

# Ultra-trace determination of silver in water samples by electrothermal atomic absorption spectrometry after preconcentration with a ligand-less cloud point extraction methodology

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## Abstract

A very simple and ligand-less cloud point extraction (CPE) methodology for the preconcentration of ultra-trace amounts of silver as a prior step to its determination by electrothermal atomic absorption spectrometry (ETAAS) has been developed. The method is based on the extraction of silver at pH 9 by using non-ionic surfactant polyethyleneglycolmono-*p*-nonylphenylether (PONPE 7.5) without adding any chelating agent. Several important variables that affect the CPE efficiency and ETAAS signal were investigated and optimized. The preconcentration of 15 ml sample solution allowed us to achieve an enhancement factor of 60. The calibration graph using the preconcentration system was linear in the range of 5–100 ng l<sup>-1</sup> with a correlation coefficient of 0.9991. The lower limit of detection ( $3s$ ) obtained in the optimal conditions was 1.2 ng l<sup>-1</sup>. The relative standard deviation (R.S.D.) for eight replicate determinations at 30 ng l<sup>-1</sup> Ag level was 4.2%. The proposed method was successfully applied to the ultra-trace determination of silver in water samples.

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**Keywords:** Silver; Cloud point extraction; Electrothermal atomic absorption spectrometry; PONPE 7.5; Water samples

## 1. Introduction

Silver is one of the industrially important elements. It is used for the preparation of corrosion-resistance alloys and its compounds are extensively used in the processing of foods, drugs and beverages and in filters and other equipments to purify water. It also has an important role in electrical and electronic application, photographic film production and the manufacturing of fungicides [1,2]. These widespread applications have resulted in increased silver content of environmental water samples. In turns, owing to the toxicity of silver to many aquatic organisms even at low concentrations, the serious environmental problems may occur. Therefore, simple and highly sensitive methods are needed to monitor the Ag levels in water samples at ever decreasing concentrations.

Several atomic spectrometric techniques such as flame and electrothermal atomic absorption spectrometry (FAAS and

ETAAS) [3–6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7] and inductively coupled plasma mass spectrometry (ICP-MS) [8–11] have been proposed for the determination of silver in different environmental samples. In order to improve the detection limit, various preconcentration procedures have also been used in combination with the above-mentioned techniques. These include solvent extraction [12,13], solid phase extraction [14–16], precipitation [17] and adsorption on tungsten wire [18]. However, most of these procedures are laborious, time-consuming and may cause sample contamination.

Cloud point extraction (CPE) is a simple and powerful technique for separation and preconcentration of metal ions [19–22] that can easily be adapted for ETAAS to improve the detection limit and selectivity of determinations. This method has been applied for silver preconcentration by using *O,O*-diethyldithiophosphate [23,24] and dithizone [25] as chelating agents and Triton X-114 as surfactant prior to its determination by FAAS and ICP-MS. However, these methodologies are rather time-consuming and take about 0.5–1 h to complete the procedures. In the present work, we have developed and optimized

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a simple CPE–ETAAS combined methodology for silver determination, which shows rapid and efficient performance. Silver was preconcentrated by using PONPE 7.5 in the absence of any chelating agent, and then determined by ETAAS. The proposed method was applied to the determination of silver in several water samples with satisfactory results.

## 2. Experimental

### 2.1. Apparatus

A Shimadzu (Kyoto, Japan) Model AA-670G atomic absorption spectrometer equipped with a GFA-4A graphite furnace atomizer, an ASC-60G autosampler and a circulating cooling unit were used for the determination of silver in the surfactant-rich phase. Deuterium lamp background correction was employed to correct for the non-specific absorbance. A silver hollow cathode lamp (Hamamatsu photonics K.K., Japan) was used as the radiation source. The operating conditions of silver hollow cathode lamp were those recommended by the manufacture. Pyrolytically coated graphite tubes were used throughout. Argon 99.999% (Roham gas Co., Tehran, Iran), with  $1.5 \text{ l min}^{-1}$  flow rate, was used as a protective and purge gas. Aliquots of  $20 \mu\text{l}$  for all samples and calibration solutions were injected directly into the graphite tube by the autosampler. Measurements were performed in the peak height mode. This mode was preferred over peak areas, since the latter gives irreproducible results. The detailed graphite furnace temperature program used for the determination of Ag(I) is shown in Table 1. A centrifuge (Hettich) was used to accelerate the phase separation process. A Metrohm model 654 pH-meter was used for pH measurements. An electronic analytical balance (Libror, AEL-200, Shimadzu) was used for weighting the solid materials.

