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PRECONCENTRATION AND SEPARATION OF Cr(III) AND Cr(VI) FROM AQUEOUS SYSTEMS USING FLOTATION BY Fe(III) HEPTYLDITHIOCARBAMATE

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Abstract

An accurate and inexpensive method for determination of total Cr in environmental waters with Zeeman electrothermal atomic absorption spectrometry (ZETAAS) following flotation preconcentration step is presented. The possibility of applying Fe(III) hepthyldithiocarbamate, $Fe(HpDTC)_3$, as a collector is studied. The experimental parameters affecting the flotation efficiency by a new collector were optimized. It is ascertained that Cr(III) and Cr(VI) can be separated simultaneously from matrix by addition of 20 mg Fe(III) and 6 ml 0.1 mol/L, hepthyldithiocarbamate anions, $HpDTC^-$, to a test sample of 1000 ml at pH 6.5. The applicability of the new proposed procedure was verified by the method of standard additions and by inductively coupled plasma atomic emission spectrometry (ICP-AES), as an independent comparative method. The limit of detection for Cr is 0.073 μg/l.

Keywords: environmental, waters, chromium, flotation, atomic absorption spectrometry.

Introduction

Chromium is an essential trace element and has a role in glucose metabolism. It seems to have an effect in the action of insulin (Manahan 2000). In anything other than trace amounts, chromium compounds should be regarded as highly toxic, especially Cr(VI) compounds which are highly toxic and carcinogenic (Grushko 1979). Consequently it is very important to know and monitor the trace concentration level of this pollutant in air, soil and aquatic systems.

Commonly the determination of Cr in traces in aquatic systems is performed by analytical methods with very low detection limits as atomic absorption spectrometry (AAS). However, in case of extremely low concentrations, a previous preconcentration step is unavoidable (Grushko 1979, Goyer 1986, Mizuike 1983, Caballero et al. 1990). Among accurate, fast and inexpensive preconcentration methods, that can be applied for Cr preconcentration before AAS is the bubble technique named flotation. The flotation as an analytical separation method has shown as very advantageous and helpful due to its rapidity and excellent recoveries of analytes. Many factors influence to perform a proper flotation, but an important role has the collector (Pavlovska et al. 2003, Ay et al. 2004, Bundalevska et al. 2005). This study describes a new flotation separation of Cr traces from water samples prior to Zeeman electrothermal atomic absorption spectrometry (ZETAAS) using a new collector Fe(III) hepthyldithiocarbamate, $Fe(HpDTC)_3$. The results of ZETAAS analyses would be compared with those obtained by inductively coupled plasma-atomic emission spectrometry (ICP–AES).

Experimental

Instrumentation and reagents: Varian SpectrAA 640Z atomic absorption spectrometer was use for AAS measurements of Cr (Table 1). High purity argon served to protect the graphite furnace during the atomization cycle. The same gas was used for ICP–AES measurements by Varian Liberty 110 (Table 2). All pH readings were carried out with Iskra pH-Meter MA 5705. The flotation cell was a glass cylinder (4 x 105 cm) with a sintered glass disc (porosity No. 4) at the bottom to produce the air bubble stream. All chemicals used were of the highest grade available except for surfactants sodium dodecylsulfate (NaDDS), sodium oleate (NaOL), sodium palmitate (NaPL), sodium stearate (NaST), benzethonium chloride (BTC) and cetyltrimethylammonium bromide (CTAB). To prepare a 50 mg/ml stock solution of $Fe(NO_3)_3$ an appropriate amount of powdered iron (Merck) was dissolved in con. HNO_3. Nitrates of Cr(III) and Cr(VI) (Merck) were used for preparation of analytes stock solutions (1 mg/ml). Intermediate standard solutions were suitably diluted daily. The 0.1 mol/l solution of heptyldithiocarbamate anions, $HpDTC^-$, was prepared daily by dissolving appropriate amount of crystalline NaHpDTC in 96 % ethanol. The solutions of surfactants were made as 0.5 % in 95 % ethanol (NaDDS, NaOL, BTC, CTAB), as well as in 99.7 % propan-2-ol (NaPL, NaST). The pH was regulated by KOH (2.5 % and 10 %) and HNO_3 (0.1 mol/l). Ionic strength (I_c) was adjusted with saturated solution of KNO_3. To transfer the content of the beaker into the flotation cell a 0.1 mol/l NH_4NO_3 solution was used.

