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Speciation of chromium in mineral waters and salinas by solid-phase extraction and graphite furnace atomic absorption spectrometry

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Abstract

A simple GF-AAS method for speciation analysis of chromium in mineral waters and salinas was developed. Cr(VI) species were separated from Cr(III) by solid-phase extraction with APDC (ammonium pyrrolidinedithiocarbamate). The APDC complexes were formed in the sample solution under proper conditions, adsorbed on Diaion HP-2MG resin and the resin was separated from the sample. After elution with concentrated nitric acid Cr(VI) was determined by GF-AAS. Total chromium was determined by GF-AAS directly in the sample and Cr(III) concentration was calculated as the difference between those results.

The detection limit of the method defined as 3 s of background variation was 0.03 $\mu g\,l^{-1}$ for Cr(VI) and 0.3 $\mu g\,l^{-1}$ for total chromium. RSD for Cr(VI) determination at the concentration of 0.14 $\mu g\,l^{-1}$ was 9%, and for total chromium at the concentration of 5.6 $\mu g\,l^{-1}$ was 5%. The recovery of Cr(VI) was in the range of 94–100%, dependently on type of the sample.

The investigation of recovery of the spiked Cr(VI) showed that at concentration levels near 1 $\mu g\,l^{-1}$ and lower recovery may be reduced significantly even by pure reagents that seem to be free from any reductants.

Keywords: Chromium speciation; Solid-phase extraction; Mineral waters; Salinas; GF-AAS

1. Introduction

Chromium is a relatively common element and occupies the 21st position on the index of elements occurring most commonly in the earth crust. It enters the environment as a result of effluent discharge from steel works, electroplating, tanning industry, oxidative dyeing, chemical industries and cooling water towers. The interest in speciation analysis of chromium is governed by the fact that its toxicity depends critically on its oxidation state. Cr(III) is considered as indispensable for the metabolism of glucose, lipids and proteins in living organisms. Cr(VI) as a strong oxidizer is highly toxic and can affect lungs, liver and kidneys. Cr(III) is also mutagenic, carcinogenic and teratogenic.

The Office of Environmental Health Hazard Assessment of the California EPA established a public health goal as 2.5 $\mu g\,l^{-1}$ of chromium in drinking water, using the assumption that hexavalent chromium does not exceed 7% of total chromium. In UK the allowable concentration of chromium is limited to 15 $\mu g\,l^{-1}$ for surface waters [1] and in the EU states its maximum allowable concentration in drinking water is 50 $\mu g\,l^{-1}$ (European Community Directive 80/778/EEC, L229/20, D48). Directive 90/3941/EEC imposes the continuous monitoring of hexavalent chromium in air, as a potent carcinogenic agent for respiratory tracts. The concentration for total chromium is limited to 0.5 $mg\,m^{-3}$ and for Cr(VI) to 0.05 $mg\,m^{-3}$ in indoor air [2].

Usually the speciation analysis of chromium is carried out by separation and determination of Cr(VI) and then by determination of total chromium. For the separation of Cr(VI) methods such as coprecipitation [3,4], solvent extraction [1,5–7], and ion exchange [8,9] were used. In the last decade HPLC separation technique [10,11] and solid-phase extraction [12–14] were used most frequently. Paleologos et al. used a new micelle-mediated methodology [15,16]. In this

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method the defined form of metal reacts with suitable ligands for the formation of hydrophobic complexes, which are subsequently entrapped in the surfactant micelles and determined by FAAS. For simultaneous separation and preconcentration of Cr(III) and Cr(VI) bi-directional electrostacking was used [17]. The chromate anions were determined by capillary zone electrophoresis with UV detection [18]. Recently one observes a growing tendency to use ICP-MS in combination with various separation methods for speciation analysis of chromium in waters [19–22].

Some authors have proposed procedures based on the separation and determination of Cr(III) and the total chromium [23–25]. However, such procedures should not be recommended for water analysis. The concentration of Cr(VI) in waters is usually about one order of magnitude lower than that of Cr(III) and its determination as a difference between two much higher values may generate large errors.

