

On-line Incorporation of Cloud Point Extraction in Flame Atomic Absorption Spectrometric Determination of Silver

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A cloud point extraction method was incorporated into a flow injection system, coupled with flame atomic absorption spectrometry, for determination of trace amounts of silver.

The analyte in the aqueous solution was acidified with 0.2 mol L⁻¹ sulfuric acid and complexed with dithizone. The cloud point extraction was performed using the non-ionic surfactant Triton X-114. After obtaining the cloud point, the surfactant-rich phase containing the dithizonate complex was collected in a mini-column packed with cotton wool. Then the complex was eluted by passing THF through the column and silver content was determined by flame atomic absorption spectrometry. All the chemical and flow variables were optimized and the enhancement factor was estimated to be 38.

The calibration curve was rectilinear in the range of 4-220 µg L⁻¹ and the limit of detection was 0.7 µg L⁻¹. The precision for 6 replicate measurements at a silver concentration of 50 µg L⁻¹ was 2.0% relative standard deviation. The proposed method was applied to the determination of silver in water samples.

Key Words: Cloud point extraction; silver; dithizone; on-line

Introduction

The silver content in environmental samples is increasing due to the use of different silver compounds in industry and medicine.¹ Therapeutic and occupational exposure to silver and its compounds results in argyria and argyrosis, which are caused by deposition of silver-protein complex in the body.² The US Environmental Protection Agency has reported that an upper limit of 50 µg L⁻¹ silver in natural waters provides protection

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against adverse health effects.³ Therefore, its determination in water samples is important for pollution control. Flame atomic absorption spectrometry (FAAS) has wide applications for determination of metal ions because of its availability in most routine laboratories. However, its sensitivity is not usually sufficient for the direct analysis of the low concentrations of Ag in water samples.⁴ Hence preconcentration of metal ion is required prior to its determination by FAAS.

Techniques such as co-precipitation,⁵ ion exchange chromatography,⁶ liquid-liquid extraction,⁷⁻⁹ and solid phase extraction¹⁰ have been reported for the preconcentration of Ag.

Diphenyl thiocarbazon, known as dithizone (H₂DZ), forms stable chelates (dithizonate) with many metal ions that are soluble in organic solvents. The reagent has been widely used in liquid-liquid¹¹ and solid phase extraction,^{12,13} spectrophotometric determination, or separation of metal ions by pH adjustment.

Being a soft base, dithizone has been used for selective extraction of soft acids such as Ag, Pd, Au, and Hg from acidic medium.¹⁴ Separations and preconcentrations based on cloud point extraction (CPE) in micellar solutions using surfactants are finding wide applications in analytical chemistry¹⁵ to determine metal species and organic molecules.⁶⁻¹⁹ The CPE of metal ions involves the formation of sparingly water soluble chelates with suitable reagents. The method is based on the entrapment of uncharged moiety within a micelle formed by heating the surfactant solution above the cloud point temperature. The principles of CPE are well documented.^{15,20} The application of CPE offers an attractive alternative to conventional liquid-liquid extraction by reducing the consumption of and exposure to the solvent, disposal cost, and extraction time.²¹⁻²³ Many metal ions have been determined by atomic absorption spectrometry such as Cd and Pb,²³ Mn,²⁴ Fe,²⁵ and Cd, Cu, Pb, and Zn²⁶ and by spectrophotometry such as Co and Ni,²⁷ and U²⁸ after CPE. Different chelating agents such as 1-(2-thiazolylazo)-2-naphthol (TAN), dialkyl dithiophosphate (DDTP), and ammonium pyrrolidine dithiocarbamate (APDC) have been used for this purpose.

