

# 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  $0.03 \mu\text{g l}^{-1}$  for Cr(VI) and  $0.3 \mu\text{g l}^{-1}$  for total chromium. RSD for Cr(VI) determination at the concentration of  $0.14 \mu\text{g l}^{-1}$  was 9%, and for total chromium at the concentration of  $5.6 \mu\text{g l}^{-1}$  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  $1 \mu\text{g l}^{-1}$  and lower recovery may be reduced significantly even by pure reagents that seem to be free from any reductants.

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## 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

$2.5 \mu\text{g l}^{-1}$  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  $15 \mu\text{g l}^{-1}$  for surface waters [1] and in the EU states its maximum allowable concentration in drinking water is  $50 \mu\text{g l}^{-1}$  (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  $0.5 \text{ mg m}^{-3}$  and for Cr(VI) to  $0.05 \text{ mg m}^{-3}$  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 Andrie and Brochaert [26]. Subramanian [6] and later Baraszkiwicz 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 M $\Omega$  cm<sup>-1</sup>) 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<sup>-1</sup>) 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<sup>-1</sup>) solution was prepared by dissolution of 0.283 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in water and dilution to 100 ml. Mg(NO<sub>3</sub>)<sub>2</sub> solution (20 mg ml<sup>-1</sup>) was prepared by dissolution of 1.66 g MgO (Koch-Light 4N8) in 20 ml 4 M HNO<sub>3</sub> 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<sup>-1</sup> Na<sup>+</sup>, 4 mg l<sup>-1</sup> K<sup>+</sup>, 20 mg l<sup>-1</sup> Mg<sup>2+</sup>, 55 mg l<sup>-1</sup> Ca<sup>2+</sup>, 124 mg l<sup>-1</sup> Cl<sup>-</sup>, 80 mg l<sup>-1</sup> (SO<sub>4</sub>)<sup>2-</sup>, 0.2 mg l<sup>-1</sup> Zn<sup>2+</sup>, 0.2 mg l<sup>-1</sup> Fe<sup>2+</sup>, 0.01 mg l<sup>-1</sup> Cd<sup>2+</sup>, 0.05 mg l<sup>-1</sup> Pb<sup>2+</sup>, 0.05 mg l<sup>-1</sup> Cu<sup>2+</sup> and 0.05 mg l<sup>-1</sup> Ni<sup>2+</sup>.

### 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  $\mu$ l of Mg(NO<sub>3</sub>)<sub>2</sub> 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  $\mu$ l 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 |

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