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Selective Determination Cloud Point Extraction Trace Amounts of Silver in Water Samples by Flame Atomic Absorption Spectrometry

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Abstract : A selective, simple and practical method has been developed for determination of traces of silver based on Cloud Point Extraction (CPE). The preconcentration of Ag(I) in aqueous solution was achieved by CPE with 1-(2-pyridylazo)-2-naphthol (PAN) as the chelating agent and Triton X-114 as the extractant. The best extraction efficiency by carbonate buffer solution (pH 10.0) 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. After phase separation, based on the cloud point of the mixture, and dilution of the surfactant-rich phase with methanol, the enriched analyte was determined by flame atomic absorption spectrometry, using discrete nebulization. The calibration graph using the preconcentration system was linear in the range of 20-500 ng ml^{-1} with a correlation coefficient of 0.9991. The enrichment factor, and the detection limit ($3SD_b/m$) were 43, and 6.5ng ml^{-1} respectively. The developed method was successfully applied to the determination of Ag (I) in water and wastewater samples.

Key words: Silver concentration, Cloud point extraction, PAN.

Introduction and Experimental

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).

Silver is vital and toxic for many biological systems and can be entered into the environment via industrial waters because it is often present as an impurity in copper, zinc, arsenic, and antimony ores. Ag is released to the environment from natural and anthropogenic sources including mining, silverware manufacturing, and the photographic industry (3).

It can cause argyria, a permanent, blue-gray discoloration of the skin and eyes that imparts a ghostly appearance. Concentrations in the range of 0.4 to 1 mg l^{-1} have caused pathological changes in the kidneys, liver, and spleen of rats. Toxic effects on fish in fresh water have been observed at concentrations as low 0.17µg l^{-1}. Relatively small quantities of silver are bactericidal or bacteriostatic and find limited use for the disinfection of swimming pool waters (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 B_{12}, 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 (7, 8), inductively coupled plasma atomic emission spectrometry (9, 10), and electrothermal atomic absorption spectrometry (11). 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, 12, 13).
Extraction preconcentration is an extensively used method for increasing the sensitivity of atomic absorption spectroscopy (14). Enhancements are obtained due to an increase in absorbance obtained in organic solvents and concentration of the metal ion in a small volume of the organic phase (15, 16, 17).

Several ligands such as 1-(2-pyridylaso)-2-naphthol (PAN), 2-(2-thiazoylazo)-4-methylphenol (TAC), 1-(2-thiazolylazo)-2-naphthol (TAN), dialkyldithiophosphates (DDTP), have been used in cloud point extraction of metal ions (6).

Among various ligands used in separation procedures, including cloud point extraction, pyridylazo reagent has been widely employed due several advantages obtained, such as, capacity to form complexes with each metal in suitable condition and low solubility in water. Some studies indicated that the hydrophobicity of ligands and complexes are the fundamental factors which regulate the extraction efficiency (18, 19).

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 environmental samples by used of 1-(2-pyridylazo)-2-naphthol (PAN) as the ligand in carbonate buffer solution.

Apparatus

A Sens AA GBC double beam atomic absorption spectrophotometer (AAS) with hollow cathode lamp operating at 4mA was used for the determination of silver in the surfactant-rich phase, which was made at 328.1 nm. An adjustable-capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomization. Deuterium lamp background correction was employed to correct for the non-specific absorbance. Operation in a double beam-background correction mode was imperative due to the complexity of the aspirated sample, which apart from the target metal and excessive chelating agent, causing a suppression of the signal. Measurements were performed in the integration mode.
A centrifuge (Shimifan) was used to accelerate the phase separation process. A Jenway model 3510 pH-meter was used for pH measurements. An electronic analytical balance (220LA, ADAM) was used for weighting the solid materials. A thermostated water bath (Fater Ltd.) model W610B was employed to maintain the experimental temperature.

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 µg 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 stock buffer solution (0.1 mol l^{-1}) was prepared by adding (0.1 mol l^{-1}) sodium carbonate solution plus (0.1 mol l^{-1}) sodium hydrogen carbonate adjusting to pH 10 by adding diluted HNO_3 solution.
A solution of 0.01 mol l^{-1}, 1-(2-pyridylazo)-2-naphthol (PAN) was prepared by dissolving 0.0249 gr 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.

Test Procedure

For the CPE, 10 ml solution of Ag (final concentration 20-500 ng ml^{-1}), 0.5ml of 0.01 mol l^{-1} PAN solution, 2 ml of 0.5% (w/v) Triton X-114 and 1 ml of 0.1 mol l^{-1} buffer solution (pH 10) were placed in a centrifuge tube and heated in thermostated water bath at $55\,^{\circ}C$ 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.

