Determination of total chromium in fresh water by atomic absorption spectrometry following flotation preconcentration

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Abstract. A flotation method is proposed for the quantitative preconcentration and determination of total chromium by electrothermal atomic absorption spectrometry in fresh water samples, without previous reduction or oxidation of the chromium ion state. Hydrated iron(III) oxide and iron(III) tetramethylenedithiocarbamate were used as precipitating collectors. The detection limit of the method is 0.01 µg/L.

Introduction

Since the total chromium concentration in fresh water is very low (1–10 µg/L) [1], preconcentration of this element is indispensable as a preliminary procedure before its analysis. Much attention has recently been paid to its separation by flotation techniques [2–8]. This paper describes the first attempt to determine total chromium in water using precipitate flotation preconcentration, after having established the experimental conditions for the successful coprecipitation separation of both chromium ions and their determination by electrothermal atomic absorption spectrometry (ETAAS). The separation and precipitation of the two chromium ions existing in natural water were performed in parallel. This simplifies the procedure and reduces the time required for the experiment. Hydrated Fe(III) oxide ($Fe_2O_3xH_2O$) and iron(III) tetramethylenedithiocarbamate ($Fe(TMDTC)_3$) were used as collectors.

Experimental

Instrumentation

Atomic absorption spectrometric (AAS) measurement of chromium was performed with a Perkin-Elmer atomic absorption spectrophotometer Model 1100 B equipped with HGA-700 graphite furnace. For flame AAS determinations air-acetylene fuel was applied. Instrumental

parameters (temperature and time) for the ETAAS determination were established by extensive testing and they are: 100 °C and 30 s (for drying), 1300 °C and 30 s (for charging), 2500 °C and 5 s (for atomizing), 2700 °C and 5 s (for cleaning). Ultraviolet/visible spectrophotometry (UV-VIS) of chromium was performed by the diphenylcarbazide method with a Pye Unicam SP6-550 spectrophotometer. The electro-kinetic (ζ) potential of the precipitated particles was determined electrophoretically using a device analogous to Chaikovskii's equipment [9]. The flotation cell used for the preconcentration was a glass cylinder (4 × 105 cm) with a sintered glass disc (porosity No. 4) at the bottom for air bubbling.

Reagents

All chemicals used were of analytical-reagent grade except for sodium dodecylsulfate (NaDDS) and sodium oleate (NaOL). Stock solutions of Cr(III) and Cr(VI), respectively, were prepared from $Cr(NO_3)_3 \cdot 9H_2O$ and K_2CrO_4 as 1 g/L solutions. Fe(III) solution (33.31 g/L) was prepared by dissolving high-purity iron metal with conc. HCl, HNO_3 and H_2O_2. Sodium tetramethylenedithiocarbamate (NaTMDTC) solution was prepared as 0.1 mol/L by dissolving an appropriate quantity of crystalline NaTMDTC. Before each flotation, the solution was filtered. 0.5% Solutions of the two tensides were prepared by dissolving appropriate amounts of NaDDS or NaOL in 95% ethanol.

Recommended procedure

The basic procedure was to utilize clear and uncontaminated spring water. The water samples had to be preserved with a few milliliters of 65% HNO_3 added to 1 L of spring water. The pH had to be ca. 2.8–3. The water sample (1 L) was placed in a 1 L beaker. After adding 6 mL of saturated KCl solution and 3 mL of Fe(III) solution, the pH was carefully adjusted to 5.3–5.5 by 10% KOH. The solution with the red-brown precipitate was stirred for 15 min (first induction time [8]). After this, 4 mL of 0.1 mol/L NaTMDTC solution were added and

the precipitate changed its colour from red-brown to black $(Fe(TMDTC)_3)$; the solution was stirred for 15 min (second induction time). Then, tenside solutions (0.6 mL of NaDDS and 1 mL of NaOL alcoholic solutions) were added and the contents of the beaker were transferred into the flotation cell. The residue in the beaker was washed into the cell with a small portion of 0.1 mol/L NH_4NO_3 solution. Air (50 mL/min) was passed from the perforated bottom of the cell for 2–3 min. Then, the glass pipette-tube was immersed into the cell through the foam layer and the water phase was sucked off. Hot 65% HNO_3 solution (10 mL) was added to the cell to destroy the scum. The solution was sucked off and collected in a volumetric flask (25 mL). The flotation cell and the glass pipette-tube in it were washed several times with 5 mL of a warm 4 mol/L HNO_3 solution. Finally, the flask was filled up to the mark with 4 mol/L HNO_3 solution and was ready for AAS measurement.

