ORIGINAL ARTICLE

Cloud point extraction-flame atomic absorption spectrometry for pre-concentration and determination of trace amounts of silver ions in water samples

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Abstract   A cloud point extraction (CPE) method was used as a pre-concentration strategy prior to the determination of trace levels of silver in water by flame atomic absorption spectrometry (FAAS) The pre-concentration is based on the clouding phenomena of non-ionic surfactant, triton X-114, with Ag (I)/diethyldithiocarbamate (DDTC) complexes in which the latter is soluble in a micellar phase composed by the former. When the temperature increases above its cloud point, the Ag (I)/DDTC complexes are extracted into the surfactant-rich phase. The factors affecting the extraction efficiency including pH of the aqueous solution, concentration of the DDTC, amount of the surfactant, incubation temperature and time were investigated and optimized. Under the optimal experimental conditions, no interference was observed for the determination of $100 \ ng \cdot mL^{-1} \ Ag^+$ in the presence of various cations below their maximum concentrations allowed in this method, for instance, $50 \ \mu g \cdot mL^{-1}$ for both Zn^{2+} and Cu^{2+}, $80 \ \mu g \cdot mL^{-1}$ for Pb^{2+}, $1000 \ \mu g \cdot mL^{-1}$ for Mn^{2+}, and $100 \ \mu g \cdot mL^{-1}$ for both Cd^{2+} and Ni^{2+}. The calibration curve was linear in the range of $1–500 \ ng \cdot mL^{-1}$ with a limit of detection (LOD) at $0.3 \ ng \cdot mL^{-1}$. The developed method was successfully applied for the determination of trace levels of silver in water samples such as river water and tap water.
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1. Introduction

Silver is a non-essential element in human body. After its ingestion or chronical topic application, silver may be deposited on human skin and mucosa, which may result in a kind of permanent blue-gray, and even lead to acute death (Renner, 1982). Therefore, the determination of silver has

become one of the important projects in the field of environmental monitoring and health epidemic prevention. In addition, the silver is an important precious metal (EPA, 1980) because of its excellence in both thermal conductivity and electrical conductivity. It has been widely used in photographic industry, chemical industry, metallurgy, medicine and accessories processing and so on, which has made silver occur in the environment at trace and ultra-trace levels. Therefore, a very sensitive method is necessary for the accurate and precise determination of silver in various matrixes.

Some atomic spectrometric techniques such as flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS) (Šrámková et al., 2000; Baron et al., 2000), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Argekar et al., 1995) as well as inductively coupled plasma mass spectrometry (ICP-MS) (Hu et al., 2002; Chang et al., 2003) have been developed for the determination of silver in different environmental samples. In order to lower the detection limit, a variety of pre-concentration processes have also been utilized prior to the analysis with the aforementioned technologies. Those sample preparation techniques include solvent extraction (Koh and Sugimoto, 1996), solid phase extraction (Dadfarnia et al., 2004; Katarina et al., 2006), precipitation (Sant'Ana et al., 2002) and adsorption on tungsten wire (Lin et al., 2010). However, most of these procedures are tedious, time-consuming and may cause sample contamination (Rahman et al., 2004).

Cloud point extraction (CPE) method is a new and environmental friendly liquid–liquid extraction technology and has gained large attention in separation science. CPE is based on the clouding phenomena of surfactants. (Bezerra et al., 2005). Changes in the experimental parameters (e.g., solution pH, temperature, concentration, and time) lead to phase separation. It can be used to separate the hydrophobic and hydrophilic material, and it is economic, safe, environmental benign, efficient and convenient (Manzoori and Bavili-Tabrizi, 2002; Carabiasmartínez et al., 1999; Liu et al., 2014). It has drawn wide application in both life science and environmental science (Jong et al., 2005; Shariati and Yamini, 2006; Liu et al., 2016; Paleologos et al., 2005; Safavi et al., 2004).

