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Determination of trace impurities in chromium matrices after separation from Cr(III) using the oxalate form of anion exchanger

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Abstract

A method has been developed for the separation and determination of a set of 11 impurities from chromium matrices using oxalate form of Amberlite IRA 93. Due to slower kinetics of formation of the anionic complex, Cr(III) passed in the effluent while impurities forming strong complexes rapidly are retained on the exchanger. The adsorption of impurities of interest is found to be uniform in pH range 2–6. The adsorbed impurities are eluted with 2 mol l^{-1} HNO_3 and determined by inductively coupled plasma-optical emission spectrometer (ICP-OES). The percentage recoveries of Al, Bi, Cd, Co, Cu, Fe, Mn, Ni, Pb, Ga and Zn are in the range 88–101% and separation of matrix is >99.9%. The method has been applied for the analysis of two samples namely $CrCl_3 \cdot 6H_2O$ and Cr. The R.S.D. of the method is 5–6% at >10 $\mu g\,g^{-1}$ level and ∼15% at <1 $\mu g\,g^{-1}$ level. The process blank values are in the range sub-$\mu g\,g^{-1}$ and detection limits are in ng g^{-1} range.

Keywords: Oxalate; Cr(III); Separation; Chromium matrix; Anion exchanger; Amberlite IRA 93; ICP-OES

1. Introduction

High purity metals/materials are known to have several applications [1,2]. The concentration of impurities present in them decides their purity as well as their suitability for specific applications. Chromium is one such metal and analysis of Cr for impurities is of great concern as impurities present in Cr segregates to the grain boundaries causing brittleness due to inter granular fracture [3]. For the determination of impurities in metals the matrix element needs to be separated in order to alleviate matrix effects and preconcentrate impurities [4–6]. The methods reported for the separation of Cr are based on ion exchange involving either as Cr(III) or Cr(VI) [7,8]. Mulokozi and Mosha reported separation of Cr as Cr(III) from Al and Fe by complexing the later as oxalates in 2% oxalic acid solution at low temperatures and passing this solution through an anion exchanger [9]. In this procedure, kinetic inertness of Cr(III) is taken as an advantage. However, this procedure is not suitable for the separation of Cr(III) from divalent transition metals as these metals form weak complexes at lower pH [10]. Hence, there is a need for a simple separation procedure for the determination of impurities present in chromium. We have reported separation of Cr(VI) from Cr(III) using oxalate form of Dowex-1 for the determination of Cr(VI) in potable water [11].

The present paper deals with the separation of impurities from Cr, present as Cr(III), using oxalate form of an anion exchanger at room temperature. The conditions for quantitative recovery of impurities, namely Al, Bi, Cd, Co, Cu, Fe, Mn, Ni, Pb, Ga and Zn, and separation of Cr are also reported. The method has been adopted for the analysis of $CrCl_3 \cdot 6H_2O$ and Cr metal procured locally.

2. Experimental

2.1. Apparatus

An inductively coupled plasma-optical emission spectrometer (ICP-OES), Jobin Yvon, system model no. JY-2000,

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Table 1
Operating parameters of ICP-OES

Power	1.0 kW
Plasma gas flow	$12\,\mathrm{l\,min^{-1}}$
Aerosol flow	$0.5\,\mathrm{l\,min^{-1}}$
Slit width	20 μm/20 μm
Wavelengths (nm)	
Al	396.152
Bi	223.061
Co	228.616
Cd	214.438
Cu	327.396
Fe	238.204
Ga	287.424
Mn	257.610
Ni	221.647
Pb	220.353
Zn	213.856

equipped with a 40.68 MHz rf generator was used for studies and determinations. The operating parameters used were given in Table 1.

2.2. Reagents

Analytical grade reagents were used throughout. Pure water (18 MΩ cm) was prepared by passing potable water through a mixed bed ion exchanger and then through a Milli Q system. Standard solutions of the impurities were procured as multi-element standard solution from E. Merck, Germany.

3. Preparation of resins

(a) *Chloride form of Amberlite IRA 93*: A column of resin (10 g, 50–100 mesh; Sigma, USA) was prepared in a 40 mm i.d. glass column and 100 ml solutions of $2\,\mathrm{mol\,l^{-1}}$ HCl and $2\,\mathrm{mol\,l^{-1}}$ NaOH were passed through it successively with a flow rate of $2\,\mathrm{ml\,min^{-1}}$ with thorough Milli Q water washings in between and finally 50 ml of $6\,\mathrm{mol\,l^{-1}}$ HCl was passed to convert it into chloride form. The chloride form of the resin thus obtained was washed free from the acid.