The same procedure was carried out to obtain data for constructing calibration curves, treating a series of chromium standard solutions with different concentrations, or to perform the standard addition method.

Results and discussion

Collector mass

The data in Table 1 show that Cr(III) was successfully floated with only 20 mg of Fe(III) added to 1 L of water, whereas Cr(VI) reached its maximum using 100 mg of Fe(III). The amount of collected Cr(III), as well as Cr(VI), has no appreciable effect on the flotation efficiency. The experimental data (obtained by flame AAS) given in Table 1 also show that the incorporation of Cr(III) and Cr(VI) into the collector particles during the induction processes depends on their ionic form. It is especially significant if these ions have been in the form of cations or anions. Since the three-valent chromium forms a cation, ion-exchange with Fe ion can occur, achieving the link between collected particle and collector very easily. It is obvious that the anion form of the hexa-valent chromium prevents its incorporation into the precipitated particles by ion-exchange. However, by increasing the collector mass, occlusion as the other type of coprecipitation occurring during the induction, becomes more frequent.

Table 1. Flotation recovery data R (%) for different mass concentrations of Cr(III) and Cr(VI) as function of the iron mass concentration $\gamma(Fe)$

$\gamma(Fe)/$ mg/L	R (%)					
	$\gamma(Cr) = 4\ \mu g/L$		$\gamma(Cr) = 8\ \mu g/L$		$\gamma(Cr) = 16\ \mu g/L$	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
2.5	92.8	72.3	80.8	56.5	65.5	51.1
5.0	92.8	72.3	85.7	85.6	79.3	59.7
10.0	89.3	75.2	92.9	78.0	96.4	64.1
20.0	100.0	67.0	94.4	78.0	94.5	76.5
40.0	100.0	75.0	97.4	93.1	100.0	88.8
60.0	100.0	75.2	100.0	96.0	100.0	91.5
80.0	100.0	75.2	100.0	97.3	100.0	92.3
100.0	100.0	100.0	100.0	100.0	100.0	100.0

Influence of the iron mass on the chromium absorbance

The 40-fold concentration of chromium made it possible to move its detection limit towards lower concentrations. However, it was important to examine the interferences resulting from a 40-fold iron mass concentrated in the final testing solutions of 25 mL on the chromium absorbance during ETAAS determinations. The results of these investigations showed that the chromium absorbance changed insignificantly up to $\gamma(Fe) = 4$ mg/mL in the final working solutions. That means that 100 mg of Fe added to 1 L of investigated water do not interfere in the final enriched solution and it is possible to perform direct chromium determinations by the proposed flotation procedure.

