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Cloud Point Extraction method for determination of Ag⁺ with 1-(2-pyridylazo)-2-naphthol (PAN)

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Abstract: A new straight forward method based on cloud-point extraction (CPE) has been developed, optimized and validated for the determination of Ag^+ in soil by Spectrophotometer at λ_{max} =715nm. The non-ionic surfactant Triton X-114 (polyethylene glycol tert-octylphenyl ether) was chosen as the extract solvent. Under the optimum conditions, the linear range of Ag^+ in soil was $0.2-2.2mgL^{-1}$ ($r^2 = 0.9995$). The limit of detection (LOD) was less than $0.22\mu gL^{-1}$ (S/N = 3). The proposed method was applied to the determination of Ag^+ in environmental sample and the results had good accuracy.

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). 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, silver ware 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 1^{-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 1^{-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 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).

The trace determination ofheavy metals in biological samples is particularly difficultbecause of the complex matrix and the usuallylow concentration of these elements in such samples, which requires sensitive instrumental techniques and frequently a pre-concentration step (7). Different methods have been studied for the pre-concentration and separation of cadmium suchas liquid–liquid extraction (8), ion-exchange techniques (9),

and electrochemical methods(10). Disadvantages, suchas significant chemical additives, solvent losses, complex equipment, large secondary wastes, prefiltrationproblems, and time-consuming, limit theapplication of these techniques. Cloud point extraction(CPE) is an attractive technique that reduces these problems and agrees with green chemistryprinciples (11). Recently, the cloud-point extraction (CPE) method has aroused much attention as a convenient alternative to the conventional extraction systems. Compared with the traditional organic liquid–liquid extraction, this CPE methodology requires a very small amount of relatively non-flammable and non-volatile surfactants. Also, compared with classical organic solvents, it offers the advantages of safety, low cost, high concentration efficiency, easy disposal of surfactants, low toxicity, less environmental pollution and simple procedure (12–20). In the present work, CPE was used for the preconcentration of Ag in soil as a step prior to its determination by Spectrophotometer using Triton X-114 as non-ionic surfactant.

2. Experimental

2.1. Reagents and Solutions

All chemicals used were of analytical-reagent grade and all solutions were prepared with double distilled water. All the plastic and glassware were cleaned by soaking in dilute HNO₃ (1+10) and were rinsed with distilled water prior to use. The non-ionic surfactant, 0.85 % (w/v) Triton X-114 (Merck, Chemise AG, Switzerland) was prepared by dissolving 0.85 g of Triton X-114 in 100 mL of distilled water. Stock standard solution of Ag⁺ at a concentration of 1000 μ g mL⁻¹ was prepared by dissolving an appropriate amount of the Ag NO₃ in distilled water and diluting to 100 ml in a volumetric flask. Working standard solution was obtained by appropriate dilution of the stock standard solution. The pH was adjusted by addition of 0.1mol L⁻¹HCl or 0.1 mol L⁻¹NaOH.

2.2. Apparatus

UV–Vis spectra were recorded on a PERKIN ELMER Lambda2 Spectrophotometer containing a thermoelectrically temperature controlled cell holder in the wavelength range of 200–800 nm with a quartz cuvette (path length = 1 cm). 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.

2.3. Test Procedure

For the CPE, 1 ml solution of Ag (final concentration $2-25\mu g l^{-1}$), 0.2ml of 2 mg l⁻¹ PAN solution, 2 ml of 0.85% (w/v) Triton X-114, pH solution adjusted 4 and solution were placed in a centrifuge tube and heated in thermostated water bath at 45°C for 10 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, 3 ml HNO₃ solutions of methanolwas added. The resultant solution was measured bySpectrophotometer at λ_{max} =715nm.

3. Results and Discussion

3.1. Effect of pH

The pH is one of the most important factors in cloud point extraction for quantitative recovery. The influence of pH on the adsorption of Ag^+ was investigated over a pH range of 1 to 6, while keeping other parameters constant. Fig. 1 shows that analyte was effectively adsorbed at a pH of 4.0, which was selected for further experiments. The pH during the analytical procedure was adjusted to 4.0 by addition of HCl and NaOH. The efficiency of Ag+ recovery increased from pH 1.0 to 6.0, and declined with further increases in the pH value. Hence, a sample pH value of 4.0 was consequently employed for the ensuing investigations.



Fig. 1. Effect of pH on the Silver extraction recovery; conditions:2 mL 0.85 % (w/v) Triton X-114, 0.2ml of 2 mg Γ^1 PAN solution,1 mL 25µgL⁻¹ of Silver, equilibration temperature 45 °C, equilibration time 10 min, Centrifugation time 10 min, Centrifugation rate 5000 rpm.

3.2. Effect of PAN Concentration



Fig. 2. Effect of the PAN Concentration on the Silver extraction recovery; conditions: pH=4, 1 mL 25 μg L-1 of Silver, 2 mL 0.85 % (w/v) Triton X-114, equilibration temperature 45 °C, equilibration time 10 min, Centrifugation time 10 min, Centrifugation rate 5000 rpm.

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 0.2to 2.5 mg Γ^1 with keeping other analytical parameters constant. Theresults were given in Fig. 2 that show the increase absorbance with increasing 0.2 mL PAN concentration which gave >99.0% recovery was selected. A higher concentration of ligand cannot be used due to its solubility.

