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ORIGINAL ARTICLE

Cloud point extraction-flame atomic absorption spectrometry for pre-concentration and determination of trace amounts of silver ions in water samples

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Abstract A cloud point extraction (CPE) method was used as a pre-concentration strategy prior to the determination of trace levels of silver in water by flame atomic absorption spectrometry (FAAS) The pre-concentration is based on the clouding phenomena of non-ionic surfactant, triton X-114, with Ag (I)/diethyldithiocarbamate (DDTC) complexes in which the latter is soluble in a micellar phase composed by the former. When the temperature increases above its cloud point, the Ag (I)/DDTC complexes are extracted into the surfactant-rich phase. The factors affecting the extraction efficiency including pH of the aqueous solution, concentration of the DDTC, amount of the surfactant, incubation temperature and time were investigated and optimized. Under the optimal experimental conditions, no interference was observed for the determination of $100 \, ng \cdot mL^{-1} \, Ag^+$ in the presence of various cations below their maximum concentrations allowed in this method, for instance, $50 \, \mu g \cdot mL^{-1}$ for both Zn^{2+} and Cu^{2+}, $80 \, \mu g \cdot mL^{-1}$ for Pb^{2+}, $1000 \, \mu g \cdot mL^{-1}$ for Mn^{2+}, and $100 \, \mu g \cdot mL^{-1}$ for both Cd^{2+} and Ni^{2+}. The calibration curve was linear in the range of $1–500 \, ng \cdot mL^{-1}$ with a limit of detection (LOD) at $0.3 \, ng \cdot mL^{-1}$. The developed method was successfully applied for the determination of trace levels of silver in water samples such as river water and tap water.

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1. Introduction

Silver is a non-essential element in human body. After its ingestion or chronical topic application, silver may be deposited on human skin and mucosa, which may result in a kind of permanent blue-gray, and even lead to acute death (Renner, 1982). Therefore, the determination of silver has

become one of the important projects in the field of environmental monitoring and health epidemic prevention. In addition, the silver is an important precious metal (EPA, 1980) because of its excellence in both thermal conductivity and electrical conductivity. It has been widely used in photographic industry, chemical industry, metallurgy, medicine and accessories processing and so on, which has made silver occur in the environment at trace and ultra-trace levels. Therefore, a very sensitive method is necessary for the accurate and precise determination of silver in various matrixes.

Some atomic spectrometric techniques such as flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS) (Šrámková et al., 2000; Baron et al., 2000), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Argekar et al., 1995) as well as inductively coupled plasma mass spectrometry (ICP-MS) (Hu et al., 2002; Chang et al., 2003) have been developed for the determination of silver in different environmental samples. In order to lower the detection limit, a variety of pre-concentration processes have also been utilized prior to the analysis with the aforementioned technologies. Those sample preparation techniques include solvent extraction (Koh and Sugimoto, 1996), solid phase extraction (Dadfarnia et al., 2004; Katarina et al., 2006), precipitation (Sant'Ana et al., 2002) and adsorption on tungsten wire (Lin et al., 2010). However, most of these procedures are tedious, time-consuming and may cause sample contamination (Rahman et al., 2004).

Cloud point extraction (CPE) method is a new and environmental friendly liquid–liquid extraction technology and has gained large attention in separation science. CPE is based on the clouding phenomena of surfactants. (Bezerra et al., 2005). Changes in the experimental parameters (e.g., solution pH, temperature, concentration, and time) lead to phase separation. It can be used to separate the hydrophobic and hydrophilic material, and it is economic, safe, environmental benign, efficient and convenient (Manzoori and Bavili-Tabrizi, 2002; Carabiasmartínez et al., 1999; Liu et al., 2014). It has drawn wide application in both life science and environmental science (Jong et al., 2005; Shariati and Yamini, 2006; Liu et al., 2016; Paleologos et al., 2005; Safavi et al., 2004).