Table 1. AAS parameters

ETAAS system	Varian SpectrAA 640Z
	Cr
Wavelength	357.9 nm
Spectral slit	0.5 nm
Lamp current	7 mA
Zeeman's *Background correction*	
Drying	85 °C, 5s
	110 °C, 40 s
	120 °C, 10 s
Atomization	2600 °C, 1.2 s, 2 s
Cleaning	2600 °C, 2 s
Sheath gas	Argon

Table 2. ICP-AES parameters

ICP system	Varian, Liberty 110		
RF generator frequency	40.68 MHz		
Spectrometer			
Optical Arrangement	CT 0.75 m focal length		
Grating	Holographic		
Groove Density	1800 Lines/mm		
Introduction Area			
Sample Nebulizer	V- groove Spray		
Chamber	Inert Sturman-Masters		
Conditions for line			
	wavelengths /nm	window /nm	view high /mm
Cr	267.72	0.01	650

Flotation procedure

A suitable ionic strength of the medium was adjusted by 6 ml saturated solution of KNO_3 added into 1000 ml sample of acidified water in a backer. Then 20 mg of Fe(III) as nitrate solution were added. By KOH solutions (at the beginning by 10 % and at the end by 2.5 %) the pH was adjusted to 6.5. A red-brown precipitate of hydrated iron(III) oxide, $Fe_2O_3 \cdot xH_2O$ was obtained. It was stirred for 5 minutes. After that 6 ml 0.1 mol/l solution of $HpDTC^-$ was introduced and a black precipitate of $Fe(HpDTC)_3$ was formed. After 5 minutes of stirring 1 ml solution of NaDDS was added and the content of the beaker was transferred quantitatively into the flotation cell with a small portion of 0.1 mol/l NH_4NO_3. Solid phase was separated from water phase by a stream of air bubbles (50 ml/min), effluxing from the perforated bottom of the cell for 1 min. The bubbles raised the precipitate flakes to the water surface. The glass pipette-tube was immersed into the cell through the froth layer build on the

top of water column and the liquid phase was sucked off by vacuum. Solid phase left in the cell was decomposed by 2.5 ml hot conc. HNO_3. The yellow solution was drawn out by vacuum through the bottom of the cell into a 25-ml volumetric flask. The flask was filled up with 4 mol/l HNO_3 and the sample was ready for AAS.

Results and Doscussion

Optimization of pH

To optimize this important parameter series of solutions (1 l), containing 25 μg of each analyte, were floated within a pH range of 5.0 to 7.5. The mass of Fe (10 mg), amount of $HpDTC^-$ (0.3 mmol), ionic strength (I_c = 0.02 mol/l) and volume of NaDDS solution (1 ml) were kept constant. The R/pH curves (Fig.1) evidence the highest recoveries for Cr(III) (91,3 %), and Cr(VI) (89,3 %) were reached at pH 6.5. Therefore pH 6.5 was selected as the most appropriate for further investigations.

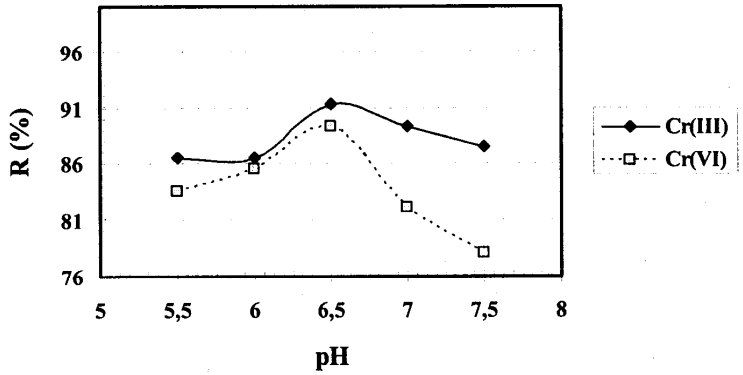

Fig. 1. Effect of pH on analyte recoveries (10 mg Fe, 0.3 mmol $HpDTC^-$)

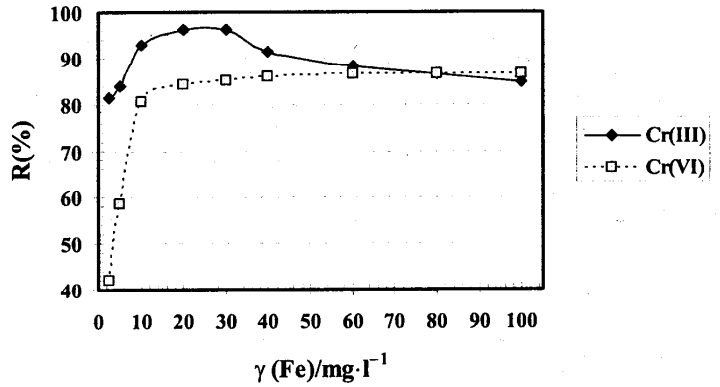

Fig. 2. Effect of iron(III) mass on Cr(III) and Cr(VI) flotation recoveries.

Effect of m(Fe) *on analyte recoveries*

Iron mass influences on formation $Fe(HpDTC)_3$ precipitate, as well as on incorporation of trace analytes in it. Therefore series of solutions (1 l) containing 25 μg of Cr(III) and

Cr(VI) were floated separately. Mass of Fe of the series of solutions varied from 2.5 to 100.0 mg per 1 l. The pH = 6.5, ionic strength (I_c = 0.02 mol/l) and amount of $HpDTC^-$ (0.3 mmol/l) were kept constant. The data show that satisfactory recoveries for two analytes were reached by 20 mg Fe (Fig. 2).

