Journal of Analytical Science and Technology

a SpringerOpen Journal

RESEARCH ARTICLE   **Open Access**

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Ultrasound-assisted emulsification microextraction and preconcentration of trace amounts of silver ions as a cyclam complex

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Abstract

Background: Silver has been recognized as a toxic element for biological systems. A low level of exposure to silver compounds is widespread owing to the use of soluble silver compounds to disinfect water for drinking and reaction purposes. The present paper describes an ultrasound-assisted emulsification microextraction method for the preconcentration and determination of silver ions in drinking water.

Methods: Determination was carried out using 1,4,8,11-tetraazacyclotetradecane as a complexing reagent and chloroform as extracting solvent, followed by flame atomic absorption determination of silver ions.

Results: The main factors affecting microextraction efficiency, such as extraction solvent type and volume, concentration of chelating reagent, concentration of picrate ions, and pH, were optimized. Under optimal conditions, a limit of detection and enrichment factor of 6.79 ng mL^{-1} and 9.8 were obtained for silver ions, respectively. The analytical curve was linear in the range of 0.055–1.5 μg mL^{-1}, with a correlation coefficient (R^2) of 0.997.

Conclusions: The use of ultrasound as a powerful energy for the microextraction and determination of silver was proposed. The main advantages of the method are as follows: minimum use of toxic organic solvent and wide linear dynamic range.

Keywords: Ultrasound-assisted emulsification microextraction, Silver extraction, 1,4,8,11-tetraazacyclotetradecane

Background

The increasing use of silver compounds and silver-containing preparations in the industry such as disinfectants and photographic films has resulted in an increased silver content of environmental samples (Kolthoff and Elving 1966; Meian 1991). Thus, accurate determination of trace quantities of silver ions by simple methods is important in chemical and environmental analysis. Direct determination of silver ions of trace level is usually very limited due to the complexity of the sample matrix and the low concentrations of silver ions; therefore, there is a crucial need for the extraction and preconcentration of this element from the sample matrix before its analysis using atomic absorption spectrometry

(Xie et al. 2005). The most widely used techniques for separation and preconcentration of trace amounts of silver ions are coprecipitation (Mao et al. 1998), solid-phase extraction (SPE) (Rofouei et al. 2009; Shamsipur et al. 2002; Safavi et al. 2004; Khayatian and Hassanpoor 2012a), liquid–liquid extraction (LLE) (Koh and Sugimoto 1996), and cloud point extraction (CPE) (Manzoori et al. 2007 and Dalali et al. 2008). However, most of these methods are laborious, time-consuming, and require large volumes of toxic organic solvents.

It is well known that ultrasound is a powerful energy for the acceleration of various steps in analytical procedures, such as homogenizing and emulsion forming (Aydin et al. 2006). This type of energy greatly helps in the processes of extraction and preconcentration because it facilitates the acceleration of the mass-transfer

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process between two immiscible phases (Ozcan et al. 2009). This leads to an increase in the extraction efficiency of the method within a minimum span of time (Luque de Castro and Priego-Capote 2006 and Khayatian and Hassanpoor 2013). As a result, the application of ultrasound radiation to an extraction method such as liquid–liquid extraction provides the advantages of both methods. This new technique is called ultrasound-assisted emulsification microextraction (USAEME). This extraction method offers advantages such as simplicity, rapidity, a high enrichment factor, and safety and low cost due to consumption of very small amounts of toxic organic solvents. In USAEME, an extraction solvent is rapidly injected into an aqueous sample with a syringe. After sonication, a cloudy solution is formed, and the analyte is extracted into the fine droplets of the extraction solvent. After extraction, the phase separation is performed by centrifugation, and the analyte is determined in the sedimented phase by instrumental methods.

In recent years, the USAEME method has been used for the separation and preconcentration of cadmium (Li et al. 2009 and Ma et al. 2009; Khan et al. 2014), palladium (Mohamadi and Mostafavi 2010), gold (De La Calle et al. 2011), silver (Wen et al. 2012), Te(IV) (Fathirada et al. 2012), mercury (Stanisz et al. 2013), and from environmental matrices. However, among many types of ligands used in microextraction of metal ions, less attention has been directed toward using macrocyclic crown ethers as an extracting agent. Therefore, we decided to study application of crown ethers as a new extracting agent for developing a sensitive microextraction method for the determination of silver ions.

