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Ultrasound enhanced air-assisted surfactant liquid–liquid microextraction based on the solidification of an organic droplet for the determination of chromium in water, air and biological samples

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ABSTRACT

Ultrasound enhanced air-assisted surfactant liquid–liquid microextraction based on the solidification of a floating organic droplet (UEAASLLM-SFO) followed by the electrothermal atomic absorption spectrometry was evaluated for extraction and preconcentration of chromium species in water, air and biological samples. Sodium dodecyl sulfate (SDS) was used as an ion-pairing age. The Cr(VI) was complexed with 1,5 diphenylcarbazide (DPC) and extracted into 1-undecanol. Fine extraction solvent drops were rapidly formed by pulling in and pushing out the mixture of sample solution and extraction solvent for 5 times repeatedly using a 10-mL glass syringe. Ultrasound irradiations enhanced the rapid formation of fine droplets of the solvent in the sample solution and promoted the mass transfer of analyte into the extractant. Cr(III) ion was determined after oxidation to Cr(VI) using $KMnO_4$ in acidic media. The effects of various parameters on the extraction process such as type and volume of extraction solvent, acidity, chelating agent concentration, concentration of surfactant, sonication time and number of extraction times were investigated. Under the optimized conditions, the limit of detection and the limit of the quantification were found 0.003 and 0.01 μg L^{-1} with preconcentration factor of 174 for Cr(VI) respectively. The relative standard deviation (RSD, n = 5) of 0.1 μg L^{-1} Cr(VI) was 3.65%. The analytical curve for Cr(VI) was linear in the range of 0.01–0.3 μg L^{-1}. The accuracy of the method was performed by an analysis of a certified reference material (CRM), the reference standard SRM1640-Natural water (NIST). The method was successfully applied to the speciation and determination of Cr(III) and Cr(VI) in water, air and biological samples.

1. Introduction

Chromium is a chemical element with toxicological and biological properties in the environment that can exist in several oxidation states includingCr(III) and Cr(VI). Cr(III) is required for the living organisms, required for living organisms through retaining the normal metabolism levels of glucose, cholesterol, and fatty acids [1,2] while Cr(VI) can easily penetrate the cell wall and exert its noxious influence on the cell. Prior studies on human have shown the carcinogenic effects of chromium (VI). [3,4]. Chromium(VI) is also an environmental contaminant associated with industrial activities such as metal manufacturing and electroplating [5]. The levels of human exposure to environmental contaminants of chromium can be measured in the ambient environments such as air, water, and land at the point of human contact. The most used techniques including cloud-point extraction [6–8], coprecipitation [9,10], solid phase extraction [11–14], liquid–liquid extraction [15], and dispersive liquid–liquid microextraction (DLLME) [16,17] have been developed for separation and preconcentration of chromium species. However, several drawbacks such as the use of large volumes of organic solvents, the use of large volume of sample, time-consuming extraction steps, low enrichment factor and the requirement to the dispersive solvent have been reported for the mentioned techniques. A novel DLLME method was introduced based on the solidification of floating organic droplets (DLLME-SFO) [18]. In this method, a solvent with low density and low toxicity and with a melting point around room temperature was used as extraction solvent [19]. In this method, the use of hazardous solvents like halogenated hydrocarbons is not required. However, both DLLME and DLLME-SFO require a large amount of toxic dispersive solvents that can decrease the partition coefficient of analytes which consequently reduces the extraction efficiency [20]. Recently, a new method of DLLME without a need for dispersive solvent called air-assisted liquid–liquid microextraction (AALLME) has been developed in which, the mixture of aqueous sample solution and extraction solvent

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is withdraw into a syringe and injected into a tube [21]. The analytes exchange into the extraction solvent via the bolus flow formed during the process of aqueous sample withdrawal and injection [22]. However, in comparison with the extraction solvents in mentioned methods, it is necessary to use low density solvents with less toxicity which can easily be collected in AALLME [20]. The application of ultrasound irradiations in AALLME leads to the rapid formation of fine droplets of the extractant in the aqueous solution, and the contact surface between both immiscible liquids is significantly enlarged. Smaller fine droplets of the extractant and enlarged interfaces lead to a significant increase in the analyte mass transfer into the extractant. Consequently, higher extraction efficiency is achieved in a short period of time. The main drawback of DLLME or AALLME is their inability to extract hydrophilic compounds into the extraction solvent. To overcome this limitation, a new method for extraction of ionic and polar compounds into an organic solvent has been reported, namely ion pair based-surfactant assisted microextraction (IP-SAME) [23]. The aim of the present work is to use the low-density and low toxic solvent, 1-undecanol in present ion pair based-surfactant and to optimize the experimental conditions of UEAASLLM-SFO and analysis by ETAAS. 1,5-diphenylcarbazide (DPC) is most exclusively usually used as reagent for Cr(VI). The Cr(VI)-DPC complex has cationic nature and cannot be extracted into solvents. To the best of our knowledge, there is not any report for the extraction of hydrophilic metal complex in UEAASLLM-SFO.

