

Separation of chromium (VI) using complexation and its determination with GFAAS

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Received 25 May 2005; received in revised form 4 July 2005; accepted 15 July 2005

Available online 18 January 2006

Abstract

In acidic medium and in the presence of chloride ions 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3H-indolium chloride forms complex with Cr(VI). The optimum conditions (pH, concentration of Cl⁻ and the complex forming reagent) of the separation and extraction of Cr(VI) into toluene using this basic dye as a complexing reagent have been determined and the possible interferences of Ca, Mg, Na, K, Cr(III), Ni, Pb, Hg, Mn, Al, Cu have been studied. An electrothermal atomic absorption spectrometer (GFAAS) was used for the determination of Cr(VI). The detection limit of the method for Cr(VI) found to be 0.15 µg dm⁻³ and RSD for spiked drinking water was better than 3%.

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Keywords: Speciation; Chromium; Extraction; GFAAS

1. Introduction

Chromium in the nature exists in two relatively stable forms, chromium(III) and chromium(VI). These forms of chromium have different influences on the medium in which they occur. They have different biological activity, which depends on chromium's oxidation state. Chromium(III) is essential for the organism, but chromium(VI) has toxic and carcinogenic effects [1–3]. The biggest sources of chromium species that enter the environment are waste-disposal companies, steel works, smelters, electroplating, timber processing and leather tanning industries [4]. The clear evidence of their different properties makes us to try to develop analytical methods, by which we can determine separately the individual chromium species in order to find out the most about the content of the occurred samples.

For a selective determination of Cr(VI) a variety of procedures were described till this time. Sperling et al. presented a reviewed introduction of the methods for the

determination of Cr(VI) and total chromium by graphite furnace atomic absorption spectrometry (GFAAS) [5], which included different preconcentration methods used for the separation of Cr(VI). The methods for the separation of chromium species and determination of Cr(III) and Cr(VI) by AAS are based on solvent extraction [7], ion-exchange [10], coprecipitation [11], electrochemical separation [12], selective volatilization [13] and solid-phase extraction [14]. Separation methods using solvent extraction are usually based on the extraction of hexavalent chromium into organic solvents. Methods using Cr(III) extraction occurs rarely [7,8], because of the inertness of Cr(III) complexes.

Diphenylcarbazide [15], pentamethylenebis(triphenylphosphonium) [16], tetramethylenebis(triphenylphosphonium) [17], benzyltributylammonium [18], O,O'-dibutyl dithiophosphate [19], crystal violet [20], nitrotetrazolium blue [21] and chromotropic acid [22] are the most frequently used reagents for the determination of chromium. In a recent work [6] complex formation was used for the preconcentration of Cr(VI) and the complex forming reagent was 2-[2-(4-methoxy-phenylamino)-vinyl]-1,3,3-trimethyl-3H-indolium chloride (MPVTI). The chemical structure of the reagent is given in Fig. 1. In acidic medium and in the presence of chloride ions this reagent forms complex with hexavalent

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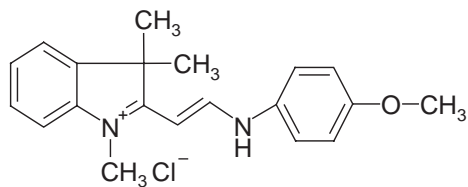


Fig. 1. Chemical structure of MPVTI.

chromium. This complex can be extracted with various organic solvents. The optimum experimental conditions were determined, and UV-VIS spectroscopy was used as detection technique [6].

The point of our work was the separation of the two chromium forms using the MPVTI complex forming reagent, investigation of the optimum conditions of the separation and the determination of chromium(VI) using another detection technique (electrothermal atomic absorption spectrometry) with a better limit of detection than UV-VIS spectroscopy. The separation of chromium(VI) was realized by using complexation and extraction. The optimum conditions were verified and specified, because we thought that the decreasing chromium concentration would cause changing of the optimum conditions. The suggested extraction-spectrometric method yields decreasing of LOD and increasing the selectivity of the method against the earlier described method [6]. The developed method was used to determine Cr(VI) in model solutions and in drinking water spiked with hexavalent chromium. These spiked concentrations of Cr(VI) are realistic for waste waters. This method should be applied in the analysis of waste waters or soil extracts.

