überhaupt nicht auszuschütteln.

Indium wurde bereits mit Diäthyläther, Methylisobutylketon und Cyclohexanon aus jodidhaltigen Lösungen als Tetrajodindat $[\text{InJ}_4]^-$ extrahiert.^{1,2,3} Geringere Mengen Kaliumjodid als in Tab. I angegeben, ergaben unvollständige Ergebnisse.

Thallium(I) läßt sich nur schlecht extrahieren, mit TI^{3+} hingegen erhielten wir sehr gute Resultate. Dieses wird nach Specker und Pappert⁴ entweder als Thalliumjodid oder im Überschuß von Jodid als Tetrajodothallat $[\text{TlJ}_4]^-$ vorliegend, mit Cyclohexanon und Tributylphosphat extrahiert.

Zinn. Bei Verteilungsversuchen von Sn^{2+} ergaben sich bedeutende Unterschiede je nach eingesetztem Lösungsmittel. Aus 0,5M kaliumjodidhaltiger- und 2N schwefelsaurer Lösung konnte Zinn nach dreimaliger Extraktion mit 1-Butoxy-2-propanol vollständig in das organische Solvens überführt werden. Auch 2-Äthyl-1-butanol und 4-Methyl-2-pentanol aus 4N schwefelsaurer Lösung extrahierten

Tellur. Nach einmaliger Extraktion mit 20 ml Lösungsmittel, ohne Zusatz von Tetrachlorkohlenstoff, läßt sich Tellur als Pentajodotellurat $[\text{TeJ}_5]^-$ quantitativ extrahieren. Ein ähnliches Ergebnis war bei Verwendung von Methylisobutylketon festzustellen.⁵

Kupfer. Die Angaben von Specker und Hartkamp⁶ sowie Specker und Pappert⁴ über das Extraktionsverhalten von Elementen der ersten Nebengruppe zeigen auch mit unseren Ergebnissen gute Übereinstimmung. Kupfer wird als $[\text{CuJ}_2]^-$ oder in konzentrierteren Lösungen als $[\text{Cu}_2\text{J}_3]^-$ nach dreimaliger Schüttelung extrahiert.

Silber konnten wir aus schwach saurer Lösung nicht quantitativ in die organische Phase überführen, wie dies mit Cyclohexanon geschieht.⁷ Das in wäßriger Phase

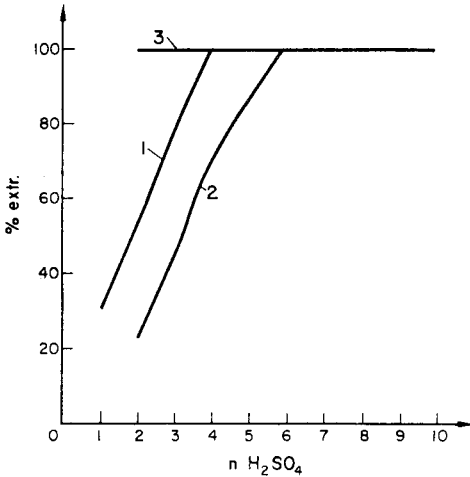


ABB. 2a

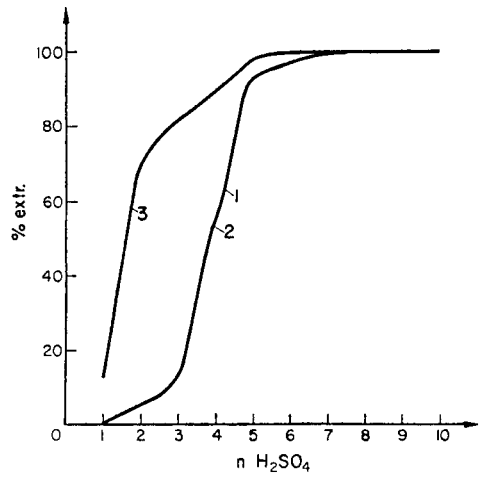


ABB. 2b

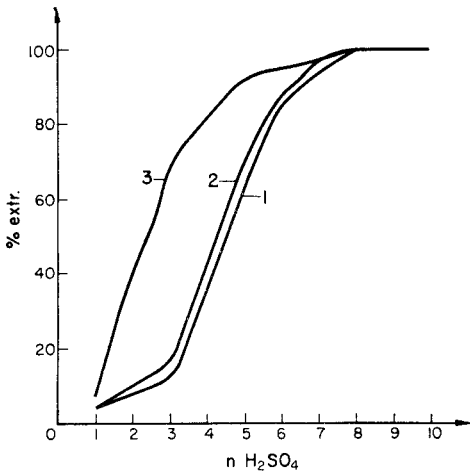


ABB. 2c

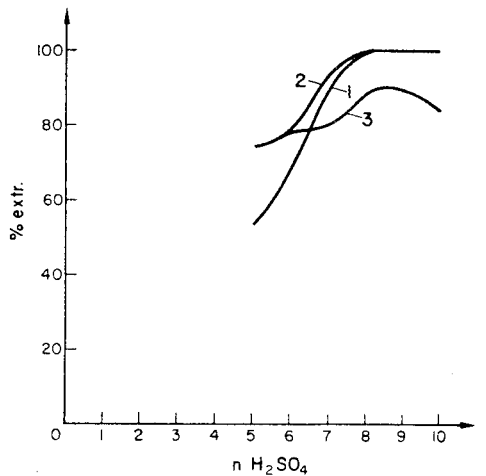


ABB. 2d

ABB. 2.—Abhängigkeit der Alkoholextraktion von der Säurenormalität:

1: 2-Äthyl-1-butanol; 2: 4-Methyl-2-pentanol; 3: 1-Butoxy-2-propanol. (a)—Zinn; (b)—Wismut; (c)—Kupfer; (d)—Silber; (e)—Cadmium; (f)—Quecksilber; (g)—Platin.

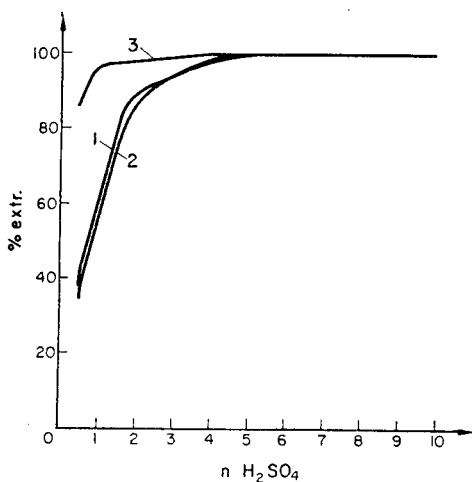


ABB. 2e

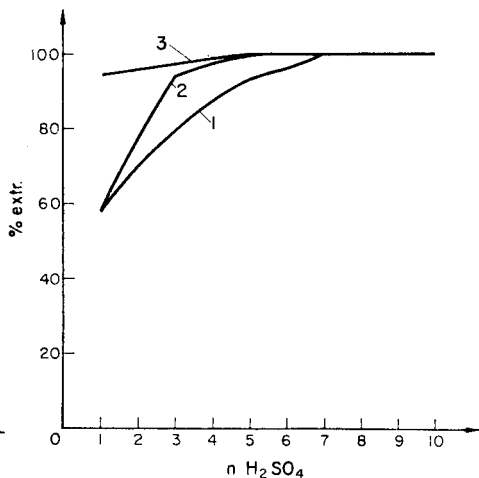


ABB. 2f

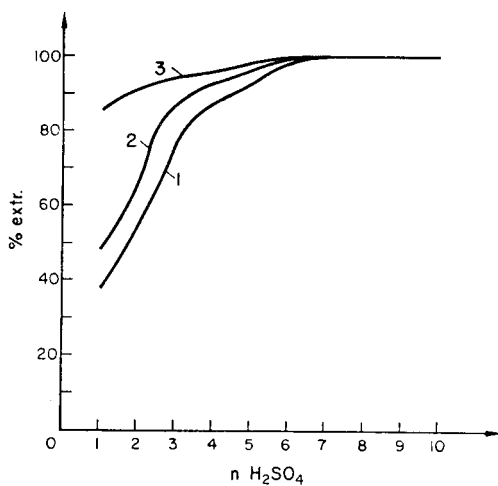


ABB. 2g

ausgefallene Silberjodid wird von den Alkoholen leicht gelöst und liegt in der organischen Phase als $[\text{AgJ}_2]^-$ oder $[\text{Ag}_2\text{J}_3]^-$ vor.

Gold. Das als $[\text{AuJ}_4]^-$ -Komplex in der organischen Phase vorliegende Metall kann nicht mit Natronlauge reextrahiert werden, da es dabei als Kolloid ausfällt. Nach Abdampfen des Lösungsmittels wird der Rückstand mit 15 ml Salzsäure und 5 ml Salpetersäure versetzt. Man kocht kurz und nimmt mit Wasser auf, neutralisiert mit Natronlauge und bringt die Lösung in einen 250 ml-Meßkolben. Hieraus werden aliquote Anteile entnommen und mit 5 ml 0,1M Komplexon-III-Lösung, 1 ml 1M Kaliumcyanonickolat-Lösung, 1 ml Ammoniak (25%ig) und SAS-SN als Indikator versetzt. Die Rücktitration erfolgt mit 0,1M Zinksulfatlösung.

Cadmium. Die Elemente der zweiten Nebengruppe sind mit verschiedenen Extraktionsmitteln eingehend untersucht und Angaben über die Zusammensetzung der jeweils extrahierten Verbindung gemacht worden.^{6,9,10} Wir konnten 100 mg

Cd^{2+} aus 0,071M Kaliumjodid- und 5N schwefelsaurer Lösung extrahieren. In diesem Fall liegt ein Verhältnis Cadmium:Jodid = 1:3 vor. Aber auch bei einem Verhältnis von 1:2 läßt sich Cadmium noch quantitativ extrahieren.

Quecksilber wird als Quecksilberjodid HgJ_2 oder als Komplex $[\text{HgJ}_3]^-$ extrahiert. Bei großem Überschuß an Jodid nimmt die Extrahierbarkeit wieder ab, da sich dann Tetrajodomercurat $[\text{HgJ}_4]^{2-}$ bildet.

Platinmetalle. Von diesen Elementen wurden Palladium(IV), Platin(IV), Rhodium(III) und Osmium(VIII) auf ihr Verteilungsverhalten untersucht. Palladium wird durch einmalige Extraktion mit Alkohol allein (ohne CCl_4) aus 0,75M Kaliumjodid- und 5N schwefelsaurer Lösung extrahiert. Ist der Alkohol mit Tetrachlorkohlenstoff "verdünnt", kann man das Metall durch dreimalige Extraktion bei gleicher Jodidkonzentration aus 3N schwefelsaurer Lösung in die organische Phase überführen.

Unter gleichen Bedingungen wurden Verteilungsversuche am Platin ausgeführt. Das Extraktionsmaximum von 98% wurde in 6N schwefelsaurem Medium ermittelt. Eine weitere Erhöhung der Säure- und Jodidkonzentration ergab eine Erniedrigung des Verteilungskoeffizienten.

Bei Osmium ergaben sich Schwierigkeiten bei der nach der Extraktion folgenden analytischen Bestimmung, da Verbindungen dieses Metalls bekanntlich sehr flüchtig sind. Mit Bestimmtheit kann jedoch gesagt werden, daß Osmium zum Großteil, Rhodium dagegen überhaupt nicht extrahiert wird.

Bei Palladium und Platin wurde der Metallgehalt nach der Extraktion jeweils in beiden Phasen analysiert. Nach Zusatz von 5 ml konz. Salpetersäure zur Entfernung des Jodids mußten die Elemente mit 5 ml konz. Salzsäure wieder in Lösung gebracht werden.

Konduktometrische Extraktionstitration

Diese dient der Aufklärung der Zusammensetzung des extrahierten Metallkomplexes, wobei es notwendig ist, daß das zu extrahierende Kation gut meßbare Änderungen der Leitfähigkeit in der organischen Phase hervorruft.

Am Beispiel des Quecksilber(II)-nitrates, das schon mit Cyclohexanon als Extraktionsmittel untersucht wurde,⁶ konnten wir die Zusammensetzung der Quecksilberjodidverbindungen, wie sie von den Alkoholen extrahiert werden, nachweisen. Aus den Knickpunkten der Leitfähigkeitskurven ist zu entnehmen, daß Quecksilber als HgJ_2 und $[\text{HgJ}_3]^-$ extrahiert wird. Quecksilber(II)-jodid hat nur eine geringe Leitfähigkeit in der organischen Phase, erst bei weiterer Zugabe von Kaliumjodid ist ein steiler Anstieg der Leitfähigkeit zu beobachten, wobei sich das Quecksilber(II)-jodid zum Trijodomercurat umsetzt.

Die Untersuchungen wurden in einem 150-ml Meßzylinder ausgeführt. Zu 20 ml einer 7N schwefelsauren Lösung, die 0,77 mMol Quecksilber enthielt, werden 40 ml Alkohol zugesetzt. Dann wird portionsweise 0,1N Kaliumjodidlösung zugegeben. Nach jeder Zugabe wird durch kräftiges Durchmischen beider Phasen das Verteilungsgleichgewicht eingestellt und die Leitfähigkeit in der organischen Phase gemessen.

Trennungen

Cadmium-Zink Diese beiden Metalle konnten mit Cyclohexanon bzw. einem Gemisch von Cyclohexanon und Tetrahydrofuran aus jodidhaltigen, schwach

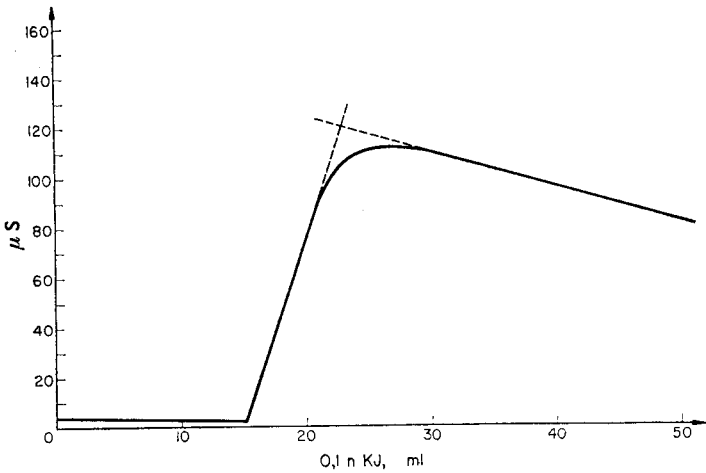


ABB. 3a

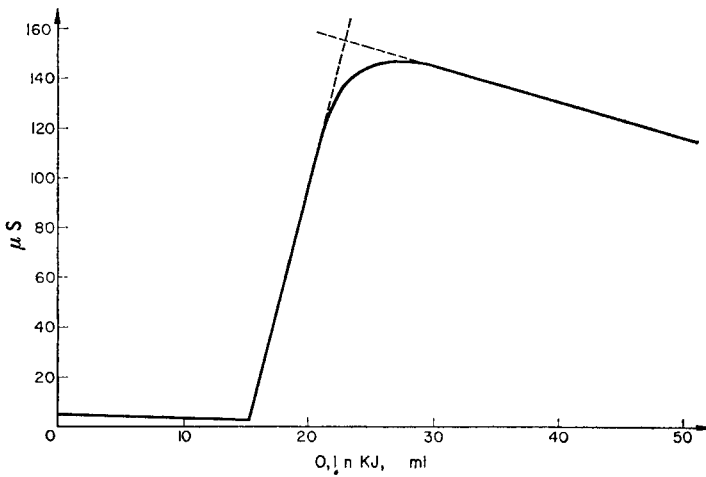


ABB. 3b

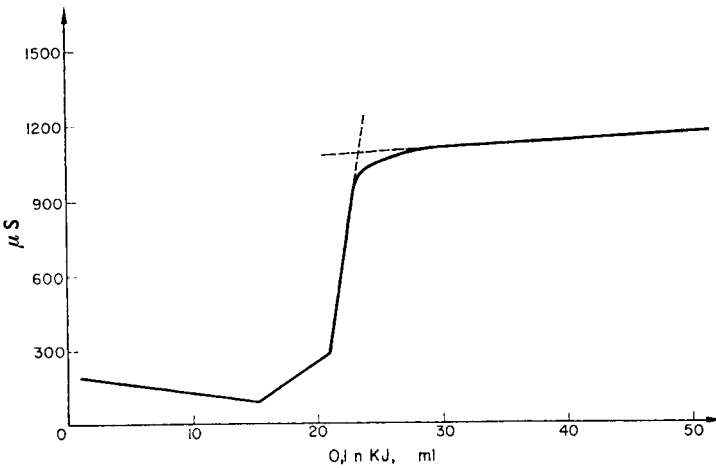


ABB. 3c

ABB. 3.—Konduktometrische Extraktionstiterung von Quecksilber (II) mit (a)—2-Äthyl-1-butanol; (b)—4-Methyl-2-pentanol; (c)—1-Butoxy-2-propanol.

