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Determination of Gallium in Red Mud after its Separation with β-Diketo Liquid Chelating Exchanger

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A selective and quantitative method for the extraction of gallium(III) in methyl *iso*butylketone medium using a β-diketo liquid chelating exchanger is described. The conditions of separation of gallium *i.e.*, pH, solvent, kinetics of extraction and the effects of various ions have been studied. The method has been applied successfully for the determination of gallium in red mud samples. To evaluate the accuracy of the method, the results were also checked with ICP–MS. Spiked recovery (98.2–101.5%) of gallium in red mud samples was also investigated.

INTRODUCTION

In animals gallium acts as a neuromuscular poison and causes renal damage. Photophobia, blindness and paralysis have been reported in rats. Aplastic changes in the bone marrow have been observed in dogs[1]. So the determination of gallium is important from environmental viewpoint. Its determination is also of significance because of the use of radiogallium as a diagnostic tool for localization of bone lesions. Gallium has been determined spectrophotometrically using various chromogenic agents[2–7] in aqueous medium or extraction into organic solvents. Gallium was also determined by ion chromatography[8]. Since gallium melts at 30°C, there is a manufacturing problem for a good hollow cathode lamp. Although atomic absorption spectrometry (AAS) is a popular method for trace analysis, because of this problem as well as due to poor sensitivity, work on gallium by AAS is scanty. Nevertheless, the influence of many ions on gallium signal in flame AAS and a spectral interference due to manganese have been reported[9, 10]. β-Diketo liquid chelating exchanger (LCE, $RCOCH_2COCH_3$ where $R = C_9H_{19}$) have been synthesised and applied for the extraction and preconcentration of various metals[11–15].

In the present work, a method for the separation of gallium has been developed using this liquid chelating exchanger (LCE) and the method has been applied for the preconcentration and trace determination of gallium in red mud samples.

EXPERIMENTAL

All inorganic chemicals used were of analytical reagent grade or comparable

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purity. Doubly distilled water was used throughout the work. A stock solution of gallium (1882 ppm) was prepared by dissolving the pure metal in minimum amount of dilute hydrochloric acid and the solution was standardized complexometrically[16]. A 0.1 M ethanolic solution of the liquid chelating exchanger was prepared.

Standard Procedure

An aliquot (0.10 ml) of gallium(III) solution containing 188.2 μg of the element was taken. The pH of the solution was adjusted to 7.0 using ammonium hydroxide solution to which 2.0 ml of tris-buffer of pH 7.0 were added. This was transferred to a separatory funnel and 1.0 ml of ethanolic solution of LCE (0.1 M) was added to it. The mixture was shaken for 2 min, then 5 ml methyl *iso*-butyl ketone (MIBK) was added and shaken again for 1 min. The resulting mixture was allowed to settle for 1.5 min to attain the equilibrium. The organic phase was transferred to another separatory funnel. The aqueous phase was again shaken and washed with 5 ml of MIBK to remove traces of organic phase entrained in the aqueous phase. Then the organic phase was stripped with 10 ml of 0.1 N hydrochloric acid. The aqueous part was then quantitatively taken for spectrophotometric measurements[17] and absorbance value was measured at 390 nm in a spectrophotometer against a reagent blank. The amount of gallium was computed from the calibration graph.

RESULTS AND DISCUSSION

Optimization of Variables

The extraction of gallium using LCE was investigated as a function of pH. The working pH range for quantitative extraction of the element was 6.0–7.0. Now the extraction behaviour of gallium was studied from aqueous solution having a definite pH into various organic solvents containing liquid exchanger. The results indicate that most quantitative extraction of gallium occurs with MIBK, the percentage of extraction being 100. Extraction with other solvents shows 90% in amyl alcohol, 88% in benzene, 72% in chloroform, 56% in cyclohexane and 50% in carbon tetrachloride.

The effect of concentration of LCE on the extraction of gallium was investigated and it was found that the extraction was quantitative with 8×10^{-3} mM of LCE for 188.2 μg of gallium. But an excess of the exchanger was used, which did not affect the separation.