### 2.2. Reagents and solutions

All chemicals used were of analytical-reagent grade and all solutions were prepared with triply distilled/deionized water (obtained from Ghazi Serum Co., Tabriz, Iran). A stock standard solution of silver ( $1000 \text{ mg l}^{-1}$ ) was prepared by dissolving

0.1575 g of silver nitrate (Merck) in deionized water containing 1 ml concentrated nitric acid (Merck) in a 100 ml volumetric flask and diluting to mark with deionized water and stored in the dark. The working standard solutions were prepared daily by stepwise diluting the stock standard solution with deionized water.

A stock buffer solution ( $0.1 \text{ mol l}^{-1}$ ) was prepared by dissolving appropriate amounts of sodium carbonate (Merck) in deionized water and adjusting to pH 9 by adding diluted  $\text{HNO}_3$  (Merck) solution.

As it is not possible to obtain a real aqueous solution of the surfactant PONPE 7.5 (polyethyleneglycolmono-*p*-nonylphenylether, Tokyo Kasei Industries, Chuo-Ku, Tokyo, Japan) since the cloud point of its micellar solution is markedly below room temperature, it was experimentally convenient to prepare a working solution (3% (v/v) PONPE 7.5) as follows: 1.5 ml surfactant PONPE 7.5 and 20 ml distilled ethanol (Merck) were mixed and made up to 50 ml with deionized water [26].

A 0.1% (w/v) chemical modifier solution was prepared by diluting  $\text{Pd}(\text{NO}_3)_2$  stock solution ( $10 \text{ g l}^{-1}$ , Merck).

The pipettes and vessels used for ultra-trace analysis were kept in 25% (v/v) nitric acid at least over night and subsequently washed three times with deionized water.

### 2.3. Cloud point preconcentration procedure

For the CPE, aliquots of working standard solution of Ag ( $1 \mu\text{g l}^{-1}$ ) (final concentration  $5\text{--}100 \text{ ng l}^{-1}$ ), 0.9 ml of  $0.1 \text{ mol l}^{-1}$  buffer solution (pH 9) and 0.4 ml of 3% (v/v) PONPE 7.5 were placed in a centrifuge tube. The mixture was diluted to 15 ml with deionized water. The resultant solution became immediately turbid at room temperature without heating. Phase separation was accelerated by centrifuging the tubes at 4000 rpm for 10 min. The aqueous phase was then separated completely by a 10 ml syringe centered in the tube without cooling in an ice bath.

### 2.4. Sample preparation

Water samples (i.e., tap water, river water, underground water and subterranean canal water), were filtered through Rund filter

Table 1  
Instrumental parameters and temperature program for silver analysis

Spectrometer				
Wavelength (nm)				328.1
Lamp current (mA)				4
Spectral bandpass (nm)				0.6
Background correction				Deuterium
Graphite furnace				
Stage	Temperature ( $^{\circ}\text{C}$ )	Time (s)		Argon gas flow ( $\text{l min}^{-1}$ )
		Ramp	Hold	
Drying	120	20	–	1.5
Pyrolysis	450	–	40	1.5
Atomization	1300	–	3	0.0
Cleaning	1800	–	2	1.5

paper (blue band, no. 300210) to remove suspended particulate matter after collection. Aliquots of 13.7 ml from each sample, 0.9 ml of 0.1 mol l<sup>-1</sup> buffer solution (pH 9) and 0.4 ml of 3% (v/v) PONPE 7.5 were placed in a centrifuge tube. The CPE procedure was carried out as described in above section.

### 2.5. ETAAS measurements

In order to reduce the viscosity of the surfactant-rich phase and facilitate sample handling prior to ETAAS analysis, the extract in the tube was made up to 250  $\mu$ l by adding methanol–water (3:1) solution. Then, 20  $\mu$ l the resulting solution and 10  $\mu$ l of Pd(NO<sub>3</sub>)<sub>2</sub> (0.1% (w/v)) as a chemical modifier were directly injected into the graphite tube by means of the autosampler and submitted to the temperature program shown in Table 1.