2. Experimental

2.1. Reagents

All reagents used were of analytical grade. A stock standard solution of Cr(VI) at a concentration of 1000 μg mL^{-1} was prepared by dissolving an appropriate amount of $K_2Cr_2O_7$(Merck, Darmstadt, Germany) in 100 mL of in double-distilled deionized water. Working standard solutions were obtained by appropriate dilution of the stock standard solution. A stock solution of Cr(III) at a concentration of 1000 μg mL^{-1} was prepared by dissolving an appropriate amount of $Cr(NO_3)_3$ (Merck, Darmstadt, Germany) in 100 mL of in double-distilled deionized water. 1-undecanol, 1-dodecanol, 1,10-dichlorodecane, and hexadecane were purchased from Merck (Darmstadt, Germany). A solution of 10^{-3} mol L^{-1} sodium dodecyl sulfate (SDS) was prepared by dissolving an appropriate amount of SDS (Sigma St. Louis, Mo, USA) in double-distilled deionized water. A solution of sulfuric acid was used for the pH adjustment. A solution of 0.001 mol L^{-1} of 1,5 diphenylcarbazide was obtained daily by dissolving an appropriate amount of DPC (Merck Darmstadt, Germany) in acetone. Sodium azide, $KMnO_4$, and H_2SO_4 were purchased from Merck (Darmstadt, Germany). $Pd(NO_3)_2$ as a chemical modifier was obtained from Merck (Darmstadt, Germany).

2.2. Apparatus

The Spectra AA from Varian 220 (Australia, http://www.varianinc.com) was equipped with a graphite furnace atomizer GTA-110 and an auto sampler (ASC-6100) for the determination of chromium. Deuterium background correction was employed to correct non-specific absorbance. A chromium hollow cathode lamp and pyrolytic graphite coated graphite tubes were used. The sample injection volume was 20 μL in all experiments. The instrumental parameters and temperature program for the graphite atomizer were given in Table 1. Argon 99.995% (from Roham Gas Co., Tehran, Iran) was used as a protective and purges gas. A Universal 320R centrifuge equipped with a swing out rotor (6-place, 5000 rpm, Cat. No. 1628A) from Hettich (Kirchlengern, Germany) was applied for separation. A 50/60 Hz, 350 W ultrasonic bath with temperature control (BANDELIN SONOREX, Germany) was used.

Table 1
Operating parameters for ET-AAS.

Instrumental parameters for chromium determination			
Spectrometer parameter			
Current(mA)			7
Wavelength (nm)			357.9
Slit width (nm)			0.2
Stage	Temperature(°C)	Time(s)	Argon gas flow(mL min^{-1})
Drying	85	30	3.0
Drying	95	10	3.0
Drying	130	15	3.0
Pyrolysis	900	5	3.0
Pyrolysis	1100	2	3.0
Pyrolysis	1200	2	0.0
Atomizing	2600	3	0.0
Cleaning	2700	2	3.0

2.3. Sample preparation

0.30 mL of blood and or 1 mL of urine samples were directly taken into Teflon polytetrafluoroethylene (PTFE) flasks. 2 mL of a freshly prepared mixture of concentrated HNO_3–H_2O_2 (2:1, v/v) was added into each of samples and heated on a hot plate at 90–95 °C for 1 h. After the required time interval, the flasks were cooled, and the resulting solutions were evaporated to dryness. Approximately 5 mL of 0.1 M nitric acid were added to the residue and then diluted to 10.0 mL. Aliquots of the obtained clear solutions were analyzed according to the described procedure.

The water samples (tap water, mineral water, and waste water) were filtered through a Millipore 0.45 μm pore-size membrane. 1 mL of the waste water sample was diluted to 10 mL and was treated according to the procedure.

A known volume of air was drawn through a filter to collect particulate chromium in workplace air. Then the collected particulates on filter were transferred into 25 mL beakers dissolved in 5 mL of concentrated HNO_3. The solution was diluted with distillated water up to 10 mL. Finally, 1.0 mL of this solutions was poured into tubes and after adjustment of pH, the volume of solution was adjusted to 10 mL.

2.4. Optimization of the furnace temperature program

To reduce matrix interferences and to increase accuracy, the use of a chemical modifier has become indispensable. Palladium nitrate is chosen as a chemical modifier, based on the obtained results, Addition of a 0.1% (w/v) $Pd(NO_3)_2$ solution is sufficient to get a good sensitivity. For aliquots larger than 10 μL, the signals were not further improved. The modifier volume was thus chosen as 10 μL. In order to obtain the maximum analytical signals, the pyrolysis and atomization temperature were optimized and the results were demonstrated in Fig. 1.

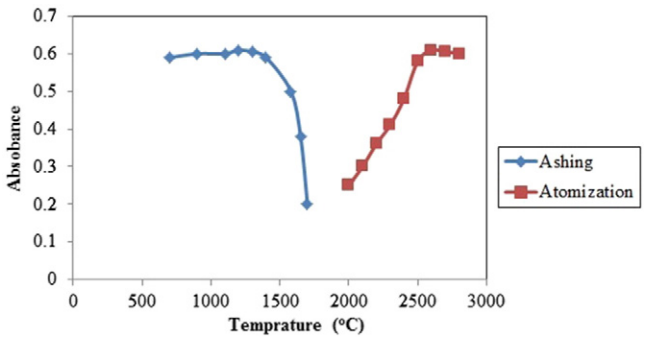

Fig. 1. Pyrolysis and atomization temperature curves after preconcentration. Concentration of Cr(VI): 0.1 μg L^{-1}.