3.3. 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, its enrichment factor must be improved. Triton X-114 close to room temperature is a proper surfactant to perform CPE for trace elements. Triton X-114 was chosen as the non-ionic surfactant because of its commercial availability in a highly purified homogeneous form, low toxicological properties, and low cost. Also, low cloud point temperature (23–26 °C) and high density of the surfactant-rich phase facilitate phase separation by centrifugation. The effect of the surfactant concentration was studied within the Triton X-114 concentration range of 0.1–1% (w/v). Fig.3 shows the effect of the surfactant concentration on the recovery. The highest extraction efficiency was obtained when the 2.5 mL Triton X-114 concentration was 0.85 % (w/v).





3.4. Effect of the equilibrium temperature and time

It is known that two phases are formed when aqueous solutions of a non-ionic surfactant are heated above the cloud-point temperature. As the equilibration temperature increases, the volumes of the surfactant-rich phase decrease because hydrogen bonds are disrupted and dehydration occurs. The amount of water in a surfactant-rich phase also decreases. Theoretically, the optimal extraction efficiency can be observed on condition that the equilibration temperature is $40-65^{\circ}$ C greater than the cloud-point temperature of the surfactant. As can be seen from Fig. 4, the highest extraction efficiency occurred when the equilibrium temperature reached 45° C. higher temperatures only led to the more difficult separation of phases due to the increasing rate of molecular thermodynamic movement. The dependence of extraction efficiency upon equilibration time was studied within a range of 5-25 min. an equilibration time of 10 min was chosen as the best to obtain quantitative extraction.



Fig.4. Effect of equilibration temperature on the Silver extraction recovery; conditions: pH=4, 1 mL 25 μ g L⁻¹ of Silver, 0.2ml of 2 mg l⁻¹ PAN solution, 2 mL 0.85 % (w/v) Triton X-114, Centrifugation time 10 min, Centrifugation rate 5000 rpm.

3.5. Selection of the dilution agent for the surfactant –rich phase:

An organic solvent should have characteristics such as low viscosity, low surface tension and combustible for use in atomic absorption. Different solvents for the surfactant–rich phase were tested so as to select the one producing the optimal results regarding sensitivity.

Acetone, methanol,HNO₃ solutions of methanol, ethanol, HNO₃ and DMF were tested for this purpose. HNO₃ solutions of methanol dissolved completely the surfactants which in its extracted complex of lead and PAN and the best recovery were obtained and an optimum volume is 1 ml.

3.6. 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 25 μ g l⁻¹ of silver and the signals were compared to that of a solution containing only Ag (I). The results showed in table 1, there is not any serious interfere in this method.

Table 1.Interference effect of various ions.

	[Foreign ions	Ion/Analyte
		K^+ , Na ⁺ ,Li ⁺ ,Ce ⁴⁺ ,Mg ²⁺ , NO ₃ ⁻		> 1000
		HPO_4^{2-} , ClO_3^{-} , IO_3^{-} , Mg^{2+} , Ca^{2+} , F^{-}		500
		Cl_، Bı،	· CH3COO · Ni ⁺ · Pd ²⁺	
SCN	300			
Mn^{2+} , Al^{3+} , Cr^{3+} , Zn^{2+} , Cd^{2+} , CrO_4^{2-}				
، Fe ³⁺ ، Pb ²⁺				
${\rm Sn}^{2+}$, ${\rm Ti}^{3+}$, ${\rm Cu}^{2+}$, ${\rm Co}^{2+}$	200			

3.7. Characteristics of the method

A calibration curve was constructed by preconcentrating 10 ml of sample standard solutions with Triton X-114. Fig. 5 shows the analytical characteristics of the method. Under the optimum experimental conditions, the calibration curve for silver was linear from 0.2 to 2.2mg Γ^1 . The relative standard deviation (RSD) for the seven replicate measurements of different concentration of Ag+ was 2.5 %. The pre-concentration factor, the ratio of initial volume to final volume, obtained was 30.The limit of detection was0.22µg 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 HNO₃ solutions of methanol.



Fig. 5.SilverCalibration curve using point cloud method.; conditions: pH=4, 0.2ml of 2 mg I^{-1} PAN solution, 2 mL 0.85 % (w/v) TritonX-114, Centrifugation time 10 min, Centrifugation rate 5000 rpm , equilibration temperature 45 °C, and equilibration time 10 min.

3.8. Determination of Silver in soil

In order to test the reliability of the proposed methodology suitable for the assaying of Ag in soil samples. For this purpose, 10ml of each of the samples were preconcentrated with 0.85% (w/v)Triton X- 114 and a PAN concentration of 2mg L^{-1} , following the proposed procedure. The results are shown in Table 2.

RSD (%)	Recovery (%)	Found ($\mu g L^{-1}$)	Added ($\mu g L^{-1}$)	Samples
-	-	4.0	-	1 ^a
2.5	100.1	14.1	10	2 ^a
1.9	100.5	24.1	20	3 ^b

Table 2. Determination of Ag⁺ in soil samples.

a) From near Road Omidiyeh petrochemical centerb) Agricultural Soil

4. Conclusion

The micellar extraction of Silver with PAN into the phase of the non-ionic surfactant Triton X-114 has been investigated. Complete metal extraction was shown to be achieved with PAN due to the hydrophobic complex compound formation. The method gives a low limit of detection and good RSD value. The sensitivity, methodological characteristic, ecological safety, simplicity, and convenience of the suggested procedure are competitive with respect to methods based on extraction with organic solvents.

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