schwefelsauren bzw. ammoniakalischen Lösungen getrennt werden.¹⁰ Auch Isoamylalkohol, Isobutylalkohol, n-Butylalkohol, Diäthyläther und Isoamylacetat aus schwach schwefelsaurer jodidhaltiger Lösung werden als Extraktionsmittel angegeben, wobei Cadmium zu 100%, aber auch ein hoher Prozentsatz (10–20%) Zink in die organische Phase übergeht.¹¹

Eigene Versuche ergaben, daß mit 1-Butoxy-2-propanol aus 0,071M Kaliumjodid- und 5N schwefelsaurer Lösung nach dreimaliger Ausschüttelung 100% Cadmium und 5% Zink extrahiert wurde. Die Beobachtung, daß auch Zink in die organische Phase überführt wird, konnte mit 2-Äthyl-1-butanol und 4-Methyl-2-pentanol nicht gemacht werden, weshalb diese beiden Alkohole zur Trennung dieser beiden Metalle Verwendung fanden. Es war jedoch notwendig, den Konzentrationsbereich von Cadmium zu ermitteln, bei dem dieses Metall aus einer konstant gehaltenen jodid- und schwefelsäurehaltigen Lösung mit einem bestimmten Volumen Alkohol extrahiert wird.

TABELLE II.—EXTRAKTIONSFÄHIGKEIT DER ALKOHOLE GEGENÜBER CADMIUM BEI GLEICHER JODIDKONZENTRATION

vorgelegt	Cadmium, mg	
	wäßrige Phase	gefunden organische Phase
5	0	5
20	0	20
50	0	49,9
100	0	100,2
200	71,6	129,4

Die angegebenen Zahlen sind Mittelwerte aus fünf Bestimmungen mit 20 ml 2-Äthyl-1-butanol und 4-Methyl-2-pentanol gelöst in 25 ml Tetrachlorkohlenstoff.

Wie Tab. II zeigt, lassen sich 100 mg Cadmium noch quantitativ extrahieren. Bei weiterer Erhöhung der Metallkonzentration muß auch die Jodidkonzentration entsprechend gesteigert werden. Die Trennung des Cadmiums vom Zink ist vollständig und gut reproduzierbar, wie aus Tab. III zu ersehen ist.

TABELLE III.—2-ÄTHYL-1-BUTANOL UND 4-METHYL-2-PENTANOL ALS EXTRAKTIONSMITTEL

vorgelegt		gefunden, nach der Extraktion	
Cadmium, mg	Zink, mg	Cadmium (org.), mg	Zink (wäß.), mg
10,1	11,6	10,3	11,6
10,1	47,2	10,1	47,2
10,1	94,2	10,4	94,1
5	94,2	5	94,2
50,5	9,5	50	9,5
101	9,5	99,2	9,8

Das in der wäßrigen Phase befindliche Zink wurde komplexometrisch bestimmt.¹²

Um diese Ergebnisse auch *in praxi* an technischen Produkten, Hüttenerzeugnissen etc. zu überprüfen, haben wir einen Blei-Cadmium-Flugstaub und Blei-Cadmium-Rückstände der Firma Dr. L. C. Marquart, Beuel/Rhein untersucht. Die Ergebnisse sind in Tab. IV zu sehen.

TABELLE IV.—ANALYSEWERTE NACH DER EXTRAKTION MIT 2-ÄTHYL-1-BUTANOL UND 4-METHYL-2-PENTANOL

	Blei-Cadmium Flugstaub		Blei-Cadmium Rückstände	
	gegeben, %	gefunden, %	gegeben, %	gefunden, %
Zink	6,43	6,25	10,06	10,18
Blei	18,24	—	41,05	—
Kupfer	0,05	—	0,3	—
Cadmium	18,57	18,35	11,19	11,19
Arsen	0,24	—	1,6	—
Antimon	0,78	—	—	—
Silber	23 ppm	—	40 ppm	—
Schwefel	—	—	2,08	—
SiO ₂	—	—	0,6	—

Die angegebene Fehlervarianz des Analysenattestes der Firma ist $\pm 0,5\%$

Es wurde 1 g Substanz in konz. Salzsäure gelöst und auf dem Sandbad bis zur Trockene eingengt, sodann mit 1N Schwefelsäure aufgenommen, um das Blei als Sulfat zu fällen, worauf filtriert und die Lösung in einem 100 ml-Meßkolben gesammelt wird; man füllt bis zur Marke mit Wasser auf und verwendet 20 ml dieser Lösung für die nachfolgende Extraktion.

Indium-Gallium. Wie Hartkamp und Specker^{1,2} berichten, lassen sich die beiden Metalle aus jodidhaltiger und mindestens 0,2N schwefelsaurer Lösung mit Cyclohexanon und mit Methylisobutylketon trennen.

Die optimalen Bedingungen für die Trennung fanden wir aus 0,75M kaliumjodidhaltiger und 2N schwefelsaurer Lösung, mit 2-Äthyl-1-butanol, 4-Methyl-2-pentanol und 1-Butoxy-2-propanol. In schwefelsaurer Lösung bei gleichbleibender Jodidkonzentration war Gallium in dem von uns untersuchten Bereich in keinem Fall in die organische Phase extrahiert worden.

Tabelle V gibt die Mittelwerte von 8 Bestimmungen für Indium und Gallium nach dreimaliger Extraktion wieder. Das in wäßriger Phase befindliche Gallium wurde entweder als Oxinat bestimmt, oder auch Galliumoxinat in heißer Salzsäure gelöst und bromatometrisch bestimmt.⁵

TABELLE V.—2-ÄTHYL-1-BUTANOL, 4-METHYL-2-PENTANOL UND 1-BUTOXY-2-PROPANOL ALS EXTRAKTIONSMITTEL

vorgelegt		gefunden nach der Extraktion	
Indium, mg	Gallium, mg	Indium (org.), mg	Gallium (wäß.), mg
19,23	18,4	19,23	18,12
98,75	18,67	99,4	18,51

Summary—A number of metal ions may be extracted quantitatively from iodide-containing sulphuric acid solutions by 2-ethyl-1-butanol, 4-methyl-2-propanol, or 1-butoxy-2-propanol, some partially extracted, and others not at all. There are many possibilities for separations, two of which—zinc-cadmium and indium-gallium—are described, and have been tested in technical products. The determination of the composition of the extracted metal complexes is described with reference to those of mercury, a conductimetric extraction titration being used.

Résumé—Un certain nombre d'ions métalliques peuvent être extraits quantitativement, quelques-uns partiellement et d'autres pas du tout à partir de solutions d'acide sulfurique contenant de l'iodure au moyen de 2-éthyl 1-butanol, 4-méthyl 2-propanol ou 1-butoxy 2-propanol. Il y a de nombreuses possibilités pour les séparations dont deux: zinc-cadmium et indium-gallium sont décrites et ont été essayées sur des produits techniques. On décrit la détermination de la composition des complexes métalliques extraits par rapport à ceux du mercure, en utilisant un titrage conductimétrique par extraction.

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SHORT COMMUNICATIONS

Spectrophotometric determination of niobium(V) with *n*-propyl 3,4,5-trihydroxybenzoate

(Received 5 May 1969. Accepted 4 August 1969)

MANY attempts have been made to determine niobium spectrophotometrically,¹⁻¹² but none avoid direct interference by such elements as platinum metals, nickel, copper, iron, hafnium, zirconium, tantalum, and manganese, which are likely to be present in niobium alloys. This paper describes the spectrophotometric determination of niobium in the presence of the commonly interfering elements, with *n*-propyl 3,4,5-trihydroxybenzoate (PTB).

EXPERIMENTAL

Reagents

All reagents and chemicals were analytical grade.

PTB solutions. A 0.1M solution was prepared by dissolving 21.2 g of reagent in 200 ml of acetone and diluting, with constant stirring, to one litre with water. Lower concentrations were prepared by proper dilution with 1:4 acetone-water mixture. These colourless solutions were stable for at least one week.

PTB solutions (0.1M) in *t*-pentanol or in isobutanol were colourless, and stable for at least two weeks.

Metal ions. An $8.0 \times 10^{-3}M$ stock solution of niobium was obtained by fusing in a silica crucible the calculated quantity of niobium pentoxide and 14 g of potassium pyrosulphate until a clear colourless liquid was formed. To the cooled melt 20 ml of 20% tartaric acid solution and 0.5 ml of concentrated sulphuric acid were added and the mixture was brought to boiling. Unbroken bits of melt were disintegrated with a stout platinum rod. The resulting solution was diluted to 1 litre with 2% tartaric acid solution. Blank solutions were similarly prepared but without niobium pentoxide.

Phosphate buffer. A mixture of 250.0 ml of 0.2M sodium dihydrogen phosphate and 37.0 ml of 0.2M sodium hydroxide was diluted to 1 litre with water, adjusted to pH 6.1 and stored in polythene bottles.

Procedure

An aliquot of the neutralized niobium solution, containing 0-100 μg of Nb, is treated in a small Kjeldahl flask with 10 ml of pH 6.1 phosphate buffer solution and 5 ml of $10^{-3}M$ PTB in acetone-water, and gently boiled for 2 mins. Two methods are then available.

A. The cooled solution is quantitatively transferred to a 25-ml volumetric flask, diluted to the mark with water and mixed, and the absorbance of the solution is measured at 333 nm against a reagent blank prepared similarly.

B. The cooled solution is placed in a separating-funnel, treated with 1 ml of 1M sodium chloride, and extracted successively with three 5-ml portions of $10^{-3}M$ PTB in *t*-pentanol. The combined extract is filtered, the filter paper is washed with 5 ml of the solvent and the volume is made up to 25 ml with *t*-pentanol. The absorbance is measured at 333 nm against a blank similarly prepared.

Procedure for alloys

A 0.1-g sample of the alloy is dissolved in 20 ml of 1:1 concentrated hydrochloric and nitric acids. The solution is evaporated to dryness and the residue is fused in a silica crucible with 2 g of potassium pyrosulphate. The cooled melt is dissolved in 20 ml of 20% tartaric acid solution containing a few drops of concentrated sulphuric acid. The resulting solution is diluted with water to 100 ml, and an aliquot that contains up to 100 μg of Nb is treated according to the recommended procedure.

RESULTS AND DISCUSSION

Conditions

Preliminary experiments showed that when a slightly acid solution, about pH 6.1, of niobium in tartrate solution was treated with PTB dissolved in acetone-water mixture a bright yellow to deep orange colour appeared, depending on the concentrations of the metal and ligand. The coloured species reached maximum intensity on boiling for 2 min and was stable in diffused light for at least three weeks. Among the common oxygen-containing organic solvents, t-pentanol and isobutanol were the most efficient extractants.

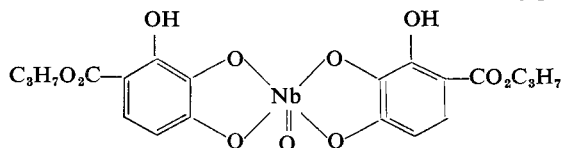
The niobium-PTB complex had a constant λ_{\max} between pH 5.4 and 6.3 with a constant molar absorptivity at 333 nm over the pH range 5.5–6.5. A minimum 3:1 ligand:metal concentration ratio was needed in acetone-water medium for full colour development, and an 8:1 ratio for the reaction with PTB in either isobutanol or t-pentanol; both solvents will extract the complex. The absorbance was higher if the metal ion solution was buffered to pH 6.1 before addition of the reagent.

To find the temperature conditions for maximum absorbance, each solution was brought to the required temperature (Table I), kept there for 2 min, then cooled to 20°. During heating the solution became pale yellow, and intensified in colour on cooling.

TABLE I—EFFECT OF TEMPERATURE ON ABSORBANCE OF COMPLEX

Temp., °C	Absorbance	Temp., °C	Absorbance	Temp., °C	Absorbance
20	0.40	50	0.42	80	0.45
30	0.40	60	0.44	90	0.45
40	0.42	70	0.45	100	0.48

Beer's law was valid over the niobium concentration range of 0–100 $\mu\text{g/ml}$ for either acetone-water or t-pentanol media, but the molar absorptivity is lower in the latter. Two methods were used to establish the composition of the Nb-PTB complex in solution, the continuous variations¹³ and the mole-ratio method.^{14–15} The results showed that an ML_2 complex is formed. The stability constant was evaluated from the results [$\log K = 10.00$ (continuous variations¹⁴); $\log K = 9.50$ (mole-ratio¹³); 10 results each]. The structure of the chelate was tentatively proposed as:



Electrophoresis and adsorption of the complex on the anion-exchange resin Amberlite IR-45(OH) showed the anionic nature of the complex. No explanation is offered for the solubility of the complex in t-pentanol and isobutanol.

Precision and accuracy

To find the repeatability of the procedure devised, 50 μg of niobium in pure solution were determined 11 times in acetone-water and t-pentanol media; the mean absorbances were 0.48 and 0.45 and the coefficients of variation for a single absorbance measurement were 2.3% and 3% respectively. Table II indicates the results (average of three) of determination of niobium in synthetic sample solutions which contained the commonly interfering ions. Analysis of an Alcomax IV sample (Al 8.0%, Ni, 13.5%, Co 24.0%, Cu 3.0%, Fe, 48.7%, Nb 2.8%) gave 2.65% Nb (5 results, relative standard deviation 1%).

TABLE II—INTERFERENCES

Al	Co	Cr	Metal added, μg				Ta	Nb, μg	
			Cu	Fe	Ni	Added		Found	
200	200	200	200	500	500	500	50.0	48.2	
							100.0	97.5	
							100.0	98.2	
150	500	300	150	200	300	300	50.0	47.8	
							50.0	48.5	

Effect of foreign ions

Measurements of the absorbances of the coloured species developed from 50- μg of niobium in the presence of 1-mg amounts of Al, Co(II), Cu(II), Fe(III), Ta, Ba, Ca, Li, Na, Rh(III), Ir(IV), Os(IV), Ni, Cr(III), Au(III), K, Zn, Re(VII), Ag, Hg, Pb, Hf and Zr, resulted in $\pm 3.8\%$ relative error. The error caused by the presence of 1-mg amounts of the following ions are given in parentheses: U(VI) (+52%), Sn(II) (+15%), Mo(VI) (+50%), Ti(III) (+15%), Pt(II) or (IV) (+20%) and Au(III) (+18%).