Dithizone has recently been used for CPE and the determination of Ag,²⁹ Cd, and Ni³⁰ by flame atomic absorption spectrometry, Bi by electrothermal atomic absorption spectrometry (ETAAS),³¹ and Hg by spectrophotometry.³²

Methods involving flow injection analysis (FIA) are preferred to those in batch, due to the advantages obtained by method automation. Flow injection atomic absorption spectrometry (FIAAS) systems offer several advantages of a purely analytical nature. These include an improvement in nebulization efficiency in certain circumstances and the ability to easily adjust the signal magnitude. The measurements performed in FIAAS systems are less influenced by differences in the viscosity of samples or differences in matrix composition.³³ Many FIA systems have been developed, most of which are on the basis of on-line solid phase extraction-FIAAS.^{34,35} Cloud point-FI systems are also reported, where the detection techniques such as UV/Vis spectrophotometry and chemiluminescence are commonly used,^{32,36} and a very few systems have used FAAS as a detection technique.³⁷ No attempt has been cited for the use of dithizone in the on-line CPE/preconcentration and determination of Ag. The goal of the present work was the incorporation of CPE into the FIAAS determination of Ag using dithizone as chelating agent and optimization of flow conditions for coupling the system to FAAS.

Experimental

Apparatus

A Varian Model SpectrAA220 (Mulgrave, Vic., Australia) flame atomic absorption spectrometer equipped with a deuterium lamp background corrector was used for the analysis of Ag. A silver hollow cathode lamp operating at 328.1 nm was used as the radiation source. The lamp current and slit width were 4 mA and 0.6 nm, respectively. The measurements were performed in an air-acetylene flame. The fuel flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal.

The reaction coil was of PTFE tubing (i.d. 0.5 mm). A mini-column, consisting of a cylindrical glass tube (3 cm × 4 mm) packed with a suitable filtering material, was used for collection of the surfactant-rich phase. A 4-way rotary valve was used for the loading/injection steps. A Julabo MP5 thermostatic bath was used to reach the cloud point temperature.

Reagents

All chemicals and reagents were of analytical reagent grade and all aqueous solutions were prepared in doubly distilled deionized water. Triton X-114 was obtained from Sigma and used as received. A stock standard solution of Ag (1000 mg L⁻¹) was prepared from pure AgNO₃ (Merck). Working standard solutions were prepared by appropriate dilution of the stock standard solution. A solution of dithizone (Merck) (1 × 10⁻³ mol L⁻¹) was prepared by dissolving appropriate amounts of the reagent in tetrahydrofuran (Merck), and kept in an amber glass bottle. A sulfuric acid (Merck) solution (2.0 mol L⁻¹) was prepared by appropriate dilution of concentrated acid in distilled water.

Procedure

The flow system is made of a peristaltic pump fitted with tygon tubes. The reaction coil (R) was kept in a thermostatic bath at 40 ± 0.5 °C, and a 4-way valve in which the injection loop was replaced by a glass mini-column packed with cotton wool (CC) was used to collect the surfactant-rich phase containing the complex (Figure 1). The system was operated in the time-based mode (where the sample flow rate and loading time govern the amount of sample loaded into the FI system) as follows: in the first stage (Figure 1a), an aliquot of the sample or standard solution containing the analyte (4-220 μg L⁻¹), 0.05% (v/v) Triton X-114, dithizone (7 × 10⁻⁶ mol L⁻¹), and sulfuric acid (0.2 mol L⁻¹) was loaded into FI manifold for 2 min at the rate of 2 mL min⁻¹. The surfactant-rich and aqueous phases were passed through the mini-column, where the surfactant-rich phase containing the complex was collected, while the aqueous phase was discharged (W). In the second stage (Figure 1b), the valve was switched on to the injection position for 15 s. The complex in the mini-column (CC) was eluted (in the reverse direction) with 50% THF solution in water (eluent) (8 mL min⁻¹) into the nebulizer of FAAS. The absorption signals were processed in the peak height mode using instrument software. The average values of peak height were obtained for 3 replicate experiments.

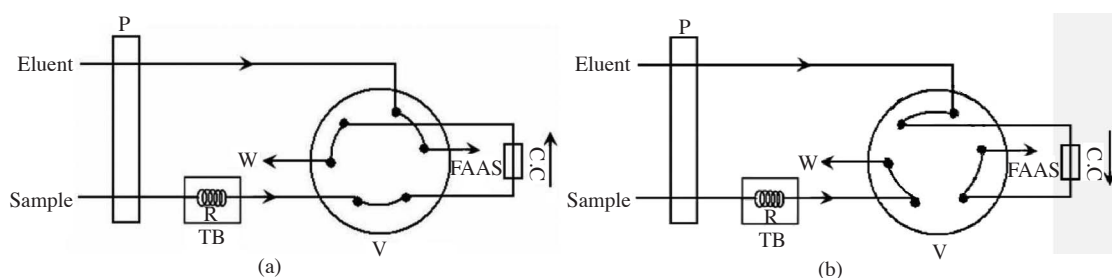


Figure 1. Schematic diagram of the CPE/ FIAAS manifold for the preconcentration and determination of Ag. P: peristaltic pump; TB: thermostatic bath; R: reactor; V: valve; FAAS: flame atomic absorption spectrometer; C.C: collection column; W: waste. Valve in the (a) loading step and (b) elution step.

