N-Octanol-Induced Phase Separation of Triton X-100 for the Extraction of Trace Silver from Environmental Samples with Flame Atomic Absorption Spectrometric Determination

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Summary: A novel and simple cloud point extraction (CPE) method for detecting trace silver has been built up with flame atomic absorption spectrometry (FAAS) through adding proper amount of n-octanol into Triton X-100 resulting in an obvious decrease of the cloud point. In the method, rhodanine was chosen as chelating agent for the preconcentration of silver. The influence of major experimental parameters such as pH, chelating agent concentration, surfactant concentration, equilibration temperature and time on the extraction of silver from aqueous solutions was investigated and optimized. Under the optimal conditions, the minimum detection was 0.18 μg/L (3σ), while the preconcentration factor could reach up to 42. The well-pleasing results of standard reference sediment analysis manifested perfect accuracy and sensitivity of the method. Also, the presented method was applied to determine the trace silver in sediment and environmental water samples with satisfactory results.

Keywords: Cloud Point Extraction; Silver; *n*-Octanol; FAAS;Rhodanine; Triton X-100.

Intrduction

Silver and its alloys are widely used in several fields such as making of corrosion resistant alloy, medicine, electronic components, sterilization of drinking water and rain making, which leads to the increasing amount of silver residue in the environment. On one hand, silver can react with a variety of necessary nutrients for human body, especially selenium, copper, vitamin E, Vitamin B12 and other substance through metabolism. On the other hand, silver deposits in the subcutaneous fatty issue which induces accumulation by metabolism as well [1]. The potential toxicity of silver to the environment and to the human health aroused peculiar concern [1, 2]. Thus, it is quite vital to determine the trace silver in water and the environmental samples. Various different methods have been employed such as flame and electrothermal atomic absorption spectrometry [3, 4], inductively coupled plasma optical emission spectrometry (ICP-OES) [5], inductively coupled plasma mass spectroscopy(ICP-MS) [6]. Among these methods, flame atomic absorption spectrometry (FAAS) is regarded as the major approach for the measurement of silver because of its many virtues such as excellent accuracy, high precision, easy operation and time-saving speed and so on [7]. However, it posses the main disadvantage of low sensitivity for direct determination of silver in complex matrices and inadequate detection limit [8]. So, the separation and preconcentration step is often adopted before detecting the ultra-trace silver.

There have been several reports on the means of separation and preconcentration of metal ions such as liquid-liquid extraction [9], solvent extraction [10, 11] and solid-phase extraction [12, 13]. However, the methods mentioned above are either expensive and time-consuming or employing toxic solvent. It is urgent to develop a cheap, time-saving and efficient method for enrichment and detection of silver ions with excellent detection limit and high sensitivity.

Cloud point extraction (CPE) preconcentration technique emerged in recent years. [14-16]. As a kind of micellar systems, researchers

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have become very interested in CPE because it meets the requirements of the green chemistry development such as high efficiency, simple operation, low cost and short analysis time [17]. It has been extensively applied in isolation and purification of biological macro-biomolecules, separation and analysis of organic molecule, and separation and enrichment of metal ions [18, 19]. The CP phenomenon is the temperature changed phase separation into aqueous and surfactant-rich phases. The CP temperature depends on the dehydration temperature of the polyoxyethylene chains and its value embodies the leading features of non-ionic micellar solutions and has close connection with the surfactant structure [20-24]. CPE technology is established on the base of the facts. Theoretically speaking, as long as the metal ion can interact with surfactant micelles or water-repellent chelating ligand, it can be extracted from the mother solution by CPE process [25]

Triton X-100 originating from polyoxyethylene and containing a phenyl hydrophobic group posses many advantages such as good extraction effect, easy separation and low price [26, 27]. But owing to its high cloud point at 66.9 degrees centigrade [28], it is inapplicable to extract some heat-labile and hydrophobic metal complex. To deal with the problem, lower alcohols were injected into Triton X-100, which could lower the cloud point of the latter [29-31]. In this work, rhodanine was used as chelating agent and the lower alcohol, n-octanol, was injected into Triton X-100 solution to lower cloud point. This approach raised the stability of rhodanine-silver complex which was extracted and detected by flame atomic absorption spectrometry.