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Summary—The use of *n*-propyl 3,4,5-trihydroxybenzoate (PTB) for the spectrophotometric determination of niobium is investigated. PTB yields a yellowish-orange ML_2 chelate with Nb(V) at pH 6.1. The formation constant at pH 6.1 is about 10^{10} . Beer's law is obeyed over the range 0–100 μg of Nb per ml.

Zusammenfassung—Die Verwendung von *n*-Propyl-3,4,5-trihydroxybenzoat (PTB) zur spektrophotometrischen Bestimmung von Niob wird untersucht. PTB bildet bei pH 6,1 mit Niob(V) ein gelborange gefärbtes ML_2 -Chelat. Die Bildungskonstante bei pH 6,1 beträgt etwa 10^{10} . Das Beersche Gesetz gilt im Bereich 0–100 μg pro ml.

Résumé—On étudie l'emploi du 3,4,5-trihydroxybenzoate de *n*-propyle (PTB) pour le dosage spectrophotométrique du niobium. Le PTB donne un chélate orangé-jaunâtre ML_2 avec Nb(V) à pH 6,1. La constante de formation à pH 6,1 est d'environ 10^{10} . La loi de Beer est suivie dans le domaine 0–100 μg de Nb par ml.

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Determination of gadolinium in sodium borate glasses

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INCREASING use of rare-earth doped glasses¹ as lasers has made analytical determination of their composition a matter of urgency. Likewise the increasing use of inorganic glasses as matrices for trapped radicals and ions in unusual oxidation states² necessitates development of a non-destructive analytical method for the determination of impurities. Gadolinium(III) introduced into inorganic crystals exhibits ultraviolet fluorescence under short wavelength excitation.³ Stimulated emission by

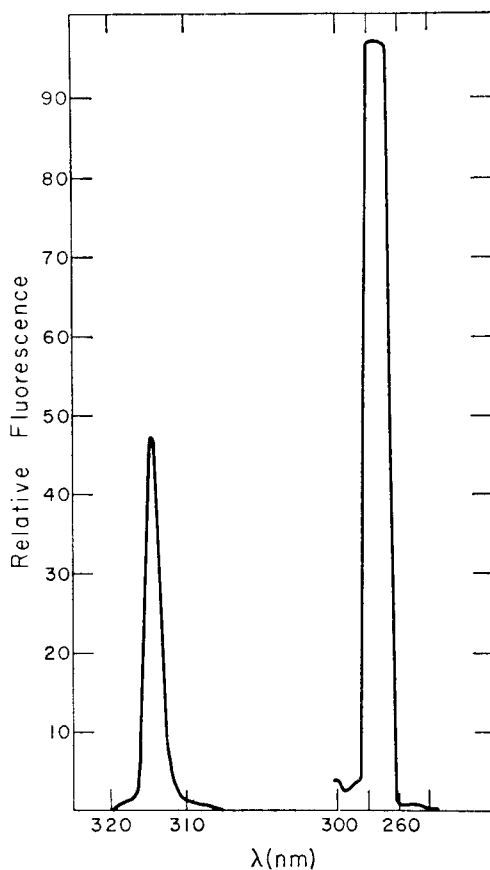


FIG. 1.—Fluorescence spectrum of a glass containing 1% w/w gadolinium.
 Left—emission (excitation 273 nm)
 Right—excitation (emission 312 nm)

TABLE I.—RELATIVE FLUORESCENCE OF GADOLINIUM IN GLASSES CONTAINING GADOLINIUM ONLY

Gd ³⁺ , ppm	Relative fluorescence, <i>I</i> ₀	Gd ³⁺ , ppm	Relative fluorescence, <i>I</i> ₀
10	5	5000	2600
50	24	6500	3350
100	48	8000	4500
500	250	10000	4800
1000	500	13000	6400
2000	1200	20000	10000
4000	2250		

gadolinium(III) in lithium magnesium aluminium silicate glass was measured by Gandy and Ginther,⁴ who observed fluorescence at 312.5 nm. Dependence of fluorescence intensity on concentration was used in this work for the quantitative determination of gadolinium.

EXPERIMENTAL

Apparatus

The spectrofluorimeter used for the measurement of excitation and fluorescence emission spectra was constructed in this laboratory and will be described in detail elsewhere.⁵ Briefly, it consists of a

500-W xenon arc lamp (Mazda), interchangeable with a medium pressure 100-W mercury lamp, an excitation monochromator (Bausch & Lomb, 250-mm focal length), the sample compartment, an analysing monochromator (Bausch & Lomb, 500-mm focal length), an EMI 9558 Q/B photomultiplier connected through a 16-ohm resistor to an EIL Vibron electrometer, and a Kipp & Zonen recorder. Slow drifts in intensity were corrected by frequent measurement of a reference glass. Fast fluctuations were filtered out. The fluorescence was viewed from the front (illuminated) side of the glass at an angle of 35° . The photomultiplier was cooled to -20° for all measurements.

Reagents

Sodium tetraborate and boric acid, 99.5% purity. Gadolinium chloride, 99.9% purity.

Preparation of glasses

Dry gadolinium chloride, was mixed with borax and boric acid (in which were taken ratio 123:62 w/w) in plastic vials containing glass balls, by means of an electric vibrator. The mixture contained gadolinium in concentrations ranging from 10 to 20000 ppm. It was established that homogeneous mixtures were obtained after 10 min. These mixtures were found to melt at temperatures lower than 1000° , but clear transparent solutions resulted only after heating at 1100° for at least 15 min. The melts were made in platinum crucibles. Drops of the hot melt were allowed to fall directly onto a clean white glazed ceramic surface. The drop was placed inside a ring 1-mm thick and pressed with a second ceramic tile so as to obtain glasses of constant 1-mm thickness. The glasses were inserted into a glass holder with a circular opening of 12-mm diameter and their excitation and fluorescence spectra were measured at room temperature.

RESULTS AND DISCUSSION

The excitation spectrum for fluorescence measured at 312 nm and the emission spectrum for 273 nm excitation are shown in Fig. 1. The 312 nm emission results from the transition from the ${}^6P_{7/2}$ state to the ${}^8S_{7/2}$ ground state of the $4f^7$ electronic configuration of Gd^{3+} . The excitation at 273 nm is due to the transition from the ground state to the levels in the 6I multiplet.

Table I presents relative fluorescence at 312 nm on excitation at 273 nm as a function of gadolinium concentration in glasses in which the only rare earth was gadolinium. Linear dependence was observed in the total range from 10–20000 ppm. The conditions of measurement were excitation 273 nm; emission 312 m μ ; voltage applied to photomultiplier 1250 V; slitwidths—excitation, entrance and exit both 0.6 mm; emission, entrance 1.0 mm, exit 0.5 mm.

TABLE II.—RELATIVE FLUORESCENCE OF GADOLINIUM AS A FUNCTION OF CONCENTRATION IN GLASS CONTAINING EQUAL AMOUNTS OF Gd AND Sm

Gd ³⁺ , ppm	Relative fluorescence, <i>I</i>	<i>I</i> ₀ / <i>I</i>
500	180	1.38
1000	390	1.28
2000	720	1.66
4000	1440	1.56
5000	1920	1.35
6500	1980	1.69
10000	2000	2.40
20000	2000	5.0

In order to test the effect of the presence of another rare earth, the fluorescence of gadolinium was measured in glasses with equal concentrations of samarium. The results are presented in Table II, conditions of measurement being as above. At concentrations up to 6500 ppm, the gadolinium fluorescence decreased by a factor of 2/3, and dependence was linear. At higher concentrations of samarium and gadolinium, quenching of fluorescence was observed.

It is therefore assumed that a non-radiative energy transfer takes place from gadolinium to samarium. Low concentrations up to 6000 ppm provide the best conditions for the analytical determination.

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Summary—A method for the determination of gadolinium in sodium borate glasses is described which utilizes the 312-nm fluorescence of gadolinium under 273-nm excitation. A linear dependence of fluorescence on concentration is found for the concentration range 10–20000 ppm. Quenching of gadolinium fluorescence by samarium is examined.

Zusammenfassung—Eine Methode zur Bestimmung von Gadolinium in Natrium Borat Gläsern, unter Benutzung der 312 nm Fluoreszenz des Gadoliniums mittels 273 nm Erregung, wird beschrieben. Eine lineare Abhängigkeit der Fluoreszenz von der Konzentration im Bereich von 10–20000 ppm wurde gefunden. Quenching der Gadolinium Fluoreszenz durch Samarium wurde untersucht.

Résumé—On décrit une méthode pour la détermination du gadolinium dans les verres au borate de sodium, qui utilise la fluorescence 312 nm du gadolinium sous l'excitation 273 nm. On trouve une relation linéaire entre la fluorescence et la concentration pour le domaine de concentrations 10–20000 ppm. On examine l'extinction de la fluorescence du gadolinium par le samarium.

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Polarographic determination of impurities in high-purity phosphorus

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SEVERAL methods have been developed for the determination of trace impurities in high-purity phosphorus used in the semiconductor industry.^{1,2} These include spectrophotometric, fluorimetric, spectrographic, voltammetric and radioactivation techniques. However, no simple method has been reported for determining copper, lead and cadmium at the ppM (parts per milliard) level. This paper describes the application of square-wave (S.W.) and radio-frequency (R.F.) polarography in a phosphoric acid base electrolyte to the simultaneous determination of these elements down to 0.1 ppm. For cadmium, higher sensitivity is achieved by the use of cation-exchange separation before polarographic determination in a potassium sulphate base electrolyte.

EXPERIMENTAL

Apparatus

Polarograph. A Yanaco PF-501 R.F./S.W. polarograph (Yanagimoto Mfg. Co., Kyoto, Japan) was used in this study. The instrumental parameters were as follows—S.W. frequency: 200 Hz; amplitude: 20 mV; time constant: 52; amplifier sensitivity: 1/2; recorder sensitivity: 0.02 or

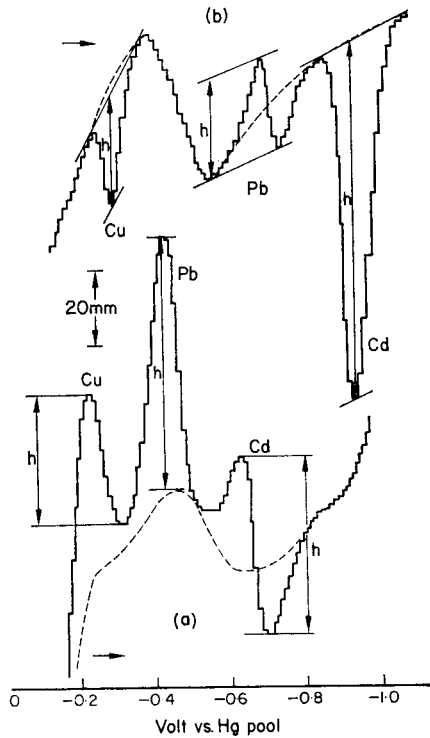


FIG. 1.—R.F. polarograms
 (a) $3M H_3PO_4$ – $0.2M KCl$ containing $0.05 \mu g$ of Cu, $0.16 \mu g$ of Pb and $0.08 \mu g$ of Cd/ml ($7.5 \times 10^{-7}M$ each, Cu, Pb and Cd).
 (b) $0.4M K_2SO_4$ containing $0.05 \mu g$ each of Cu, Pb and Cd/ml (ca. $7.5 \times 10^{-7}M$ Cu, $2.5 \times 10^{-7}M$ Pb and $4.5 \times 10^{-7}M$ Cd).
 Broken lines: base electrolyte alone. *h*: peak height.

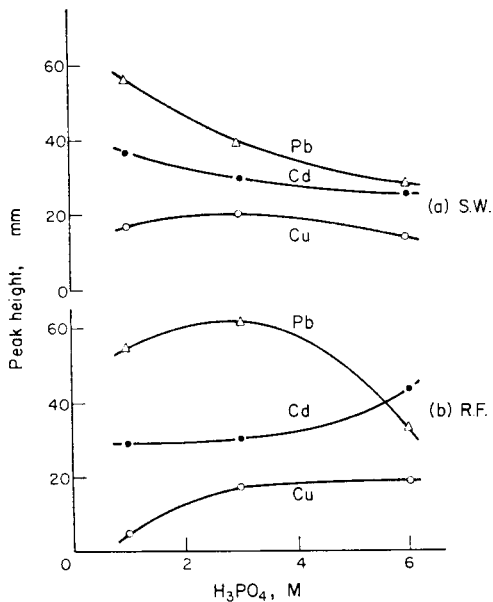


FIG. 2.—Effect of phosphoric acid concentration on peak-height in $0.2M KCl$. ($0.03 \mu g$ of Cu, $0.1 \mu g$ of Pb and $0.06 \mu g$ of Cd/ml)

0.04 (for the S.W. polarography); and R.F. frequency: 455 kHz; S.W. modulation: 200 Hz; amplitude: 4 V; amplifier sensitivity: 1/1; recorder sensitivity: 0.02 or 0.04 (for the R.F. polarography). All measurements were carried out at $20 \pm 0.5^\circ$ after deaeration with nitrogen for 15 min.

Cation-exchange column. Columns were prepared from Amberlite IR 120 B strongly acidic cation-exchange resin, 30–50 mesh. After careful conditioning, the resin was converted into the hydrogen form with 3M hydrochloric acid and washed free from acid with water. The flow-rate was adjusted to ca. 1 ml/min.

Reagents

Water was purified by ion-exchange followed by repeated distillation. Nitric acid was purified by distillation; ca. 5 ppM of copper and 0.6 ppM of lead were found after purification. Potassium sulphate, 0.5M, was purified by electrolysis with a mercury cathode.

Potassium chloride. Potassium chloride solution (100 ml, 3M) was shaken with two lots of 4 ml of 0.1% sodium diethyldithiocarbamate solution and 20 ml of chloroform, and then with 20 ml of chloroform. The aqueous phase was evaporated to dryness in a quartz beaker and heated to ca. 400° to destroy organic matter.

Phosphoric acid 6M. Phosphoric acid (90 ml, 6M) was poured onto a 14-mm diam. \times 150-mm cation-exchange column. The first 10-ml fraction of the effluent was discarded, and the following 80-ml fraction was collected for use. The breakthrough capacity of the column was ca. 100 ml.

All the reagents used were of reagent grade. A quartz condenser was used in the distillations.

Procedure

Dissolution of sample. Elementary phosphorus was converted into phosphoric acid as follows. Place a weighed sample (0.5–2 g) in a 50-ml quartz tall beaker, add 5 ml of water and then 10 ml of nitric acid per g of sample, in small portions, and heat gently until the sample has dissolved. Continue heating to evaporate the solution to 1–2 ml. Add 10 ml of water, evaporate to 1–2 ml, and repeat this operation twice more. To minimize airborne contamination, carry out the dissolution and evaporation inside a small chamber, which is continuously flushed with purified nitrogen.

Cation-exchange separation of copper, lead, and cadmium in phosphoric acid. Pour a sample (5–20 ml of 3M phosphoric acid) onto a 12-mm diam. \times 60-mm cation-exchange column, and wash the column with 20 ml of water. Pass 30 ml of 4M hydrochloric acid through the column, and collect the effluent in a 50-ml silica dish. Evaporate the effluent to dryness.