In recent years, cloud point extraction was successfully used in enrichment, separation and determination of the metal elements. In the present study, we applied CPE for the separation and pre-concentration of Ag(I) ions from aqueous solutions using a Triton X-114 as a non-ionic surfactant and a sodium diethyl dithiocarbamate (DDTC) as a chelating agent, followed by its determination with FAAS. The parameters influencing the efficiency of CPE such as effects of pH, the concentrations of both Triton X-114 and DDTC, incubation temperature and time were systematically studied and optimized. The developed CPE procedure has been successfully applied to the determination of the concentration of Ag(I) ions in water samples.

2. Material and methods

2.1. Materials and chemicals

Stock standard solutions of 1000 mg·L^{-1} Ag$^+$ were prepared by dissolving AgNO$_3$ in 2% (v/v) HNO$_3$. Working standard solutions were obtained daily by the serial dilution of standard stock solution with Double Distilled Water (DDW). The chelating reagent solution at 1×10^{-2} mol·L^{-1} was prepared by dissolving sodium diethyldithiocarbamate (DDTC) in DDW. The non-ionic surfactant Triton X-114 purchased from Aladdin was further diluted to 50 g·L^{-1} prior to use in this work. The pH of the solutions was adjusted with 0.2 mol·L^{-1} sodium acetate (NaAc) and 0.2 mol·L^{-1} of acetic acid (HAC). DDW was used throughout the work.

2.2. Apparatus

A WFX-120 FAAS (Beijing Ruili Analytical Instrumental Co., Beijing, China) was used for quantitative analysis of silver while a TDZ5-WS centrifuge (Shanghai Lu Xiangyi centrifuge Instrument Co., Ltd, Shanghai, China) for facilitating phase separation. The pH was measured by Ohaus Starter 3C pH meter (Pine Brook, NJ, USA).

2.3. Operating procedure

To a 10-mL centrifuge tube, were added a certain amount of standard solution of silver, 0.5 mL of 0.01 mol·L^{-1} DDTC solution, 1.0 mL of pH = 5 buffer solution, and 0.7 mL of 50 g·L^{-1} Triton X-114 solution followed by diluting the mixture to the 10-mL mark with DDW and mixing them well. The resulting solution containing the analyte was incubated in the water bath at 40 °C for 20 min. Separation of the phases was achieved by centrifugation at 4000 rpm for 10 min. After centrifugation, it was cooled in an ice bath for 10 min to increase the viscosity of the surfactant-rich phase. The aqueous phases could readily be discarded by inverting the tube. A volume of nitric acid (0.1 M) in methanol was added to the surfactant-rich phase (200 μL) to reduce its viscosity and to promote sample treatment prior to FAAS assay. The final solution (5 mL) was brought in the nebulizer of the spectrometer. Blank solution was also operated with a similar procedure and measured in parallel to the sample solutions. Cloud point extraction procedure is shown in Fig. 1.

