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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 μg g^{-1} level and ∼15% at <1 μg g^{-1} level. The process blank values are in the range sub-μg 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	$12\,l\,min^{-1}$
Aerosol flow	$0.5\,l\,min^{-1}$
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 $2\,mol\,l^{-1}$ HCl and $2\,mol\,l^{-1}$ NaOH were passed through it successively with a flow rate of $2\,ml\,min^{-1}$ with thorough Milli Q water washings in between and finally 50 ml of $6\,mol\,l^{-1}$ 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 $1\,ml\,min^{-1}$. 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 ($1–4\,mol\,l^{-1}$) 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 $1\,ml\,min^{-1}$. After adsorption of impurities, the resin was washed with 10 ml de-ionized water. The adsorbed elements were eluted using 25 ml of $2\,mol\,l^{-1}$ 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.