RESULTS AND DISCUSSION

Because copper(II) gives low peak-heights in S.W. and R.F. polarograms in 3M or 6M phosphoric acid, a small amount of potassium chloride was added (0.2M). A typical R.F. polarogram is shown in Fig. 1(a). The effect of phosphoric acid concentration on peak-height is summarized in Fig. 2.

TABLE I.—DETERMINATION OF IMPURITIES IN 99.9999% RED PHOSPHORUS

Expt. no.	Sample taken, g	Base electrolytes	Polarography	Found, ppm		
				Cu*	Pb	Cd
1	0.91	3M H ₃ PO ₄ – 0.2M KCl	S.W.	0.1	0.1	Not detected
			R.F.	0.1	0.1	Not detected
2	1.12	3M H ₃ PO ₄ – 0.2M KCl	S.W.	0.1	0.1	Not detected
			R.F.	0.1	0.1	Not detected
3	2.06	6M H ₃ PO ₄ – 0.2M KCl	R.F.	0.1 ₂	—	—
4	0.59	0.4M K ₂ SO ₄ , 2.5 ml	R.F.	—	—	0.01
5	0.90	0.4M K ₂ SO ₄ , 2.5 ml	R.F.	—	—	0.00 ₆

* Blank values, 0.1–0.2 μ g, were subtracted. No correction was required for the other two elements.

As reproducibility of R.F. polarograms of lead and cadmium in 6M phosphoric acid-0.2M potassium chloride was poor, 3M phosphoric acid-0.2M potassium chloride was chosen as the base electrolyte for the simultaneous determination of the three elements.

The lower limits of determination in 3M phosphoric acid-0.2M potassium chloride were (in $\mu\text{g/ml}$): 0.005 (S.W.) 0.01 (R.F.) for Cu, 0.01 (S.W., R.F.) for Pb, and 0.01 (S.W., R.F.) for Cd. The calibration curves (peak-height vs. concentration) were linear up to at least 0.1 $\mu\text{g/ml}$, with a maximum deviation of ca. 5% at 0.05 $\mu\text{g/ml}$. All of them passed through the origin except for R.F. polarograms of copper. However, in 6M phosphoric acid-0.2M potassium chloride, R.F. polarographic peak heights were proportional to copper concentrations over the range 0.005-0.1 $\mu\text{g/ml}$.

In S.W. and R.F. techniques in 3M phosphoric acid-0.2M potassium chloride, the following elements may be present in at least the amounts ($\mu\text{g/ml}$) indicated without causing appreciable error: Pb, 10; Cd, 5; As(III), 0.7; Fe(III), 5; Sb(III), 0.04 (in the determination of 0.03 μg of Cu/ml); Cu, 6; Cd, 5; As(III), 0.4; Fe(III), 2.5; Sb(III), 0.05 (in the determination of 0.1 μg of Pb/ml); Cu, 3; Pb, 1; As(III), 0.7; Fe(III), 2.5; Sb(III), 0.05 (in the determination of 0.05 μg of Cd/ml). Also, nitric acid more dilute than 0.1M does not interfere with the determination.

A sample of high-purity red phosphorus was analysed by these techniques with the results shown in Table I (Expts. 1-3). Phosphorus, ca. 1 or 2 g, was converted into ca. 10 ml of 3M or 6M phosphoric acid as described above. As little as 0.1 ppm of these elements can be determined simultaneously within 5-6 hr.

In order to extend the lower limits of determination, cation-exchange separation was combined with the polarographic determination in a small volume of 0.4M potassium sulphate. A typical R.F. polarogram in this base electrolyte is shown in Fig. 1(b). The lower limits of determination in 0.4M potassium sulphate were (in $\mu\text{g/ml}$): 0.002 (S.W.) 0.01 (R.F.) for Cu, 0.01 (S.W., R.F.) for Pb, and 0.005 (S.W.) 0.002 (R.F.) for Cd. In both S.W. and R.F. techniques, peak-heights of copper, lead, and cadmium were proportional to concentrations of the elements up to at least 0.1 $\mu\text{g/ml}$, with a maximum deviation of ca. 5% at 0.05 $\mu\text{g/ml}$.

In the cation-exchange separation described above, the breakthrough capacity of the column for the desired impurity elements was ca. 50 ml in 3M phosphoric acid, and these elements were completely eluted with ca. 25 ml of 4M hydrochloric acid. Copper and lead, 0.1-1 μg each, and cadmium, 0.01-1 μg , added to 10-20 ml of purified 3M phosphoric acid, were almost completely recovered. Because of the relatively large contamination of copper and lead, this method was successfully applied only to the determination of cadmium in high-purity phosphorus. The results are given in Table I (Expts. 4 and 5). Since cadmium contamination is negligible, less than 5 ppm of cadmium in phosphorus can be determined by this technique. The time required for a determination is approximately 8 hr.

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Summary—Square-wave and radio-frequency polarographic techniques in phosphoric acid-potassium chloride media are applied to the simultaneous determination of copper, lead and cadmium in high-purity red phosphorus down to a level of 0.1 ppm. In addition ca. 0.01 ppm of cadmium is determined by R.F. polarography in potassium sulphate base electrolyte after cation-exchange separation.

Zusammenfassung—Square-wave- und Radiofrequenzpolarographie in Phosphorsäure-Kaliumchlorid-Medien werden zur gleichzeitigen Bestimmung von Kupfer, Blei und Cadmium in hochreinem rotem Phosphor bis herunter zum Bereich 0,1 ppm verwendet. Ferner läßt sich etwa 0,01 ppm Cadmium nach Kationenaustausch-Abtrennung in Kaliumsulfat-Trägerelektrolyt durch Radiofrequenzpolarographie bestimmen.

Résumé—On applique les techniques polarographiques d'onde carrée et de radio-fréquence en milieux acide phosphorique-chlorure de potassium à la détermination simultanée des cuivre, plomb et cadmium dans le phosphore rouge de haute pureté jusqu'à des teneurs aussi faibles que 0,1 ppm. De plus, on détermine environ 0,01 ppm de cadmium par la polarographie R.F. en électrolyte de base sulfate de potassium après séparation par échange cationique.

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Submicro determination of cobalt, manganese or nickel in organometallic compounds

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LITTLE attention has been devoted to the determination of metals in organometallic compounds on the submicro scale. A method for the determination of iron¹ appears to be the only one studied so far; in this method, the organic material was digested in a sealed tube with a nitric/sulphuric acid mixture and the iron determined spectrophotometrically.

It has subsequently been shown^{2,3} that a more rapid mineralization procedure, with a perchloric/sulphuric acid mixture in an open tube, is effective in the submicro determination of phosphorus. Some photometric EDTA titration methods for microgram quantities of various metals have recently been described⁴ and it was suggested that these might be applicable to the analysis of organometallic compounds.

These techniques have been examined for the analysis of compounds containing cobalt, manganese or nickel.

EXPERIMENTAL

Photometric titration

Standard solutions, which had been treated to simulate the residues from digestion of organometallic materials, gave variable, high results when titrated by the methods described previously,⁴ probably because titratable impurities were introduced during the processing of the solutions. Some improvement might be achieved by the use of purified reagents, masking agents or more selective titrations. In refining the titrimetric methods, however, much of their simplicity might be lost and it was considered better to seek suitable spectrophotometric methods; titrimetry, including the use of the mercury electrode,⁵ would only be reconsidered if spectrophotometry proved unsuitable.

Spectrophotometric methods

Cobalt. Nitroso-R-salt⁶ was found to be a satisfactory reagent.

Manganese. Attempts to determine manganese by the catalytic method of Almásy and Dežšo⁷ failed to achieve the desired repeatability. Satisfactory precision was obtained by oxidation to permanganate with ammonium hexanitratocerate.⁸ Owing to the poor sensitivity of this method, however, the largest final volume that could be used was 10 ml, which allows barely sufficient volume for washing digestion vessels. The formaldoxime method proposed by Marzenko⁹ gave a precision as good as the permanganate method and, because of its higher sensitivity, was preferred.

Nickel. Sodium diethyldithiocarbamate¹⁰ was briefly examined for nickel determination, but results were very erratic. The dimethylglyoxime method proposed by Yamasaki and Matsumoto¹¹ had been used previously with some success; it was found that the higher pH recommended by Blackwell *et al.*¹² was preferable and consistency of results was improved by an alteration in the order of addition of the reagents.

Mineralization procedures

Portions of aqueous solutions of metal salts containing 4–20 µg of metal were evaporated in digestion tubes and treated by the open- and sealed-tube mineralization procedures. Excellent recoveries were obtained with both for all three metals tried, the spectrophotometric finishes being used. However, when the open-tube digestion was applied to organometallic compounds, consistent but slightly low recoveries were obtained from cobalt and nickel compounds and variable, high results from a manganese compound. Variations in the amounts of acids and time and temperature of heating did not consistently improve results, so the lengthier sealed-tube digestion procedure was adopted.

Recommended procedures

Mineralization. Digest the samples, containing 4–20 μg of metal, in sealed tubes by the procedure described elsewhere.^{1,3} It is particularly important to ensure that the last traces of nitric acid are removed from the opened tube before nickel is determined.

Determination of cobalt. Transfer the residue from the digestion tube into a 50-ml conical flask with about 10 ml of water. Add 25 μl of concentrated sulphuric acid followed by 2 ml of 50% sodium acetate trihydrate solution and 2 ml of 0.05% nitroso-R-salt solution. Boil the contents of the flask for 1 min, add 1 ml of concentrated nitric acid and again boil for 1 min. Cool the solution rapidly in running water and transfer it into a 25-ml volumetric flask. Dilute to the mark and measure the absorbance at 500 nm in a 40-mm cell against a reference blank solution taken through the whole procedure. Prepare a calibration curve by evaporating portions of standardized¹³ cobalt solution to dryness in digestion tubes, and applying the complete procedure.

Determination of manganese. Transfer the residue from the digestion tube into a 25-ml volumetric flask with about 10 ml of water. Add 1 ml of formaldoxime solution (8.4 ml of 36% formaldehyde + 70 ml of 10% hydroxylamine hydrochloride solution diluted to 100 ml) followed immediately by 3 ml of 1.25M sodium hydroxide. After 10–15 min, dilute to the mark and measure the absorbance at 455 nm in a 40-mm cell against a reference blank solution taken through the whole procedure. For the calibration curve apply the whole procedure to portions of standardized¹⁴ manganese solution, diluted to 10 ml and to which concentrated sulphuric acid has been added to make the total acid volume 5 μl .

Determination of nickel. Transfer the residue from the digestion tube into a 25-ml volumetric flask with about 10 ml of water. Add 1 ml of 20% tartaric acid solution and 0.5 ml of saturated bromine water. Allow the solution to stand for 1–2 min, add concentrated ammonia solution dropwise to decolorize the solution and then 5 or 6 drops in excess. Allow the solution to stand for 1–2 min, then add, in quick succession, 1 ml of 3M sodium hydroxide, 5 ml of buffer solution (100 ml of 0.2M disodium hydrogen phosphate + 65 ml of 0.2M sodium hydroxide) and 1 ml of 1% ethanolic dimethylglyoxime solution, swirling the flask well during each addition. After 15 min, dilute to the mark and measure the absorbance at 466 nm in a 40-mm cell against a reference blank solution subjected to the whole procedure. Prepare a calibration curve by applying the colour development procedure to a standard nickel solution.

Note. The bromine water should be prepared daily and allowed to stand for 1 hr before use. The 3M sodium hydroxide should be renewed weekly and the tartaric acid and buffer solutions monthly.

RESULTS AND DISCUSSION

The results of the analysis of a number of organometallic compounds are summarized in Table I. Only two of the forty determinations done came outside the normally accepted limits, of $\pm 0.3\%$ absolute, for analysis of organic materials. The range of compounds listed is limited; other materials analysed by the recommended methods were either of uncertain composition, in which case similar precision was obtained, or were clearly inhomogeneous.

TABLE I.—ANALYSIS OF ORGANOMETALLIC COMPOUNDS

Compound	Range of weight, μg	Metal, %		No. of detns.	Range of errors % absolute
		Calc.	Found (mean)		
Ni-dimethylglyoxime	28.0–69.4	20.32	20.3 ₀	4	–0.3 ₈ to +0.1 ₇
Ni-nioxime	48.1–100.5	17.21	17.2 ₁	4	–0.0 ₆ to +0.1 ₃
Ni-oxime	27.3–91.5	16.91	16.8 ₉	4	–0.1 ₁ to +0.0 ₆
Ni- α -naphthol	34.7–98.5	14.01	14.0 ₉	4	+0.0 ₁ to +0.1 ₆
Ni-di-isopropyl-dithiophosphate	46.7–92.5	12.10	12.0 ₇	4	–0.1 ₈ to +0.2 ₇
Co-anthranilic acid	32.0–69.8	17.79	17.8 ₆	4	–0.2 ₇ to +0.0 ₇
Co- α -nitroso- β -naphthol	63.4–89.9	9.95	9.9 ₅	4	–0.0 ₅ to +0.0 ₇
Co-acetylacetone	30.1–85.8	16.54	16.5 ₄	4	–0.0 ₄ to +0.0 ₇
Mn-acetylacetone	43.3–84.4	15.60	15.6 ₁	4	–0.0 ₈ to +0.1 ₀
Mn-anthranilic acid	33.7–90.7	16.79	16.9 ₀	4	–0.1 ₄ to +0.3 ₁

The reason for the failure of the open-tube digestion procedure is not known. Deviations from the mean for the cobalt and nickel compounds mineralized by this technique were similar to those obtained by sealed-tube digestion but mean recoveries of only about 98% were obtained. The manganese compound tested gave a mean recovery of about 107% and results were very variable. It is thought that higher oxidation states of manganese may be formed during the digestion.

TABLE II.—POOLED STANDARD DEVIATIONS FOR TITRIMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF METALS

	Pooled standard deviation, μg		
	Co	Mn	Ni
Spectrophotometry	0.06	0.09	0.05
Photometric titration	0.13	0.09	0.13

A comparison of the pooled standard deviations for the two finishes is of interest and is shown in Table II. In each case the figures are based on 8 determinations at 4 levels of metal content in the range 4–20 μg . The improvement in precision by the spectrophotometric procedure is significant for cobalt and nickel, although no improvement is obtained for manganese.

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Summary—Methods for the determination of cobalt, manganese or nickel in samples of organometallic compounds weighing 30–100 μg have been developed. Spectrophotometric determination following digestion with nitric and sulphuric acids in a sealed tube is recommended, all results obtained from the analysis of standard compounds being within $\pm 0.4\%$ absolute error. Digestion in an open tube with perchloric and sulphuric acids gives slightly low results for cobalt and nickel compounds and is inappropriate for manganese compounds.

Zusammenfassung—Verfahren zur Bestimmung von Kobalt, Mangan oder Nickel in Proben metallorganischer Substanzen mit 30–100 μg wurden entwickelt. Nach Aufschluß mit Salpeter- und Schwefelsäure im abgeschmolzenen Rohr wird spektrophotometrische Bestimmung empfohlen; alle Ergebniss der Analyse von Standardverbindungen lagen innerhalb von 0,4% absolutem Fehler. Aufschluß im offenen Rohr mit Überchlor- und Schwefelsäure gibt für Kobalt- und Nickelverbindungen etwas zur niedrige Werte; für Manganverbindungen ist er nicht geeignet.

Résumé—On a élaboré des méthodes pour la détermination du cobalt, du manganèse ou du nickel dans des échantillons de composés organo-métalliques pesant 30–100 μg . On recommande le dosage spectrophotométrique suivant la digestion avec les acides nitrique et sulfurique en tube scellé, tous les résultats obtenus de l'analyse de composés étalons étant compris dans les limites d'erreur absolue $\pm 0,4\%$. La digestion en tube ouvert avec les acides perchlorique et sulfurique donne des résultats légèrement faibles pour les composés du cobalt et du nickel et ne convient pas aux composés du manganèse.