3. Results and discussion

3.1. Effect of pH

It is of high importance to select appropriate chelating agent and metal ions to form a hydrophobic complex when metal ions are extracted by the cloud point extraction. The complex is extracted to surfactant phase. The extraction efficiency depends on the acidity of the solution as the pH has an impact on the overall charges of the analyte, thus affecting the generation of the complex between the metal and the surfactant active functional groups. Therefore, the different pHs on the extraction efficiency of Ag$^+$ were investigated. Cloud point extraction of Ag$^+$ was carried out in the pH range of 3–8. The results are shown in Fig. 2. The recovery for Ag$^+$ increased with increasing pH from 3 to 5, and reached a maximum with pH at 5.0. At low pH, the low recoveries for Ag$^+$ were observed owing to the decomposition of DDTC in acidic media to liberate CS$_2$. When the solution pH is higher than 7, it could be a problem for the hydrolysis of Ag$^+$. Taking into account all these factors, a pH value of 5.0 was chosen for further studies.
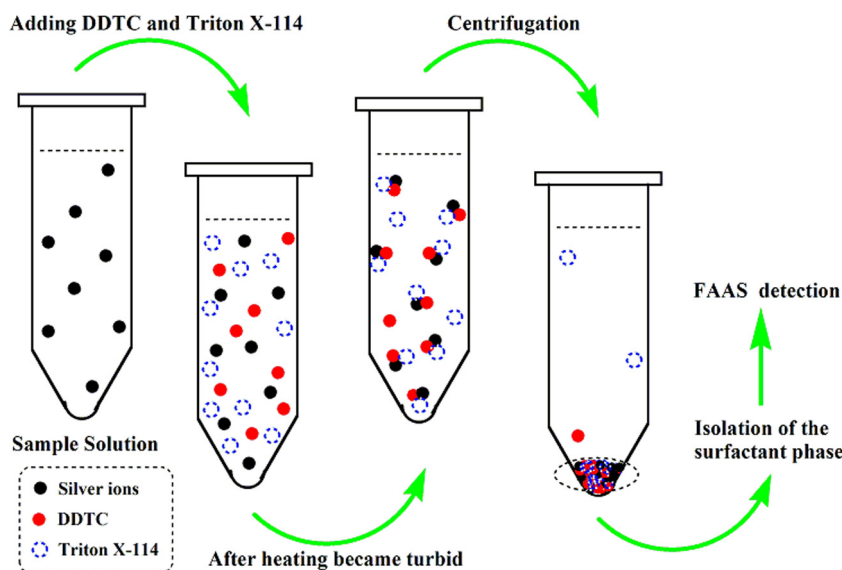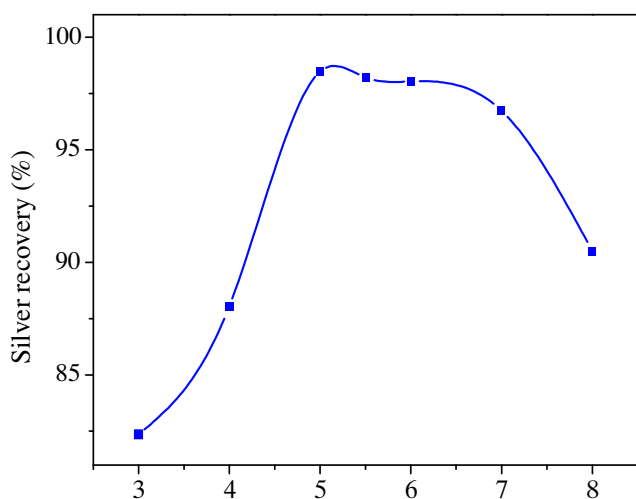
Figure 1   Cloud point extraction procedure.

Figure 2   Effects of pH on the cloud point extraction of Ag^+ (100 ng·mL^{-1}). Experimental conditions: 0.35% (v/v) Triton X-114 and 5×10^{-4} mol·L^{-1} DDTC.

Figure 3   Extraction efficiency of the complex as a function of DDTC concentration. Experimental conditions: Ag^+ (100 ng·mL^{-1}), 0.35% (v/v) Triton X-114 and pH 5.

3.2. DDTC concentration

Chelating agent is one of the key factors influencing the extraction efficiency. As shown in Fig. 3, cloud point extraction of Ag^+ was carried out in the DDTC concentration ranging from 1.0 to 7.0×10^{-4} mol·L^{-1}. The recovery for Ag^+ increased with increasing DDTC concentration from 1.0 to 5.0×10^{-4} mol·L^{-1}, and reached a maximum (99% ??) at 5.0×10^{-4} mol·L^{-1}. However, when DDTC concentration is higher than 6.0×10^{-4} mol·L^{-1}, the recoveries decline. It could be due to more free DDTC and less Ag^+ into the surfactant-rich phase and more Ag^+ entering into main water phase. Therefore, the optimum concentration for DDTC was taken as 5.0×10^{-4} mol·L^{-1} for further experiments.
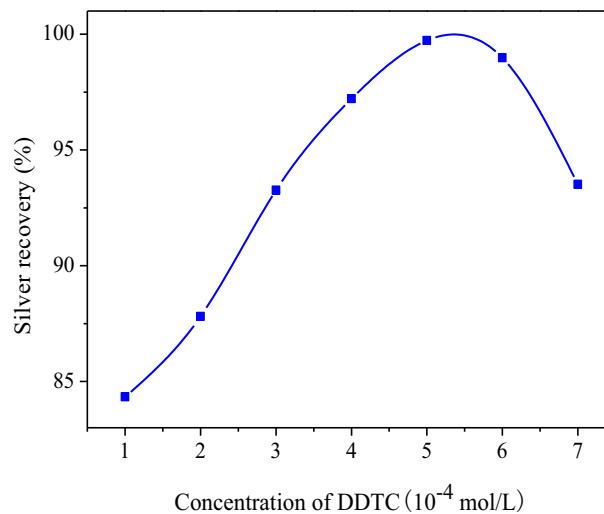
3.3. Concentration of Triton X-114