(b) *Oxalate form of Amberlite IRA 93*: The above resin was converted to the oxalate form by passing 100 ml of 10% potassium oxalate, washed free from excess of oxalate and air-dried.

3.1. Adsorption

A column of 10 mm i.d. was prepared with 2 g of oxalate form of Amberlite IRA 93. Solutions containing a mixture of 25 μg each of analytes of interest in 50 ml at varying pH (1–6) was passed through the column with a flow rate of $1\,\mathrm{ml\,min^{-1}}$. After complete adsorption, the eluate was analyzed by ICP-OES. The percentage adsorption was computed by comparing the signal of unprocessed standards with that of processed standards of analytes. The procedure has been repeated with 1 g of $CrCl_3{\cdot}6H_2O$ solution spiked with 25 μg each of analytes of interest (400 μg in case of Al and Fe) in 50 ml of de-ionized water.

3.2. Elution

After adsorption the adsorbed elements were eluted with varying volumes (5–25 ml) and concentrations ($1\text{–}4\,\mathrm{mol\,l^{-1}}$) of HNO_3 and the eluate was analyzed for impurities as well as Cr against unprocessed standards by ICP-OES.

4. Analytical procedure

Both the samples were dissolved as mentioned below:

(i) $CrCl_3{\cdot}6H_2O$ (1 g) was dissolved in 50 ml water and passed through the resin as such (the pH of the solution was between 2.5 and 3).

(ii) Cr metal (250 mg) was dissolved in 5 ml concentrated HCl on a hot plate at about 200 °C. After complete dissolution, 1 ml HNO_3 was added to it. The mixture was evaporated to dryness on a water bath, diluted to ∼50 ml and pH was adjusted to 2.5–3 using dilute NaOH solution.

The sample solutions prepared as above were passed through a column of the oxalate form of Amberlite IRA 93 (10 mm column i.d.) with a flow rate of $1\,\mathrm{ml\,min^{-1}}$. After adsorption of impurities, the resin was washed with 10 ml de-ionized water. The adsorbed elements were eluted using 25 ml of $2\,\mathrm{mol\,l^{-1}}$ HNO_3 and evaporated to 10 ml before analysis. Sample solutions spiked with known amounts of standards were also processed as mentioned above to establish a standard addition calibration plot. A process blank was also prepared as mentioned above. The solutions after separation of Cr matrix were analyzed for impurities by ICP-OES.

4.1. Validation

The sample solutions [$CrCl_3{\cdot}6H_2O$ (1 g) in 50 ml water, Cr metal (250 mg) in 5 ml concentrated HCl] taken in different beakers were evaporated to near dryness on hot plate and treated with HCl and $HClO_4$. A red color residue was obtained due to the oxidation of Cr(III) to Cr(VI). It was evaporated till the red color disappeared. It was treated with HCl, $HClO_4$ and evaporated till the beaker appeared empty due to the complete oxidation of Cr(III) to Cr(VI) and evaporation of Cr(VI), i.e., CrO_2Cl_2. The contents of the beaker were dissolved with HNO_3 and diluted to 10 ml and analyzed by ICP-OES.

5. Results and discussion

The kinetics of Cr(III) is known to be slow [9,12]. Once Cr(III) solution containing impurities is passed through the oxalate form of Amberlite IRA 93, impurities forming strong complex rapidly with oxalate are sorbed along with the anions present in the solution. Sorption depends on the ease of formation of anionic oxalato complexes, which depend on stability constant and kinetics. Stability constants depend on pH, and increase with increase in pH. At pH 1–2, the divalent cations form weaker complexes and sorption is rather poor. In 2% oxalic acid, pH is ∼1.5 at which the complexation of divalent cations with oxalic acid is poor, and hence cannot be applied for the separation of these ions from Cr(III). In the present procedure, the sample solution is taken at pH 2.5–3 and passed through the oxalate form of the resin, which is a suitable condition for the complexation.

Sorption of metal cations along with anions present in the solution is confirmed by the following experiment. A solution containing 2 mg of Al as chloride is passed through the resin and the effluent is analyzed. It is found that no Al, chloride and oxalate are present in the effluent. The process of sorption can be explained by the following equation:

$$6R_2C_2O_4 + 2AlCl_3 \leftrightarrow 2R_3Al[C_2O_4]_3 + 6RCl$$

where R indicates species retained on the resin phase.