## 3. Results and discussion

### 3.1. Study of the CPE conditions

In the conventional CPE methodology a chelating agent is needed to form a hydrophobic complex with the metal ions, which then is extracted by using a suitable surfactant of high density and low cloud point. Recent studies have shown that some non-ionic surfactants, especially PONPE 7.5, can acts as both the extracting and complexing agent, thereby making the CPE procedure is very simpler [27,28].

PONPE 7.5 is a polyoxyethylene non-ionic surfactant with molecular formula of HO (CH<sub>2</sub>CH<sub>2</sub>O)<sub>7.5</sub> C<sub>6</sub>H<sub>4</sub>C<sub>9</sub>H<sub>19</sub> and critical micellar concentration (CMC) of 0.085 mM. The cloud point temperature of PONPE 7.5 depends on its concentration and for a 5% (w/w) solution has been reported to be 5 °C [29]. This temperature can be modified by the presence of alcohols, salts, alkalis, acids, polymers and other surfactants. In the appropriate conditions, PONPE 7.5 may form a complex with Ag<sup>+</sup> through their polyoxyethylene groups and thereby can be extracted in surfactant-rich phase. Complex formation between ether linkage of some non-ionic surfactants and cations such as Ag<sup>+</sup> has also been reported by other researchers [30,31]. The cloud point of the studied system is near room temperature; therefore, the phase separation can be made without heating the micellar solutions. Moreover, for this system, after centrifugal settling, the two phases are easily separated without cooling in an ice bath. Therefore, PONPE 7.5 was chosen as a micellar system for experiments.

The effect of pH upon the extraction of silver ions from the solution was studied within the pH range of 2–12. Each pH value was adjusted by the addition of diluted HNO<sub>3</sub> and/or NaOH solutions. The results are shown in Fig. 1a. As can be seen, the extraction efficiency was increased with the increase of the pH value and the quantitative extraction begins at pH 8, being constant until pH 12. Since the pK<sub>a</sub> value for the hydrolysis of silver is about 11.7 [32], therefore, in the pH range studied here the silver ions exist mainly in the form of Ag<sup>+</sup>. The lower extraction efficiency in acidic media may be due to the fact that H<sup>+</sup> ions can also bind to polyoxyethylene groups of surfactant [31],