Table 1. The influences of the pH and various buffer of the aqueous solution on the recovery % of Ag (I)

		pH				
		7	**8**	**9**	**10**	**11**
% Recovery	Universal buffer	26.5	33.0	36.5	49.0	50.0
	Boric Acid	18.0	22.5	26.0	31.5	32.0
	Carbonate buffer	60.1	65.4	70.0	>99.0	75.0
	Phosphate buffer	36.8	41.5	46.0	58.0	52.5

Table 2: Optimization of practical parameters

Equilibration temperature for CPE	$55\,^{\circ}C$
Equilibration time for CPE	15 min
Centrifuge time	10 min
Centrifuge rate	5000 rpm
Time of cooling in ice bath	10 min

Table 3. Analytical characteristics of the prorposed method

Concentration range (ng ml^{-1})	20-500
Slope	0.0354
Intercept	0.0231
Correlation coefficient (r)	0.9991
RSD (%) (n=3)[a]	2.80
LOD (ng ml^{-1})[b]	6.50
Enrichment factor[c]	43.0

[a] Silver concentration was 30 ngml^{-1} for which the R.S.D. was obtained.

[b] Limit of detection. Calculated as three times the S.D.(3σ) of the blank signal.

[c] Calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration.

Table 4. Interference effect of various ions

Foreign ions	**Interferent-to-analyte ratio**
K^+, Na^+,Li^+,Ce^{4+}،Mg^{2+}, NO^-_3	> 1000
HPO_4^{2-} ،ClO^-_3 ،IO^-_3 ،Mg^{2+} ،Ca^{2+} ،F^- ، Cl^-، Br^-، CH_3COO^-، Ni^+، Pd^{2+}	500
SCN^- ،Mn^{2+} ،Al^{3+} ،Cr^{3+} ،Zn^{2+} ،Cd^{2+} ،CrO_4^{2-}، Fe^{3+}، Pb^{2+}	300
Sn^{2+}، Ti^{3+}، Cu^{2+}، Co^{2+}	200

Table 5. Determination of Ag^+ in various water samples

Sample	Ag^+(ng ml^{-1})		Recovery (%)
	Added	Found	
Photographic Wastewater [a]	-	300.5 ± 0.4	-
	20	320.4 ± 0.3	99.9
	30	330.0 ± 0.4	99.8
Wastewater [b]	-	89.5 ± 0.5	-
	20	109.3 ± 0.3	99.8
	30	119.0 ± 0.6	99.5
River water [c]	-	ND[d]	-
	20	20.0 ± 0.5	100.0
	30	29.9 ± 0.4	99.6
Lake water [e]	-	28.8 ± 0.2	-
	20	48.5 ± 0.5	99.4
	30	58.4 ± 0.4	99.3

[a] From a rinse water of photography ± standard deviation (n=3)

[b] dental clinic wastewater

[c] From Kor river water (local river).

[d] Not detected

[e] From Parishan lake water (Fars, Iran).

Table 6. Comparative some recent studies on preconcentration–separation of silver

Complexing Reagent	Detetermination	LDR	Recovery (%)	Sample	Reference
bis(2-mercaptoanil) acetylacetone (BMAA)	(FAAS)	2-200 ng ml^{-1}	97.2-101.8	water	3
Dithizone (diphenylthiocarbazone)	(FAAS)	3-200 ng ml^{-1}	96.5-102.0	water	6
2-mercaptobenzothiazole (MBT)	(FAAS)	10-200 ng ml^{-1}	>99.0	water	14
1-(2-phyridylazo)-2-naphthol (PAN)	(FAAS)	20-500 ng ml^{-1}	>99.0	water & wastewater	Proposed method

