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Cloud point extraction combined with high-performance liquid chromatography for speciation of chromium(III) and chromium(VI) in environmental sediment samples

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ABSTRACT

A sensitive and simple method for high-performance liquid chromatography (HPLC) determination of traces of chromium species in lake sediments after preconcentration by cloud point extraction (CPE) has been developed. Simultaneous preconcentration of Cr(III) and Cr(VI) in sediment samples was achieved by CPE with 1-(2-thiazolylazo)-2-naphthol (TAN) as the chelating agent and non-ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114) as the extractant. Baseline separation of the TAN chelates of Cr(III) and Cr(VI) was realized on a RP-C_{18} column by using a mixture of methanol–water (69:31, v/v) solution and 4.5 mmol L^{-1} CTMAB buffered with 0.03 mol L^{-1} NaAc–HAc solution (pH 5.5) as the mobile phase at a flow rate of 0.8 mL min^{-1}. The variables affecting the complexation and extraction steps were examined. The precision (R.S.D.) for seven replicate injections of a mixture of 100 μg L^{-1} of Cr(III) and Cr(VI) was 1.2 and 0.9% for the retention time, 4.7 and 2.7% for the peak area, respectively. The concentration factor was 45 for Cr(III) and 40 for Cr(VI). The detection limit (LOD) of this method, calculated as three times the standard deviation of the blank signals was 7.5 μg L^{-1} for Cr(III) and 3.5 μg L^{-1} for Cr(VI), respectively. The proposed procedure was applied to the speciation of chromium in sediment samples with satisfactory results.

1. Introduction

Chromium occurs naturally in the earth crust, but its extensive use in various industrial processes and products has led to widespread chromium contamination in the environment. It is well known that the toxicological as well as biological properties of element chromium depend strongly on its chemical forms. In fact, while Cr(III) is an essential component having a vital role in the metabolism of glucose, lipids and protein, Cr(VI) is considered to be a more toxic form [1]. Total chromium does not provide sufficient information to understand its toxicity, bioavailability, biotransformation and ways of circulation. Therefore, an accurate and reliable method for the determination of chromium species is more important than the total chromium measurement. Different approaches have been reported for the speciation analysis of Cr being the combination of a powerful separation technique in environmental and biological samples such as flame atomic absorption spectrometry (FAAS) [2,3], inductively coupled plasma atomic emission spectrometry (ICP-AES) [4], inductively coupled plasma atomic emission spectrometry (ICP-OES) [5,6], inductively coupled plasma-mass spectrometry (ICP-MS) [7], electrothermal atomic-absorption spectrometry (ET-AAS) [8], electrochemical [9], fluorometry [10,11] and chemiluminescence [12].

Despite increasingly sensitive analytical instrumentation, the determination of Cr at trace levels usually requires previous preconcentration [13,14]. Cloud point extraction (CPE), based on the clouding phenomena of non-ionic surfactants, has become an alternative to conventional solvent extraction due to a number of possible advantages such as low cost, environmental safety, a high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and high concentration factors. CPE occurs in aqueous solutions of non-ionic surfactants that become turbid when heated to a temperature known as the cloud-point temperature (CPT), thus forming a two-phase system. During the formation of the two phases, hydrophobic complexes can be entrapped "in situ" in the surfactant phase. Mere centrifugation and decanting of the aqueous phase can easily separate the two phases. The first use of the CPE technique for preconcentration of metals was pioneered by Watanabe et al. [15], who studied the extraction of manganese with 1-(2-pyridylazo)-2-naphthol (PAN) as a complexing agent. Extracting ligands such as 1-(2-thiazolylazo)-2-naphthol (TAN) [16], 8-hydroxyquinoline (8-HQ) [17] and lately,

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dibromophenylfluorone (Br-PF) [8] have been used for cloud point extraction in several procedures.

In recent years CPE has been used as a preconcentration step in conjunction with detection by atomic absorption spectrometry for the speciation analysis of Cr [3], Fe [18], Sb [19], As [20] and Sn [21] species. Atomic absorption spectrometry can easily detect the total amount of chromium, but it can not distinguish between Cr(III) and Cr(VI). Many of these methods have the disadvantage that one of the species is determined as the difference between total and the other chemical form of the element. The separation of element species prior to determination is necessary if independent results are to be obtained. In some cases, chromatographic systems techniques can be used for simultaneous determination of the most important element species in a single step [22].

The aim of the present work was to apply CPE as a preconcentration step for chromium species combined with high-performance liquid chromatographic determination. In the developed system, 1-(2-thiazolylazo)-2-naphthol (TAN) was used as the chelating agent and Triton X-114 as the extractant. Potential factors affecting the CPE preconcentration of Cr(III) and Cr(VI) were investigated in detail. The developed method was applied for chromium speciation in lake sediments with satisfactory results.

2. Experimental

2.1. Instrumentation

A Waters Breeze HPLC system (Waters, USA) equipped with a Waters 1525 Binary Pumps, a Waters 2487 Dual λ Absorbance Detector, and injector was employed to determine the concentration of Cr(III) and Cr(VI) species in extract phase. All separations were performed on a C18 column (Waters ODS 5 μm, 150 cm × 4.6 mm i.d.) at room temperature. The Breeze software was used to acquire and process spectral and chromatographic data from the detector 2487. The chromatograms were monitored at 490 nm for optimization experiments and peak area measurements.