Experimental

Instruments and Chemicals

Absorbance of silver was recorded using WFX-1E2 flame atomic absorption spectrometry from Beijing Rayleigh Analytical Instrument Corporation. A pH meter (Mettler Toledo FE20, Switzerland) was used for measuring pH. All of the chemicals (such as triton X-100, rhodanine, sodium chloride, silver nitrate, nitric acid, acetic acid, sodium acetate,n-octanol etc) used are of the analytical-reagent grade from Sinopharm Chemical Reagent Co., Ltd. (China) and without further purification. Stock solution of 1g/L silver ion was prepared by adding suitable amount of silver nitrate into a concentration of 0.1mol/L nitric acid and deliquated to the scale. It was calibrated by using standard NaCl solution. Working solution was diluted from stock solution. The water used was all of the deionized water.

Methods

First, a certain amount of standard silver working solution was added into a 50 mL colorimetric tube, and 0.5mL of 0.5mol/L Rhodanine, 2.0mL of 10% Triton X-100, 1.2mL of n-octanol and 5.0 mL of HAc-NaAc buffer solution that was pH 4.0 were added into the above colorimetric tube in turn, which was diluted to the scale. Then, the prepared solution was incubated in a constant 40℃ water bath after adequately oscillating. The solution was cooled down after water bath 30 minutes. When the phase was completely separated, the water phase was entirely removed and the content of the precipitated silver was measured by flame atomic absorption spectrometry.

Preparation of Water Samples

In the present study different water samples utilized were gathered from Huancheng River in Hefei. The standard stream sediment samples were accurately labeled as GBW 07301, GBW 07311 and GBW 07312 separately. 0.5000 g of each was weighed and injected 30 mL of aqua regia. Every sample was made to evaporate until it became almost dry. The above procedure was repeated for twice. Then the samples were respectively dissolved with 10 mL of deionized water and diluted and adjusted the pH to the scale of 25 mL.

Results and Discussion

Volume of n-octanol

It is supposed that it is essential for reaching efficient extraction to add some salt or organic solvent prior to the extraction step [32]. Herein, to investigate the change of the cloud point, n-Propanol, n-Butanol, n-Hexanol, n-Octanol and n-Decanol were injected into the Triton X-100-Rhodanine system, respectively. Results suggested that n-Octanol could dramatically lower the cloud point temperature from 66.9℃ to 36℃, while the others can only lower the range of 5-10℃. The volume effect of n-Octanol on the extraction of silver ion was also explored. The experiments were conducted as following: 5.0 mL of HAc-NaAc buffer solution with pH 4.0, 10% Triton X-100 2.0 mL, 0.5 mL of Rhodanine with 0.5 mol/L, and 50 μg/L of Ag^+, the volume of n-Octanol was added into solution from 0.4 to 1.8 mL. The experimental results were shown in Fig. 1. It is observed that the presence of n-Octanol not only decreased the cloud point but also shortened the phase separation time of the Triton X-100-Rhodanine-Ag^+ system, which was attributed to the lowered viscosity of the surfactant. In addition, when 1.2 mL of n-Octanol was injected, the extraction rate of silver reached as high as 96.4 %, and showed a tendency toward stabilization. Therefore, a volume of 1.2 mL of n-Octanol was selected as the most appropriate value in the further experiments.