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Spectrophotometric extractive titrations—VII.* Titrations with di-2-naphthylthiocarbazone

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DITHIZONE has been successfully applied as titrant in extractive titrations.¹⁻⁴ It was considered that the use of its analogue, di-2-naphthylthiocarbazone (DNZ), would be advantageous: the molar absorptivities of the reagent and its chelates are higher than those of dithizone and of dithizonates,^{5,6} and DNZ does not form secondary chelates. Thus, it would be most advantageous to use DNZ in the analysis of samples readily soluble in alkaline medium and for the consecutive titration of two metal ions, because it is more likely that there will be a pH range within which both metal ions are extracted successively than in the case of dithizone, and the titration employing the measurement of absorbance due to free reagent should be easier because of the lower tendency of DNZ to pass into ammoniacal aqueous solutions from organic solvents such as carbon tetrachloride or chloroform. The disadvantages that were envisaged stemmed from the lower stability of DNZ solutions and the lack of reliable equilibrium constants to enable prediction of optimum conditions.⁷

The reagent was evaluated by titrating traces of silver in germanium dioxide and successively titrating mercury and zinc. During the titrations, the solutions were kept in a dark bottle placed in a Dewar flask kept cold by being filled with water with ammonium chloride dissolving in it.

EXPERIMENTAL

Apparatus

As described earlier.^{1,8}

Reagents

The common reagents and solutions were as indicated earlier.^{1,8}

Standard silver solution, 100 ppm. Reagent grade silver sulphate was dissolved in water on the day of use and diluted to the required concentration.

Di-2-naphthylthiocarbazone. A sample was prepared by the procedure of Grzhehorzhevsky⁹ and was purified by dissolving 0.1 g in 50 ml of carbon tetrachloride, then re-extracting with five 50-ml portions of aqueous ammonia (1 + 9). The combined aqueous phases were cooled in an ice-bath, and then acidified with dilute acetic acid. The green precipitate was filtered off on filter paper and dried in the dark at room temperature. The DNZ so precipitated was dissolved in 25-ml of freshly distilled, water-free chloroform or carbon tetrachloride and this stock solution was stored in a dark bottle in a refrigerator. Solutions of DNZ, $1^{-8} \times 10^{-2}M$, were prepared by diluting the stock solution with either chloroform or carbon tetrachloride. The titre of solutions was checked absorptometrically, by taking the absorptivity at 650 nm to be $6.70 \times 10^4 \text{ l.mole}^{-1}\text{cm}^{-1}$.^{10,11}

Procedures

Titration of silver. Ten ml of chloroform were placed in the titration cell, followed by 50 ml of the solution to be analysed, containing up to 10 μg of silver, and 1 ml of 0.1% sodium ethylenedinitri-tetra-acetate. The solution was adjusted with 2M ammonia to a suitable pH between 3 and 11.

* Part VI—*Talanta*, 1969, **16**, 201.

In the comparison cell, 10 ml of chloroform and 50 ml of water were placed. The solutions were agitated with a mixer for 2 min, then the titration was started. After each addition of DNZ, the mixer was applied for 1 min. When the organic phase in the lower arm of the titration cell clarified, the absorbance at 650 nm was measured against a blank of pure chloroform. During the titration the absorbance rises negligibly up to the end-point, but thereafter it increases markedly with each addition of titrant.

Consecutive titration of mercury and zinc. Thirty ml of the solution to be analysed, containing up to 5 μg of mercury and 2 μg of zinc, were placed in the titration cell, followed by 20 ml of 30% w/v sodium acetate trihydrate solution. Ten ml of carbon tetrachloride were added to the comparison and titration cells, then the comparison cell was filled with aqueous sodium acetate solution and the phases were equilibrated for 2 min. When the phases settled, the spectrophotometer was checked with the comparison cell, and then the titration, with $5 \times 10^{-5}M$ DNZ, was begun. After each increment of titrant was added, the solutions were agitated for 100 sec and then the absorbance of the organic layer was measured at either 580 or 590 nm. It was observed that during the titration of mercury there is a slight increase in the absorbance until the end-point is reached and thereafter it increases markedly until the second end-point is reached. Thereafter the slope of the curve decreases sharply, but remains positive.

The buffers and the vessels used were carefully purified with a solution of DNZ in chloroform.

RESULTS AND DISCUSSION

Silver

In order to find the pH range for titration of silver with DNZ it was necessary to reinvestigate the pH-dependence of the extraction of this element, because the reported data are contradictory.^{8,12} A series of 50-ml aliquots of 0.015M EDTA, each containing 20 μg of silver, were either acidified with a few drops of 1M sulphuric acid or made ammoniacal and, after measurement of pH, transferred into 100-ml separatory funnels and shaken for 30 sec with 5 ml of $1.3 \times 10^{-5}M$ DNZ in chloroform. The absorbance of the extracts was measured at 500 and at 650 nm. Treatment of the results in the manner described by DuBois and Knight¹¹ showed that DNZ is quantitatively bound over the pH range 2-11. The discrepancy between these findings and those of earlier authors might be due to the replacement of sodium hydroxide with aqueous ammonia, which suppresses the precipitation of silver oxide.

The procedure for spectrophotometric extractive titration of silver with DNZ was designed by taking into account this pH range. Because of addition of EDTA, the procedure should be selective against interferences other than mercury(II) and gold(III).¹² In order to check the accuracy of the method the absorptiometric titre was compared with that obtained by the titration of standard silver sulphate solution. The technique of simultaneous titration of the standard sample and of the blank solution was applied, and the shape of the titration curve was quite similar to that reported earlier,⁴ if the absorbance of the blank was measured with the spectrophotometer zero being set for the sample. The results of titrations listed in Table I indicate that the DNZ was still not pure; it obviously contained some metal chelate which absorbs negligibly at 650 nm and which is less stable than the chelate

TABLE I.—TITRATION OF SILVER

Silver present, μg	Volume of DNZ solution, ml calculated,* <i>A</i>	Volume of DNZ solution, ml found, <i>B</i>	Difference, % $100(A - B)/A$
7.0	0.389	0.348	10.5
5.0	0.298	0.260	6.5
4.5	0.250	0.230	8.0
3.5	0.194	0.170	12.4
2.5	0.139	0.128	7.9
1.0	0.056	0.050	10.7

* Using Beer's law and molar extinction coefficient $6.70 \times 10^4 \text{ l. mole}^{-1} \text{ cm}^{-1}$ at 650 nm.

of silver with DNZ. Further purification of DNZ by adsorption might seem useful, but it might result in another shortcoming—lower stability of titrant solutions.¹¹

With the application of the procedure for silver to the analysis of germanium dioxide being in mind, the extraction of silver with DNZ from 1M ammonium tartrate in 0.5% EDTA solution was investigated. It was found that DNZ is bound by silver quantitatively only between pH 8.6 and 11. The narrowing of the pH range cannot be explained by the complexing effect of tartrate ions; it is more likely that the ammonium tartrate contains an anionic impurity which binds silver more strongly

than tartrate does. Fortunately, even the narrower pH range coincides with that best suited for dissolution of germanium dioxide,⁴ at the same time the measurement of the absorbance at the wavelength of maximum absorptivity of free DNZ remains possible because of the large partition coefficient of DNZ between chloroform and water. The application of the procedure for silver, modified by addition of ammonium tartrate, to the analysis of germanium dioxide was proven to be satisfactory, the only shortcoming being the necessity to check frequently the titre of DNZ solutions by titration of standard silver solution.

Consecutive titration of mercury and of zinc

The choice of suitable wavelength and organic solvent for the consecutive titration of mercury and of zinc with DNZ was made on the basis of measurements of absorption spectra of equimolar solutions of pure mercury and zinc chelates in chloroform and in carbon tetrachloride. It was found that the ratio of absorbance of the zinc and mercury chelates is most favourable at 585 nm with carbon tetrachloride as solvent.

There must be a large difference between the stability of the chelates involved for successful successive titration.³ The ratio of the extraction constant of the mercury chelate to that of the zinc one is $>10^{16}$ with chloroform as solvent.¹¹ This high value, which presumably applies also to carbon tetrachloride systems, indicates that in consecutive titration at any pH zinc will be titrated only after all mercury has been completely extracted. The titration of zinc may then be treated as if it is present alone and the minimum pH for successive titration may be calculated according to equations derived earlier,⁷ but with modification taking into account the complexing effect of buffer.

$$\text{pH}_t = 2.14 - \frac{1}{2} \log K_{\text{Zn}(\text{DNZ})_2}^{\text{CCl}_4} + \frac{1}{2} \log (1 + K_{\text{ZnAc}}[\text{Ac}]) \quad (1)$$

Here K_{ZnAc} is the stability constant of zinc acetate. Employing the value of the extraction constant found by Grzechorzhevsky⁵ and the stability constant of zinc acetate referred to by Jazimirski and Wasiljew,¹² the threshold pH for consecutive titration of mercury and of $10^{-6}M$ zinc solutions in $0.88M$ acetate medium is 6.72.

These predictions were verified experimentally (Table II). For the reasons mentioned in connection

TABLE II.—CONSECUTIVE TITRATION OF MERCURY AND ZINC

Mercury, μg		Zinc, μg	
present	found	present	found
5.0	4.9	0.8	0.7 ₃
3.2	3.4	1.1	1.1 ₅
3.2	3.3	1.1	1.2
2.2	2.2	2.0	2.0 ₆
1.9	1.8	0.6	0.5
0.9	0.7 ₇	0.6	0.6 ₆

with silver, the DNZ solutions were standardized by separately titrating either mercury or zinc standard solutions.

Lead and thallium(I), in 50- μg amounts, did not interfere with the titration, but metal ions such as nickel, cobalt and copper, or large amounts of citrate, did. The consecutive titration therefore requires the separation of mercury and of zinc from the bulk of any sample.

It may be concluded that the spectrophotometric extractive titrations with DNZ are feasible; in comparison with titrations with dithizone they have advantages mainly related to the absence of the formation of secondary chelates, so that, e.g., silver can be determined in an ammoniacal medium. The higher values of molar absorptivity of DNZ chelates did not lead to higher absolute sensitivity, because of the limiting effect of the variability of blanks. A serious shortcoming of titrations with DNZ is the necessity of carefully protecting the titrant both from light and heat.

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Summary—An investigation of the possibilities of the use of di-2-naphthylthiocarbazon as titrant in spectrophotometric extractive titrations has been undertaken. A selective procedure for successive titration of silver in an ammoniacal medium has been developed and applied to the analysis of germanium dioxide. It has been established that the consecutive titration of mercury and zinc in the microgram range is possible. Because of low selectivity of this titration, a separation of mercury and zinc from other ions is necessary.

Résumé—On a entrepris une investigation des possibilités d'emploi de la di-2-naphtylthiocarbazon comme agent de titrage dans les titrages par extraction spectrophotométriques. On a élaboré une technique sélective pour le dosage courant de l'argent dans un milieu ammoniacal et on l'a appliquée à l'analyse du bioxyde de germanium. On a établi que le titrage consécutif du mercure et du zinc dans le domaine du microgramme est possible. A cause de la faible sélectivité de ce titrage, une séparation des mercure et zinc des autres ions est nécessaire.

Zusammenfassung—Die Verwendungsmöglichkeiten von Di-2-naphthylthiocarbazon als Titrant bei spektrophotometrischen extraktiven Titrationen wurden untersucht. Eine selektive Vorschrift zur Titration von Silber in ammoniakalischem Medium wurde entwickelt und auf die Analyse von Germaniumdioxid angewandt. Es wurde festgestellt, daß die Titration von Quecksilber und Zink nacheinander im Mikrogrammbereich möglich ist. Da die Titration wenig selektiv ist, müssen Quecksilber und Zink von anderen Ionen abgetrennt werden.

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Determination of atmospheric iron particulates by X-ray fluorescence spectroscopy

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ATMOSPHERIC iron particulates as iron oxides present a serious hazard to human beings. Iron oxide fumes are generated, for example, in welding operations. It has been shown that continued exposure to concentrations above 30 mg/m³ may cause chronic bronchitis.^{1,2} Atmospheric iron particulates have been determined by emission spectrography³ and by atomic-absorption spectroscopy.⁴ The former has relatively poor precision and accuracy compared with the latter, though that suffers from inter-element effects.

The good precision and accuracy of X-ray fluorescence spectroscopy have been well documented in other articles⁵⁻⁹ on trace analysis. The inter-element effects in the present method were neglected because of the lack of heavy elements, the abundance of lighter elements as matrix, and the thinness¹⁰ of samples collected on membranes.

EXPERIMENTAL

Reagents

All chemicals used were of reagent grade. Distilled demineralized water was used throughout.

Preparation of standards

Pure iron wire (1.000 g) was dissolved in 10 ml of hydrochloric acid (1 + 1) and diluted to 1 litre with water. This solution contained 1000 μg of iron per ml, and was diluted further as required. Portions containing 1000, 300, 100, 30 and 10 μg of iron, were added each to 10 ml of water, and ammonia solution was then added dropwise to precipitate hydrous iron(III) oxide. After checking by atomic-absorption spectroscopy for completeness of precipitation, the precipitates were filtered off on membranes which could be used as iron standards with or without a Mylar film covering¹¹ and which were reasonably permanent.

Apparatus

A Norelco air-path X-ray fluorescence spectrometer with tungsten tube operated at 50 kV and 40 mA, lithium fluoride analyser crystal and scintillation counter was used. For the preparation of the standards, a Pyrex filter holder (Millipore Corp. cat. no. XX10 047 00) with 47-mm PH membranes of 0.30 μm pore size was used.

Procedure

An inverted polyethylene cup is pressed on to the membrane disk so that the precipitate of hydrous iron(III) oxide or unknown sample is exposed through the opening. The sample holder with disk and sample backing is then inverted in the X-ray unit and the intensity of the $\text{FeK}\alpha$ line is measured. A blank membrane is used to obtain a correction for background.

RESULTS AND DISCUSSION

Background interference

Since blanks may cause significant errors in trace analysis, an investigation was made into the contribution of $\text{FeK}\alpha$ intensity from the tungsten target tube, Mylar, precipitating reagent, membrane and sample backing. Compared with about 5 cps from 10 μg of iron in the sample, none of the blanks showed any significant contribution to the $\text{FeK}\alpha$ signal.

A similar study was also made on various filters. Neither regular filter paper nor a Millipore membrane showed any detectable iron while a glass-fibre filter appeared to contain about 5 μg of iron. A silver membrane also showed very little iron but the back-scattering was so serious that the metallic membrane was considered unsuitable for the present work.

Back-scattering

In order to improve signal-to-noise ratio a sample backing was sought which would give the least back-scattering. Of those studied an inverted polyethylene cup was found to be the most suitable. Metallic backings enhanced the $\text{FeK}\alpha$ radiation by approximately 15%, but were unsuitable because of their higher back-scattering.

Inter-element effects

Based on information about the chemical compositions of the atmospheric particulates reported,¹² a study was made of some inter-element effects. No significant inter-element effects were observed that were greater than the experimental error of approximately 5% (Table I).