In the present work, we report a simple USAEME method for the preconcentration and flame atomic absorption spectrometry (FAAS) determination of silver ions using 1,4,8,11-tetraazacyclotetradecane (cyclam) as a complexing agent and $CHCl_3$ as an extraction solvent.
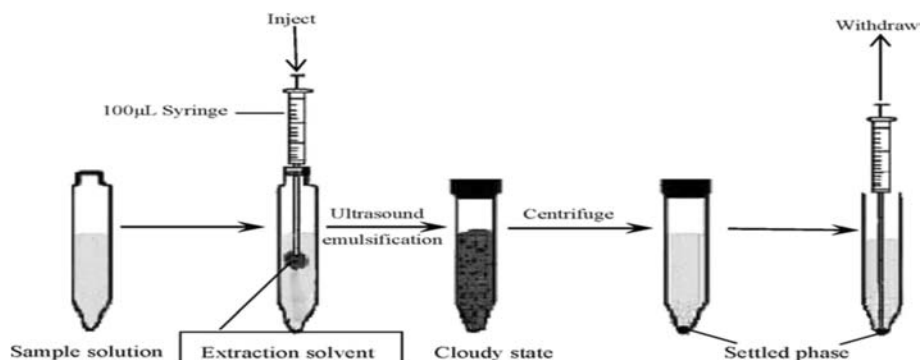
Methods
Chemicals and reagents
Extra pure methanol ≥95.5 %, acetonitrile (AN) ≥99 %, nitric acid 65 %, and hydrochloric acid 32 % were used as received. Stock standard solution (1.000 g L^{-1}) of Ag^+ was prepared by dissolving corresponding $AgNO_3$ (Merck) (99.8–100.5 %) in distilled water. The ligand that was used for the extraction procedure was 1,4,8,11-tetraazacyclotetradecane (cyclam, Merck) ≥92.0 % and used without any further purification, except for vacuum drying over P_2O_5.

Determination of silver and other cations was performed on a Shimadzu AA-670 atomic absorption spectrometer (Kyoto, Japan) under the recommended conditions (wavelength of 328.1 nm and bandwidth 0.6 nm). All pH measurements were made using a Metrohm E-691 digital pH meter with a combined glass electrode. A model Labofuge 400 (Germany) centrifuge was used to accelerate phase separation. A model Parsonic 7500S, 28-kHz, 100-W (220 VAC max) ultrasonic bath with temperature control was used to assist the emulsification process of the microextraction technique.

General procedure
A 5.0-mL sample containing 2.5 µg L^{-1} of silver ion standard solution or real sample adjusted at pH = 2 was placed in a 15-mL conical-bottom glass centrifuge tube and then 200 µL of cyclam in chloroform (9.27×10^{-4} M) was added. After sonication for about 14 min at 35 °C, a stable cloudy solution was obtained and Ag^+-cyclam 1:1 complex was extracted into the fine droplets of the $CHCl_3$. The mixture was then centrifuged for 5 min at 2500 rpm. Consequently, the fine droplets of the $CHCl_3$ settled at the bottom of the centrifuge tube. After removing the whole sedimented phase with a microsyringe, the sedimented phase was evaporated to dryness (Scheme 1). After evaporation of the organic phase, 0.5 mL of $Na_2S_2O_3$ 1.0 M was added and Ag^+ in this

Scheme 1 Schematic representation of USAEME enrichment method

solution was determined by FAAS (Khayatian and Hassanpoor 2012b and Khayatian and Hassanpoor 2013).