Ammonium pyrrolidinedithiocarbamate (APDC) is known as an agent chelating the Cr(III) and Cr(VI) species in different ways and was used for their separation. The properties of the formed complexes were investigated and discussed in detail by Andrle and Brochaert [26]. Subramanian [6] and later Baraszkiewicz and Siepak [5] applied liquid extraction for separation of Cr(VI) basing on the fact that Cr(III) ions are strongly hydrated and at normal temperature their reaction with APDC is very slow, whereas under proper conditions Cr(VI) species are reduced by APDC to Cr(III) that immediately forms complexes with APDC.

In this work we used APDC for separation of Cr(VI) from Cr(III) in mineral waters by solid-phase extraction. Since the sorbent prepared by fixation of APDC on the solid bed did not give the satisfactory results we applied the formation of the complex in solution followed with its sorption on the resin. This procedure enables a simple separation and determination of Cr(VI) in the presence of Cr(III) in mineral waters. Determination of Cr(III) concentration is calculated as the difference between the concentrations of total chromium and Cr(VI).

2. Experimental

2.1. Apparatus

A Thermo-Jarrell Ash (Franklin, MA, USA) SH 4000 atomic absorption spectrometer, equipped with a controlled furnace atomiser (CTF 188) and a Smith-Hieftje correction system. A Visimax II (Thermo Jarrell Ash) chromium hollow-cathode lamp and pyrolytic coated graphite tube were used. A Mettler Delta 340 pH-meter, a laboratory shaker type WL-1 (Poland), and glass columns of 4 mm in internal diameter with the stopper were used for the separation process.

2.2. Reagents

All solutions were prepared from high purity analytical-reagent grade compounds using ultra-pure water (resistivity 18 MΩ cm^{-1}) obtained with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Nitric and hydrochloric acids were purified by sub-boiling distillation.

Cr(III) stock standard solution (10 mg ml^{-1}) was prepared by dissolution of 1 g metallic chromium (Koch-Light 5N) in concentrated hydrochloric acid and dilution with water to 100 ml. Cr(VI) stock standard (1 mg ml^{-1}) solution was prepared by dissolution of 0.283 g $K_2Cr_2O_7$ in water and dilution to 100 ml. $Mg(NO_3)_2$ solution (20 mg ml^{-1}) was prepared by dissolution of 1.66 g MgO (Koch-Light 4N8) in 20 ml 4 M HNO_3 and dilution with water to 50 ml.

The buffer solution, pH 3.5, was prepared by dissolution of 1.0209 g potassium hydrogen phthalate in 50 ml of water, addition of 8 ml of 0.1 M HCl, and dilution with water to 100 ml. The 3% APDC (ammonium pyrrolidinedithiocarbamate) water solution was prepared fresh every day.

Diaion HP-2MG polymethacrylate resin (Supelco) was used after washing with 0.1 M HCl and air drying.

The prepared artificial test water contained the following components: 15 mg l^{-1} Na^+, 4 mg l^{-1} K^+, 20 mg l^{-1} Mg^{2+}, 55 mg l^{-1} Ca^{2+}, 124 mg l^{-1} Cl^-, 80 mg l^{-1} $(SO_4)^{2-}$, 0.2 mg l^{-1} Zn^{2+}, 0.2 mg l^{-1} Fe^{2+}, 0.01 mg l^{-1} Cd^{2+}, 0.05 mg l^{-1} Pb^{2+}, 0.05 mg l^{-1} Cu^{2+} and 0.05 mg l^{-1} Ni^{2+}.

2.3. Recommended analytical procedure

Place 100 ml of the mineral water sample or 100 ml of 20% salina solution in ultra-pure distilled water into the separatory funnel and acidify with hydrochloric acid to pH about 3.5, then add 5 ml of buffer solution, 3 ml of APDC solution, 1 g of resin and adjust the final pH value to 4. Shake for 10 min using a mechanical shaker, then transfer the resin into the column, drain off the aqueous phase and wash the column twice with 2 ml of water acidified to pH 4. To elute the retained chromium pass 1 ml of concentrated nitric acid through the column and collect the effluent in a 10 ml volumetric flask. Place a second portion of 1 ml concentrated nitric acid into the column and allow it to react for 30 min. After this time drain the acid into the same volumetric flask and wash the column bed with 5 ml of water. Add 150 μl of $Mg(NO_3)_2$ solution and dilute to the mark with the water. Use the solution for determination of Cr(VI) by ET AAS method using a pyrolytic coated graphite tube and 10 μl of sample and measuring the integrated absorbance. The analytical parameters are presented in Tables 1 and 2. Any series of samples should be accompanied by a blank. Prepare the standards by addition of a suitable amount of Cr(III) standard solution to acidified distilled water.

