

Cloud Point Extraction and Determination of Trace Amounts of Silver by Flame Atomic Absorption Spectrometric Method

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Abstract: A selective, simple has been developed for determination of traces of silver based on Cloud Point Extraction (CPE). The preconcentration of Ag(I) using 4,2 pyridylazo resorsinol (PAR) as chelating agent and Triton X-114 as the extractant. The best extraction efficiency by carbonate buffer solution (pH 9.0) with good recoveries (>99.0%) was achieved. The effect of experimental conditions such as pH, concentration of chelating agent and surfactant, equilibration temperature and time on cloud point extraction was studied. The analyte was determined by flame atomic absorption spectrometry, after dilution with methanol. The calibration graph using the preconcentration system was linear in the range of 20-350 $\mu\text{g L}^{-1}$. The detection limit (3SDb/m) 6.0 $\mu\text{g L}^{-1}$ respectively. The developed method was successfully applied to the determination of Ag (I) in water samples.

Key words: Cloud Point Extraction, Trace Amounts, Silver, Flame Atomic Absorption Spectrometric Method.

1. Introduction

Silver is a heavy metal that its content in environmental samples is increased with the increasing use of silver compounds and silver-containing products in industry, in medicine and in commerce [1]. This element and its compounds and alloys are widely used in the production of jewelry, photographic films or paper, mirrors and dental fillings, among other applications. Moreover, because of its antibacterial properties, Silver compounds are added to a great variety of products, such as drinking water, polymeric materials or clothing [2-4].

Toxicity of silver to many aquatic organisms even at low concentrations, the serious environmental problems may occur [5]. Interaction of silver with essential nutrients, especially selenium, copper, Vitamins E and B₁₂, have focused attention on its potential toxicity [6]. Therefore, the determination of traces of Ag is needed in several fields. The monitoring of this element in a great variety of environmental and biological samples is also required due to its potential toxicity, which raises some concern owing to its widespread use in the industry [2].

Trace amounts of silver can be determined in different media by expensive analytical methods such as inductively coupled plasma mass spectrometry, inductively coupled plasma atomic emission spectrometry [3], and electrothermal atomic absorption spectrometry [7]. Flame atomic absorption spectrometry (FAAS) is not sufficiently sensitive for the direct determination of silver traces and it needs previous separation and preconcentration [3].

Cloud point extraction is a simple and powerful technique for separation and preconcentration of metal ions and it has many advantages, such as low cost, safety, and a high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and high concentration factors [5, 8, 9].

Several ligands such as 1-(2-pyridylazo)-2-naphthol (PAN), 2-(2-thiazoylazo)-4-methylphenol (TAC), 1-(2-thiazoylazo)-2-naphthol (TAN), dialkyldithio phosphates (DDTP), have been used in cloud point extraction of metal ions [6].

The goal of this work was to apply CPE as a preconcentration step for flame atomic absorption spectrometric selective determination of traces of

silver ion in real samples by used of 4,2 pyridylazo resorsinol (PAR) as the ligand.

2-Experimental

2.1 Instruments

Atomic absorption determinations were made with Sens AA GBC scientific equipment spectrophotometer equipped with a hollow cathode lamp and a deuterium background correction respective wavelengths using air-acetylene flame for measurements of analytes. All pH readings were carried out with JENWAY pH-meter model 3510 with combined glass electrode.

2.2. Reagents and Solutions

All chemicals used were of analytical-reagent grade (Merck) and all solutions were prepared with double distilled water. A stock standard solution of silver ($1000 \mu\text{g l}^{-1}$) was prepared by dissolving 0.1574 g of silver nitrate in distilled water containing 1ml concentrated nitric acid in a 100 ml volumetric flask and diluting to mark with distilled water and stored in the dark. The working standard solutions were prepared daily by stepwise diluting the stock standard solution with distilled water.

A solution of 0.01 mol l^{-1} , 4,2 pyridylazo resorsinol (PAR) was prepared by dissolving of appropriate amount of this reagent in Ethanol.

It was experimentally convenient to prepare a working solution (0.5% (w/v) Triton X-114) as follows: 0.53 gr surfactant Triton X-114 made up to 100 ml with distilled water.

2.3. Test Procedure

For the CPE, 10 ml solution of Ag (final concentration $20\text{-}350 \mu\text{g L}^{-1}$), 0.5ml of 0.01 mol l^{-1} PAR solution, 2 ml of 0.5% (w/v) Triton X-114 and 1 ml of 0.1 mol l^{-1} buffer solution (pH 9) were placed in a centrifuge tube and heated in thermostated water bath at 55°C for 15 min. The resultant solution became turbid by heating. Phase separation was accelerated by centrifuging the tubes at 5000 rpm for 10 min. The aqueous phase was then separated completely by a 10 ml syringe centered in the tube after cooling in an ice bath. To decrease the viscosity of the surfactant rich phase and facilitate sample handling, 1 ml of methanol was added. The resultant solution was introduced into the flame by conventional aspiration.

3. Results and Discussion

3.1. The effect of pH

The effect of pH was examined by varying the pH of solution in the range of 5-10 (Fig 1). The absorbance

measurements represent a maximum at pH of 9. Hence this pH was chosen for the future studies. Absorbance and recovery decreasing at the pH less and more than 9 is due to the protonated complex and participation of silver.