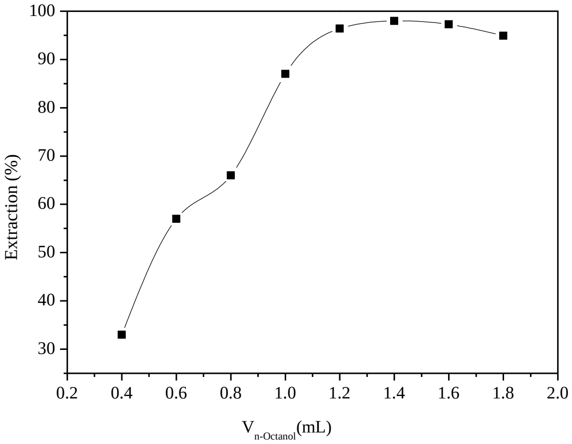

Fig. 1: Effect of n-Octanol on the extraction of Ag^+.

pH value

pH value plays quite an important role both in the agglomeration of the micelles and in the coordination reaction between the ligand and the silver ions. The influence of the pH on the extraction rate of silver were evaluated under the condition with and without n-Octanol respectively by altering the pH from 1.0 to 8.0. The pH was adjusted by dilute hydrochloride acid, HAc-NaAc buffer solution and dilute sodium hydroxide. The results were showed in Fig. 2. As can be seen, the extraction rates of silver were improved at the presence of n-Octanol in the pH ranging from 1.0 to 8.0. Interestingly, the highest extraction rates were both at pH 4.0 under the two above conditions. With the increase of pH from 1 to 4, the extraction rate kept increasing all the time. When the pH was 4, the extraction rate reached the highest (90.4%) without n-Octanol, it could be the reason that the poor stability of the complex prevented it from quantitative extraction (Extraction rate higher than 95%). However, it is near to 98 % in the same experimental condition except for adding 1.2 mL n-Octanol. Coincidentally, both the extraction rate showed a decreasing trend as the pH was beyond 4.0. The results showed that n-Octanol could lower the cloud point of the extraction system, also improved the stability of the complex. Moreover, because of the existence of n-Octanol there was co-extraction effect in the system which allowed the quantitative extraction of silver [33]. According to the above, in the following experiments, a pH of 4.0 was always employed.

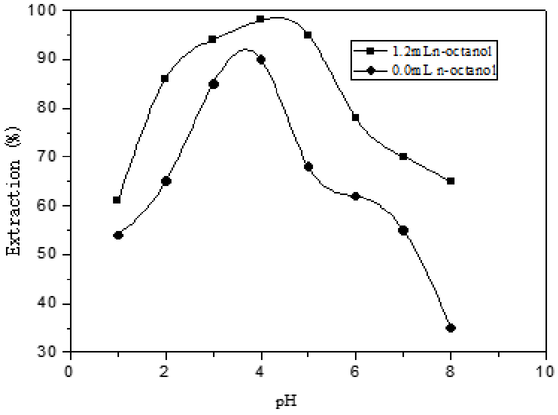

Fig. 2: Effect of pH on the extraction of Ag^+.

Optimum volume of Rhodanine and Triton X-100

Rhodanine reacted with silver ions to form complexes, which prompted the silver ions to be effectively extracted to the surfactant micelle phase. Under the precondition of keeping the surfactant in a certain amount, owing to the strong hydrophobicity Rhodanine, excessive use of it might lead to competitive extraction between Rhodanine and its complex on the surfactant phase in the system. The competition would result in the inefficient extraction of silver. Hence, the effect of the volume of Rhodanine at fixed concentration of 0.5 mol/L on the extraction rate was inspected in range of 0.2-1.6 mL, and the results were showed in Fig. 3. It could be observed that the extraction rate increased quickly with the increase of Rhodanine volume from 0.2 to 0.6. After this volume, the extraction rate decreased. When 0.6 mL of Rhodanine with concentration of 0.5 mol/L was injected to the system, the extraction rate reached the highest. Based on the above findings, 0.6 mL was the optimum volume of rhodanine solution (0.5mol/L) and was selected for further studies.