Table 1
Parameters for AAS determination

Wavelength (nm)	265.9
Band pass width (nm)	0.4
Lamp current (mA)	6
Integration time (s)	6
Background correction	Smith-Hieftje

Table 2
Atomization temperature–time program

	Temperature (°C)	Ramp (s)	Hold (s)	Purge Ar
Drying	120	40	20	Low
Pyrolysis I	700	20	5	Medium
Pyrolysis II	1000	10	10	Medium
Atomization	2550	0	4	Off
Cleaning	2600	–	3	Medium

Determine the concentration of total chromium directly by placing into the 10 ml volumetric flask 150 μl of $Mg(NO_3)_2$ solution, 850 μl of concentrated nitric acid, and filling it up to the mark with 9 ml of the mineral water or salina solution to be analysed. Calculate the concentration of Cr(III) as the difference between concentrations of the total chromium and Cr(VI).

3. Results and discussion

3.1. Parameters for the separation process

Some parameters of the APDC reaction with Cr(VI), such as the optimum range of pH, APDC concentration, and buffer solution, were accepted from the investigation of the extraction data described in the literature [6] after checking theirs correctness under our conditions. The crucial parameter for the proposed procedure is the time of reaction and adsorption on the resin of the complex formed only with Cr(VI), i.e. the shaking time of the sample, because APDC is able to react with both species of chromium. Cr(VI) species are immediately reduced by APDC to Cr(III) and quickly form complexes with it, whereas, strongly hydrated Cr(III) ions, present in the solution, require a significantly longer time for reaction at normal temperatures. Since this phenomenon is the basis for the applied separation procedure, the proper reaction time must be estimated and adhered very carefully.

For estimation of the shaking time effect on the separation of both types of chromium species artificial test water with composition corresponding to that of natural river water was used. The 100 ml samples of this water were spiked with 200 ng either of Cr(VI) or Cr(III) and treated according to the normal analytical procedure with varying shaking time. The results, presented in Table 3, indicate unambiguously that the maximum amount of Cr(VI) is separated after 10 min and is stable at the longer shaking time, whereas, the first small amount of Cr(III) does not appear before 15 min. Using 10 min shaking time we are able to separate completely both the forms.

We have found it most convenient to transfer the resin with the adsorbed APDC–Cr complex into the column for decomposition end elution of the retained chromium. However, this process may be carried out in any other way, e.g. in a backer.

Table 3
Effect of shaking time on the retention of Cr(VI) and Cr(III) 100 ml test water samples spiked with 200 ng either of Cr(VI) or Cr(III); $n = 3$

Shaking time (min)	Retention (%)	
	Cr(VI)	Cr(III)
5	55–58	n.d.
10	65–70	n.d.
15	68–72	2
20	68–70	10

n.d.: not detected.

3.2. Recovery of Cr(VI)

The results from Table 3 demonstrate that the recovery of the spiked amount of Cr(VI) is about 70%. Although similar results have been reported by other authors [6,27], such results are unacceptable for quantitative analysis. Since all components contained in the test water are removed during the separation process and cannot affect the results, such poor recoveries could be caused either by incomplete separation of Cr(VI) from the sample or by suppression of the analytical signal by the disintegration products of the APDC by the concentrated nitric acid. However, the significantly larger amount (5 μg) of Cr(VI), added to the test water is recovered at the level of 95–100%, and 200 ng of Cr(VI) added to the blank solution is recovered at the level of about 100%. Moreover, the recovery of Cr(VI) in distilled high purity water is equal to 100% (see Table 4). These results suggest that the poor recovery observed in Table 3 cannot depend on the above mentioned reasons but they are caused by partial reduction of the spiked chromium in the test water solution. To test this hypothesis we first oxidized the test water by addition of potassium permanganate or by hydrogen peroxide and UV-radiation [28] before spiking it with chromium. The results presented in Table 4 show that in these experiments the recovery was 90–95%. Addition of Cr(VI) to natural mineral waters, in which Cr(VI) and Cr(III) exist in equilibrium, enables its recovery at a level above 95%. The reduction of Cr(VI) was reported also by Vercoutere et al. [2] in their work on certification of chromium in lyophilised solution. They explained it as changes during storage.