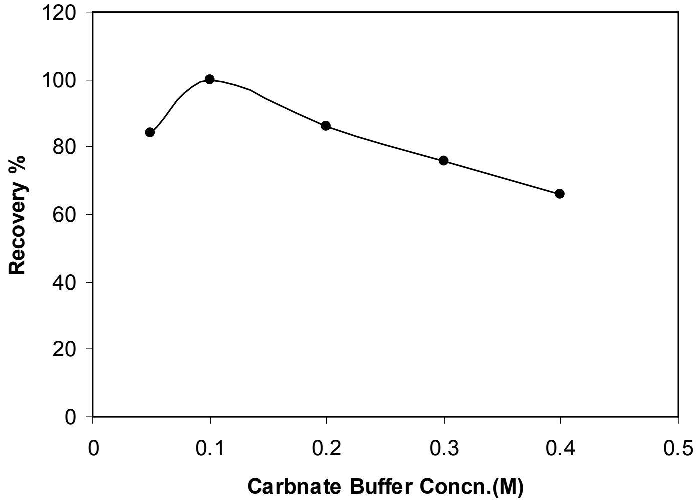

Fig 1. Effect of buffer concentration on the CPE-preconcentration performance

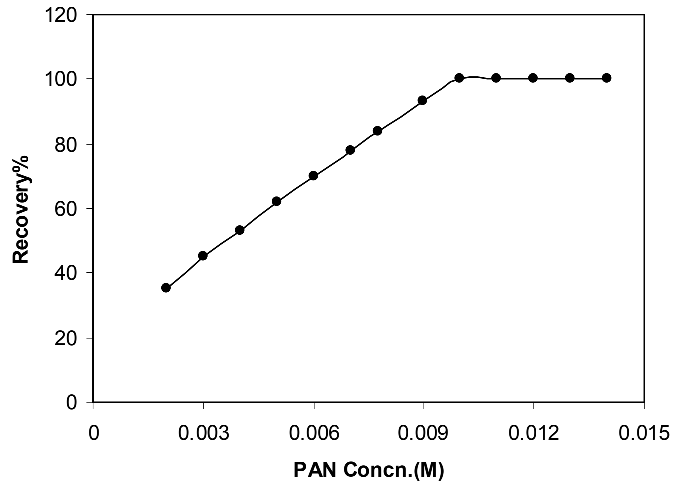

Fig. 2. The influences of the PAN Concentration on the recovery of Ag (I) ion

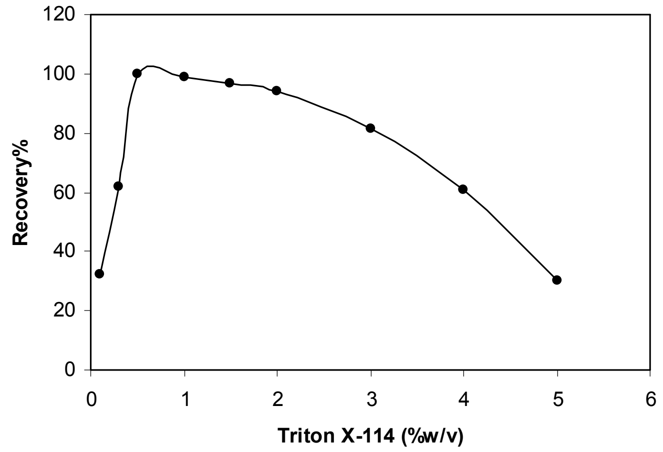

Fig. 3. Effect of Triton X-114 concentration on the extraction recovery of silver

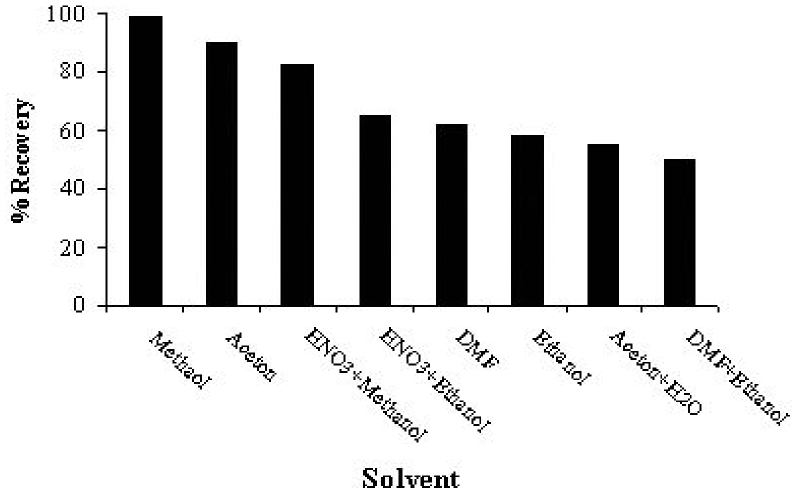

Fig. 4 . Effect of various solvents on dissolving the surfactant-rich phase

Results and Discussion

Effect of pH and Buffer

The formation of metal-chelate and its chemical stability is two important influences for CPE. The pH plays a unique role on metal-chelate formation and subsequent extraction, and is proved to be a main parameter for CPE (20). The influences of pH of the aqueous solutions on the recoveries of Ag (I) as PAN chelate was investigated in the pH range 7–11. For obtain better sensitivity pH values, several buffer agents such as phosphate, carbonate, boric acid/sodium hydroxide, and universal buffer were tested for pH adjustment. The quantitative recovery (>99.0 %) for silver was found only at carbonate buffer. As a result carbonate buffer solution at pH 10 was chosen for the pH adjusting and all subsequent studies were carried out at pH 10. The result was depicted in Table 1. The effect of addition of different concentrations of buffer was studied by varying concentration buffer in the range of 5×10^{-2} to 4×10^{-1} mol l^{-1}. The results in Fig. 1 show that the maximum sensitivity was achieved by using 0.1 mol l^{-1} carbonate.