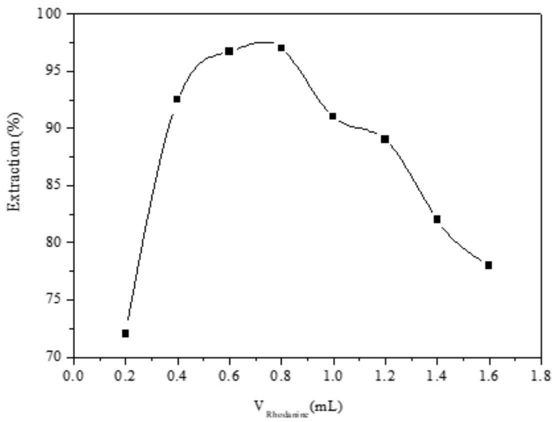

Fig. 3: Effect of Rhodanine on the extraction of Ag^{+}.

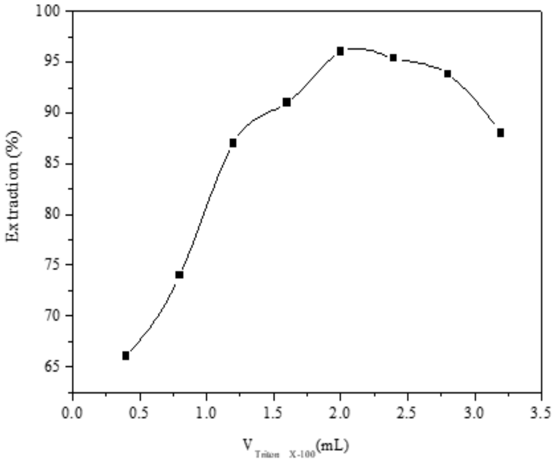

Fig. 4: Effect of Triton X-100 on the extraction of Ag^{+}

In the process of metal ions of cloud point extraction, now that the solubilization of the complexes generated is bound up with the volume of the surfactant applied, it is significant to discuss how the surfactant concentration affects the extraction extent of silver. Thus, to optimize the TritonX-100 concentration, a string of experiments was conducted. In the above experiments, the volumes of TritonX-100 were changed from 0.4mL to 3.2mL. The concentration of silver ions was 50 μg/L. The change of extraction rate caused by different volumes of Triton X-100 was depicted in Fig. 4. As it was shown, the extraction rate kept increasing with Triton X-100 volume increasing until the volume reached 2.0 mL. Beyond 2.0 mL, the extraction rate showed a downward trend. It was probably the reason that low concentration of Triton X-100 led to the incomplete extraction while high concentration of Triton X-100 resulted in the incomplete separation of phases. Furthermore, the high viscosity of the enriched micelle was detrimental to the accuracy of measurement. Thus, 2.0 mL of Triton X-100 was the optimum volume chosen in the subsequent experiments.

Equilibrium temperature and Time

Equilibrium temperature had closely connected with incubation time. It was desirable to make use of the shortest incubation time and to keep the equilibration temperature as low as possible, which compromised complete reaction and efficient separation of the phases [33]. As it was known that the higher the equilibrium temperature in the cloud point extraction system was, the shorter the time to reach maximum extraction was. How the temperature affected the extraction of silver was also investigated under optimized conditions for determination of optimum equilibrium temperature. In this work, the experiments were executed in the range of 25-70℃ using 2.0 mL of Triton X-100, 1.2 mL of n-Octanol, 0.6 mL of 0.5 mol/L Rhodanine, and 50 μg/L Ag^{+}. The pH value in the solution was adjusted to 4.0. The results were illustrated in Fig. 5. It was easily seen that extraction rate increased with the increase of the equilibrium temperature below 40℃ and almost stabilized in the range of 40-50℃. Obviously, when the temperature increased further, the extraction rate decreased. The behavior could be the reason that the equilibrium temperature was too low to achieve the cloud point. As a result, phase separation had poor effects, which resulted in incomplete extraction. Also, too high equilibrium temperature had an impact on the distribution of Rhodanine-Ag^{+} complex in the n-octanol solution thus lowered the extraction rate. In the experiments, 40℃ was chosen as the equilibrium temperature.