The described observation indicates unambiguously that for the determination of Cr(VI) at low nanogram-concentrations particular precautions should be taken. Even pure reagents, e.g. artificially prepared test water, which

Table 4
Recovery of Cr(VI) spikes from various water samples and salinas 100 ml water or 20% salina solution samples spiked with 200 ng of Cr(VI); $n = 3$

Type of water	Recovery (%)
Distilled water	∼100
Test water	65–70
Test water + $KMnO_4$	90–96
Test water + H_2O_2 + UV-irradiation	96–98
Mineral water “Franciszek”	95–98
Mineral water “Nałęczowianka”	94–97
Salina “Ciechocinek”	96–99
Salina “Bochnia”	95–98

Table 5
Speciation analysis of chromium in various mineral waters and salinas

Type of sample	Name of sample	Cr(VI) ($\mu g\,l^{-1}$)	Cr total ($\mu g\,l^{-1}$)	General composition declared by suppliers ($mg\,l^{-1}$)					
				Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}
Mineral waters	Jan	0.09	0.6	152	25	15	6	525	18
	Henryk	0.17	0.9	164	42	1282	28	2900	7
	Zuber[a]	n.d.	5.6	132	331	6495	320	18550	975
	Franciszek	0.14	1.6	191	28	4650	90	8930	2520
	Nałęczowianka	0.06	1.2	112	23	13	5	483	n.dcl.
	Buskowianka	0.45	3.0	119	28	34	10	578	32
		Cr(VI) ($ng\,l^{-1}$)	Cr total ($ng\,l^{-1}$)	%					
Salinas	Ciechocinek	2.8	30	30% ($Na^{+} + K^{+}$); 50% Cl^{-}; 2% Ca^{2+}; 0.6% Mg^{2+}					
	Bochnia	29	307	90% NaCl; 1.6% Ca^{2+}; 0.9% Mg^{2+}					

n.d.: not detected; n.dcl.: not declared.
[a] Water contains $0.99\,mg\,l^{-1}$ of Fe(II).

formally does not contain any reducing substances, can reduce significant amounts of chromium at this concentration level and bias the results.

3.3. Evaluation of the method

The precision of the method was estimated by multiple determinations ($n = 7$) of chromium at two concentration levels in natural mineral waters. For Cr(VI) at $0.14\,\mu g\,l^{-1}$ the R.S.D. was equal to 9%, and for total chromium at $5.6\,\mu g\,l^{-1}$ the R.S.D. was equal to 5%.

The accuracy of the method was estimated by determining a known amount of Cr(VI) spiked into oxidized test water and into two natural mineral waters. The recovery was in the range of 94–98% (Table 4) and is considered satisfactory. The accuracy of the total chromium determination was estimated in the same way by spiking natural mineral waters. In all cases the recovery was about 100%. All results were inside the range limited by the precision of the method.

The detection limit of the method defined as 3 s of background variation was $0.03\,\mu g\,l^{-1}$ for Cr(VI) and $0.3\,\mu g\,l^{-1}$ for total chromium.

Tests for interferences showed that all cations and anions usually present in most mineral waters or natural salinas do not affect the results of chromium determination with the exception of reductants, e.g. iron(II), that can reduce Cr(VI). However, in waters containing such substances chromium in this form is absent. Table 5 presents the results of the speciation analysis of chromium obtained by this method for some commercially available Polish drinking mineral waters and two salinas used for therapeutic purposes.

4. Conclusion

The presented method enables a simple and quick separation and determination of Cr(III) and Cr(VI) species present in mineral waters and salinas at a low $\mu g\,l^{-1}$ and $ng\,l^{-1}$ concentrations. It should be emphasised, however, that all operations with Cr(VI) require a special precaution and careful checking of the applied reagents for ultra trace amounts of reductants. Even pure reagents, those should be absolutely inert and those do not reduce Cr(VI) to an observable degree on high $\mu g\,l^{-1}$-level, can reduce a significant amount of chromium at a ultra-trace concentration level and introduced bias in the results. This is particularly important for the preparation of standard solutions and for the testing of the recovery of Cr(VI). It seems that the poor recoveries reported by some authors may result from reduction of small amounts of Cr(VI) in their experiments.