Results and Discussion

Optimization of chemical variables

The influence of chemical variables such as acidity of sample solution, and concentrations of dithizone, Triton X-114, and THF on the preconcentration efficiency of 10 mL of solution containing $100 \mu\text{g L}^{-1}$ of silver was investigated and optimized. Sulfuric acid was chosen for pH adjustment due to the stability of dithizone in the presence of H_2SO_4 . HCl is not recommended since the percentage of extraction will decrease either by precipitation of Ag^+ ion or by chloride complex formation of Ag. HNO_3 can decompose dithizone. The reason for choosing Triton X-114 was its low cloud point temperature and high density of the surfactant-rich phase. The results are summarized in Table 1.

Table 1. Optimization of chemical variables.

Variable	Studied range	Selected value
THF final concentration (% v/v)	0.5-5	0.7
Dithizone concentration (mol L^{-1})	$1 \times 10^{-6} - 1 \times 10^{-5}$	7×10^{-6}
Triton X-114 concentration (% v/v)	0.01-0.2	0.05
Sulfuric acid concentration (mol L^{-1})	0.001-1	0.2

Optimization of FI and preconcentration variables

The home-made mini-column was packed with different filtering materials in order to obtain phase separation by entrapping larger surfactant aggregates and allowing the smaller components in the aqueous phase to pass through. Aliquots (10 mL) of standard solutions containing $100 \mu\text{g L}^{-1}$ silver, $7 \times 10^{-6} \text{ mol L}^{-1}$ dithizone, $0.2 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, and Triton X-114 (0.05% v/v) were passed through the column at the flow rate of 2.0 mL min^{-1} for 120 s. The retained complex was then eluted with 40% THF solution at the flow rate of 6.0 mL min^{-1} for 15 s. Since cotton wool provided the best absorption signals and reproducibility, it was chosen as the filtering material for further evaluation of the performance of the system (Table 2).

The silver elution from the CC column (packed with cotton wool) was studied using different solvents such as pure ethanol, methanol, and their nitric acid solutions ($0.01\text{-}1 \text{ mol L}^{-1}$), and THF³⁰ (5%-80% v/v) as eluting agent at the rate of 6.0 mL min^{-1} . The complete elution and highest absorbance signal were

achieved with THF at concentrations above 25%; hence 50% THF was chosen for subsequent experiments (Figure 2).

Table 2. Effect of filtering material on the absorption signal and precision.

Filtering material	Dry amount	Absorbance	R.S.D (% n = 4)
Glass wool	90 mg	0.3	2.5
Cotton wool	90 mg	0.40	1.8
Cigarette filter	3 cm × 4 mm	0.19	3.3

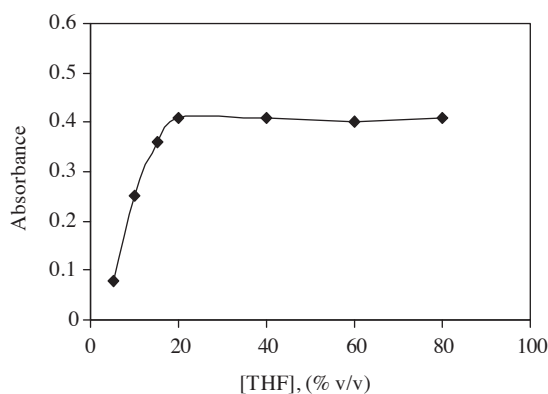


Figure 2. Effect of THF concentration on the elution of Ag. Conditions: Initial concentration of Ag, $100 \mu\text{g L}^{-1}$; Column, 3 cm × 4 mm packed with 90 mg cotton; Sample flow rate, 2 mL min^{-1} ; Sample loading time, 120 s; Eluent flow rate, 6 mL min^{-1} .