Preparation of radiological film

A 2-cm^2 sheet of a developed film (0.0504 g) was cut into several strips and put into a 100-mL beaker. Then, 0.5 mL of concentrated sulfuric acid was added, followed by six to eight drops of concentrated nitric acid. The beaker was placed on the hot plate and heated until evolution of brown fumes was no longer observed. This procedure was repeated until the radiological film was digested. After complete decomposition, the contents of the beaker should consist of a white to very light tan precipitate and a clear yellowish liquid. The hot plate was set on high heat, and the contents of the beaker were boiled until white fumes appeared (Gansel 1959; Sarafraz-Yazdi and Amiri 2010). Then, the analysis was performed as mentioned previously after diluting the solution 50 times and adjusting the pH with sodium hydroxide to pH 2.

Results and discussion

Optimization of parameters

To obtain high extraction efficiency, the effects of different parameters such as type and volume of the extracting solvent, pH, amount of cyclam, amount of counter ion, extraction time, salt addition, and centrifuging time were optimized. Then, the effect of interfering ions was investigated, and different natural water samples and a radiological film sample were subjected to analysis via the recommended method to evaluate the concentration of silver ions.

The effect of type and volume of the extraction solvent

The extracting solvent in USAEME should be able to form a cloudy solution in the aqueous phase; in addition, it must have high extraction efficiency and low water solubility (Manzoori et al. 2007; Safavi et al. 2004). Thus, to study the type of extraction solvent, different solvents such as chloroform, dichloromethane, carbon tetrachloride, chlorobenzene, and tetrachloroethylene were examined. For this purpose, 200 μL of each solvent was added to 5.0 mL of deionzed water containing 0.5 μg mL^{-1} of silver ions, and the extraction efficiency of silver ions was measured by the increase in absorbance in the extracted solvent. The obtained results showed that chloroform has the highest extraction efficiency for the silver ions; thus, chloroform was selected as the extraction solvent for further experiments, Table S1 (in Additional file 1).

The influence of the amount of chloroform used in USAEME of silver ions was also investigated. Experiments were performed using volumes of chloroform ranging from 30 to 400 μL. The results are shown in Fig. 1. As can be seen, the absorbance of silver ions increased along with the increase of volume of chloroform from 30 to 100 μL and then remained constant when the volume was continuously increased. The increase in the absorbance is due to the increase in the volume of chloroform. This can increase the amount of extracted silver-cyclam ion complex. Thus, in the further studies, 200 μL of chloroform was selected as the optimum volume of the extraction solvent.

Effect of pH on the extraction of silver ions

The effect of the pH of the sample solution on the recovery of 0.5 μg mL^{-1} of silver ions from the 5.0-mL solution was investigated in the pH range of 2.0–7.0. The pH was adjusted by using 0.1 M of either nitric acid or sodium hydroxide solutions. The results of percent of extraction versus pH value are shown in Figure S1 (Additional file 1). As can be seen, the results indicated that the silver ions can be quantitatively extracted at pH 2.0 (≥95 %), and then, at higher pH values, percent extraction slowly decreased. Low extractions that occur at lower pH values (pH 1.0) are probably due to protonation of the ligand. At higher pH values (pH > 3.0), the extraction efficiency gradually decreases, which may be
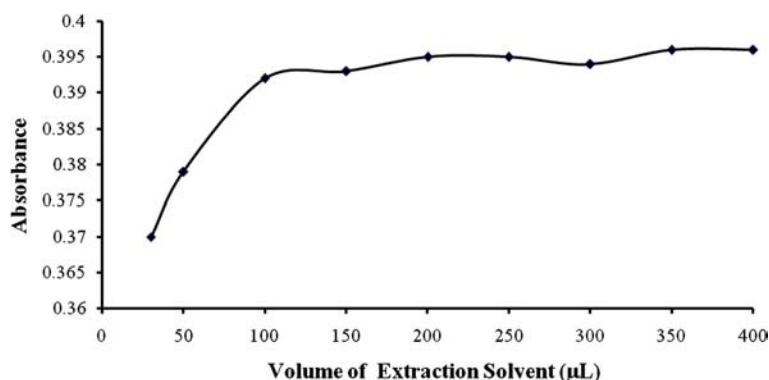

Fig. 1 Effect of volume of extraction solvent. Conditions: sample volume 5.0 mL; sample concentration 0.5 μg mL^{-1}; picric acid concentration 1×10^{-3} M

due to the addition of sodium hydroxide for the adjustment of higher pH values and the competition of this ion with silver ion for complex formation with cyclam. Thus, pH 2.0 was chosen as the optimum pH for further studies.