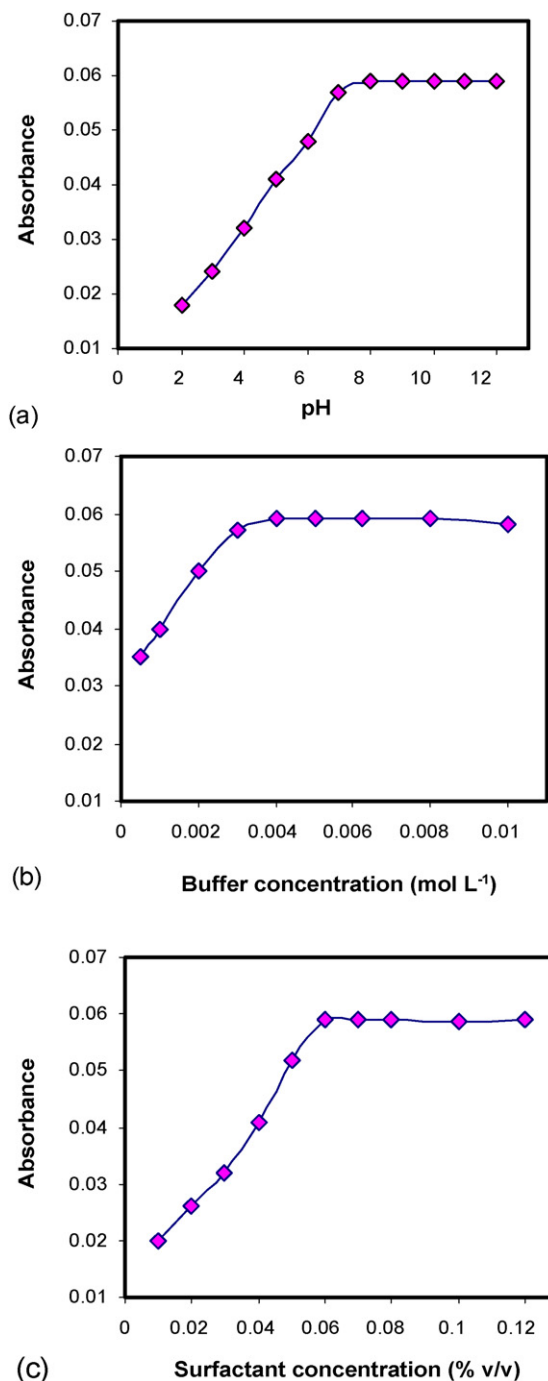


Fig. 1. Effect of: (a) pH, (b) buffer concentration and (c) surfactant (PONPE 7.5) concentration on the cloud point extraction of 30 ng l<sup>-1</sup> Ag<sup>+</sup>.

thereby hinders the complex formation of Ag<sup>+</sup> ions. As a result pH 9 was selected as the working value. Several buffer agents such as phosphate, carbonate, boric acid/NaOH, NH<sub>4</sub>Cl/NH<sub>3</sub> and borax were tested for pH adjustment. In the presence of the latter three buffers no considerable signals were obtained. The suitable absorbance signal can be achieved using both the phosphate and carbonate buffers but the latter gives the highest signal. Therefore, carbonate buffer solution was chosen for the pH adjusting.

The influence of buffer concentration in the range of  $5 \times 10^{-4}$  to  $1 \times 10^{-2} \text{ mol l}^{-1}$  was investigated while the other experimental variables remained constant. The results are illustrated in Fig. 1b. It could be seen that with the increase of buffer concentration, the absorbance increases and a maximum is obtained after the buffer concentration approaches to  $4 \times 10^{-3} \text{ mol l}^{-1}$  and remains constant up to  $1 \times 10^{-2} \text{ mol l}^{-1}$ . Therefore,  $6 \times 10^{-3} \text{ mol l}^{-1}$  buffer concentration was employed for further experiments.

The variation of the analytical signal as a function of the concentration of PONPE 7.5 in the range of 0.01–0.12% (v/v) was also investigated. Fig. 1c indicates that PONPE 7.5 can quantitatively extract the silver ions from aqueous sample in the concentration range of 0.06–0.12% (v/v), using a single step extraction procedure. In order to achieve a good enhancement factor, 0.08% (v/v) was chosen as optimal.

The effect of the equilibration temperature was investigated from room temperature to  $50^\circ\text{C}$ . It was found that the increase of temperature has no considerable effect upon the extraction efficiency and analytical signal. Thus, room temperature used as an equilibration temperature in CPE process. Keeping the room temperature, the influence of incubation time on CPE was studied within a range of, from immediately after the preparation to 20 min. It was observed that, in this system, the incubation time before centrifugation has no significant effect upon the extraction efficiency. So, in order to keep analysis time as short as possible the turbid solution was centrifuged immediately after the preparation at room temperature.

The effect of centrifugation time upon analytical signal was also studied in the range of 5–20 min. A centrifugation time of 10 min at 4000 rpm was selected for the entire procedure, since complete separation occurred for this time and no appreciable improvements were observed for longer times.

Finally, different solvents such as methanol, ethanol, acetone, THF and acidic solutions of methanol and ethanol were tried for dissolving the surfactant-rich phase and reducing its viscosity. The best results were obtained for methanol and, to prevent its vaporization during the experiments at room temperature, methanol–water (3:1) mixture solution was employed.

### 3.2. Study of the ETAAS conditions

In order to reduce interferences and increase the accuracy, the use of a chemical modifier or a modifier mixture has become indispensable in ETAAS measurements. In the present work, we used  $\text{Pd}(\text{NO}_3)_2$  as a chemical modifier. When the palladium modifier was not added, the analytical signal was gradually decreased until 40% of the initial signal. The influence of the palladium modifier on the background level was also important. Based on the experimental results, addition of 0.1% (w/v)  $\text{Pd}(\text{NO}_3)_2$  solution allowed increasing the analytical signal with considerable background reduction, without increasing the pyrolysis temperature. Because for portions larger than  $10 \mu\text{l}$  the signals were not further improved, the palladium modifier injection volume was chosen as  $10 \mu\text{l}$ .