The concentration of surfactant used in the CPE plays key roles. Triton X-114 is one of the non-ionic surfactants extensively used in CPE due to its advantages such as commercial availability with high purity, low toxicity and cost as well as high density of the surfactant-rich phase thus promoting the phase separation by centrifugation, and relatively low cloud point temperature. As a result, different concentrations of Triton X-114 were investigated ranging from 0.1 to 0.6% (v/v) for checking the extraction efficiency. The results are presented in Fig. 4. The recovery for Ag^+ increased with an increase in Triton X-114 concentration from 0.1% to 0.35%, and reached a maximum at 0.35% Triton X-114. The recovery
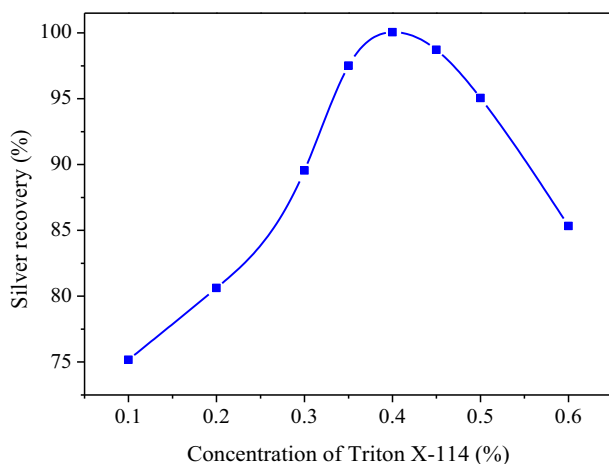
Figure 4 Extraction efficiency of the complex as a function of Triton X-114 concentration. Experimental conditions: Ag^+ (100 ng·mL^{-1}), 5×10^{-4} mol·L^{-1} DDTC and pH 5.

Table 1 Investigation of interferences from co-existing metal ions for the determination of 100 ng·mL^{-1} Ag$^+$ by using CPE pre-concentration followed by FAAS determination.

Iron	Interference/metal ratio	Recovery (%)
Mg(II)	2000	98
Cu(II)	50	95
Zn(II)	50	97
Pb(II)	80	100
Mn(II)	1000	94
Fe(III)	2000	96
Cd(II)	100	101
Na(I)	8000	98
Ni(II)	100	97
Ba(II)	2000	100
K(I)	8000	101
Ca(II)	2000	102

drops when the concentration of Triton X-114 is higher than 0.4%. Such observations can be ascribed an increase in volume and viscosity of the micellar phase. Thus, a concentration of 0.35% (v/v) Triton X-114 was used for subsequent experiments

in order to achieve the greatest recoveries and thereby the highest extraction efficiency.

3.4. Incubation time and temperature

The largest analyte pre-concentration factor is possible when the CPE process is performed with equilibration temperature well above the cloud point temperature of the system. Therefore, the incubation temperatures ranging from 35 °C to 60 °C and time between 5 and 40 min were studied. The results showed that an equilibration time of 20 min, and 40 °C were enough to reach the highest recovery.