Though Cr(III) also forms a strong complex with the oxalate, in the present experimental conditions it does not form the complex due to its slow kinetics and hence elutes out along with the effluent. However, the conditions need to be optimized in order to achieve quantitative recoveries of impurities of interest.

Table 2
Percentage recovery of impurities on oxalate form of Amberlite IRA 93 with change in pH

Element	Recovery (%) ($n = 3$)			
	pH 1	pH 2	pH 4	pH 6
Al	97	98	99	98
Bi	43	92	88	93
Cd	70	97	94	88
Co	74	98	92	90
Cu	30	97	88	87
Fe	82	101	97	98
Ga	72	91	88	84
Mn	12	96	94	91
Ni	18	101	98	102
Pb	42	88	89	90
Zn	86	100	88	87

All the values are average values of three independent experiments.

Table 3
Percentage elution of impurities with concentration of HNO_3 (mol l^{-1})

Element	Elution (%) ($n = 3$)		
	1	2	3
Al	88	98	109
Bi	84	92	91
Cd	92	97	93
Co	91	98	95
Cu	78	97	98
Fe	88	101	105
Ga	74	91	88
Mn	95	96	93
Ni	92	101	99
Pb	78	88	87
Zn	89	100	88

pH of loading solution is 2.5–3, volume of HNO_3 is 25 ml.

6. Optimization of conditions

6.1. Adsorption

The adsorption conditions have been optimized using 2 g of resin. The pH of the adsorbing solution has been optimized by studying the adsorption as a function of pH. As seen in Table 2, near quantitative adsorption has been obtained in pH range 2–6 and lower adsorptions are found at pH 1. A flow rate of 1 ml min^{-1} is found to be adequate for the adsorption of all the analytes and to avoid complexation of Cr(III) with oxalate. The removal (or elution) of Cr(III) is found to be 99.9% at these conditions.

6.2. Elution

The adsorbed analytes are eluted with varying concentrations of HNO_3. It is found that 25 ml of 2 mol l^{-1} HNO_3 is required to obtain near quantitative recovery of all the analytes (Table 3). A decrease in volume of the eluting solution results in an increase in the preconcentration factor. Hence, the elution has been carried out at different volumes (5–25 ml) of 2 mol l^{-1} HNO_3. Though 10 ml of 2 mol l^{-1} HNO_3 is sufficient to elute all the analytes quantitatively, the recovery of Al is poor (Table 4). To accommodate Al, elution has been carried out using 25 ml of 2 mol l^{-1} HNO_3.

Table 4
Percentage of elution of impurities with change in volume of 2 mol l^{-1} HNO_3

Element	Volume of HNO_3 (ml) ($n = 3$)		
	5	10	25
Al	20	57	98
Bi	31	91	92
Cd	19	98	97
Co	19	97	98
Cu	32	99	97
Fe	8	97	101
Ga	9	89	91
Mn	98	98	96
Ni	63	101	103
Pb	38	101	88
Zn	26	98	100

Table 5
Recoveries of impurities (25 μg) spiked to 1 g of $CrCl_3{\cdot}6H_2O$ or 250 mg of Cr metal

Element	%Recovery	
	$CrCl_3{\cdot}6H_2O$	Cr metal
Al	98.1 ± 2.2[a]	97.4 ± 3.0[b]
Bi	92.0 ± 1.7	90.8 ± 2.1
Cd	97.2 ± 2.6	96.7 ± 3.0
Co	98.1 ± 2.3	97.0 ± 2.8
Cu	97.4 ± 2.0	96.0 ± 1.9
Fe	101.5 ± 1.8[a]	101.9 ± 2.2[a]
Ga	91.8 ± 1.4	93.0 ± 1.1
Mn	96.7 ± 1.9	96.0 ± 1.8
Ni	103.1 ± 2.0	103.0 ± 1.8
Pb	88.7 ± 2.0	89.0 ± 1.5
Zn	100.4 ± 1.8	100.0 ± 1.0

[a] Spiked 400 μg.
[b] 100 μg.