2. Experimental

2.1. Apparatus

A Perkin Elmer AAnalyst 600 atomic absorption spectrometer with Zeeman background correction equipped with a transversely heated graphite atomizer (THGA) and an AS 800 autosampler, and a Varian SpectrAA 10 atomic absorption spectrometer with deuterium background correction equipped with a heated graphite atomizer (HGA) were used throughout the measurements. They were equipped with a Narva Cr hollow cathode lamp operated at 8 mA. The wavelength at 357.9 nm was used with a slit-width of 0.7 nm with the Perkin Elmer and 0.2 nm with the Varian type of spectrometer. The graphite furnace heating program is given in Table 1. The measured volume of the sample solution was 20 μL . For the measuring of the needed weights a Precisa 240A analytical balance was used. The deionized water was prepared by a Millipore Milli-Q RG device. Some of the solutions were prepared by the help of a Transsonic 460/H ultrasonic unit. For the on-line separation of the two chromium species and their determination in order to find out the yield of the extraction of the Cr(VI) complex into the toluene the following equipment was used: Knauer HPLC pump, hydraulic high pressure nebulizer (HHPN), RP18 column (5 cm, 4.6 mm inner

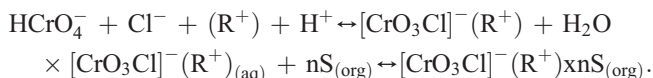
diameter, Knauer), flame AA spectrometer Pye Unicam SP 1900 AAS.

2.2. Reagents

Deionized water was used throughout for preparing the solutions and diluting the stock solutions. All chemicals used were p.a. purity and the organic solvent (toluene) was purity for UV spectroscopy. The chromium(VI) stock solution ($0.1 \text{ mol dm}^{-3} \text{ K}_2\text{Cr}_2\text{O}_7$) was prepared by dissolving 2.9418 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 100 mL of deionized water. The working solution ($10^{-3} \text{ mol dm}^{-3} \text{ K}_2\text{Cr}_2\text{O}_7$) was prepared from the stock solution by diluting with deionized water. A 0.5 mol dm^{-3} working solution of H_2SO_4 was used for the adjustment of pH. The effect of the chloride ions was set by using a 4 mol dm^{-3} aqueous solution of NaCl. A $1 \cdot 10^{-3} \text{ mol dm}^{-3}$ aqueous solution of the complexing reagent was prepared by dissolving 34.3 mg of MPVTI in 100 mL of deionized water.

2.3. General procedure

It was found that the mole ratio of Cr(VI):chloride:dye reagent is 1:1:1. For the extraction mechanism the following was suggested by Andruch et al. [6], where S stands for toluene, (aq) for aqueous phase and (org) for organic phase:



The needed volumes of $10^{-3} \text{ mol dm}^{-3} \text{ K}_2\text{Cr}_2\text{O}_7$ were placed into glass test tubes. Acidity of the solution was adjusted by adding 0.3 mL 0.5 mol dm^{-3} of sulfuric acid. The concentration of the chloride ions and the complexing reagent were adjusted by adding 1.25 mL of 4 mol dm^{-3} NaCl and 1.1 mL of $10^{-3} \text{ mol dm}^{-3}$ MPVTI. The concentrations of sulfuric acid, sodium chloride and MPVTI have been varied during the investigation of the optimum conditions of the separation and extraction of the Cr(VI) complex. After adding the reagents, the solution was filled with deionized water to 5 mL and extracted for 30 s with 5 mL of toluene by manual shaking. After the extraction, the organic phase was separated, and the absorbance was measured by GFAAS. The blank test was prepared under the same conditions without an addition of chromium.

Table 1

Graphite furnace heating program of the Perkin Elmer Analyst 600 for the determination of hexavalent chromium in the organic phase after extraction into the toluene

Step	Temperature [°C]	Time [s]		Argon flow rate [cm ³ min ⁻¹]
		Ramp	Hold	
1	110	1	30	250
2	130	15	30	250
3	1500	10	20	250
4	2300	0	5	0
5	2450	1	3	250

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