3.5. Interference study

The potential interference from co-existing positive ions on the silver determination was studied with 100 μg·L^{-1} Ag$^+$ so that it can demonstrate the selectivity of the proposed method. The investigation of interferences with the determination of Ag$^+$ arising from other possible interfering species in the cloud point extraction is shown in Table 1. These results indicate that the general co-existing positive ions have no significant effect on the separation and determination of the Ag$^+$ under testing conditions. In addition, the stability constants of metal-DDTC complexes decrease in the following order: Hg(II) > Pd(II) > Ag(I) > Cu(II) > Tl(III) > Ni(II) > Bi(III) > Pb(II) > Co(III) > Co(II) > Cd(II) > Tl(I) > Zn(II) > In(III) > Sb(III) > Fe(III) > Te(IV) > Mn(III) > Mn(II). Therefore, the effects of other ions at given concentrations are ignorable.

3.6. Analytical figures of merit

Under the optimal conditions, the analytical performance of the proposed method was studied. This method exhibited the detection of Ag$^+$ with a wide linear range from 1 to 500 ng·mL^{-1} and an excellent linearity with correlation coefficient value of 0.9996. The corresponding equation was found to be A = 0.20163C + 0.00579, where A is ??? and C is the concentration of silver, respectively. The limit of detection (LODs, 3σ) was 0.3 ng·mL^{-1} for Ag$^+$ with enrichment factor at 33. The precision of (RSD) of the CPE procedure was found to be 3.6% for Ag$^+$ (100 ng·mL^{-1}, $n = 11$). The comparison of the results found in the presented study and some works

Table 2 Comparison of the relative standard deviation, limit of detection, linear range, and enrichment factors found for the cloud point extraction of silver enrichment in this work with those reported previously.

Relative standard deviation (%)	Limit of detection (ng·mL^{-1})	Linear range (ng·mL^{-1})	Enrichment factors	Refs.
2.14	0.56	3–200	43	Manzoori and Karim-Nezhad (2003)
4.9	0.004	0.01–0.5	20	Silva and Curtius (2000)
4.2	0.0012	0.005–0.1	60	Manzoori et al. (2007)
2.6	1	5–450	24	Gao et al. (2010)
–	6.0	20–350	–	Sabzevari (2013)
2.0	0.7	4–220	–	Javadi and Dalali (2011)
2.6	2.2	10–200	20	Shariati and Yamini (2006)
–	1.7	–	48	Ghaedi et al. (2009)
–	10	28–430	35	Tavallali et al. (2010)
–	0.006	0.1–146	100	Liu et al. (2009)
3.6	0.3	1–500	33	This work

Table 3 Determination of silver in the water samples by the proposed method ($n = 3$).

Sample	Silver (ng·mL^{-1})				Recovery (%)
	None	Added	Found	R.S.D (%)	
Tap water	2.03	15	16.8	1.2	98.5
	2.03	115	116.6	1.5	99.6
	2.03	415	422.61	2.0	101.3
River water (Huatan River)	9.47	15	24.6	1.4	100.9
	9.47	115	126.52	1.1	101.8
	9.47	415	418.14	1.7	98.5
River water (Jialing River)	8.48	15	23.45	1.8	99.8
	8.48	115	125.03	1.6	101.3
	8.48	415	420.13	1.1	99.2

in literature is given in Table 2. The proposed cloud point extraction method is better in terms of LOD and linear range when compared to other methods.

3.7. Application of the method

In order to evaluate the accuracy and selectivity of the method, it was applied for the determination of Ag (I) ions in three natural water samples including river water (Huatan River), river water (Jialing River) and tap water (China West Normal University). The results (Table 3) show that the proposed CPE method can be successfully applied for the recovery, pre-concentration and determination of Ag (I) in the tested water samples, which further indicates the capability of the method in the determination of the Ag$^+$ in real samples containing different matrices under the developed conditions.

4. Conclusions

A cloud point extraction (CPE) procedure was developed for preconcentration of silver (I) ions by using sodium diethyldithiocarbamate as a chelating agent and Triton X-114 as a surfactant. The developed protocol has been successfully employed for the determination of silver in various water samples via flame atomic absorption spectrometry. With respect to its values, the proposed method is simple, rapid, cost effective, low in LOD (0.3 ng·mL^{-1}), wide in linear range (1–500 ng·mL^{-1}) and highly reproducible (RSD < 4%).

Acknowledgments

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