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Speciation and determination of ultra trace amounts of chromium by solidified floating organic drop microextraction (SFODME) and graphite furnace atomic absorption spectrometry

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ABSTRACT

Solidified floating organic drop microextraction (SFODME) method in combination with graphite furnace atomic absorption spectrometry (GFAAS) has been used for the determination of chromium species in water and urine samples. 1-undecanol containing 2-thenoyltrifluoroacetone (TTA) was used as a selective chelating agent for the extraction of Cr(III). The total Cr was determined after the reduction of Cr(VI) to Cr(III) with hydroxylamine. The concentration of Cr(VI) was determined from the difference between the concentration of total chromium and the Cr(III). Several variables such as the sample pH, concentration of TTA, salt concentration, extraction time and the sample volume were investigated in detail. Under the optimum conditions, the limit of detection of the proposed method was 0.006 $\mu g\,l^{-1}$ for Cr(III) and the relative standard deviation for six replicate determinations at 0.1 $\mu g\,l^{-1}$ Cr(III) was 5.1%. The proposed method was successfully applied for the determination of chromium species in tap water, well water, mineral water, and urine samples.

1. Introduction

Speciation of chromium as a trace element in environmental and biological samples has become an interesting topic in analytical techniques. The interest in speciation is governed by the fact that toxicological and biological characteristics of this element are related to its oxidation states. Although chromium can exist in several oxidation states, Cr(III) and Cr(VI) are known as the only stable species in solution [1,2]. Cr(III) appears to be essential for the living organisms especially human beings. It has an important role in glucose, lipid and protein metabolism [3], while Cr(VI) is known as a toxic species that can easily penetrate the cell wall and exert its noxious influence in the cell. Cr(VI) is also known as a cause of various cancer diseases [4,5]. Thus, due to the difference in toxicities of Cr(III) and Cr(VI), their separate determination is necessary.

Various analytical techniques such as atomic absorption spectrometry (AAS) [6–8], spectrophotometry [9], spectrofluorometry [10], stripping voltametry [11], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [12], inductively coupled plasma-mass spectrometry (ICP-MS) [13,14], and high performance liquid chromatography (HPLC) [15] have been frequently used for accurate determination of chromium in various samples. However, due to its good sensitivity, graphite furnace atomic absorption spectrometry (GFAAS) is one of the most extensively used techniques for the determination of trace amounts of various elements, but it suffers from matrix interferences and the direct determination of the species of the elements presented in the samples is not possible. Thus, speciation of trace elements at sub-ppb level by GFAAS requires a separation and preconcentration step.

The most widely used techniques for separation and preconcentration of chromium are cloud-point extraction [16–18], coprecipitaton [19,20], solid phase extraction [21–23], ion exchange separation [24] and liquid–liquid extraction [25]. Although satisfactory results can be obtained with the above mentioned separation/preconcentration techniques, they have some drawbacks such as large consumption of reagent, low enrichment factor, multistage operation and lengthy separation.

Microextraction methods such as drop-in-drop system [26], single-drop microextraction (SDME) [27], homogenous liquid–liquid microextraction (HLLME) [28], solid phase microextraction (SPME) [29], dispersive liquid–liquid microextraction (DLLME) [30,31], and solidified floating organic drop microextraction (SFODME) [32] have been developed to overcome these problems. The major idea behind these techniques is a great reduction in the volume ratio of acceptor to donor phase.

Solidified floating organic drop microextraction (SFODME) that was reported by Khalili Zanjani et al. [32] is a new liquid phase microextraction technique in which small volume of an organic solvent with a melting point near the room temperature (in the range of 10–30 °C) is floated on the surface of aqueous solution.

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The aqueous phase is then stirred for a prescribed period of time, and the sample is transferred into the ice bath. When the organic solvent is solidified, it is transferred into a small conical vial and the melted organic solvent is used for the analytes determination. This method is inexpensive, sensitive and effective for the removal of the interfering matrices. Compared with conventional solvent extraction, it also has the advantage of great reduction in the amount of organic solvent and subsequently great enhancement of the preconcentration factor [33,34]. Recently, our research group were able to successfully combine SFODME with GFAAS and flame atomic absorption spectrometry (FAAS) for trace elements separation and determination [35–37]. Later, this method was also used by other researchers for the determination of trace metals in various samples [38–41]. However, to the best of our knowledge there is no report on the use of the SFODME technique for speciation of elements. Thus, in this study the possibility of implementation of SFODME for trace metal speciation was considered and a simple method for speciation of chromium(III) and (VI) was developed. Thenoyltrifluoroacetone (TTA) was used as a selective chelating agent for the extraction of chromium(III). Furthermore, the applicability of the approach was demonstrated for the determination of chromium in urine and water samples.