It should be emphasised that when the above precaution are followed the proposed method enables the correct determination of both forms of chromium in many natural waters and salinas.

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References

[1] M. Gardner, S. Comber, Analyst 127 (2002) 153.
[2] K. Vercoutere, R. Cornelis, L. Mees, Ph. Quevauviller, Analyst 123 (1998) 965.
[3] C.L. Lan, M.H. Yang, Z.B. Alfassi, Analyst 116 (1991) 35.
[4] P. Gopi Krishna, J. Mary Gladis, U. Rambabu, T. Prasada Rao, G.R.K. Naidu, Talanta 63 (2004) 541.
[5] D. Baraszkiewicz, J. Siepak, Chem. Anal. (Warsaw) 44 (1999) 879.
[6] K.S. Subramanian, Anal. Chem. 60 (1988) 11.
[7] G.J. de Jong, U.A.Th. Brinkman, Anal. Chim. Acta 98 (1978) 243.
[8] D.M. Adria-Cerezo, M. Llobat-Estelles, A.R. Mauri-Aucejo, Talanta 51 (2000) 531.
[9] A.G. Coedo, T. Dorato, I. Padilla, F.J. Alguacil, J. Anal. Atom. Spectrom. 51 (2000) 1564.
[10] J. Posta, H. Berndt, S. Luo, G. Schaldach, Anal. Chem. 63 (1993) 2590.
[11] C.M. Andrle, J.A.C. Broekaert, J. Fres, Fres. J. Anal. Chem. 346 (1993) 653.

[12] O. Rychlovsky, M. Krenželok, R. Volhejnova, Collect. Czech. Chem. Commun. 63 (1998) 2015.
[13] E. Vassileva, K. Hadjiivanov, T. Stoychev, Ch. Daiev, Analyst 125 (2000) 693.
[14] B. Demirata, Microchim. Acta 136 (2001) 143.
[15] E.K. Paleologos, C.D. Stalikas, S.M. Tzouwara-Karayanni, A.G. Pilidis, M.I. Karayannis, J. Anal. Atom. Spectrom. 15 (2000) 287.
[16] E.K. Paleologos, C.D. Stalikas, M.I. Karayannis, Analyst 126 (2001) 389.
[17] Z.Y. He, M.L. Cervera, A. Pastor, M. de la Guardia, Anal. Chim. Acta 447 (2001) 135.
[18] B. Baraj, L.F. Hax Niencheski, J.A. Soares, M. Martinez, A. Merkoci, Fres. J. Anal. Chem. 367 (2000) 12.
[19] Y.-L. Chang, S.-J. Jiang, J. Anal. Atom. Spectrom. 16 (2001) 858.
[20] M.F. Giné, A.P.G. Gervasio, A.F. Lavorante, C.E.S. Miranda, E. Carrilho, Anal. Atom. Spectrom. 17 (2002) 736.
[21] H. Louie, M. Wu, P. Di, P. Snitch, G. Chapple, J. Anal. Atom. Spectrom. 17 (2002) 587.
[22] F. Séby, S. Charles, M. Gagean, H. Garraud, O.F.X. Donard, J. Anal. Atom. Spectrom. 18 (2003) 1386.
[23] H. Filik, Microchim. Acta 140 (2002) 205.
[24] Z.-H. Wang, M. Sond, Q.-L. Ma, H.-M. Ma, S.-C. Liang, Microchim. Acta 134 (2000) 95.
[25] F. Shemirami, M. Rajabi, Fres. J. Anal. Chem. 371 (2001) 1037.
[26] C.M. Andrle, J.A.C. Brochaert, Fres. J. Anal. Chem. 346 (1993) 653.
[27] A. Syty, R.G. Christensen, T.C. Rains, J. Anal. Atom. Spectrom. 3 (1998) 193.
[28] J. Golimowski, K. Golimowska, Anal. Chim. Acta 325 (1996) 111.