Working curve

The count-rate was plotted on a log-log scale for amounts of iron between 10 and 1000 μg . The recorded peaks and the calibration curve are shown in Fig. 1. It appears that the working curve is

TABLE I.—INTENSITIES (cps) OF $\text{FeK}\alpha$ LINE FROM 100 μg OF IRON IN THE PRESENCE OF SOME OTHER ELEMENTS

Element	Amount added, μg			
	0	100	500	1000
Silicon	49.5	45.6	45.9	47.8
Aluminium	47.5	45.5	48.2	46.2
Magnesium	47.5	48.2	48.0	46.5
Calcium	49.5	48.2	46.5	47.0

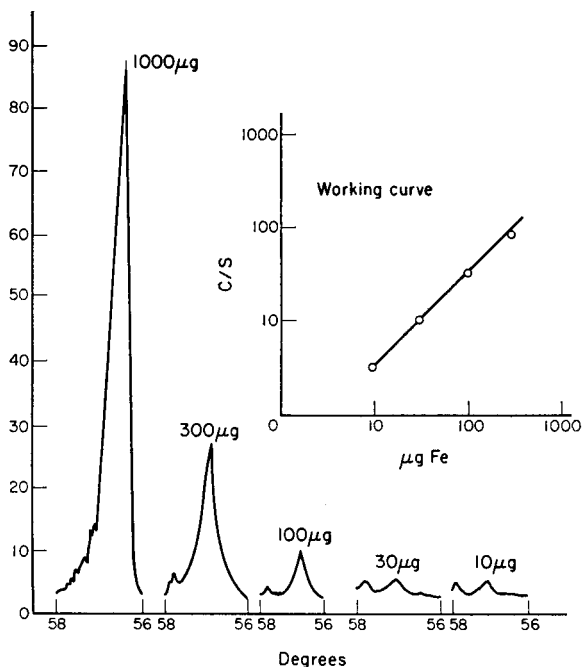


FIG. 1.—X-ray fluorescence spectra of iron standards, and the calibration graph.

linear up to 1000 μg of iron as hydrous iron(III) oxide, but it is doubtful whether the linearity will still hold up to 1000 μg of iron in actual atmospheric samples, because of increasing thickness of the samples collected on the membranes. No further attempt was made to ascertain the linearity beyond 1000 μg of iron.

Precision and accuracy

The precision for five different standard samples of 100 μg of iron determined by this method was checked, and a relative standard deviation of $\pm 5.4\%$ was obtained at a concentration level of 100 μg of iron, with an average count-rate of 46.5 cps.

Table II shows the results of analyses by this method and by a wet chemical method for various collected samples. Samples 1-4 were taken in a wet-chemical laboratory for the analysis of alloys, and samples 5-10 were taken near a machine workshop. The average error of $\pm 6.7\%$ in the concentration ranges shown compares favourably with that of atomic-absorption spectroscopy⁴ for this concentration range.

TABLE II.—ACCURACY OF THE X-RAY FLUORESCENCE METHOD

Sample No.	Iron found, $\mu\text{g}/\text{m}^3$		Difference, %
	X-ray method	Chemical method	
1	23	25	-8.0
2	29	32	-9.4
3	42	40	+5.0
4	45	49	-8.2
5	88	82	+7.3
6	87	91	-4.4
7	125	115	+6.1
8	141	133	+6.0
9	265	282	-6.0
10	340	359	-5.3

In conclusion the present method was found to be suitable for the determination of iron in the atmospheric samples with satisfactory precision and accuracy. The sensitivity of the method could be improved by using a thinner beryllium window in the X-ray chamber, by utilizing smaller membranes for sample-collection and by the use of a better detector system. The disadvantages of the X-ray fluorescence method are the complications due to inter-element effects, especially when large amounts of sample are collected, and the difficulty in preparing proper standards.

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JAE Y. HWANG

Summary—A method is described for the determination of atmospheric iron particulates by X-ray fluorescence spectroscopy. Samples are collected, with a low-volume air sampler, on organic membranes which are used directly for measurement by comparison with standards prepared by precipitation of hydrous iron(III) oxide on similar membranes. The method is simple and rapid, and offers a precision and error of about 6% for the range 10–200 μg of iron.

Zusammenfassung—Ein Verfahren zur Bestimmung atmosphärischer Eisen-Schwebeteilchen durch Röntgenfluoreszenzspektroskopie wird beschrieben. Die Proben werden mit einem kleinvolumigen Luft-Probenahmegerät auf organischen Membranen gesammelt; diese werden direkt zur Messung verwendet und mit Standards verglichen, die durch Fällern von Eisen(III)oxidhydrat auf gleichartige Membranen hergestellt werden. Das Verfahren ist einfach und schnell. Genauigkeit und Fehler betragen etwa 6% im Bereich 10–200 μg Eisen.

Résumé—On décrit une méthode pour la détermination de particules de fer atmosphérique par spectroscopie de fluorescence de rayons X. Les échantillons sont collectés, avec un échantillonneur d'air de faible volume, sur des membranes organiques que l'on utilise directement pour la mesure par comparaison avec des étalons préparés par précipitation d'oxyde de fer(III) hydraté sur des membranes similaires. La méthode est simple et rapide, et offre une précision et une erreur d'environ 6% dans le domaine 10–200 μg de fer.

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NOTICES

SECOND CONFERENCE ON PARTICLE SIZE ANALYSIS

9-11 SEPTEMBER 1970 AT THE UNIVERSITY OF BRADFORD

Papers are invited dealing with original work on methods of particle size and surface area measurement, and their applications in practice.

Abstracts (not more than 300 words) should be submitted by September 30th, 1969, to the Conference Secretary, Society for Analytical Chemistry, 9/10 Savile Row, London, W1X 1AF. The full texts of papers that are accepted will be required by February 1st, 1970.

Further information can be obtained from the Conference Secretary.

SYMPOSIUM ON NON-AQUEOUS ELECTROCHEMISTRY

under the auspices of

THE INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Paris, France, 8-10 July 1970

Topics: Solvation, Electroanalytical Methods in Non-Aqueous Solvents, Electrochemical Investigation of Ionic Equilibria (acid-base, redox, complexation, *etc*), Organic Electrode Reactions.

Note: Studies encompassing these subjects in fused salts will be included in the coverage.

The number of participants is restricted to 200: registration fee; \$30.

For further information apply to the Executive Chairman, Dr. J. Badoz-Lambling, Laboratoire de Chimie Analytique, ESPCI 10 rue Vauquelin, PARIS 5, France.

INTERNATIONAL SOLVENT EXTRACTION CONFERENCE 1971

This Conference will be held under the auspices of The Society of Chemical Industry, Koninklijk Instituut van Ingenieurs, The Institution of Chemical Engineers, and Koninklijk Nederlandse Chemische Vereniging, in The Hague, Holland, 19-23 April 1971. Offers of papers must be made by 28 February 1970. Further information may be obtained from ISEC '71, 14 Belgrave Square, London, S.W.1.

PAPERS RECEIVED

- 2,1,3-Naphtho(2,3-c)-selenadiazole as a reagent for the determination of macro to sub-micro quantities of palladium:** HERBERT K. Y. LAU and PETER F. LOTT. (23 October 1969)
- Determination of Co, Cu, Fe, Ga, W and Zn in rocks by neutron-activation and anion exchange-separation:** O. JOHANSEN and E. STEINNES. (27 October 1969)
- Theory of titration curves—VII. The properties of derivative titration curves for strong acid—strong base and other isovalent ion-combination titrations:** THELMA MEITES and LOUIS MEITES. (27 October 1969)
- Spectrophotometric determination of niobium by 8-hydroxyquinoline-5-sulphonic acid:** G. C. SHIVAHARE and M. K. MATHUR. (28 October 1969)
- Spectrophotometric determination of nickel(II) with phosphomolybdic acid:** R. L. HELLER and J. C. GUYON. (28 October 1969)
- Contributions to the analytical chemistry of osmium and ruthenium—IX. The dimercapto derivatives of asymmetric triazine as colour reagents for osmium:** GR. POPA, C. LAZĂR and C. CRISTESCU. (3 November 1969)
- Studies on a new 2,2'-bipyridyl hexathiocyanato chromate(III):** M. L. ANAND. (3 November 1969)
- Molar absorptivity and stability of some complex compounds of the form BA_n:** I. PARALESCU. (3 November 1969)
- Studies on extraction into nitrobenzene—II. On the mechanism of the extraction of phosphomolybdic acid and traces of caesium:** J. RAIS and P. SELUCKÝ. (5 November 1969)
- Sulphoxides as solvating reagents for the separation of metal ions:** DAVID C. KENNEDY and J. S. FRITZ. (7 November 1969)
- Extraction chromatography of uranium with dioctylsulphoxide:** J. S. FRITZ and DAVID C. KENNEDY. (7 November 1969)
- Spectrophotometric determination of ruthenium(III) and iridium(IV) and spectral characteristics of other noble metal complexes with 8-hydroxyquinoline N-oxide:** R. D. GUPTA, G. S. MANKU, A. N. BHAT and B. D. JAIN. (10 November 1969)
- Rapid ion-exchange determination of caesium-137 in natural waters with inorganic exchange materials supported on silica gel—II. Ammonium phosphomolybdate-silica gel:** KIKUO TERADA, KIYOSHI SAWADA and TOSHIYASU KIBA. (11 November 1969)
- Composition of the thorium(IV)-8-hydroxyquinoline adduct:** A. CORSINI and J. ABRAHAM. (11 November 1969)
- Kinetchromic spectrophotometry—III. Determination of fluoride via catalysis of the zirconium-Methylthymol Blue reaction:** R. V. HEMS, G. F. KIRKBRIGHT and T. S. WEST. (12 November 1969)
- Alizarin Red S as metallochromic indicator:** RAJINDER PAL SINGH. (17 November 1969)
- Determination of platinum, palladium and silver in geological materials and their concentrates by fire assay and emission spectrography:** E. G. KOLEVA and S. H. ARPADJIAN. (19 November 1969)

PUBLICATIONS RECEIVED

XXIst International Congress of Pure and Applied Chemistry, Prague, 1967. Congress Lectures Butterworths, London, 1969. pp. 273. £5.00.

Three fields of chemistry received special attention at this Congress: Automation in Analytical chemistry, Toxicological chemistry, and Chemistry of nucleic acid components. The topics covered in the second section are of considerable interest to a very wide group of readers, including the many analytical chemists whose job it is to detect and determine traces of toxic compounds. The lectures are entitled Dangers de l'ère chimique, The fate of foreign compounds in man and animals, Exposure tests in industrial toxicology, Diagnosis of poisoning by products in the home, and Analysis of biological material in industrial toxicology.

The first section includes lectures on more familiar topics with a general discussion of Analytical chemistry and automation, and more specific papers on Automation of analytical processes (in steel works), Controlled-potential electrolysis and the rates of homogeneous reactions, Automation in functional group analysis, and Automation in the elucidation of the structure of organic compounds. The contents of the book also appear in *Pure and Applied Chemistry*, 1969, Vol. 18.

Solute-solvent interactions: Eds. J. F. COETZEE and CALVIN D. RITCHIE, Dekker, New York and London, 1969. pp. 653. \$29.50.

The rapidly increasing interest in the nature of solutions and the thorough physicochemical study of their properties in connection with other branches of chemistry such as acid-base work, non-aqueous solutions, and reaction kinetics has prompted the publication of this book. The interest among analytical chemists in this field is obviously growing, too, and many will find a perusal of some of the chapters of this book worthwhile and stimulating. The first two chapters, on Heats and entropies of ionization (a critical survey of published data for Brønsted acids in aqueous solution) and Medium effects and pH in non-aqueous solvents (dealing with the theory and problems of pH scales and pH measurement) serve as an introduction to the subsequent six chapters on Acidity functions, Interactions in dipolar aprotic solvents, The selective solvation of ions in mixed solvents, Solvent isotope effect on thermodynamics of non-reacting solutes, Solvent isotope effects for equilibrium and reactions, and Organoalkali compounds in ethers. This is a useful up-to-date reference book for the research worker.

Introduction to the Chemical Analysis of Plastics: A. KRAUSE and A. LANGE, Iliffe, London, 1969. Pp. x + 225. 60s.

This is essentially a laboratory handbook on the identification of plastics, plasticizers and fillers by simple chemical and physical tests. No theory is given and methods such as spectrophotometry, polarography and gas chromatography are intentionally omitted. A wide range of materials is covered and the volume, which keeps within the limits stated, should be of value for identification and in the preparation of more complex methods of analysis.

Pharmaceutical Chemistry, Vol. 2: Ed. L. G. CHATTEN. Pp. xiv + 773 Dekker, New York and London, 1969. Pp. xiv + 773. £14; \$29.50.

This comprehensive book is the second of two volumes and deals with the theory and application of instrumental techniques in pharmaceutical analysis. Although directed mainly at the senior undergraduate and postgraduate student of pharmacy, it should serve as a valuable reference work for the practising pharmaceutical chemist himself. This volume contains chapters on the following topics: ultraviolet, visible and infrared spectrophotometry, Raman spectroscopy, fluorimetry, mass spectrometry, nuclear magnetic resonance, gas chromatography, polarography, atomic-absorption, X-ray and radiochemical methods, turbidimetry and nephelometry, optical crystallography, refractometry, polarimetry, potentiometric and amperometric titrations, current flow methods, coulometric methods and chronopotentiometry. Most chapters provide a comprehensive list and some chapters include questions, problems and practical experiments to demonstrate certain applications. Each monograph is clearly written and well illustrated, containing many photographs and diagrams of modern analytical instruments.

A Programmed Introduction to Gas-Liquid Chromatography: J. B. PATTISON. Heydon, London, 1969. Pp. xv + 303. 45s.

This book contains a great deal of very familiar data presented in a rather unusual form. The approach is that of an elementary textbook on physical chemistry dealing with the vapour-liquid equilibria. There is a fair amount of practical detail, some rather trivial in character and a series of questions and answers. The book is suitable for sixth-form students and first-year degree courses.

Liquids and Liquid Mixtures, 2nd Ed.: J. S. ROWLINSON. Butterworths, London, 1969, pp. xv + 371. £6 10s.

This is a revised second edition of a definitive work by the world authority on the subject. The scope of the book is largely unchanged, but all tables have been recalculated. The material includes the thermodynamic treatment of vapour-liquid equilibria for pure liquids and an interpretation of the phenomena associated with mixing in terms of inter-molecular forces. The book provides an excellent basis for an advanced course for graduate students.

Outline of Industrial Organic Chemistry: ALFRED RIECHE. Butterworths, London, 1968. Pp. xix + 572. 98s.

This is a translation of the 3rd edition (1964) of "Grundriss der technischen organischen Chemie" originally based on lectures by the author at Jena University. The coverage is very wide and the text is supplemented by numerous tables of technical and economic data. The chemistry of coal, oil and natural gas, hydrocarbons and derivatives occupies one half of the book, the second half being divided in approximately equal parts between carbohydrates, fermentation chemistry, and fats and soaps (100 pp) synthetic organic chemistry and plastics (85 pp) and pharmaceuticals, dyestuffs and explosives (90 pp). This is both a useful reference work and an interesting history of the organic chemical industry.

Electrochemistry at Solid Electrodes: RALPH N. ADAMS. Dekker, New York, 1969. Pp. 402. \$18.75.

The aim of this book is to discuss the use and application of solid electrodes, the approach being essentially that of the experimentalist. The first half covers the theoretical considerations, and the second has chapters on Investigation of electrode processes, Fabrication of electrode systems, and Applications to organic compounds. The large amount of valuable practical information in the second part reflects the author's wide experience in this field. The book is aimed at graduates and research students, particularly those in the field of organic electrochemistry.

Lipid Chromatographic Analysis, Vol. 2: Ed. GUIDO V. MARINETTI. Dekker, New York, 1969. Pp. xii + 596. \$27.50.

