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Determination of trace silver in water, wastewater and ore samples using dispersive liquid–liquid microextraction coupled with flame atomic absorption spectrometry

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ABSTRACT

A fast and reliable dispersive liquid–liquid microextraction (DLLME) method for the determination of trace levels of silver by flame atomic absorption spectrometry (FAAS) was developed. The method is based on highly-efficient separation and preconcentration of silver by the complex formation of Ag(I) with 2-mercaptobenzimidazole and extracted by DLLME procedure using carbon tetrachloride as extraction and acetone as disperser solvent. After establishment of a cloudy solution, the phase separation is achieved and Ag(I) is determined in the enriched phase by FAAS. The method yields a linear calibration curve in the concentration range of 1–100 ng mL^{-1} of Ag(I), and the limit of detection is 0.41 ng mL^{-1}. The proposed method was successfully applied to determine the trace amounts of silver in water, radiology film processing wastewater and ore samples.

1. Introduction

Metal ions play a crucial role in different fields of science and technology. Silver, as a precious metal finds an extensive use in accessories, tableware, coins and is widely utilized in the photographic and imaging industry. Due to its antibacterial properties, silver is usually used as an antiseptic agent and disinfectant, as filter for purification of water, in food processing and drugs [1].

Although the benefits of this valuable element are undeniable, its extended use results in being released into the environment and hence the chance of exposure to silver increases, causing serious health effects in living organisms [2]. Silver has interaction with amino acids, proteins and essential nutrients, especially vitamins E and B12. The excess amounts of silver in human body shows toxic effect and result in skin diseases and blood disorder [3,4]. The potential toxicity of silver depends on its forms. The ionic form of silver has been shown to be more toxic than other silver forms. The World Health Organization (WHO) has considered a maximum allowable limit of 0.1 mg L^{-1} of silver ions in drinking water, but the recommendations of the United States Environmental Protection Agency (USEPA) permits concentration of 0.05 mg L^{-1} as the maximum [5].

Silver is also present in some minerals in trace amounts and can be introduced into the environment through geochemical activities [6]. Therefore, the development of analytical methods for accurate determination of trace amounts of silver is an important task for environmental monitoring and exploration.

Flame atomic absorption spectrometry (FAAS) [7–9], graphite furnace atomic absorption spectrometry (GFAAS) [10], inductively coupled plasma atomic emission spectrometry (ICP-AES) [11], inductively coupled plasma mass spectrometry (ICP-MS) [12] and electroanalytical techniques [13] have been used for the determination of trace heavy metals. Application of instrumental analysis has some limitations because of the presence of metal ions at lower concentration than the detection limits of instrumental techniques, complexity of sample and high cost. Preconcentration and separation procedures including liquid–liquid extraction (LLE) [14,15], cloud point extraction (CPE) [16], stripping voltammetry [17], co-precipitation [18], membrane filtration [19] and solid-phase extraction (SPE) [20,21] can be used to overcome these problems. LLE is one of the oldest preconcentration techniques which is widely employed for sample preparation, because of its simplicity and low cost.

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However it suffers from various factors, particularly time-consuming and requiring large volumes of organic solvents. Due to using toxic organic solvents, LLE produces hazardous laboratory waste making great threat to the environment and human body. A drastic reduction of the extractant phase volume can miniaturized LLE which reduces both time and organic solvent consumption. This purposed statement has been sued for the development of a new environment-friendly method known as liquid phase microextraction (LPME). Recently LPME has been recognized as a powerful technique for separation and enrichment of various inorganic and organic analytes [22–24]. An attractive mode of LPME is dispersive liquid–liquid microextraction (DLLME) which has received much attention for sample pretreatment since 2006 [25]. In this method a few microliters of solvents mixture containing an extraction solvent and a disperser solvent with high miscibility in both extractant and aqueous phase is rapidly injected into the sample. The result of this injection is the formation of a cloudy solution which consists of minute droplets of the extraction solvent. Due to extremely large area of emulsified droplets the extraction equilibrium is reached rapidly. The application of DLLME for the determination of trace metals in different matrices resulted in high enrichment factors for analytes [26–29].

In the present paper, a new DLLME method combined with FAAS was developed for the determination of Ag(I) based on the complex formation with 2-mercaptobenzimidazole. The effective parameters on extraction recovery such as type and amount of extraction and disperser solvents were optimized.