Effect of cyclam concentration on the extraction of silver ions

The effect of cyclam concentration on the absorbance of silver ions has been studied in the concentration range of 9.27×10^{-3} to 9.27×10^{-5} M, and the results are shown in Fig. 2. As can be seen, the absorbance signal increases with the increase of the ligand concentration, and then, a maximum is obtained after the ligand concentration approaches to 9.27×10^{-4} M. However, the signal was not altered by the addition of ligand up to 9.27×10^{-5} M. This observation may be due to the quantitative extraction of silver ions in such a condition (Khayatian and Hassanpoor 2012a and Shamsipur et al. 2002). Thus, a concentration of 9.27×10^{-4} M was selected as a suitable amount of the cyclam for further studies.

Effect of counter ions on silver ions absorbance

The silver ion extraction depends not only on the various kinds of counter anions used but also on the concentration of these ions; therefore, different types of counter ions, such as NO_3^-, ClO_4^-, and picrate ion (from picric acid), were chosen for the extraction of silver ions. Among the different counter ions studied, the picrate ion was the best for the extraction of silver ions from the sample solution. This observation is due to a more lipophilic character of picrate ions that not only neutralize the charged (Ag^+-cyclam) complexes but also increase a more lipophilic character to the silver-cyclam complex. These effects cause greater extraction of silver

ions than the inorganic anions such as NO_3^- and ClO_4^- can provide (Shamsipur and Khayatian 2001 and Shamsipur et al. 2003; Rounaghi et al. 2008).

The effect of concentration of picric acid in the silver ion extraction was investigated in the concentration range of 0.001–0.025 mol L^{-1}, and the results are shown in Fig. 3. As seen, the absorbance signal increases with increasing picric acid concentration in the sample solution. The maximum absorbance occurs when the concentration of picric acid is about 0.006 mol L^{-1} and then it decreases gradually with increasing picric acid concentration. The decrease in the extraction of silver ions at a higher concentration of picric acid may be due to a competitive effect between hydronium ions (from picric acid) with silver ions, which causes a decrease in extraction efficiency of silver ions from aqueous phase to organic phase.

Effect of extraction time

In USAEME, extraction time is defined as the time between the addition of extraction solvent and the end of the sonication stage (Zhang et al. 2011). Enough sonication time will make the extraction solvent disperse more finely into the aqueous solution and results in an excellent cloudy solution and better extraction efficiency. So, the effect of extraction time on the extraction of silver ions was evaluated in the range of 4–20 min. The results are shown in Fig. 4. It was observed that the highest absorbance signal was obtained at 14 min (under constant ultrasonic power) and then it decreased with the increase in sonication time. The decrease in the absorbance signals at a time greater than 14 min may be due to an increase in the solubility of the ligand in the aqueous
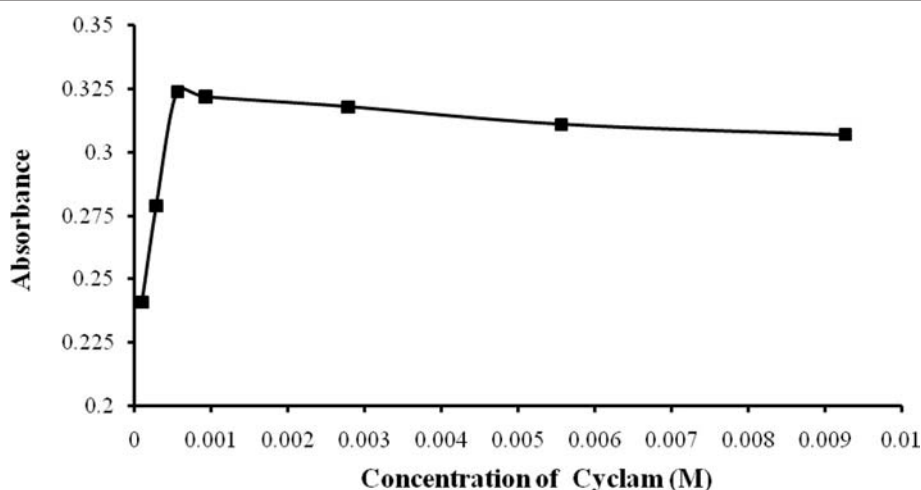