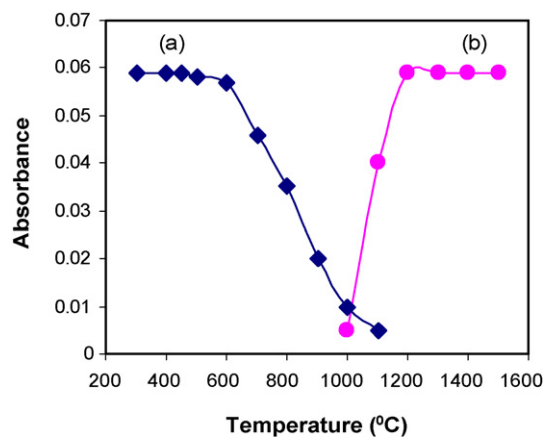


Fig. 2. (a) Pyrolysis curve and (b) atomization curve for the cloud point extraction of  $30 \text{ ng l}^{-1} \text{ Ag}^+$ .

The selection of an appropriate pyrolysis temperature is very important for removing as much the matrix as possible and preventing the pyrolysis loss of the analytes prior to atomization. Fig. 2a shows the influence of pyrolysis temperature, in the range of  $300\text{--}1100^\circ\text{C}$ , on the absorbance. As could be seen, the maximum absorbance was achieved in the range of  $300\text{--}450^\circ\text{C}$  in the presence of chemical modifier. However, when the pyrolysis temperature was over  $500^\circ\text{C}$ , the signal of analyte decreased rapidly with the increase of the pyrolysis temperature. Therefore,  $450^\circ\text{C}$  was selected as the optimized pyrolysis temperature for the determination of silver.

In the selected pyrolysis temperature of  $450^\circ\text{C}$ , the effect of pyrolysis time on the absorbance of Ag was investigated. The results showed that the absorbance was increased when the pyrolysis time was changing from 10 to 40 s and no appreciable improvements were observed for longer times. As a result, a pyrolysis time of 40 s was chosen.

Using a pyrolysis temperature of  $450^\circ\text{C}$  and pyrolysis time of 40 s, the effect of the atomization temperature, in the range of  $1000\text{--}1500^\circ\text{C}$ , on analytical signal of Ag was also studied and the results are shown in Fig. 2b. As can be seen, in the presence of chemical modifier, the maximum signal was obtained at about  $1200^\circ\text{C}$  and remained unchanged with the further increasing of temperature up to  $1500^\circ\text{C}$ . So, the atomization temperature of  $1300^\circ\text{C}$  was selected for the further experiments. The experimental results show that atomization time has little effect on the atomic signal of Ag. Therefore, an atomization time of 3 s was selected. The unusual low pyrolysis and atomization temperatures used in this work is probably due to the fact that the components used in the CPE procedure are reducing the thermal stability of Ag.

### 3.3. Analytical figures of merit

The analytical characteristic data for the present CPE–ETAAS system are shown in Table 2. In the optimum conditions a calibration graph was constructed by preconcentrating 15 ml of the standard solutions in the presence of PONPE 7.5, without adding any chelating agent, according to procedure under experimental. The limit of detection ( $3s$ ) was  $1.2 \text{ ng l}^{-1}$ . Table 2 also

Table 2  
Analytical characteristics of the proposed method

Analytical parameters	Without CPE preconcentration	With CPE preconcentration
Linear range (ng l <sup>-1</sup> )	500–20,000	5–100
Intercept	0.001	0.001
Slope	0.032	1.927
Correlation coefficient	0.9998	0.9991
Detection limit (ng l <sup>-1</sup> )	76.3	1.2
Relative standard deviation (R.S.D. %) ( <i>n</i> = 8)	3.1 (5 μg l <sup>-1</sup> )	4.2 (30 ng l <sup>-1</sup> )
Enhancement factor	–	60

shows the calibration obtained with standard solutions of Ag not subjected to the CPE preconcentration step. The enhancement factor, calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration, was 60. The number of determinations per hour was approximately 20.