2. Experimental

2.1. Reagents and standard solutions

All reagents used were of analytical reagent grades and were purchased from the Merck Company (Darmstadt, Germany). Doubly distilled deionized water was used throughout this study. Stock standard solution (1000 mg l^{-1}) of Cr(VI) and Cr(III) was prepared by dissolving proper amount of $K_2Cr_2O_7$ and $CrCl_3{\cdot}6H_2O$ in water. Thenoyltrifluoroacetone (TTA) solution (0.1 mol l^{-1}) was prepared by dissolving 0.111 g of TTA in 5 ml of 1-undecanol, and then 0.001 mol l^{-1} of TTA solution was prepared by proper dilution with 1-undecanol. Hydroxylamine hydrochloride solution (4 mol l^{-1}) was prepared by dissolving 6.95 g of the reagent in 25 ml of distillated water. Sodium fluoride solution (1 mol l^{-1}) was prepared by dissolving sufficient amount of NaF in distillated water. Buffer solution (pH = 3.5) was prepared by dissolving 13.609 g of KH_2PO_4 and an appropriate amount of hydrochloric acid, adjusting the pH and diluting to the mark by distillated water in a 100 ml volumetric flask.

2.2. Apparatus

Varian Zeeman spectra atomic absorption spectrometer, model 220Z was used for all metal measurements throughout this study. A PC computer was used to record the absorbance signal profile. A Varian Spectra-AA hollow cathode lamp for chromium was used as the light source. The furnace tube was a standard plateau tube with a pyrolytic graphite coating. The analytical wavelength (357.9 nm), spectra bandwidth (0.5 nm) and lamp current (7 mA) were used as recommended by manufacturers. The sample injection volume was 10 μl in all experiments. The pH measurements were carried out with a Metrohm pH meter (model 691, Switzerland) using a combined glass calomel electrode.

2.3. Extraction procedure

(A) Determination of Cr(III): Ten ml solution of the Cr(III) and Cr(VI), 0.2 ml of 1 mol l^{-1} NaF and 1 ml of phosphate buffer solution (pH = 3.5) were added to a suitable vial containing a stirring bar. 30 μl of TTA in 1-undecanol (0.001 mol l^{-1}) was added, the magnetic stirrer was turned on and the solution was mixed for 30 min at 1250 rpm. In this step the organic drop was dispersed to some extents in the sample solution, the Cr(III) reacted with TTA and extracted into 1-undecanol while Cr(VI) remained in the aqueous solution. After the extraction time was over, the stirring rate was lowered so that the drop was coagulated. The stirring was then terminated and the sample vial was transferred into an ice bath for 5 min. The solidified solvent was transferred into a conical vial where it melted immediately. 10 μl of the extract was manually injected into graphite furnace atomic absorption spectrometer for quantification.

(B) Determination of total Cr and Cr(VI): To determine the total concentration of chromium in the solution, Cr(VI) was efficiently reduced to Cr(III) upon the addition of 1 ml of 0.05 mol l^{-1} of the hydroxylamine hydrochloride solution. The solution was then treated according to the procedure given in part A.

The concentration of Cr(VI) was determined from the difference between the concentration of total chromium and Cr(III).

3. Results and discussion

In the preliminary analysis of the extract with GFAAS, it was illustrated that 2-thenoyltrifluoroacetone (TTA) dissolved in 1-undecanol can extract Cr(III) via the solidified floating organic drop microextration (SFODME) method, while Cr(VI) remained in aqueous phase, a similar behavior was reported by the other workers [16,42]. TTA forms a complex with Cr(III) as follows:

1-Undecanole was used as an extracting solvent because of its low volatility, low water solubility and melting point (13–15 °C) near to room temperature. Furthermore, to obtain a high enrichment factor, different parameters affecting the complex formation, extraction and analysis process were optimized in a univariable approach. The percentage of extraction and enhancement factors was calculated according to the Eqs. (1) and (2) as described earlier [35–37].

$$\text{Percent of extraction} = \left(\frac{C_O V_O}{C_{aq} V_{aq}}\right) \times 100 \qquad (1)$$

$$\text{Enrichment factor} = \frac{C_O}{C_{aq}} \qquad (2)$$

where V_O, C_O and V_{aq}, C_{aq} are the volumes and the concentration in organic and initial aqueous phases, respectively. C_O was calculated from the calibration graph of standard solution of Cr(III)–TTA complex in ethanol.

3.1. Optimization of furnace temperature program

It was previously reported that TTA complex of Cr(III) is volatile and vaporized at 700 °C [16,42]. Thus, in order to avoid the loss of the interested metal ion and to eliminate or alleviate the background signal during the pyrolysis step, the time and temperature program of GFAAS during the analysis process were optimized, the results of which are demonstrated in Fig. 1. The optimal ashing and atomization temperatures were 550 and 2400 °C respectively. Under these conditions the background was low and the Cr peak had a normal shape. The optimum temperature program of GFAAS used for the determination of chromium in the extract is given in Table 1.

3.2. Selection of organic solvent

Several extracting solvents, including 1-undecanol (m.p. 13–15 °C), 1-dodecanol (m.p. 22–24 °C), 1,10-dichlorodecane (m.p. 14–16 °C) and n-hexadecane (m.p. 18 °C) which fulfill the needed conditions for extracting solvents of SFODME, were investigated [35–37]. 1-Undecanol was found to give the best extraction efficiency, with 2-dodecanol the extraction efficiency was about 65%