Fig. 2 Effect of cyclam concentration on USAEME of silver ions. Conditions: sample volume 5.0 mL; sample concentration 0.5 μg mL^{-1}; picric acid concentration 1×10^{-3} M
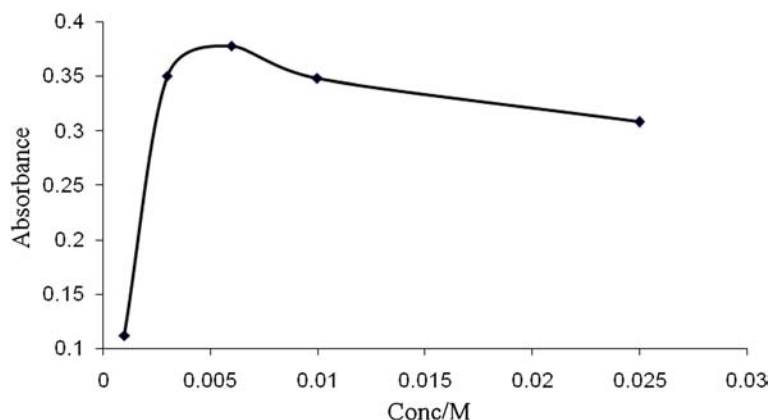
Fig. 3 Effect of picric acid concentration on the USAEME of silver ions. Conditions: sample volume 5.0 mL; sample concentration 0.5 μg mL^{-1}; extraction solvent volume (CHCl$_3$) 200 μL; different concentrations of picric acid

phase (Hashemi et al. 2013). Based on these observations, an extraction time of 14 min was chosen for further experiments.

Effect of ionic strength

In the extraction methods, due to salting-out effect, the solubility of metal chelates in aqueous solutions decreases with increasing ionic strength. Thus, for this purpose, extraction efficiency was investigated by the addition of varying concentrations of NaNO$_3$ and NaClO$_4$ salts from 0 to 10 %. Increasing the salt concentration had no significant effect on extraction efficiency, perhaps because of the dual effects of salt addition in USAEME: one involves increasing the volume of the extracted phase, which decreases the enrichment factor, and the other is the salting-out effect that increases the enrichment factor (Zeini Jahromi et al. 2007 and Bidari et al. 2007). These two effects cancel each other out; therefore, the enrichment factor is nearly constant by increasing the amount of the salts, and the extraction experiments were carried out without additional salt.

Effect of time and rotational speed of the centrifugation step on extraction

The effect of centrifugation time on extraction of silver ions was evaluated in the range of 3–9 min, while all of the experimental parameters were kept constant. The obtained results showed that absorbance signals increase slowly by increasing the centrifugation time until 5 min and then it remains constant with further increase in centrifugation time (Additional file 1: Figure S2). The effect of centrifugation speed was also investigated in a rotational speed of 1000–3500 rpm (Additional file 1: Figure S3). The results showed that the best rotational speed for extraction is 2500 rpm. Therefore, a centrifugation time of 5 min at a rotational speed of 2500 rpm was chosen for further experiments.
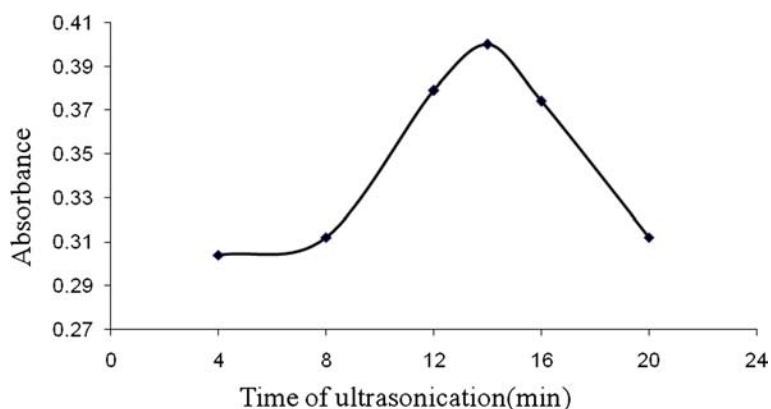