### 3.4. Effect of foreign ions

The effect of typical potential interfering ions on the analytical signal was investigated. Different amounts of ions were added to the test solution containing 30 ng l<sup>-1</sup> of silver and then operated as described previously. An ion was considered to interfere when its presence produced a variation of more than 5% in the absorbance of the sample. The results are given in Table 3. Some of cations and common anions were found not to affect silver signal in the CPE–ETAAS system when they are present in 1000-fold excess. As shown later, these results permit the application of the proposed system for interference-free determination of ultra-trace silver in water samples.

### 3.5. Determination of silver in real samples

The proposed CPE–ETAAS methodology was applied to the determination of Ag in several water samples. In order to validate the proposed method, recovery experiments were also carried out by spiking the water samples with different amounts of silver before any pretreatment. The solutions were analyzed using the standard additions calibration and the percentage recoveries were calculated. Table 4 shows the obtained results. Statistical analysis of these results using Student's *t*-test showed that there are no significant differences between actual and found concentrations at 95% confidence level. The slopes of the standard

Table 3  
Tolerance limits of interfering ions in the determination of 30 ng l<sup>-1</sup> Ag

Ions	Interferent-to-analyte ratio
Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Cd <sup>2+</sup> , Cr(VI), Pd <sup>2+</sup> , Ba <sup>2+</sup> , Mn <sup>2+</sup> , As <sup>3+</sup> , Hg <sup>2+</sup> , Ce <sup>4+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> , F <sup>-</sup> , Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	>1000:1
Tl <sup>+</sup> , Ni <sup>2+</sup>	800:1
Co <sup>2+</sup> , Cu <sup>2+</sup>	500:1
Cr <sup>3+</sup> , Pb <sup>2+</sup> , Al <sup>3+</sup> , Fe <sup>3+</sup>	300:1
Sn <sup>2+</sup> , Ru <sup>3+</sup> , Bi <sup>3+</sup> , Zn <sup>2+</sup>	200:1
Au <sup>3+</sup> , Pt(IV)	100:1

Table 4  
Determination of silver in water samples (results of recoveries of spiked samples)

Samples	Ag added (ng l <sup>-1</sup> )	Ag found <sup>a</sup> (ng l <sup>-1</sup> )	Recovery (%)
Tap water <sup>b</sup>	–	15.3 ± 0.4	–
	10	25.3 ± 0.5	100.0
	20	35.9 ± 0.6	101.7
Subterranean canal water <sup>c</sup>	–	40.0 ± 1.0	–
	10	49.8 ± 1.0	99.6
	20	58.7 ± 0.6	97.8
Underground water <sup>d</sup>	–	25.9 ± 0.5	–
	10	35.0 ± 0.6	97.5
	20	45.2 ± 0.3	98.5
River water <sup>e</sup>	–	32.7 ± 0.8	–
	10	42.8 ± 0.6	100.2
	20	52.2 ± 0.5	99.0

<sup>a</sup> Mean of three experiments ± standard deviation.

<sup>b</sup> From drinking water system of Tabriz, Iran.

<sup>c</sup> Obtained from Tasoji, Iran.

<sup>d</sup> Obtained from Sharafkhaneh, Iran.

<sup>e</sup> From Almas river, Iran.

additions graphs for water samples did not have any significant difference with that of calibration graph and also the corresponding detection limits for each water sample were found to be the same as that obtained from standard solutions. Therefore, we can conclude that there are no interferences from the sample matrices.

## 4. Conclusions

This paper proposes a new method for the preconcentration and determination of ultra-trace levels of silver by CPE combined with ETAAS. The proposed procedure does not need any chelating agent, heating, long incubation time and cooling after centrifugation. Phase separation can be achieved at room temperature and the extraction efficiency is high, resulting in low detection limits and high enhancement factors. The preconcentration of only 15 ml of samples in the presence of PONPE 7.5 gives an enhancement factor of 60. Therefore, the proposed CPE technique can effectively improve the sensitivity of ETAAS. This method is characterized with simplicity, rapidity, reliability, safety and low cost, and is suitable for the determination of ultra-trace silver in environmental water samples.



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