6.3. Recovery

The recoveries of analytes of interest, namely Al, Bi, Cd, Co, Cu, Fe, Mn, Ni, Pb, Ga and Zn, at optimum conditions (i.e., pH of loading solution 2.5–3; flow rate 1 ml min^{-1}; elution using 25 ml of 2 mol l^{-1} HNO_3) are found to be near quantitative. Similar recoveries are observed when the sample solution spiked with all analytes are also passed through the column with a flow rate of 1 ml min^{-1} (Table 5). As the expected levels of Fe and Al are high, the sample solutions are spiked with an excess of these two elements (400 μg each of Fe, Al and 25 μg each of rest of the elements to 10 ml of the sample solution). The recovery of Fe in case of Cr metal is found to be low (60%). To enhance the recovery of Fe (101.9%, Table 5), the sample solution after dissolution in HCl and evaporation, is treated with concentrated HNO_3 to convert any Fe(II) to Fe(III), as Fe(III) forms a stronger oxalato complex than Fe(II). This treatment did not affect the recoveries of other analytes. However, this treatment is not required for the analysis of $CrCl_3{\cdot}6H_2O$ sample. The percentage recoveries have been computed by comparing the value obtained, on subtraction of the actual concentrations of individual elements present in sample from the total concentration of individual elements in the sample spiked with known amounts of standards, i.e., [sample + spike] − [sample] = recovered spike, with that of the actual value of standard spiked. The following equation is used to compute the %recovery:

$$\%\text{Recovery} = \frac{(\text{signal of sample} + \text{spike}) - \text{signal of sample}}{\text{signal of spike}} \times 100$$

7. Application

As the recoveries of analytes are adequate to carry out the separation and preconcentration in Cr matrix, the method has been applied for the analysis of two samples, namely, $CrCl_3{\cdot}6H_2O$ and Cr metal procured locally. The concentrations of impurities present in these samples are given in Table 6. The concentrations reported are per gram of the sample, i.e., per gram of $CrCl_3{\cdot}6H_2O$ in case of $CrCl_3{\cdot}6H_2O$ and per gram of Cr in case of Cr metal. The process blank values and limits of detection calculated as three times the standard deviation (3σ) in the repeated measurements (six) of blank solution for $CrCl_3{\cdot}6H_2O$ sample are given in Table 7.

8. Validation

The results obtained in the present procedure are validated for the accuracy using volatilization procedure in which Cr is volatilized as CrO_2Cl_2 [13]. The comparison of results obtained by the present and volatilization procedures are given in Table 6.

Table 6
Comparison of concentrations of impurities in samples using the present method and volatilization method

Element	$CrCl_3{\cdot}6H_2O$ (μg g^{-1})		Cr metal (μg g^{-1})	
	Present method ($n = 3$)	Volatilization method ($n = 3$)	Present method ($n = 3$)	Volatilization method ($n = 3$)
Al	395 ± 22	357 ± 38	387.7 ± 16	376.0 ± 28
Bi	<1.0	<1.0	16.0 ± 2	20.0 ± 3
Cd	<0.5	<0.5	<2.0	<2.0
Co	<0.1	<0.1	<0.4	<0.4
Cu	0.95 ± 0.13	1.27 ± 0.24	19.7 ± 0.2	22.4 ± 0.3
Fe	305 ± 18	364 ± 36	3509 ± 186	3285 ± 224
Ga	1.6 ± 0.2	2.1 ± 0.5	43.8 ± 0.4	44.1 ± 0.5
Mn	1.5 ± 0.2	1.9 ± 0.4	54.2 ± 0.3	63.3 ± 0.4
Ni	10.7 ± 0.7	11.8 ± 0.9	16.1 ± 0.8	18.8 ± 0.9
Pb	<1.5	<1.5	<5	<5
Zn	2.1 ± 0.3	2.9 ± 0.9	17.6 ± 0.6	17.5 ± 0.9

Uncertainties are given as 1σ variation in measurements of three independent experiments.

Table 7
Process blank and limits of detection values of the present method

Element	Process blank ($\mu g\,g^{-1}$) ($n = 6$)	Limit of detection ($\mu g\,g^{-1}$) ($n = 6$)
Al	4.30	1.00
Bi	1.10	0.23
Cd	0.50	0.16
Co	0.10	0.03
Cu	0.20	0.10
Fe	3.32	1.20
Ga	0.18	0.50
Mn	0.37	0.21
Ni	0.72	0.30
Pb	1.30	0.50
Zn	0.80	0.30

9. Conclusion

The separation of Al, Bi, Cd, Co, Cu, Fe, Mn, Ni, Pb, Ga and Zn as oxalate complexes from Cr matrix has been achieved by taking advantage of kinetic inertness of Cr(III). The procedure reported can be applied to any Cr(III) salt such as nitrate, sulphate, chloride, etc., for the analysis of impurities that form strong complex with oxalate. The method is simple and rapid and can be easily applied for routine sample analysis.

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