The various authors have produced a compilation of established and new techniques of value in the chromatographic analysis of steroids, sterols, bile acids, alcohols, prostaglandins, vitamins A and D, tocopherols and other compounds. One of the main advantages of the book is that minor, but important, manipulative and other practical points are explained. There is considerable and valuable critical appraisal of the various methods, and literature up to 1966 is well covered in addition to a few references to more recent literature. The literary style is uneven. There are numerous laboratory colloquialisms and several misprints. The book will serve as a valuable concise handbook on the subject.

Molten Salts: Ed. GLEB MAMANTOV. Dekker, New York, 1969. Pp. xvi + 611. \$16.75; £6.

This collection of essays on the chemistry of molten salts gives a useful picture of current research and thinking in this field of chemistry, and may prove fruitful in catalysing analytical thought on the application of molten salt systems to analysis.

SUMMARIES FOR CARD INDEXES

Comparative distribution coefficients and cation-exchange behaviour of the alkaline earth elements with various complexing agents: F. W. E. STRELOW and C. H. S. W. WEINERT, *Talanta*, 1970, 17, 1. (National Chemical Research Laboratory, P.O. Box 395, Pretoria, S. Africa.)

Summary—Equilibrium distribution coefficients are presented for the alkaline earth metals Be(II), Mg(II), Ca(II), Sr(II) and Ba(II) with the complexing agents acetate, formate, lactate, citrate, tartrate, α -hydroxyisobutyrate, malonate, malate, acetylacetonate, EDTA, EGTA and DCTA, and the AG50W-X8 cation-exchange resin. Coefficients in HCl, HNO₃, HClO₄ and NH₄Cl are included for the sake of completeness. The merits of the various complexing agents for the separation of adjacent element pairs are discussed and experimental elution curves are presented for selected separations. Separation factors for adjacent elements are calculated at eluting agent concentrations corresponding to a distribution coefficient of 10 for the less strongly absorbed element and are presented together with the eluting agent concentrations to form a basis for comparison.

Analytical applications of ternary complexes—VIII. An improved reagent system for the spectrophotometric determination of aluminium: J. E. CHESTER, R. M. DAGNALL and T. S. WEST, *Talanta*, 1970, 17, 13. (Chemistry Department, Imperial College, London, S.W.7, U.K.)

Summary—Aluminium ions form a ternary complex with Catechol Violet (CV) and cetyltrimethylammonium bromide (CTAB) in which an Al³⁺:CV:CTAB ratio of 1:2:5 is observed. The sensitivity of the binary complex between aluminium and Catechol Violet $\epsilon_{615\text{nm}} = 1.50 \times 10^3 \text{ l. mole}^{-1} \cdot \text{mm}^{-1}$ is enhanced on ternary complex formation to $\epsilon_{670\text{nm}} = 5.30 \times 10^3 \text{ l. mole}^{-1} \cdot \text{mm}^{-1}$. The colour is formed instantaneously, stabilizes within 20 min, and may be used for the detection of aluminium in the range 0.27–54 μm in the presence of EDTA which prevents the interference of most ions. A benzoate extraction procedure for aluminium is used to prevent interference from hundred-fold amounts of Cr(VI), Fe(II), Fe(III), Hg(II), Sb(III), Ti(IV) and acetate, but Be, Cr(III), rare earths, V(V), Zr and tartrate must be absent, as must high concentrations of phosphate and fluoride ions.

**СРАВНИТЕЛЬНЫЕ КОЭФФИЦИЕНТЫ
РАСПРЕДЕЛЕНИЯ И КАТИОНООБМЕННЫЕ
ХАРАКТЕРИСТИКИ ЩЕЛОЧНОЗЕМЕЛЬНЫХ
ЭЛЕМЕНТОВ С РАЗНЫМИ
КОМПЛЕКСООБРАЗУЮЩИМИ АГЕНТАМИ:**

F. W. E. STRELOW and C. H. S. W. WEINERT, *Talanta*, 1970, 17, 1

Резюме—Приведены равновесные коэффициенты распределения для щелочноземельных элементов Be(II), Mg(II), Ca(II), Sr(II) и Ba(II) с комплексообразующими агентами ацетатом, формиатом, лактатом, цитратом, тартаратом, α -оксиизобутиратом, малонатом, малатом, ацетилацетонатом, ЭДТА, ЭГТА и ДЦТА, и катионообменной смолой AG50W-X8. В качестве комплетности также включены коэффициенты в HCl, HNO₃, HNCIO₄ и NH₄Cl. Обсуждены преимущества различных комплексообразующих агентов для разделения соседних пар элементов и приведены экспериментальные кривые элюирования для отобранных разделений. Вычислены факторы разделения соседних элементов для концентраций элюирующего агента отвествующих коэффициенту распределения 10 для менее сильно абсорбированного элемента и приведены вместе с концентрациями элюирующего агента, с целью послужить в качестве основы для сравнения.

**ПРИМЕНЕНИЕ ТРОЙНЫХ КОМПЛЕКСОВ В
АНАЛИЗЕ—VIII. УЛУЧШЕННАЯ СИСТЕМА
РЕАГЕНТОВ ДЛЯ ОПРЕДЕЛЕНИЯ АЛЮМИНИЯ
СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ:**

J. E. CHESTER, R. M. DAGNALL and T. S. WEST, *Talanta*, 1970, 17, 13.

Резюме—Ионы алюминия образуют тронной комплекс с катехиновым фиолетовым (КФ) и цетилтриметиламмонийбромидом (ЦТАБ) в котором отношение Al³⁺:КФ:ЦТАБ равно 1:2:5. Чувствительность двойного комплекса алюминия и катехинового фиолетового $\epsilon_{615\text{nm}} = 1,50 \times 10^3$ л.моль⁻¹.мм⁻¹ повышается образованием тройного комплекса до $\epsilon_{670\text{nm}} = 5,30 \times 10^3$ л.моль⁻¹.мм⁻¹. Окраска появляется мгновенно, стабилизируется в течение 20 мин и ее можно пользоваться для обнаружения алюминия в пределах 0,27–54 мг/л в присутствии ЭДТА который уклоняет влияние большинства ионов, Экстракция алюминия бензоатом использована для уклонения влияния 100-кратного избытка Cr(VI), Fe(II), Fe(III), Hg(II), Sb(III), Ti(IV) и ацетата, но Be, Cr(III), редкоземельные элементы, V(V), Zr и тартарат надо отсутствовать, так же как и высокие концентрации фосфат- и фторидионов.

Performance characteristics of analytical methods—I: A. L. WILSON, *Talanta*, 1970, 17, 21. (Water Research Association, Ferry Lane, Medmenham, Nr. Marlow Bucks, U.K.)

Summary—The ever-increasing volume of analytical literature makes it important to be able to compare unambiguously the advantages and disadvantages of analytical methods. To this end, a set of consistent definitions and methods for determining quantitative performance-characteristics (*e.g.*, precision, sensitivity, bias) is needed. The aim of this series of papers is to review the definition and determination of such parameters, and to suggest criteria for general use. This first paper discusses the general problem, considers those general aspects of analytical methods that are important, and establishes the performance-characteristics to be considered in detail.

The performance-characteristics of analytical methods—II: A. L. WILSON, *Talanta*, 1970, 17, 31. (Water Research Association, Ferry Lane, Medmenham, Nr. Marlow, Bucks. U.K.)

Summary—Statements on the errors of analytical results are an important aspect of characterizing the performance of analytical methods. The general nature of random and systematic errors is briefly discussed, and methods of numerically defining the former are considered. It is suggested that the standard deviation of analytical results be used exclusively as the quantitative measure of precision within the context of performance-characteristics. Techniques for, and precautions to be observed in, estimating standard deviation are critically discussed. On this basis, general principles are proposed that should be observed whenever possible in experimental tests to estimate standard deviation.

***N*-Acetylsalicyloyl-*N*-phenylhydroxylamine as an analytical reagent. Determination of niobium and tantalum in the presence of each other:** C. P. SAVARIAR and JOY JOSEPH, *Talanta*, 1970, 17, 45. (Department of Chemistry, University of Calicut, Kerala, India.)

Summary—*N*-Acetylsalicyloyl-*N*-phenylhydroxylamine is proposed for the separation of niobium(V) and tantalum(V) and their gravimetric determination. Niobium is precipitated at pH 5.5–6.5 by the reagent and the complex is weighed directly. Tantalum is precipitated from 1–2*M* hydrochloric acid solutions and the complex is ignited to tantalum pentoxide. The method is fairly selective. In the presence of thiocyanate the reagent forms an extractable complex with niobium. The reaction forms the basis of a selective and sensitive spectrophotometric determination of niobium.

ХАРАКТЕРИСТИКИ ВЫПОЛНЕНИЯ АНАЛИТИЧЕСКИХ МЕТОДОВ—I:

A. L. WILSON, *Talanta*, 1970, 17, 21.

Резюме—Резко увеличивающийся объем аналитической литературы вызывает потребность сравнивать однозначно преимущества и невыгодности аналитических методов. В этом качестве надо иметь последовательные дефиниции и методы определения количественных характеристик выполнения (на пример точности, чувствительности, склонности). Цель этого ряда статей сделать обзор дефиниций и определения этих параметров и предложить критерии для общего применения. Предлагаемая статья обсуждает общую проблему и важные общие виды аналитических методов, и обозначает изучаемые подробно характеристики выполнения.

ХАРАКТЕРИСТИКИ ВЫПОЛНЕНИЯ АНАЛИТИЧЕСКИХ МЕТОДОВ—II:

A. L. WILSON, *Talanta*, 1970, 17, 31.

Резюме—Сообщение ошибок аналитических результатов представляет собой важный вид охарактеризования аналитических методов. Коротко обсужден общий характер случайных и систематических ошибок и сравнены методы цифрового определения этих ошибок. Предложено исключительное применение стандартного отклонения аналитических результатов в качестве количественной меры точности в смысле характеристик выполнения. Критически обсуждены методы определения стандартного отклонения и меры предосторожности в этом определении. На этой основе предложены общие принципы которые надо почитать—если обстоит возможность—в опытах определения стандартного отклонения.

N-АЦЕТИЛСАЛИЦИЛОИЛ-*N*-ФЕНИЛГИДРОКСИЛАМИН В КАЧЕСТВЕ АНАЛИТИЧЕСКОГО РЕАГЕНТА: ОПРЕДЕЛЕНИЕ НИОБИЯ И ТАНТАЛА ОДНОГО В ПРИСУТСТВИИ ДРУГОГО:

C. P. SAVARIAR and JOY JOSEPH, *Talanta*, 1970, 17, 45.

Резюме—*N*-Ацетилсалицилоил-*N*-фенилгидроксиламин предложен для разделения ниобия(V) и тантала(V) и их определения весовым методом. Ниобий осаждают реагентом при рН 5,5–6,5 и комплекс прямо взвешивают. Тантал осаждают из 1–2*M* содянокислых растворов и комплекс обзоливают до пятиокиси тантала. Метод является довольно избирательным. В присутствии роданида реагент образует экстрагируемый комплекс с ниобием. На этой реакции основан селективный и чувствительный спектрофотометрический метод определения ниобия.

Determination of deuterium in heavy water by secondary deuteron activation: R. PRETORIUS and R. E. WAINERDI,[®] *Talanta*, 1970, 17, 51. (Activation Analysis Research Laboratory, Texas A & M University, College Station, Texas, U.S.A.)

Summary—The deuterium concentration of heavy water was determined by utilizing recoiling deuterium nuclei from n-d collisions to induce the reaction $^{18}\text{O}(\text{d}, \text{n})^{17}\text{F}$. The internal ratio of 66-sec fluorine-17 to 7.35-sec nitrogen-16 activity, formed by the reaction $^{18}\text{O}(\text{n}, \text{p})^{18}\text{N}$, was found to vary linearly with deuterium concentration. When such an internal ratio of activities is measured, the neutron flux and sample weight need not be known. Deuterium was determined over the range from 2.6 to 94.5 atom %, with a relative standard deviation of 2.8%. The effect of sample size was investigated and it was found that the relative amount of fluorine-17 activity formed became less as sample size decreased, due to the loss of recoiling deuterons from the sample. A simple relationship to account for this effect was obtained.

Rapid spectrophotometric determination of boron in steel: OM P BHARGAVA and W. GRANT HINES, *Talanta*, 1970, 17, 61. (Chemical and Metallurgical Laboratories, The Steel Company of Canada Ltd., Wilcox Street, Hamilton, Ontario, Canada.)

Summary—A rapid spectrophotometric method is presented for the determination of boron in steel by use of the fluoborate-Methylene Blue complex. The method is in principle similar to that of Rosotte, but modifications simplify the operation, obviate contamination and avoid problems with emulsion formation. Up to 20% Cr, 10% Ni, and 1% each of V, Mo and W present either individually or collectively do not interfere in the determination, making it applicable to alloy steels. The determination limit of the method has been lowered from 5 to 0.2 ppm boron. Samples are dissolved at room temperature in polythene bottles, solubilizing all forms of boron including boron nitride, and avoiding loss of relatively volatile boron compounds. The precision of the method is good. Six samples can be analysed in less than 2 hr.

ОПРЕДЕЛЕНИЕ ДЕЙТЕРИЯ В ТЯЖЕЛОЙ ВОДЕ
МЕТОДОМ ВТОРИЧНОЙ ДЕЙТЕРОННОЙ
АКТИВАЦИИ:

R. PRETORIUS and R. E. WAINERD[®], *Talanta*, 1970, 17, 51.

Резюме—Концентрация дейтерия в тяжелой воде определена использованием ядер дейтерия отдачи из $n - d$ сразов для индуцирования реакции $^{16}\text{O}(d, n)^{17}\text{F}$. Обнаружена линейная зависимость концентрации дейтерия от внутреннего отношения активности 66-сек фтор-17 в 7,35-сек азот-16, образованной реакцией $^{16}\text{O}(n, p)^{16}\text{N}$. При измерении такого внутреннего отношения активностей не надо определять поток нейтронов ни вес образца. Дейтерий определен в пределах 2,6 до 94,5 атомных %, с относительной стандартной ошибкой 2,8 %. Изучено влияние веса образца и обнаружено что относительная активность фтора-17 уменьшается с уменьшением веса образца в результате потер дейтронов отдачи из образца. Обнаружено простое отношение для объяснения этого эффекта.

БЫСТРОЕ СПЕКТРОФОТОМЕТРИЧЕСКОЕ
ОПРЕДЕЛЕНИЕ БОРА В СТАЛИ:

Om P. BHARGAVA and W. GRANT HINES, *Talanta*, 1970, 17, 61.

Резюме—Предложен быстрый спектрофотометрический метод определения бора в стали, пользующийся комплексом фторобората с метиленовым синим. В принципе метод похожий методу Розотта, но модификации упрощают процедуру, избегают загрязнение и проблемы образования эмульсий. До 20 % Cr, 10 % N и 1 % V, Mo или W не мешают определению если присутствуют индивидуально или коллективно, этим образом позволяя применение метода в анализе легированных сталях. Чувствительность метода снижена от 5 до 0,2 мкг/г бора. Пробы растворяют при комнатной температуре в полиэтиленовых склянках, с растворением Всехформ бора включая нитрид бора, а избегая потери довольно летучих соединений бора. Метод дает хорошую воспроизводимость, а позволяет анализировать шесть проб в меньше чем 2 ч.

Anion-exchange separation and spectrophotometric determination of molybdenum and tungsten in silicate rocks: KAZUAKI KAWABUCHI and ROKURO KURODA, *Talanta*, 1970, 17, 67. (Laboratory for Analytical Chemistry, Faculty of Engineering, University of Chiba, Yayoi-cho, Chiba, Japan.)