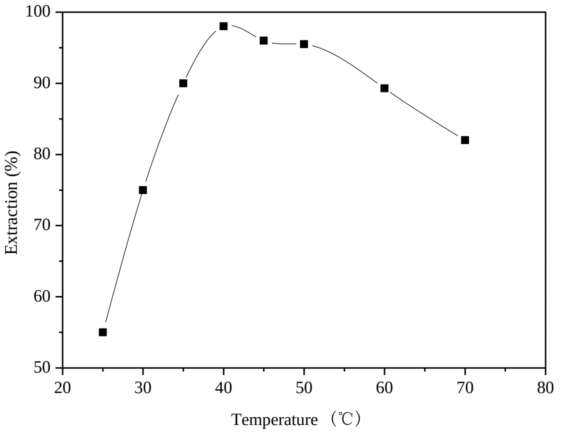

Fig. 5: Effect of equilibrium temperature on the extraction of Ag^+

How the equilibrium time exerted an influence on the extraction rate was investigated as well. The experiments were performed in the range of 10-60 min under the above most suitable conditions. As is shown in Fig. 6, the extraction rate rose with the extension of equilibrium time in the range of 10-30 min. When the equilibrium time was longer than 30 min but less than 60 min, the extraction rate almost kept steadily and the best extraction rate attained as high as 98.1 %. To follow the guide of simple, fast and effective extraction, 30 min was chosen as optimal equilibrium time.

Calibration curve, Detection limit and Stability

Under the optimum condition, the detection of Ag^+ ions was performed, and the intensity of atomic absorption was linear to the concentrations of Ag^+ ions. The calibration curve was obtained in from 5 to 50 μg/L. The equation of linear regression is A = 0.262C + 0.0241 with a correlation coefficient of 0.9992 in Fig. 7. The present method possessed a preferable detection limit of silver ion which was 0.18 μg/L on the basis of the ten times the standard deviation of the blank readings (n = 10，3σ/k）with the enrichment factor of 42. The 50 μg/L of standard solution of silver ions enriched was successively measured for 8 times and the RSD was 4.6%, which indicaded that the method presented high sensitivity and strong stability.

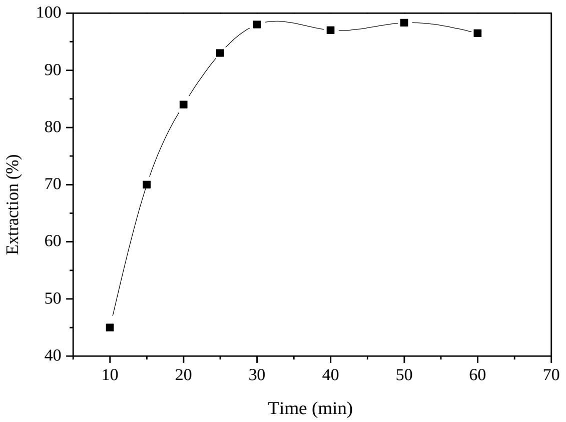

Fig. 6: Effect of equilibrium time on the extraction of $Ag^{+.}$

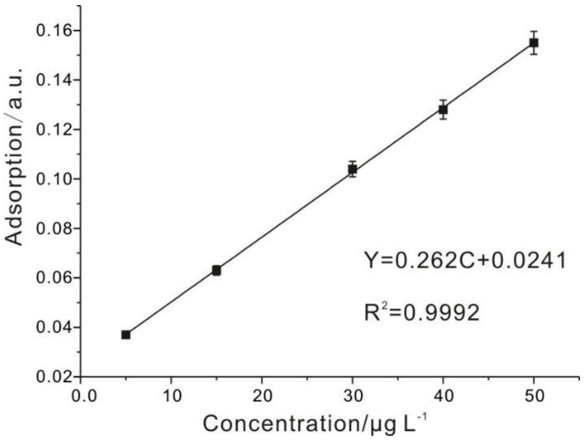

Fig. 7: The relationship of adsorption intensities and concentrations of $Ag^{+.}$