Fig. 4 Effect of time of extraction on USAEME of silver ions. Conditions: sample volume 5.0 mL; sample concentration 0.5 μg mL^{-1}; extraction solvent volume (CHCl$_3$) 200 μL; picric acid concentration 6×10^{-3} M

Table 1 Tolerant limits of coexisting ions for the extraction of 0.5 μg mL^{-1} silver ions

Interference ion	Added as	Tolerance limit ion ratio(Cion/CAg)	% Recovery
Mg^{2+}	$Mg(NO_3)_2$	1000	96 ± 3
K^+	KNO_3	100	95.1 ± 2.2
Ca^{2+}	$Ca(NO_3)_2.4H_2O$	10	95.4 ± 2.5
Co^{2+}	$Co(NO_3)_2.6H_2O$	10	97.1 ± 3.4
Cd^{2+}	$Cd(NO_3)_2.6H_2O$	10	96.0 ± 1.5
Hg^+	$Hg_2(NO_3)_2$	5	95.4 ± 2.3
Al^{3+}	$Al(NO_3)_3$	5	97.32 ± 2.4
Na^+	$NaNO_3$	5	96.3 ± 3.3
Mn^{2+}	$Mn(NO_3)_2.4H_2O$	5[a]	95.0 ± 2.3
Pb^{2+}	$Pb(NO_3)_2$	1	94.0 ± 3.5
Hg^{2+}	$Hg(NO_3)_2$	1[a]	98.8 ± 1.4
Ni^{2+}	$Ni(NO_3)_2$	5[a]	95.35 ± 2.5
Fe^{3+}	$Fe(NO_3)_3.9H_2O$	1[b]	95.76 ± 3.4
NO_3^-	KNO_3	100	95.2 ± 3.5
CO_3^{2-}	K_2CO_3	100	95.0 ± 4.3
OAC^-	CH_3COOK	25	100.4 ± 1.3
Cl^-	KCl	10	95.06 ± 3.2

[a]The interference effect in the presence of EDTA
[b]The interference effect in the presence of F^-

Effect of interfering ions

In order to investigate potential interferences on the recovery of silver ions, a 5.0-mL aliquot solution containing 0.5 μg L^{-1} silver ions with various amounts of diverse ions was treated according to the recommended procedure. A given species was considered to interfere if it resulted in a ± 5 % variation of the absorbance signal. The results are given in Table 1. As can be seen, some of the investigated ions have no significant influence on the extraction of silver ions under the selected conditions. Sil et al. (2001) showed that cyclam has a greater preference for silver ions over other cations. This behavior is due to substitution of NH groups in a macrocyclic ring that increases the stability of Ag$^+$ complexes significantly.

Analytical performance and method validation

The analytical characteristics of the recommended method, including linear range, limit of detection (LOD), limit of quantification (LOQ), relative standard deviation (RSD), correlation coefficient (R^2), and enrichment factor, were obtained. Under the optimum experimental conditions, the analytical curve was achieved by analyzing 5.0 mL of silver