Gallium was completely stripped back from the MIBK layer using 0.1 M hydrochloric acid solution. Two minutes and thrity seconds were enough for extraction and back-extraction respectively. In both cases two minutes were allowed to attain the equilibrium.

Separation from Various Ions

Gallium (188.2 μg) was separated from the binary mixtures of various ions within an error of not more than ±2% (the ion concentration is indicated in parentheses): Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-} (1000 μg each); Pb^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, Tl^{3+}, F^-, In^{3+} (2000 μg each); La^{3+}, Th^{4+}, Al^{3+}, Cr^{3+}, MoO_4^{2-}, VO_3^- (1500 μg each); Ti^{4+}, Zr^{4+}, PO_4^{3-} (1000 μg each); Fe^{3+} (200 μg).

The separation of gallium (188.2 μg) was possible in the presence of more than one foreign ion in the following mixtures within an error of not more than ± 2%:

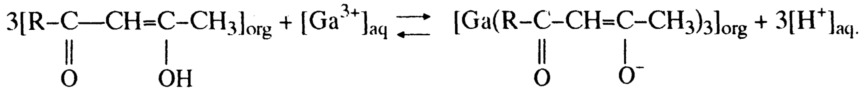
(a) Ca^{2+} (2000 μg) + Mg^{2+} (1000 μg) + F^- (500 μg);
(b) Na^+ (10000 μg) + Ti^{4+} (500 μg) + VO_3^- (500 μg);
(c) Mn^{2+} (1000 μg) + Zn^{2+} (1000 μg) + Ca^{2+} (1000 μg);
(d) Ba^{2+} (2000 μg) + Tl^{3+} (1000 μg) + MoO_4^{2-} (2000 μg).

Nature of the Extracted Species

The composition of the extracted species was determined by using a definite amount of gallium and varying the pH of the medium. The stoichiometry of the complex was determined using the following equation[18]

$$\log D = \log K_{ex} + (m + n) \log [HLCE] + npH$$

The plot of log D against pH gives a straight line having a slope value of 2.8. This suggests that the extraction mechanism is as follows:



$$3[\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}CH{=}\underset{\underset{OH}{|}}{C}{-}CH_3}]_{org} + [\mathrm{Ga}^{3+}]_{aq} \rightleftharpoons [\mathrm{Ga(R{-}\underset{\underset{O}{\|}}{C}{-}CH{=}\underset{\underset{O^-}{|}}{C}{-}CH_3)_3}]_{org} + 3[\mathrm{H}^+]_{aq}.$$

Application

The method was applied for the determination of gallium in red mud samples. The samples were also analysed by ICP-MS technique. The results have been shown in Table 1. In the case of determination of gallium without separation lower values are obtained due to the presence of matrix elements present in red mud samples. To check the reliability of the method reference samples (marine sediment) were analysed and a second method of analysis (*i.e.* ICP-MS) was also employed. The results obtained were in good agreement with the certified value. Spiked recovery of gallium from the red mud sample (No. 1) was performed to evaluate the accuracy of the method also (Table 2).

TABLE 1
DETERMINATION OF GALLIUM IN RED MUD SAMPLES

Sample	Direct (Without separation)	Amount of gallium* (μg/g)	
		Present method	ICP-MS
Red mud–1	9.48	21.07	20.38
Red mud–2	4.29	7.50	6.90
Red mud–3	7.16	13.75	13.07
Red mud-4	68.47	118.71	117.17
Marine sediment[a] (MESS–1, NRC, Canada)	65.14	20.76	—
Marine Mud[b] (MAG–1, US Geol. Surevey)	—	—	20.27

*Average of three determinations
[a]Certified value: 20 μg/g
[b]Certified value: 20.4 μg/g

TABLE 2
RECOVERY OF GALLIUM FROM RED MUD

Gallium added (μg)	Red mud–1	
	Gallium found (μg)	% Recovery
0.0	21.06	—
9.40	30.29	98.2
18.80	40.15	101.5
28.20	48.85	98.5
37.60	58.40	99.3

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