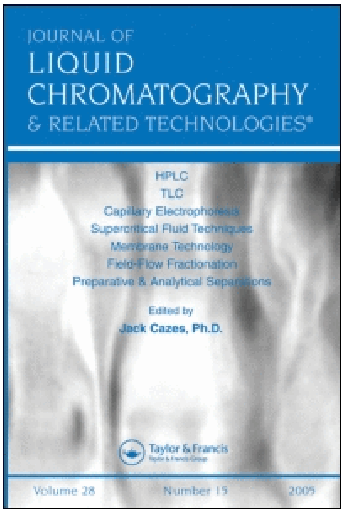

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QUANTITATIVE DETERMINATION OF IRON AND ALUMINIUM IN SOME ALLOYS AND SILICATE ROCKS AFTER A CATION EXCHANGE SEPARATION ON ZIRCONIUM(IV) PHOSPHO AND SILICO ARSENATES

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ABSTRACT

A rapid and quantitative method has been developed for the analysis of some iron and aluminium based alloys and silicate rocks using zirconium(IV) based arsenophosphate and arsenosilicate cation exchangers. The method is simple, reproducible and precise with a standard deviation $<3\%$, for the direct determination of iron and aluminium in rocks and alloys. The low standard deviation values suggest that the method should be useful for the standardization purposes.

INTRODUCTION

Analysis of alloys and rocks is important in chemical technology as the presence of various constituents play a vital role in their applications. Although several papers have earlier been published in this field using well known analytical techniques (1-5), the ion-exchange technique is more useful as it gives fast separation of the ionic species present. However such studies have been made mostly on organic

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resins (6,7) probably because of their excellent reproducibility and stability.

Inorganic ion-exchangers are well known for their high selectivity for metal ions and stability at elevated temperatures (8). Zirconium(IV) arsenophosphate (ZAP) and Zr(IV) arsenosilicate (ZAS) prepared in these laboratories (9,10) possess exceptionally good chemical stability and reproducibility in ion-exchange behaviour which improve further for ZAP on heating. A possibility of using these materials for the quantitative separation of metal ions from their synthetic mixtures and from some real samples has already been explored earlier in these laboratories (10). The present article summarizes our efforts for a quantitative separation of aluminium and iron from some alloys and rocks on their columns.

EXPERIMENTAL

Chemicals and Reagents

Zirconyl chloride used in these studies was of J.T.Baker Chemical Co.Philipsburg (USA), while tri-sodium orthophosphate was of BDH, Poole (London). Di-sodium arsenate and sodium silicate were E-Merck (Dermstadt) products and all other reagents and chemicals were of analaR grade.

Apparatus

A pye unichem model SP-2900 atomic absorption spectrophotometer was used for the quantitative determination of various elements present in rocks and alloys.

Synthesis and Ion-Exchange Capacity of ZAP and ZAS

These materials were synthesized by the methods reported earlier (9,10) and were thermally treated by putting them at various temperatures for one hour each in a muffle furnace. They were washed thoroughly with dil.HNO_3 and then with demineralized water (DMW) till the effluents were free of any metallic or non metallic impurities as tested by atomic absorption spectrophotometry. The Na^+-ion-exchange capacities of various samples thus obtained are reported in Table 1. On this basis a heated phase of ZAP upto 200 °C (α-ZAP) and normal ZAS were used for further studies.

Distribution Studies

The distribution coefficients (Kd) for various metal ions were determined as usual by the batch process on α-ZAP and ZAS (10). Table 2 shows a comparative statement of these values in DMW and HNO_3.

TABLE 1

Ion-Exchange Capacity of ZAP and ZAS After Thermal Treatment

Heating temperature (°C)	Ion-exchange capacity (meq./dry g.)		% Retention in ion-exchange capacity	
	ZAP	ZAS	ZAP	ZAS
45	0.94	1.30	100.0	100.0
100	0.95	1.30	101.1	100.0
200	1.03	1.25	109.6	96.2
400	0.94	0.46	100.0	35.4
600	0.84	0.20	89.4	15.4

TABLE 2

Kd values of Various Metal Ions on α-ZAP and ZAS in DMW and HNO_3 Media

Metal ions	DMW		0.01M HNO_3		0.1M HNO_3		1M HNO_3	
	α-ZAP	ZAS	α-ZAP	ZAS	α-ZAP	ZAS	α-ZAP	ZAS
Ba(II)	1900	110	83	105	65	91	0	0
Cd(II)	5400	8030	1750	186	507	130	0	0
Pb(II)	5650	5430	360	1580	268	1460	0	0
Mg(II)	4400	367	20	77	3	63	0	0
Sr(II)	3150	218	0	35	0	3	0	0
Hg(II)	326	52	30	58	20	41	0	0
Mn(II)	3530	69	52	13	45	9	0	0
Ca(II)	3700	314	0	81	0	36	0	0
Zn(II)	3280	1000	28	57	8	36	0	0
Ni(II)	5150	8000	68	206	20	190	0	0
Co(II)	5150	600	5	700	5	409	0	0
Cu(II)	3250	85	126	2	3	0	0	0
Sn(II)	1800	61	2	1	0	0	0	0
Fe(II)	3900	3850	3900	293	630	210	0	0
Al(II)	3900	4350	3900	3880	320	320	0	0