Effect of PAN Concentration

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 PAN concentration on the reaction was determined. The concentration of PAN was varied from 1.0×10^{-4} to 1.5×10^{-2} mol l^{-1} with keeping other analytical parameters constant. The results were given in Fig. 2 that show the increase absorbance with increasing PAN concentration. 1×10^{-2} mol l^{-1} PAN concentration which gave >99.0% recovery was selected. A higher concentration of ligand cannot be used due to its solubility.

Effect of Triton X-114 Concentration

A successful CPE should maximize the extraction efficiency by minimizing the phase/volume ratio ($V_{org}/V_{aqueous}$), thus improving the concentration factor. The effect of surfactant concentration on the extraction was investigated, the concentration being varied from 0.1 to 5% (w/v) using. As can be seen by increasing the Triton X-114 concentration above 2% (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^{+}–PAN was at 0.5% (w/v) surfactant (Fig. 3).

Practical Parameter

The practical parameters such as equilibration temperature and time, centrifuge time and rate, time of cooling in the cloud point extraction were thoroughly optimized (Table 2). It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and efficient phase separation. It was found that the formation of Ag^{+}–PAN does not require high temperatures. In pervious works, it has been reported that, by increasing the temperature, a reduction in the phase volume ratio of surfactant can be achieved (21). An increase in temperature from 45 to 65°C caused an increase in extraction, but there is the best sensitivity at 55°C. The time for measuring the change in absorbance was also optimized and it was found that sensitivity increases up to 20 min, and further increase in time resulted in a significant decrease of the efficiencies probably due to the thermal instability of the formed PAN complexes. At 15 min the reaction has good sensitivity, so 15 min was selected.

The optimized reagent concentration after heating for 15 min in 55°C, it was found that increases up to 20 min and centrifuging by 10 min at 5000 rpm and cooling for 10min in ice bath lead to highly recovery of silver.

Study of Various Solvent

An organic solvent should have the following characteristics for use in atomic absorption: (a) the solvent should be combustible so as not to lower flame temperature; (b) the solvent should have a favourable aspiration rate, i.e., low viscosity; (c) the solvent should not absorb radiation from the hollow cathode lamp; and (d) the solvent should have a low surface tension allowing the production of a smaller droplet size distribution. (15). Finally, different solvents such as methanol, ethanol, acetone, DMF, DMF-ethanol (1:1), acetone–water (3:1), and acidic solutions of methanol and ethanol were tried for dissolving the surfactant-rich phase and reducing its viscosity. Fig. 4 shows the best results was obtained for methanol.

Characteristics of the method

A calibration curve was constructed by preconcentrating 10 ml of sample standard solutions with Triton X-114. Table 3 shows the analytical characteristics of the method. Under the optimum experimental conditions, the calibration curve for silver was linear from 20 to 500 ng ml^{-1}. The enhancement factor of about 43 obtained by preconcentrating a 10 ml of sample volume can be considered highly satisfactory compared with other CPE methodologies. The limit of detection was sufficiently low. 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.

Interferences

PAN is a non-selective chelating agent and favourably reacts with many metal ions. In an ambience of competitive reactions of the chelating agent with various metallic species, a reduction of the extraction efficiency of the target metal species should be expected. In this respect, interfering studies were conducted to determine whether other trace elements or anions interfere with the determination of silver during the proposed pre-concentration scheme. Different amounts of ions were added to the test solution containing 30 ng ml^{-1} of silver and the signals were compared to that of a solution containing only Ag (I). The results showed in table 4, there is not any serious interfere in this method.

Application to real samples

A simple and accurate spectrophotometric method was applied to the determination of trace amounts of silver ion in various water sample solutions of dental clinic, photographic solutions, and several spiked water samples with different amounts of silver before any pre-treatment. Samples of photographic wastewater, lake and river water and wastewater were collected. They were filtered through Whatman 42 filter to remove the suspended particulate matter and were stored in glassware bottles at 4°C in the dark, a photographic and dental clinic wastewater was diluted with distilled water. The results are shown in Table 5.

Conclusion

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. In Table 6 we have compare the present method with other reported Atomic Absorption spectrometric methods. The separation occurred efficiently, resulting in good enrichment factor 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 environmental samples.

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