In recent years, cloud point extraction was successfully used in enrichment, separation and determination of the metal elements. In the present study, we applied CPE for the separation and pre-concentration of Ag(I) ions from aqueous solutions using a Triton X-114 as a non-ionic surfactant and a sodium diethyl dithiocarbamate (DDTC) as a chelating agent, followed by its determination with FAAS. The parameters influencing the efficiency of CPE such as effects of pH, the concentrations of both Triton X-114 and DDTC, incubation temperature and time were systematically studied and optimized. The developed CPE procedure has been successfully applied to the determination of the concentration of Ag(I) ions in water samples.

2. Material and methods

2.1. Materials and chemicals

Stock standard solutions of 1000 mg·L^{-1} Ag$^+$ were prepared by dissolving AgNO$_3$ in 2% (v/v) HNO$_3$. Working standard solutions were obtained daily by the serial dilution of standard stock solution with Double Distilled Water (DDW). The chelating reagent solution at 1×10^{-2} mol·L^{-1} was prepared by dissolving sodium diethyldithiocarbamate (DDTC) in DDW. The non-ionic surfactant Triton X-114 purchased from Aladdin was further diluted to 50 g·L^{-1} prior to use in this work. The pH of the solutions was adjusted with 0.2 mol·L^{-1} sodium acetate (NaAc) and 0.2 mol·L^{-1} of acetic acid (HAC). DDW was used throughout the work.

2.2. Apparatus

A WFX-120 FAAS (Beijing Ruili Analytical Instrumental Co., Beijing, China) was used for quantitative analysis of silver while a TDZ5-WS centrifuge (Shanghai Lu Xiangyi centrifuge Instrument Co., Ltd, Shanghai, China) for facilitating phase separation. The pH was measured by Ohaus Starter 3C pH meter (Pine Brook, NJ, USA).

2.3. Operating procedure

To a 10-mL centrifuge tube, were added a certain amount of standard solution of silver, 0.5 mL of 0.01 mol·L^{-1} DDTC solution, 1.0 mL of pH = 5 buffer solution, and 0.7 mL of 50 g·L^{-1} Triton X-114 solution followed by diluting the mixture to the 10-mL mark with DDW and mixing them well. The resulting solution containing the analyte was incubated in the water bath at 40 °C for 20 min. Separation of the phases was achieved by centrifugation at 4000 rpm for 10 min. After centrifugation, it was cooled in an ice bath for 10 min to increase the viscosity of the surfactant-rich phase. The aqueous phases could readily be discarded by inverting the tube. A volume of nitric acid (0.1 M) in methanol was added to the surfactant-rich phase (200 μL) to reduce its viscosity and to promote sample treatment prior to FAAS assay. The final solution (5 mL) was brought in the nebulizer of the spectrometer. Blank solution was also operated with a similar procedure and measured in parallel to the sample solutions. Cloud point extraction procedure is shown in Fig. 1.

3. Results and discussion

3.1. Effect of pH

It is of high importance to select appropriate chelating agent and metal ions to form a hydrophobic complex when metal ions are extracted by the cloud point extraction. The complex is extracted to surfactant phase. The extraction efficiency depends on the acidity of the solution as the pH has an impact on the overall charges of the analyte, thus affecting the generation of the complex between the metal and the surfactant active functional groups. Therefore, the different pHs on the extraction efficiency of Ag$^+$ were investigated. Cloud point extraction of Ag$^+$ was carried out in the pH range of 3–8. The results are shown in Fig. 2. The recovery for Ag$^+$ increased with increasing pH from 3 to 5, and reached a maximum with pH at 5.0. At low pH, the low recoveries for Ag$^+$ were observed owing to the decomposition of DDTC in acidic media to liberate CS$_2$. When the solution pH is higher than 7, it could be a problem for the hydrolysis of Ag$^+$. Taking into account all these factors, a pH value of 5.0 was chosen for further studies.