Effect of Co-exist ions

During the cloud point extraction of silver ions, other coexisting ions could compete with silver ions to form hydrophobic complex and affect the extraction of silver ions. To test the selectivity of the method proposed, the effect of twelve common metal ions on the extraction of silver in the Rhodanine cloud point system was investigated. The solution which contains target analyte and different concentrations of interfering species were prepared separately. The proposed procedure was applied to extract ions in the solution and the results were listed in Table-1. An ion was deemed to be impervious when it brought about a variation exceeding 5 % in the sample absorbance. As descried in Table-1, except for sodium and magnesium, the other ten kinds of common metal ions did not disturb the determination on trace of silver ion in the current system.

Table-1: Effect of twelve common metal ions on the extraction and determination of 50μg/L Ag^+

Ion	M^{n+}/Ag^+	Recovery, %
Na^+	1000	109.4
K^+	1000	103.5
Ca^{2+}	1000	105.7
Mg^{2+}	1000	109.2
Mn^{2+}	500	95.2
Cu^{2+}	200	96.1
Cd^{2+}	200	88.6
Zn^{2+}	500	99.1
Pb^{2+}	500	98.8
Hg^{2+}	200	82.9
Al^{3+}	500	96.2
Fe^{3+}	500	97.3

Table 2 Determination results of Ag^+ in standard reference samples (n = 3)

Sample names	Standard value（μg/g）	Measured value（μg/g）
GBW07301	1.05±0.09	0.98±0.04
GBW07311	3.2±0.5	3.11±0.36
GBW07312	1.15±0.06	1.15±0.06

Table-3: Determination results of Ag^+ in real environmental samples (n = 3)

Samples	Added（μg/L）	Found	Recovery/%
Lake bed sediments	0	0.38±0.06μg/g	-
Waste water	0	54.9±2.99μg/L	-
	10	63.5±4.53μg/L	97.9%
	20	70.8±4.22μg/L	94.4%
Lake water	0	ND	-
	10	9.8±0.09μg/L	98.7%
	20	20.02±0.12μg/L	102.3%

Sample Analysis

Three standard water sediment samples were accurately measured and labeled as GBW 07301, GBW 07311 and GBW 07312 separately. Each of them weighed 0.5000g and injected 30 mL of aqua regia . The three samples were made to evaporate until the samples became almost dry. The above procedure was repeated for twice. Then the samples were respectively dissolved with 10 mL of deionized water and diluted to the scale of 25 mL. The Ag^+ concentration of samples was measured by the low temperature CPE established, and the corresponding results were exhibited in Table 2. It is clearly shown that the measurement is in keeping with the reference data, which means the detection and enrichment of silver ions in the samples are very accurate. To further verify the viability of the method, recovery experiments on the samples of the lake sediment, waste water and lake water were carried out to analyze the silver ions. As Table 3 is demonstrated, the adding standard recovery of silver is between 94.4% and 102.3 %, which reveals high precision and good accuracy of the proposed CPE method.

Conclusion

A new and simple CPE method for detecting trace silver has been established with FAAS based on that Octanol induced to significantly decrease the cloud point of Triton X-100. The method is fairly accurate, which leads to an effective separation. It constitutes an inexpensive alternative to other pre-concentration methods. The satisfactory results of standard reference sediment analysis manifested perfect accuracy and sensitivity of the method. The presented method was also applied to determine trace silver in sediment and environmental water samples.

Acknowledgements

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