Effect of n($HpDTC^-$) on analyte recoveries

To study this effect, series solutions (1 l), containing 25 μg of each analyte were floated by different amounts $HpDTC^-$ (0.3–1.2 mmol) at constant pH (6.5) and I_c (0.02 mol/l). Each solution contained 20 mg Fe. As can be seen analytes recovery increases with rising of n($HpDTC^-$) (Fig. 3). The best recoveries of analytes were obtained when 0.6 mmol $HpDTC^-$ was added to 1 l of test solution.

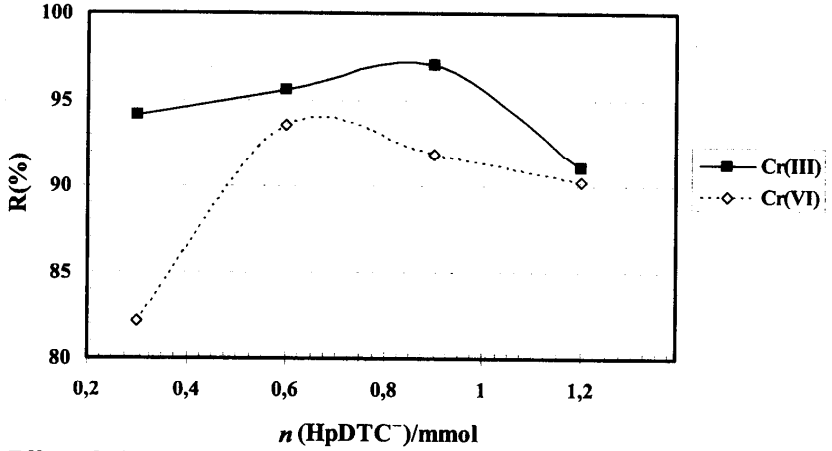

Fig. 3. Effect of n($HpDTC^-$) on analyte flotation recoveries (pH 6.5, 20 mg Fe)

Choice of surfactant

To select the most suitable surface active substance series of flotations under previously optimized conditions (pH = 6.5, I_c = 0.02 mol/l, 20 mg/l Fe, 0.6 mmol/l $HpDTC^-$) were carried out. The results (Table 3) evidence that cationic surfactants froth very well at pH 6.5, but can't perform flotation. This is the sign that the collector particles are positive charged and consequently can't made micelles with cationic surfactants. The anionic surfactants, having the opposite charge of $Fe(HpDTC)_3$ particles, were more effective. The flotation recoveries of Cr(III) and Cr(VI) obtained by NaDDS were the highest, and so it was selected as the most appropriate for the procedure.

Table 3. Selection of surfactant for flotation of Cr(III) and Cr(VI) (pH = 6.5, I_c = 0.02 mol/l, 20 mg/l Fe, 0.6 mmol/l $HpDTC^-$)

	Cationic surfactant		Anionic surfactant			
	BCT	CTAB	NaDDS	NaOL	NaPL	NaST
	R (%)					
Cr(III)	Foam, but no flotation		95.6	87.7	65.4	92.4
Cr(VI)	Foam, but no flotation		93.5	92.1	65.4	72.1

Limits of detection

The limit of detection, *LOD,* of Cr was determined floating series of blanks by the new developed flotation method. After that analytes were determined by ZETAAS and *LOD* of Cr was estimated as three values of the standard deviation of the blank. It is 0,073 Cr μg/l, while the precision of the method expressed by means of the relative standard deviations was 1,54%.

Verification of the method

To confirm the separation and preconcentration method with $Fe(HpDTC)_3$ a few samples of environmental waters were analyzed. The method of standard additions was applied. For this purpose, known amounts of chromium were added to 1 l aliquots of each water sample. After flotation 40-fold concentrated water samples were analyzed by ZETAAS. The results are given in Table 4. As seen the proposed flotation method achieves quantitative recoveries of chromium (94.5-101.1 %). The data show that ZETAAS results agree with those obtained by ICP-AES. The water samples tested by ICP-AES were concentrated by evaporation.

Table 4. ZETAAS determinations of total chromium in natural water samples after flotation with $Fe(HpDTC)_3$ verified by the method of standard additions and AES-ICP

Water sample	Flotation/Zeeman ETAAS				Evaporation/AES-ICP
	Added μg/l Cr	Estimated μg/l Cr	Found μg/l Cr	R (%)	Found μg/l Cr
Pantelejmon	-	-	0,210	-	
15,17 dH° [a]	1,25	1,460	1,380	94,5	0,20
pH = 7,45	2,50	2,710	2,682	98,9	
Sreden Izvor	-	-	1,060	-	
20,23 dH°	1,25	2,310	2,240	96,9	1,04
pH = 7,2	2,50	3,560	3,381	94,9	
Rašče	-	-	2,440	-	
12,25 dH°	1,25	3,690	3,641	98,6	2,40
pH = 7,17	2,50	4,940	4,821	97,6	
Demir Kapija	-	-	0,540	-	
8,79 dH°	1,25	1,790	1,810	101,1	0,55
pH = 7,47	2,50	3,040	2,880	94,7	
Veles	-	-	0,027	-	
1,86 dH°	1,25	1,277	1,280	100,2	<0,10
pH = 6,56	2,50	2,527	2,515	99,5	

[a]dH° – German degree of water hardness

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