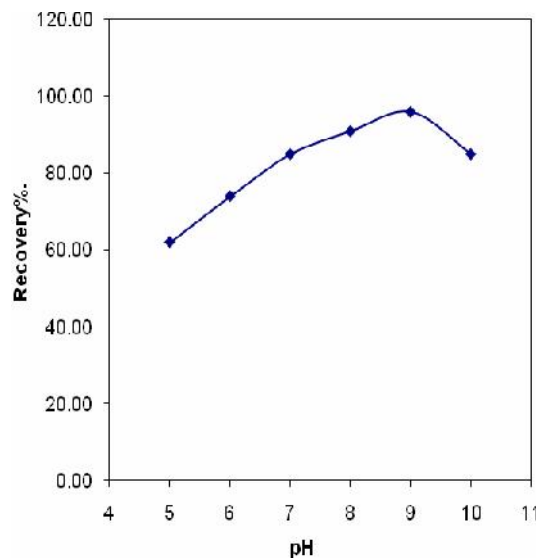


Fig. 1. Effect of pH on recovery of analytes

3.2: Selection of surfactant

A successful CPE should maximize the extraction efficiency by minimizing the phase/volume ratio ($V_{\text{org}}/V_{\text{aqueous}}$), thus improving the concentration factor. The effect of surfactant concentration on the extraction was investigated, the concentration being varied from 0.02 to 0.1% (w/v) using. By increasing the Triton X-114 concentration above 0.07% (w/v), the signals decrease because of the increment in the overall analyte volumes and the viscosity of the surfactant phase. In order to achieve the optimal analytical signal, the maximum enrichment factor could be attained with Ag-PAR was at 0.07% (w/v) surfactant

3.3. Effect of PAR amount on recovery

Due to the amount of ligand, which is also an important factor in the preconcentration studies for the quantitative recoveries of analyte ions from the working media, the effect of PAR concentration on the reaction was determined. The concentration of PAR was varied from 1.0×10^{-4} to $1.5 \times 10^{-2} \text{ mol l}^{-1}$ with keeping other analytical parameters constant. The results were given in Fig. 2 that show the increase absorbance with increasing PAR concentration. $4.0 \times 10^{-3} \text{ mol l}^{-1}$ PAR concentration which gave >99.0% recovery was selected. A higher concentration of ligand cannot be used due to its solubility.

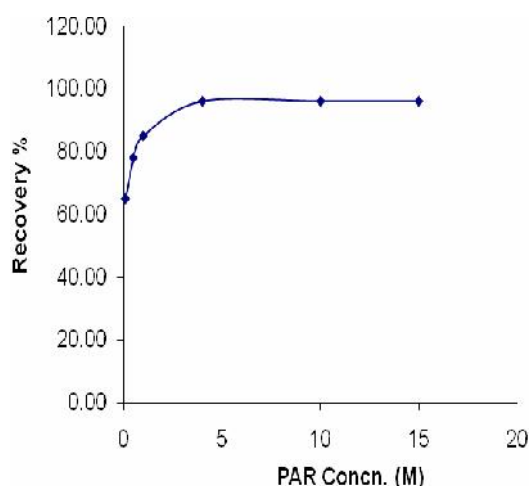


Figure 2. Effect of PAR concentration

3.4. Effect of foreign ions

The interfering effects of various cations that may react with PAR or species that may react with analytes and decrease the extraction efficiency. Flotation procedures for trace of analytes in samples can be affected by the matrix constituents of the sample. Before the flotation for preconcentration of analyte ion in samples, the influence of some alkaline and earth alkaline ions on the recoveries of silver ion was investigated. The results are given in Table 1.

3.5. Characteristics of the method

A calibration curve was constructed by preconcentrating 10 ml of sample standard solutions with Triton X-114. Under the optimum experimental conditions, the calibration curve for silver was linear

from 20-350 $\mu\text{g L}^{-1}$. The limit of detection was sufficiently low ($6 \mu\text{g L}^{-1}$). Further improvement is also feasible, either by preconcentrating larger amounts of the sample solution or diluting the surfactant rich phase to a smaller volume of the methanol solution.

3.6. Application to real samples

Water samples after adjustment of samples pH to desired value the flotation were performed. The results are shown in Table 2.

4. Conclusions

This paper proposes a new method for the preconcentration and determination of trace levels of silver by CPE in a wastewater and spiked water by different matrices combined by FAAS. The separation occurred efficiently, and the method is relatively has wide range as compared with previously reported procedures for the enrichment of analyte ions. This method is characterized with simplicity, rapidity, reliability, safety and low cost, and is suitable for the determination of trace silver in water samples.

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Table 1. Effect of foreign ions on the determination of silver

Ion	Ion / Analyts ($\mu\text{g L}^{-1}$)
Li^+ , k^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- , NO_3^-	800
Ni^{2+} , Cu^{2+}	500
Fe^{3+} , Al^{3+} ,	450

Table 2. Determination of silver⁺ in water samples by purposed method

Sample	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	R.S.D (%)	Recovery (%)
Water	0.0	-	-----	-----
(ghreghazh rever)	50.0	52.0	2.6	104.0
	100.0	103.0	1.3	103.0
Tap water	0.0	-	-	-----
	70.0	69.5	2.9	101.5
	150.0	152.0	1.2	98.0

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