ion standard solution containing a known amount of target ion in the range of 0.01–2.5 μg mL^{-1}. The analytical curve was linear in the range of 0.055–1.5 μg mL^{-1} with a correlation coefficient (R^2) of 0.997. The regression equation was $A = 0.853C - 0.019$, where A is the absorbance and C is the concentration of silver in micrograms per milliliter. The limit of detection ($n = 10$, LOD $= 3\ \sigma_{blank}/m$) and limit of quantification ($n = 10$, LOQ $= 10\ \sigma_{blank}/m$), where m is the slope of the analytical curve in accordance to IUPAC recommendation, were obtained 6.79 and 22.77 ng mL^{-1}, respectively. The RSD for 15 replicate measurements of 0.5 mg L^{-1} of silver ions was 5.50, and the recovery of extraction calculated according to $(C_{org}\ V_{org})/(C_{aq}\ V_{aq}) \times 100$, where C_{org} and C_{aq} are the concentrations of silver in the organic phase and sample solution, respectively, and V_{org} and V_{aq} are the volumes of the organic and the sample solutions, respectively, was about 98.5 %.

Applications

The developed method was applied for the extraction and determination of silver ions in well water and radiological film, and the results along with the recovery for the spiked

Table 2 The application of the USAEME method for determination silver ions in water and radiological film samples

Sample	Added (μg mL^{-1})	Found (μg mL^{-1})	Recovery (%)
Well water	0.00.1	<LOD[a]0.0943 $\pm$ 0.012[b]	93
Radiological film	0.00.5	0.575 $\pm$ 0.0181.103 $\pm$ 0.016	-105

[a]Below limit of detection
[b]Mean $\pm$ standard deviation (SD) for ($N = 3$)

Table 3 Comparison of the published preconcentration methods for silver ion with the recommended method

Enrichment method	Detection method	Enrichment factor	Linear range (µg L^{-1})	Detection limit (µg L^{-1})	Reference
LLE[a]	FAAS	30	-	13	(Campagong and Honjo 2002)
CPE[b]	FAAS	-	10–200	2.2	(Shemirani et al. 2007)
DLLME[c]	UV-Vis	-	70–2100	30	(Kocúrova et al. 2011)
SPE[d]	FAAS	25	-	1.05	(Tuzen and Soylak 2009)
USAEME	FAAS	9.8	55.0–1500	6.8	This work

[a]Liquid–liquid extraction
[b]Cloud point extraction
[c]Dispersive liquid–liquid microextraction
[d]Solid-phase extraction

samples are given in Table 2. The average spiked recoveries of the analytes in water and radiological film samples were in the range of 93–105 %. The results indicated that the developed preconcentration method for the silver ion was not affected by potential interferences from the matrix components of the analyzed samples.

Comparison with other methods

The characteristics of the developed method have been compared with the other preconcentration methods, and the results are shown in Table 3. Table 3 indicates that characteristics are comparable in some cases or even better in other cases.

On the other hand, the USAEME method has many advantages over the other methods in Table 3, such as it uses little toxic organic material and it is faster than LLE methods. Compared to CPE, this method is faster and does not need heating and cooling of sample solution, which is a tedious process in the CPE. Compared to DLLME, the USAEME method does not need to use a third solvent (disperser solvent) for emulsification, which usually decreases the partition coefficient of the analytes into the extractant solvent (Sarafraz-Yazdi and Amiri 2010). Compared to SPE, the organic phase used for extraction is small (200 µL), cheap, and more available than SPE sorbents that are more expensive than solvents used in the liquid extraction.

Conclusions

The use of ultrasound as a powerful energy for the microextraction and determination of silver was proposed. The main advantages of the method are as follows: minimum use of toxic organic solvent and wide linear dynamic range. In addition to these advantages, USAEME is simple, easy to use, inexpensive, and environmentally friendly.

Additional files

Additional file 1: Supplementary information. Table S1. effect type of extraction solvent. **Figure S1.** effect of pH on the extraction of silver ions. **Figure S2.** effect of centrifugation time on the extraction of silver ions. **Figure S3.** effect of centrifugation speed on the extraction of silver ions. (DOCX 20.5 KB)

Abbreviations

CPE: cloud point extraction; LLE: liquid–liquid extraction; LOD: limit of detection; LOQ: limit of quantification.; SPE: solid-phase extraction; USAEME: ultrasound-assisted emulsification microextraction.

Competing interests

The authors declare that they have no competing interests.

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