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Preconcentration/separation of lead at trace level from water samples by mixed micelle cloud point extraction

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ABSTRACT

A mixed micelle-mediated cloud point extraction procedure was developed for lead. Triton-X114 and benzyldimethyl hexadecyl-ammonium chloride were used as mixed micellar medium. Lead(II) was reacted with 4-(2-pyridylazo) resorcinol at pH 6.0 to form hydrophobic chelates. The parameters including pH, ligand volume, concentrations of surfactants and centrifugation time were optimized. The effect of some common ions was also tested. The limit of detection was 1.15 $\mu g\,L^{-1}$ with preconcentration factor of 50. The accuracy of method was evaluated by the analysis of certified reference materials. The method was successfully applied to determination of levels of lead in water samples.

Introduction

The pollution is caused by heavy metals which are great concern due to their potentially toxic effects on living beings and ecosystem [1–3]. Among the heavy metals Pb(II) is one of the most toxic and dangerous metal and it causes the several toxic effects on human health and as well as animal. Therefore, the concentration of Pb(II) is detected in the environmental samples due to increasing of urbanization, industrial development and heavy traffic lead to contamination of water with heavy metals [4,5]. These heavy metals may disturb the metabolic process of human body and also damage the IQ level [6–8].

Several techniques including atomic absorption spectrometry (AAS) [9], inductively coupled plasma atomic emission spectrometry (ICP-AES) [10], inductively coupled plasma mass spectrometry (ICP-MS) [11], electrothermal atomic absorption spectrometry (ETAAS) [12] and flame atomic absorption spectrometry (FAAS) [13] have been widely used for the determination of trace amount of Pb(II). However, there are some disadvantages such as expensive, time consuming and require skilled operators arising from the above mentioned techniques. On the contrary, FAAS has a several advantages including good selectivity, speed and fairly low operational cost [14].

A number of separation and preconcentration methods such as liquid-phase microextraction (LPME) [15], dispersive liquid–liquid microextraction (DLLME) [16], solid phase extraction (SPE) [17,18] and cloud point extraction (CPE) [19] have been widely used in analytical chemistry. CPE extraction technique is one the most popular sample pretreatment approach. This extraction technique is based on the mixing either cationic/anionic surfactant with nonionic surfactants, formation of covalent hydrophobic chelates of the respective metal ion with suitable reagents. All these methods have some limitations. While, CPE offers many advantages such as cost effective, easy and rapid related to sample preparation. These techniques also overcome the few drawbacks of conventional techniques [20–22].

In the present study, CPE extraction based on mixed micelle mediated was developed for the preconcentration and determination of Pb(II) after the formation of a complex with chelating agent PAR in acidic media and later analysis by FAAS using non-ionic and cationic surfactant. The proposed method was applied for the determination trace level of Pb(II) in different water samples.

Materials and methods

Reagents and glass wares

Analytical grade reagents and chemicals (Merck, Darmstadt, Germany) were used. Ultra-pure water (Milli-Q Millipore 18.2 MO cm^{-1} resistivity) was used in the experimental work.

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Nitric acid (65%) and 4-(2-pyridylazo) resorcinol (PAR) as chelating agent (Merck, Darmstadt, Germany) were used. Stock standard solution (1000 mg L^{-1}) of Pb(II) was prepared with the addition of an appropriate amount of nitrate salts in 1% nitric acid. While working standards of corresponding metal ion were prepared from the dilution of stock standard solution with distilled water. Benzyldimethyl hexadecyl-ammonium chloride as cationic surfactant (Merck, Darmstadt, Germany) was used as cationic surfactant.

Buffer solutions were prepared by using combination of salts and solutions as follows: phosphate buffer solution (pH 3.0–4.0, sodium dihydrogen phosphate/phosphoric acid), phosphate buffer solution (pH 5.0–8.0 sodium dihydrogen phosphate/disodium hydrogen phosphate).

PAR solution was prepared by dissolving 0.1 g of (0.1% w/v) in 100 mL of ethanol/water on daily basis. Triton X-114 and benzyldimethyl hexadecyl-ammonium chloride (0.2%, v/v) were prepared by dissolving 0.2 g in 100 mL of distilled water. The accuracy of proposed method was evaluated by analyzing of CRM fortified water (TMDA 53.3) and waste water (SPS-WW2).

Instrumentation

A Perkin Elmer Model 3110 flame atomic absorption with air–acetylene flame was used for determination of trace amount of lead. Hollow cathode lamp was used and operated at recommended current. The calibration curves (1.0–10 $\mu g\ mL^{-1}$) was established by using of working standard solutions. The instrumental parameter was adjusted according to the manufacturer's recommendations. After applied the proposed procedure, all measurements were subjected to FAAS using microinjection system. A model Nel pH 900 digital pH meter equipped with a combined glass electrode was used for the pH adjustment.