A thermostated water bath maintained at the desired temperatures (Jincheng guosheng Science Instrument, Jiangsu, China) was used for equilibration temperature experiments and the phase separation was accelerated with a centrifuge (Xiangyi Laboratory Instrument Co., Ltd., Hunan, China). All the pipettes and vessels used for trace analysis were soaked in 10% nitric acid for at least 12 h and subsequently at least three times with pure water.

2.2. Reagents

All chemicals were of analytical or better grade, and water used to prepare sample and buffer solutions was freshly deionized by EASYpure water purification system with a 0.2 mm fiber filter (Barnstead, USA). Triton X-114 (>99%), cetyltrimethylammonium bromide (CTMAB) and TAN were purchased from Sigma (St. Louis, MO, USA) and used without further purification. A 2.0 mmol L^{-1} of TAN solution was prepared by dissolving suitable amount of the reagent in methanol. A mixture of methanol (Chromatographic Grade, Acros Organics, Morris Plains, NJ)–water (69:31, v/v) and 4.5 mmol L^{-1} CTMAB buffered with 0.03 mol L^{-1} NaAc–HAc solution (pH 5.5) was employed as the mobile phase at a flow rate of 0.8 mL min^{-1}. The pH of the sample solution was adjusted to 5.5 with 1 mol L^{-1} acetic acid. The mobile phase was filtered through a 0.45 μm filter, and was degassed in an ultrasonic bath for 20 min just prior to use. To ensure good day-to-day precision for the HPLC separation, methanol at 1.0 mL min^{-1} was used to wash the HPLC column for 50 min to remove residual surfactant adsorbed on the column after 1-day experiment.

Stock standard solutions of Cr(III) and Cr(VI) at a concentration of 1000 mg L^{-1} were prepared from $Cr(NO_3)_3$ and $K_2Cr_2O_7$, respectively. Working standard solutions were prepared by stepwise diluting the stock solutions just before use.

2.3. Procedure for cloud point extraction

For the CPE, aliquots of 10.0 mL of a solution containing the analytes, 2.0 mmol L^{-1} TAN and 1.25% (v/v) Triton X-114 at a suitable pH 5.5 were heated in a thermostatic water bath maintained at 40 °C for 20 min. The mixture was centrifuged at 4000 rpm for 15 min for phase separation, and then cooled in an ice-bath for 10 min so that the surfactant-rich phase became viscous and was retained at the bottom of the tube. In this way, the supernatant aqueous phase was easily decanted. In order to reduce the viscosity and facilitate sample handling prior to HPLC separation, 0.5 mL of methanol was added to the remaining surfactant-rich phase.

2.4. Sample collection and preparation

The investigated area is located in the Chaohu Lake in the middle of Anhui Province (China). The localization of the main sampling sites is presented in Fig. 1. Sediment samples were collected from six sites of the Chaohu Lake. The samples were dried in an oven at 105 °C and homogenized with a sieve. Then a 1.0 g sediment sample was weighed and transferred into conical flask. Sample solution was obtained by exchanging the contaminated sediment with water in a 1:5 ratio (soil:deionized water) for 2 h in an end-over-end shaker, 4000 rpm for 15 min and filtering through 0.45 μm Schleicher and Schuell syringe filters [23]. Then, cloud point extraction procedure given above was applied to the final solutions.

3. Results and discussion

3.1. Effect of pH on CPE

Cr(III) and Cr(VI) reacts with TAN in acidic medium to form hydrophobic complexes which are subsequently trapped in the surfactant micelles (e.g. Triton X-114) and separated from the aqueous phase. The formation of metal complexes and its chemical stability are the two important influence factors for the CPE and the pH of the sample solution plays a critical role on metal chelate formation and subsequent extraction efficiency. Thus, the effect of pH ranged from 3.0 to 9.0 on extraction efficiency of Cr(III) and Cr(VI) was evaluated and the results are shown in Fig. 2. As can be seen, the optimum pH for Cr(III) and Cr(VI) maximum extraction efficiency was 5.5. In more acidic solutions, absorbance decrease may be attributed to some hydronium ions trapped in cage of TAN which avoids interaction between metal ion and TAN. On the other hand, when the pH of solution is higher than 5.5, the signal intensity of analyte is decreased obviously due to the degradation of TAN complexing. Hence, pH of 5.5 was preferred for all subsequent studies.

3.2. Effect of Triton X-114 concentration on CPE

The non-ionic surfactant Triton X-114 was chosen for the formation of the surfactant-rich phase due to its low cloud-point temperature (22–30 °C), low UV absorbance and high density of the surfactant-rich phase, which facilitates phase separation by centrifugation. The effect of Triton X-114 concentration was investigated within the range of 0.25–1.5% (v/v) on the extraction efficiency and the results are shown in Fig. 3. It was found that the extraction efficiency of analytes increased as the concentration of Triton X-114 increased from 0.5 to 1.25% (v/v), and remained