Summary—A combined ion-exchange spectrophotometric method has been developed for the determination of molybdenum and tungsten in silicate rocks. After the decomposition of samples with a mixture of sulphuric, nitric and hydrofluoric acids, traces of molybdenum and tungsten are separated from other elements by anion-exchange in acid sulphate media containing hydrogen peroxide. The adsorbed molybdenum and tungsten can easily be stripped from the column by elution with sodium hydroxide-sodium chloride solution. The adsorption and desorption steps provide selective concentration of molybdenum and tungsten, allowing the simultaneous spectrophotometric determination of the two metals with dithiol. Results on the quantitative determination of molybdenum and tungsten in the U.S. Geological Survey standard samples are included.

Use of 3-hydroxy-1,3-diphenyltriazine in the spectrophotometric determination of copper, palladium, iron, cobalt, nickel, and molybdenum: B. DAS and S. C. SHOME, *Talanta*, 1970, 17, 75. (Chemical Laboratory, Presidency College, Calcutta, India.)

Summary—3-Hydroxy-1,3-diphenyltriazine (HDPTA) forms brightly coloured complexes with copper, palladium, iron, cobalt and nickel ions, which are readily extractable in benzene. The deep yellow molybdenum complex is completely soluble in 60% ethanol. All the chelates have a definite absorption maximum between 398 and 422 nm, the reagent absorption being negligible above 415 nm. The molar composition of the chelates is ML_2 , except for iron and cobalt which form ML_3 complexes. Microquantities of these metals can be determined spectrophotometrically with HDPTA.

АНИОНООБМЕННОЕ РАЗДЕЛЕНИЕ И
ОПРЕДЕЛЕНИЕ СПЕКТРОФОТОМЕТРИЧЕСКИМ
МЕТОДОМ МОЛИБДЕНА И ВОЛЬФРАМА В
СИЛИКАТНЫХ ГОРНЫХ ПОРОДАХ:

KAZUAKI KAWABUCHI and ROKURO KURODA, *Talanta*, 1970, 17, 67.

Резюме—Разработан комбинированный ионообменно-спектрофотометрический метод для определения молибдена и вольфрама в силикатных горных породах. После разложения образцов с смесью серной, азотной и фтороводородной кислот, следы молибдена и вольфрама отделяют от других элементов анионным обменом в сернокислой среде, содержащей перекись водорода. Адсорбированные элементы молибден и вольфрам легко элюируют из колонки раствором гидроксида натрия и хлорида натрия. Фазы адсорбции и десорбции позволяют селективное концентрирование молибдена и вольфрама и одновременное спектрофотометрическое определение этих металлов с дитиолом. Приведены результаты количественного анализа молибдена и вольфрама в эталонах U.S. Geological Survey.

ИСПОЛЬЗОВАНИЕ 3-ОКСИ-1,3-ДИФЕНИЛТРИАЗИНА
ДЛЯ СПЕКТРОФОТОМЕТРИЧЕСКОГО
ОПРЕДЕЛЕНИЯ МЕДИ, ПАЛЛАДИЯ, ЖЕЛЕЗА,
КОБАЛЬТА, НИКЕЛЯ И МОЛИБДЕНА:

V. DAS and S. C. SHOME, *Talanta*, 1970, 17, 75.

Резюме—3-Окси-1,3-дифенилтриазин (ОДФТА) образует яркоокрашенные комплексы с ионами меди, палладия, железа, кобальта и никеля, которые легко извлекаются бензолом. Темножелтый комплекс молибдена полностью растворимый в 60% спирте. Все комплексы имеют определенный максимум светопоглощения в пределах 398–422 нм, не принимая во внимание поглощение реагента выше 415 нм. Молекулярный состав хелатов ML_2 исключая железо и кобальт, которые образуют комплексы ML_3 . ОДФТА позволяет определять микроколичества этих металлов спектрофотометрическим методом.

A separation scheme for the analysis of multicomponent samples: JAMES S. FRITZ and GARY L. LATWESEN, *Talanta*, 1970, 17, 81. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—A sequential separation scheme has been devised for the quantitative analytical separation of 27 different metal ions. Five different chromatographic and ion-exchange columns are used to separate the metal ions into groups. The metal ions of each group are eluted separately from each column by means of selective eluents. Following separation, the metal ions are determined by titrimetry, flame spectrometry or other appropriate analytical methods. The reliability of the proposed scheme has been demonstrated by extensive testing, including the analysis of U.S. National Bureau of Standards samples. The scheme can be used for macro or micro quantities.

Metallextraktionen mit aliphatischen Alkoholen: EUGEN GAGLIARDI and PETER TÜMLER, *Talanta*, 1970, 17, 93. (Institut für Anorganische und Analytische Chemie der Universität Graz, Österreich.)

Summary—A number of metal ions may be extracted quantitatively from iodide-containing sulphuric acid solutions by 2-ethyl-1-butanol, 4-methyl-2-propanol, or 1-butoxy-2-propanol, some partially extracted, and others not at all. There are many possibilities for separations, two of which—zinc-cadmium and indium-gallium—are described, and have been tested in technical products. The determination of the composition of the extracted metal complexes is described with reference to those of mercury, a conductimetric extraction titration being used.

Spectrophotometric determination of niobium(V) with n-propyl 3,4,5-trihydroxybenzoate: FADHIL JASIM, *Talanta*, 1970, 17, 103. (Department of Chemistry and Food Technology, College of Agriculture, University of Baghdad, Baghdad, Iraq.)

Summary—The use of n-propyl 3,4,5-trihydroxybenzoate (PTB) for the spectrophotometric determination of niobium is investigated. PTB yields a yellowish-orange ML_2 chelate with Nb(V) at pH 6.1. The formation constant at pH 6.1 is about 10^{10} . Beer's law is obeyed over the range 0–100 μg of Nb per ml.

СХЕМА РАЗДЕЛЕНИЯ ДЛЯ АНАЛИЗА МНОГОКОМПОНЕНТНЫХ ОБРАЗЦОВ:

JAMES S. FRITZ and GARY L. LATWESSEN, *Talanta*, 1970, 17, 81.

Резюме—Разработана последовательная схема разделения для количественного аналитического разделения 27 различных ионов металлов. Использовано пять различных хроматографических и ионообменных колонок для разделения ионов металлов в группы. Ионы металлов каждой группы элюируются отделенно из каждой колонки с использованием селективных элюентов. После разделения ионы металлов определены титриметрическими или пламенно-фотометрическими методами или другими подходящими аналитическими. Прочность предложенной схемы подтверждена тщательным испытыванием, включая анализ образцов U.S. National Bureau of Standards. Схема применима на макро- или микрошкале.

ЭКСТРАКЦИЯ МЕТАЛЛОВ С АЛИФАТИЧЕСКИМИ СПИРТАМИ:

EUGEN GAGLIARDI and PETER TÜMMLER, *Talanta*, 1970, 17, 93.

Резюме—Ряд ионов металлов можно экстрагировать количественно из иодидсодержащих растворов серной кислоты 2-этил-1-бутанолом, 4-метил-2-пропанолом или 1-бутоксид-2-пропанолом, некоторые ионы экстрагированы частично, некоторые совсем не экстрагированы. Даны многие возможности разделения, две из них—цинк-кадмий и индий-галлий—были испытаны на технических продуктах. Описано определение состава экстрагированных комплексов металлов, ссылаясь на комплексы ртути, с применением кондуктометрической экстракционной титрации.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИОБИЯ(V) Н-ПРОПИЛ-3,4,5-ТРИОКСИБЕНЗОАТОМ:

FADHIL JASIM, *Talanta*, 1970, 17, 103.

Резюме—Исследовано применение н-пропил-3,4,5-триоксибензоата (ПТБ) в спектрофотометрическом определении ниобия. ПТБ дает желтооранжевый ML_2 комплекс с Nb(V) при pH 6,1. Константа образования при pH 6,1 равна приблизительно 10^{10} . Закон Бера почитается в пределах 0–100 мкг/мл Nb.

Determination of gadolinium in sodium borate glasses: RENATA REISFELD and EHUD BIRON, *Talanta*, 1970, 17, 105. (Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel.)

Summary—A method for the determination of gadolinium in sodium borate glasses is described which utilizes the 312-nm fluorescence of gadolinium under 273-nm excitation. A linear dependence of fluorescence on concentration is found for the concentration range 10–20000 ppm. Quenching of gadolinium fluorescence by samarium is examined.

Polarographic determination of impurities in high purity phosphorus: T. MIWA, T. KONO, R. ISOMURA and A. MIZUIKE, *Talanta*, 1970, 17, 108. (Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan.)

Summary—Square-wave and radio-frequency polarographic techniques in phosphoric acid-potassium chloride media are applied to the simultaneous determination of copper, lead and cadmium in high-purity red phosphorus down to a level of 0.1 ppm. In addition *ca.* 0.01 ppm of cadmium is determined by R.F. polarography in potassium sulphate base electrolyte after cation-exchange separation.

Submicro determination of cobalt, manganese or nickel in organometallic compounds: R. BELCHER®, BARBARA CROSSLAND and T. R. F. W. FENNELL, *Talanta*, 1970, 17, 112. (Department of Chemistry, The University, P.O. Box 363, Birmingham 15, U.K.)

Summary—Methods for the determination of cobalt, manganese or nickel in samples of organometallic compounds weighing 30–100 μg have been developed. Spectrophotometric determination following digestion with nitric and sulphuric acids in a sealed tube is recommended, all results obtained from the analysis of standard compounds being within $\pm 0.4\%$ absolute error. Digestion in an open tube with perchloric and sulphuric acids gives slightly low results for cobalt and nickel compounds and is inappropriate for manganese compounds.

ОПРЕДЕЛЕНИЕ ГАДОЛИНИЯ В НАТРИЙБОРАТНЫХ СТЕКЛАХ:

RENETA REISFELD and EHUD BIRON, *Talanta*, 1970, 17, 105.

Резюме—Описан метод определения гадолиния в натрийборатных стеклах, основан на флуоресценции гадолиния при 312 нм с возбуждением при 273 нм. Обнаружена линейная зависимость флуоресценции от концентрации в пределах 10–20000 частей на миллион. Изучено погашение самарием флуоресценции гадолиния.

ОПРЕДЕЛЕНИЕ ПРИМЕСЕЙ В ВЫСОКОЧИСТОТНОМ ФОСФОРЕ ПОЛЯРОГРАФИЧЕСКИМ МЕТОДОМ:

T. MIWA, T. KONO, R. ISOMURA and A. MIZUKE, *Talanta*, 1970, 17, 108.

Резюме—Полярографические методы квадратной волны и радиочастоты использованы в средах фосфорной кислоты и хлорида калия для одновременного определения меди, свинца и кадмия в высокочистотном красном фосфоре до концентрации 0,1 мкг/г. Кроме того можно определять около 0,01 мкг/г кадмия методом радиочастотной полярографии на фоне сльфата калия после выделения катионообменным методом.

СУБМИКРОМЕТОД ОПРЕДЕЛЕНИЯ КОБАЛЬТА, МАРГАНЦА ИЛИ НИКЕЛЯ В МЕТАЛЛООРГАНИЧЕСКИХ СОЕДИНЕНИЯХ:

R. BELCHER®, BARBARA CROSSLAND and T. R. F. W. FENNELL, *Talanta*, 1970, 17, 112.

Резюме—Разработаны методы определения кобальта, марганца или никеля в 30–100 мкг пробы металлоорганических соединений. Предложено дигерирование с азотной и серной кислотами в закрытой трубке с последующим спектрофотометрическим определением; ошибка полученных на стандартных соединениях результатов составляла меньше чем $\pm 0,4\%$ абс. Дигерированием в открытой трубке с хлорной и серной кислотами получают незначительно низкие результаты в случае соединений кобальта и никеля, а метод неприемлем в случае соединений марганца.

Spectrophotometric extractive titrations—VII. Titrations with di-2-naphthylthiocarbazone: A. GALÍK, *Talanta*, 1970, 17, 115. (Lachema, N.C., Kaznějov, Czechoslovakia.)

Summary—An investigation of the possibilities of the use of di-2-naphthylthiocarbazone as titrant in spectrophotometric extractive titrations has been undertaken. A selective procedure for successive titration of silver in an ammoniacal medium has been developed and applied to the analysis of germanium dioxide. It has been established that the consecutive titration of mercury and zinc in the microgram range is possible. Because of low selectivity of this titration, a separation of mercury and zinc from other ions is necessary.

Determination of atmospheric iron particulates by X-ray fluorescence spectroscopy: JAE Y. HWANG, *Talanta*, 1970, 17, 118. (Applications Laboratory, Instrumentation Laboratory Inc., 113 Hartwell Avenue, Lexington, Mass. 02173, U.S.A.)

Summary—A method is described for the determination of atmospheric iron particulates by X-ray fluorescence spectroscopy. Samples are collected, with a low-volume air sampler, on organic membranes which are used directly for measurement by comparison with standards prepared by precipitation of hydrous iron(III) oxide on similar membranes. The method is simple and rapid, and offers a precision and error of about 6% for the range 10–200 μg of iron.

ЭКСТРАКЦИОННО-СПЕКТРОФОТОМЕТРИЧЕСКИЕ
ТИТРАЦИИ—VII. ТИТРАЦИИ С
ДИ-2-НАФТИЛТИОКАРБАЗОНОМ:

A. GALÍK, *Talanta*, 1970, 17, 115.

Резюме—Исучена применимость ди-2-нафтилтиокарбазона в качестве титрационного раствора для экстракционно-спектрофотометрических титраций. Разработан селективный метод последовательного титрования серебра в аммиачной среде и применен в анализе двуокиси германия. Последовательное титрование микрограммовых количеств ртути и цинка оказалось осуществимым. Вследствие низкой селективности этой титрации надо провести отделение ртути и цинка от других ионов.

ОПРЕДЕЛЕНИЕ ЧАСТИЦ ЖЕЛЕЗА В ВОЗДУХЕ
МЕТОДОМ РЕНТГЕНОВСКОГО ФЛУОРЕСЦЕНТНОГО

JAЕ Y. HWANG, *Talanta*, 1970, 17, 118.

Резюме—Описан метод определения частиц железа в воздухе методом рентгеновского флуоресцентного анализа. Пробы собирают при помощи прибора для пропускания небольших объемов воздуха на органических мембранах, которые служат для прямого измерения в сравнении с эталонами, приготовленными осаждением гидроокиси железа(III) на подобных мембранах. Метод является несложным и быстрым, его точность и ошибка равны 6% в области 10–200 мкг железа.

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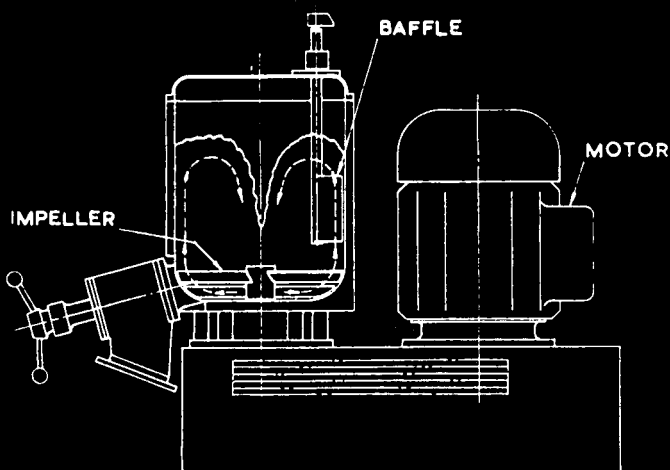
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