2. Experimental

2.1. Apparatus

A GBC flame atomic absorption spectrometer (FAAS) model Avanta (Australia) fitted with a silver hollow cathode lamp (Unicam, Franklin, MA) was used to perform atomic absorption measurements. The wavelength of 328 nm, lamp current of 4 mA and spectral band pass of 0.50 nm were used throughout. An air-acetylene flame was used for the determination of the Ag(I). A Metrohm 632 (Switzerland) pH-meter was used to measure pH with a combined glass electrode. A model BHG HERMLE centrifuge (Germany) was used for the phase separation.

2.2. Reagents

All chemicals were of analytical grade and double distilled water was used throughout. A stock solution of Ag(I) (1000 μg mL^{-1}) was prepared by dissolving of 1.5748 g pure silver nitrate (Merck, Darmstadt, Germany) in water and diluting to 1000 mL in a volumetric flask. Working standard solutions were obtained daily by successive dilutions of this stock solution. Buffer solution at pH 5.5 was prepared from 0.2 mol L^{-1} sodium acetate (Merck) and 0.2 mol L^{-1} of acetic acid (Merck). A solution of 2-mercaptobenzimidazole (MBI), 0.026 mol L^{-1}, was prepared by dissolving of 12 mg of MBI (Merck) in 3 mL of acetone containing 200 μL of carbon tetrachloride.

2.3. Dispersive liquid–liquid microextraction procedure

In order to perform DLLME, 12 mL of the sample or standard solution containing Ag(I) was placed in a glass test tube with a conical bottom and 1.0 mL of acetate/acetic acid buffer at pH 5.5 was added. Then, a mixture of 3 mL of acetone (as disperser solvent) and 200 μL of carbon tetrachloride (as extraction solvent) containing 2-mercaptobenzimidazole (MBI) (0.026 mol L^{-1}) was rapidly injected into the sample solution by a microsyringe. A stable cloudy solution (water, acetone and CCl_4) was formed. During this stage the Ag(I)–MBI complex is extracted into the fine droplets of CCl_4. Then the mixture was centrifuged for 5 min at 5000 rpm to achieve phase separation. The dispersed fine droplets of the extraction phase were sedimented at the bottom of the conical test tube. After removal of aqueous solution, by means of a microsyringe, all the sedimented phase (150 ± 5 μL) was removed and diluted with 350 μL of methanol. This final solution was aspirated directly into the flame of AAS for the determination of Ag(I). A blank solution was also run under the same analytical conditions without adding any Ag(I).

2.4. Preparation of samples

Two water samples including tap water (Ahvaz, Iran) and river water (Khuzestan Province, Iran) were collected, filtered using a filter paper (Whatman No. 40) and acidified with HNO_3 prior to use. An aliquot of water samples was treated under the recommended procedure.

A radiology film processing wastewater sample was obtained from the local hospital (Ahvaz, Iran) and filtered using a filter paper (Whatman No. 40).Then it was acidified with HNO_3 and stored in the dark at 4 °C. An aliquot of this solution was treated for determination of Ag(I) using the proposed DLLME procedure.

Five grams of a powdered ore sample (Dehdasht, Iran) was accurately weighed into a 50 mL glass beaker, to which 25 mL of concentrated nitric acid was added. The sample was gently heated on a sand bath at a low boiling temperature until dense white fumes disappeared. After cooling, 5 mL of 5 mol L^{-1} nitric acid and 10 mL of water were added into the beaker to dissolve the analyte. The solution was filtered into a 50 mL volumetric flask, and after washing the filter paper with water, the solution was diluted to the mark [30].

3. Results and discussion

In order to achieve the quantitative extraction of Ag(I) by DLLME method, 2-mercaptobenzimidazole (MBI) was selected as a complexing agent in the organic phase. MBI forms stable complexes with a number of metals and has found many applications in trace element separation and preconcentration methods [31–33]. Therefore, this reagent was chosen for preconcentration of Ag(I) using DLLME method.

3.1. Selection of extraction solvent and its volume

Careful attention should be paid to the selection of the extraction solvent. A suitable extractant needs to meet the following characteristics: (1) immiscible in water, (2) higher density than water and (3) high extraction capability for target analytes. Generally, the choice of an extraction solvent is based on the physical and chemical properties of the solvents. For this purpose, chloroform, carbon tetrachloride and dichloromethane were tested as extraction solvents. The study was performed using 3.0 mL of acetone containing different volumes of the extraction solvent to achieve about 150 μL of the sedimented phase. The results revealed that carbon tetrachloride has the highest extraction efficiency in comparison with the other tested solvents. In addition CCl_4 can form a stable cloudy solution and has less consumption of volume. Therefore, CCl_4 was selected as extraction solvent in the subsequent experiment.

To examine the effect of extractant solvent volume, solutions containing different volumes of carbon tetrachloride in the range of 100–350 μL and fixed volume of acetone as disperser were used