Model of work

For the CPE, an aliquot of 10 mL of solution containing 100 $\mu g\ L^{-1}$ target analyte was transferred into 50 mL of conical bottom vials. Added 2.0 mL of phosphate buffer (pH 3.0–8.0) into the solution. The pH of the sample solution was adjusted to desired pH 6.0 with the addition of nitric acid or sodium hydroxide (1 mol L^{-1}). After adjusting the pH, 100–400 μL of 0.1% PAR, 200 μL 0.05–0.5 (w/v) % of Triton X-114, 200 μL of benzyldimethyl hexadecyl-ammonium chloride 0.05–0.5 (w/v) % and 1.0 mL of KI (0.1%) were added to extract the metallic chelates into the miceller solution. After this, the extracted solution was placed in a thermostatic bath at 50 °C for 30 min. For the separation of two phases, the solution was centrifuged for 10 min at 4000 rpm. Then the aqueous phase was carefully removed by decantation and the surfactant rich phase was diluted in 500 μL of acidic methanol (HNO_3 1.0 mol L^{-1}) and finally the solution was aspirated into FAAS using microinjection system for the determination of Pb(II). Blank samples were also treated in same way as the samples were treated.

Applications

In the present study different water samples including were collected from Turkey. The samples were collected into polyethylene plastic bottles (1.5 L capacity). Before analysis all the collected samples were filtered through a 0.45 μm pore size membrane filter (Millipore Corporation, Bedford, MA, USA) to remove suspended particulate matter. The developed procedure was applied to water certified reference material and some water samples. After adjusting the pH of the water samples to 6.0, the method as described in the section "Model of work" was performed to water samples.

Results and discussion

Effect of pH

pH is one of the most important and key factor in metal–chelate formation and preconcentration technique [23–29]. Hence, the effect of pH on CPE extraction procedure was investigated in the range of 3.0–8.0. The quantitative recovery was achieved at pH 6.0 (Fig. 1). The recovery of Pb(II) was decreased at more acidic and more alkaline pH because of incomplete complex formation. The all subsequent studies were carried out at pH 6.0.

Effect of ligand volume

The amount of ligand is the second important factor in the present study. The effect of the different amounts of PAR on the quantitative recoveries of analyte was examined ranging from 100–400 μL of ligand as shown in Fig. 2. From the results it was observed that the analytical signals of Pb(II) were decreased at the beginning and then were increased with the increasing of LV. Thus, 200 μL of LV was chosen as optimum.

Effect of the concentration of surfactants

Several concentrations of the Triton X-114 and benzyldimethyl hexadecyl-ammonium chloride surfactants were tested in order to ensure quantitative recovery of analyte. The effect of Triton X-114 concentration and benzyldimethyl hexadecyl-ammonium chloride concentration on the quantitative recoveries of Pb(II) were investigated in the range of 0.05–0.5 (w/v) %. The results are shown in Fig. 3 for Triton X-114 concentration and Fig. 4 for benzyldimethyl hexadecyl-ammonium chloride concentration. The recovery of studied metal was increased by increasing of Triton X-114 and benzyldimethyl hexadecyl-ammonium chloride concentrations up to higher concentration.

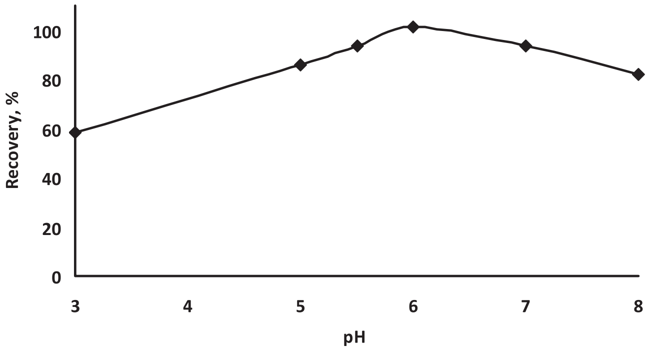

Fig. 1. Effect of the pH on the recovery of Pb(II).

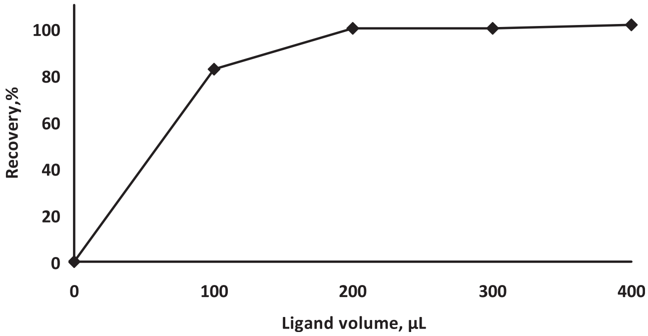

Fig. 2. Effect of the ligand volume on the extraction efficiency of Pb(II).