Influence of pH

The optimal pH interval was determined with regard to the coprecipitation. The significant effect of pH on the chromium (III and VI) recovery from water via flotation indicated a maximum recovery at pH 5.5 (Fig. 1). The different mass of collected chromium had no appreciable effect on the flotation efficiency. During the flotation
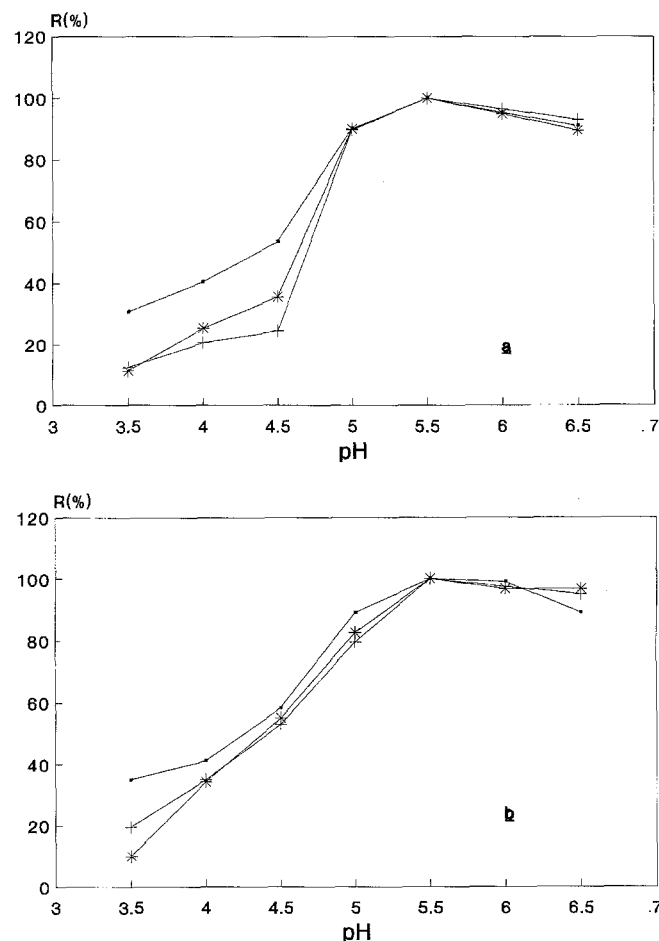

Fig. 1a, b. Dependence of the chromium recovery (R%) on pH by flotation with 100 mg/L Fe and 4 mL 0.1 mol/L NaTMDTC solution for **a** Cr(III) and **b** Cr(VI). Concentration of 4 (·), 8 (*) and 16 μg/L (+)

Table 2. Results of total chromium ETAAS determination in some spring waters of the Skopje neighbourhood compared with the results obtained by UV-VIS

Spring name	Sample number	Added µg/L Cr	Estimated µg/L Cr	Found µg/L Cr	R (%)	UV-VIS µg/L Cr
Rašče (20.26 DH°)[a]	1	0.00	–	2.50	–	2.6
	2	1.25	3.75	3.80	101.4	
	3	2.50	5.00	4.95	99.0	
	4	5.00	7.75	7.70	99.3	
Jegunovce (7.32 DH°)	1	0.00	–	0.75	–	
	2	0.50	1.25	1.26	100.8	
	3	1.00	1.75	1.78	101.7	
Rotince (7.04 DH°)	1	0.00	–	0.50	–	
	2	1.00	1.00	0.99	99.0	
Pršovečka jurija (6.19 DH°)	1	0.00	–	0.40	–	
	2	1.25	1.65	1.69	102.4	

[a] DH (*Deutsche Härte*) German degree of water hardness

the acidity influenced only the stability of the tensides because of their hydrolysis at lower pH. So the recoveries within the pH-range of 3.5 to 4.5 were poor.

Choice of tenside

The particles of hydrated iron(III) oxide had a positive ζ-potential of 0.025 V at pH 5.5. The ζ-potential of the second collector, at the same pH, was also positive and its value was 0.046 V. According to the signs of the ζ-potentials of the two collectors, they needed anionits as surfactants during the flotation. The combination of two anionits, NaOL and NaDDS, was successful.

Analysis of natural waters

For investigating the applicability of the proposed flotation procedure for water analysis, the method of standard additions was used. Several spring water samples with varying hardness from the neighbourhood of the city of Skopje were tested (Table 2). The recovery of 99.0 to 102.4% shows that the preconcentration and separation of total chromium by the proposed method is satisfactory without any conversion of one state of chromium ion into the other. The precision and accuracy of the proposed method applied to spring water from Rašče was confirmed by an UV-VIS determination as an independent method (Table 2). The detection limit (0.01 µg/L) was estimated as three values of standard deviation (0.0026)

from ten successive blank measurements. The relative standard deviation was estimated to be 4.3%.

Conclusion

The results confirm that the recommended procedure can be used for a successful total chromium analysis of fresh waters. The most important condition for the accurate determination is the quantitative relation of the two collector masses used for the coprecipitation step. The results of all tests prove that the use of $Fe(TMDDC)_3$ as additional collector improves the precipitation and makes the flotation more successful.

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