Analysis of the Samples for Iron and Aluminium

A. Preparation of the Standard Solutions:

The standard solutions were prepared as follows:

Synthetic Alloy Samples

Various metallic solutions were mixed in certain ratios so that they correspond to the actual metallic proportions in the standard alloys.

Standard Alloy Samples

An accurately weighed amount of the alloy was dissolved in a minimum amount of aquaregia followed by the dilution to a desired volume with DMW.

Rock Samples

Twenty milliliters of 15% NaOH were heated in a Ni-crucible until melted and then fused with 100 mg. of the sample for 5-6 minutes at dull red heat ($\sim 600^{\circ}C$). The melt was cooled and 100 ml of DMW was added. After keeping overnight the liquid was transferred to a 1 liter volumetric flask containing 40 ml of 1:1 HCl and the volume made upto the mark with DMW.

B. Separation and Determination of Fe(III) and Al(III)

It was done as follows:
Two grams of the 60-100 mesh sized particles of the ion exchanger in H^+-form were packed in a glass tube having an internal diameter ~ 0.6 cm and fitted with glass wool at the bottom. The sample solution (1-5 ml) was evaporated to almost dryness to remove the excess acid and the residue was dissolved in a small amount (1-3 ml) of DMW which was then loaded on the column.

TABLE 3

Quantitative Separation of Iron/Aluminium from Some Synthetic Alloys Using α-ZAP and ZAS Columns

Synthetic alloy and its composition (μg) per ml of the solution		Aluminium/iron obtained* in the effluent (μg)				% Error				% Standard deviation			
		α-ZAP		ZAS		α-ZAP		ZAS		α-ZAP		ZAS	
		Al	Fe	Al	Fe	Al	Fe	Al	Fe	Al	Fe	Al	Fe
Dow metal	(Al 40, Mn 15, Mg 945)	41.2	-	40.3	-	+3.00	-	+0.75	-	0.50	-	0.90	-
-do-	(Al 120, Mn 10, Mg 870)	118.3	-	122.4	-	-1.42	-	+2.00	-	0.80	-	0.95	-
Aluminium-zinc binary alloy	(Al 750, Zn 250)	745	-	743	-	-0.67	-	-0.93	-	1.40	-	2.30	-
-do-	(Al 950, Zn 50)	939	-	941	-	-1.16	-	-0.95	-	2.10	-	1.60	-
Aluminium bronze	(Al 100, Cu 900)	99.5	-	101.5	-	-0.50	-	+1.50	-	0.46	-	1.20	-
-do-	(Al 120, Cu 875, Sn 5)	122.4	-	123.0	-	+2.00	-	+2.50	-	0.75	-	1.20	-
Magnalium	(Al 850, Mg 150)	843.6	-	847.6	-	+0.75	-	-0.28	-	1.80	-	2.80	-
-do-	(Al 900, Mg 100)	890.9	-	904.2	-	-1.01	-	+0.47	-	1.30	-	0.30	-
-do-	(Al 925, Mg 75)	932.4	-	918.9	-	+0.80	-	-0.66	-	0.65	-	0.34	-
Y-alloy	(Al 940, Ni 20, Mn 10, Cu 50)	937.3	-	946.1	-	-0.29	-	+0.65	-	0.70	-	0.46	-
Duralumin	(Al 950, Mn 5, Mg 6, Cu 40)	944.9	-	959.1	-	-0.54	-	+0.95	-	0.15	-	0.42	-
Manganese steel	(Fe 879, Mn 120)	-	887.2	-	884.2	-	+0.93	-	+0.59	-	1.03	-	0.94
-do-	(Fe 849, Mn 150)	-	841.6	-	853.6	-	-0.87	-	+0.54	-	1.20	-	0.58
Nickel steel	(Fe 944, Ni 36, Mn 18)	-	921.8	-	-	-	-2.35	-	-	-	0.66	-	-
Chrome steel	(Fe 965, Mn 19, Cr 15)	-	957.0	-	-	-	-0.83	-	-	-	0.85	-	-
-do-	(Fe 960, Mn 19, Cr 20)	-	949.9	-	-	-	-1.05	-	-	-	0.30	-	-
Invar	(Fe 620, Ni 360, Mn 19.5)	-	609.8	-	-	-	-1.65	-	-	-	1.40	-	-
Stainless steel	(Fe 734, Ni 80, Mn 5, Cr 180)	-	730.5	-	-	-	-0.48	-	-	-	1.98	-	-
Nichrome	(Fe 120, Ni 750, Mn 20, Cr 110)	-	119.2	-	-	-	-0.67	-	-	-	0.21	-	-

*Average value of four replicates.

TABLE 4

Quantitative Separation of Iron from Some Standard Steel Samples Using α-ZAP Columns

Steel analysed	Volume of the stock solution loaded (Ml)	Elements present as per the standard composition of the steel (µg)						Iron determined in the effluent*** (µg)	% Error	% Standard deviation
		Fe	Cr	Ni	Cu	Mn	Si			
AISI-303*	1.0	222.80	56.52	26.69	-	4.71	1.57	230.46	+3.44	0.17
	2.0	445.60	113.04	53.38	-	9.42	3.14	454.40	+1.97	0.94
	2.5	557.00	141.30	66.725	-	11.775	3.925	566.40	+1.69	0.81
AISI-347*	1.0	219.40	56.52	31.40	-	4.71	1.57	225.13	+2.61	0.96
	2.0	438.80	113.04	62.80	-	9.42	3.14	446.26	+1.70	1.26
	2.5	548.50	141.30	78.50	-	11.775	3.925	554.43	+1.08	0.57
	3.0	658.20	169.56	94.20	-	14.13	4.71	626.42	-4.83	0.44
Inconel-600**	1.0	66.60	155.80	769.3	1.6	2.0	-	64.80	-2.70	0.75
Inconel-800**	1.0	451.4	209.90	319.8	2.9	8.1	-	450.20	-0.27	0.58

*A.I.S.I. Standard Steels.

**Huntington Alloy Products, Division of International Nickel Co., U.S.A.

***Average value of five replicates.

TABLE 5

Quantitative Separation of Aluminium and Iron from Various U.S.G.S. Standard Rocks Using α-ZAP and ZAS Columns

Rock analysed	Standard composition of the rock for Al and Fe per 5 ml of the stock solution (µg)		Al_2O_3 and Fe_2O_3 obtained* in the effluent (µg)				% Error				% Standard deviation			
			α-ZAP		ZAS		α-ZAP		ZAS		α-ZAP		ZAS	
	Al_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3
G-2	77.00	13.45	78.00	13.80	79.00	18.80	+1.30	+2.60	+2.59	+2.60	1.94	0.65	1.64	1.06
AGV-1	85.95	38.90	85.40	39.20	87.00	38.50	-0.64	+0.77	+1.22	-1.02	1.38	1.97	0.94	1.10
BHVO-1	68.50	60.00	69.45	61.00	71.00	59.25	+1.39	+1.67	+3.64	-1.25	2.99	2.99	1.89	2.10
BCR-1	68.60	67.05	69.45	69.00	69.80	68.10	+1.24	+2.91	+1.74	+1.56	1.75	1.86	2.14	1.40
PCC-1	3.65	41.40	3.57	40.35	3.60	40.70	-2.19	-2.54	-1.36	-1.69	0.47	1.31	0.68	0.95

*Average values of five replicates.

All the elements except Al and Fe were eluted out either in DMW or 0.01M HNO_3 (max.volume ~150 ml). These metals were then leached out with 1M HNO_3 (max. volume ~100 ml) and determined quantitatively by atomic absorption spectrophotometry. The observations are summarized in Tables 3-5.

RESULTS AND DISCUSSION

The essential feature of these studies is to use inorganic ion exchangers for the analysis of some alloys and silicate rocks. As it is clear from Table 2, the distribution behavior of ZAP is significantly affected on heating. The heated phase of this material (α-ZAP) becomes highly selective for Al(III) and Fe(III). Also, zirconium(IV) arsenosilicate preferentially holds these two ions (10). This property of these two ion-exchangers has been successfully utilized for the separation and quantitative determination of Al(III) and Fe(III) in some alloys and silicate rocks. When a solution of these samples (synthetic or real) is passed through the ion-exchange column with a very slow rate, only Al(III) and Fe(III) ions are retained and others are completely excluded by the column simply in DMW or 0.01M HNO_3. They are then eluted out in 1M HNO_3. (Tables 3-5). The method is quite simple and requires much less time as compared to the classical methods. Furthermore, quite a large number of samples can be analyzed using a single column because these materials have shown the excellent reproducibility in their ion exchange behavior, and then ion exchange capacity is not affected even after several recycling processes. Since ZAS has a high Kd value for Ni(II) ions it could not be used for the separation of iron in the nickel containing steels. For such analyses, however, α-ZAP is quite suitable (Tables 3,4).

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