The effect of sample flow rate on the preconcentration efficiency was studied in such a way that 10 mL of a solution containing $100 \mu\text{g L}^{-1}$ of silver was pumped through the system at flow rates of 0.5 to 5 mL min^{-1} . It was observed that the analytical signal decreased slightly by increasing the sample flow rate above 2.5 mL min^{-1} , which must be due to the incomplete reaction in the coil as well as insufficient detainment of the micellar phase on the mini-column. Therefore, a sample flow rate of 2.5 mL min^{-1} was selected for further studies. The performance of the flow system was investigated by varying the loading time from 30 to 240 s. The analytical signal increased with increase in loading time up to 100 s, above which there was no significant change in signal (Figure 3). Hence, a loading time of 120 s was chosen. The length of the column was another parameter optimized for its effect on the preconcentration efficiency. Columns 1, 2, 3, and 5 cm in length packed with cotton wool were tested. A 3 cm length column was chosen, since it gave the highest absorption signal. The shorter columns were inadequate for retaining the surfactant-rich phase, while the longer column decreased the signal due to insufficient elution of the micellar aggregates. The amount of cotton wool in the mini-column is important for collecting the surfactant-rich phase; hence it was optimized for the selected column by testing different amounts of dry cotton wool. The best results were obtained when ca. 100 mg was used. Larger amounts of cotton wool led to the deterioration of the signal due to blockage of tubes and insufficient elution of the retained complex; when a smaller amount was used, collection was not efficient. The influence of elution rate was also investigated in the range of $2\text{-}10 \text{ mL min}^{-1}$. Figure 4 shows that the absorption peak increased with increases in the flow rate and reached a maximum at flow rates in the range of $6\text{-}10 \text{ mL min}^{-1}$. At flow rates below 6 mL min^{-1} , the signal decreased considerably, resulting in

broader peaks. This must be due to the incompatibility between elution and nebulization flow rates, which can cause a significant dispersion when eluent flow rate is smaller than nebulizer flow rate. Hence, a flow rate of 7 mL min⁻¹ was selected for elution. The optimization results are summarized in Table 3.

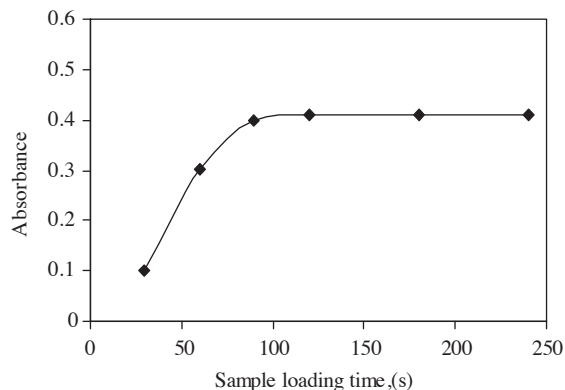


Figure 3. Effect of sample loading time on the absorbance of Ag. Conditions: Initial concentration of Ag, 100 $\mu\text{g L}^{-1}$; Column, 3 cm \times 4 mm packed with 90 mg cotton; Sample flow rate, 2.5 mL min⁻¹; Eluent, THF 50 % (v/v); Eluent flow rate, 6 mL min⁻¹.

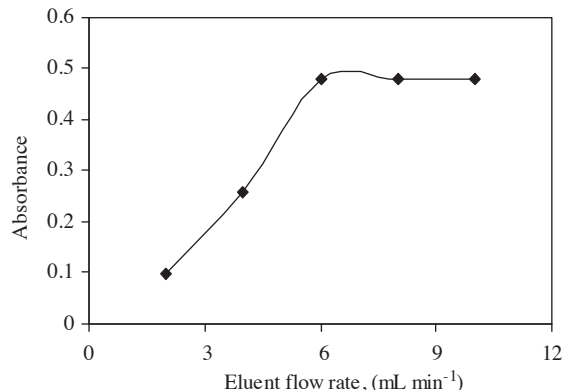


Figure 4. Absorbance vs. eluent flow rate. Conditions: Initial concentration of Ag, 100 $\mu\text{g L}^{-1}$; Column, 3 cm \times 4 mm packed with 100 mg cotton; Sample flow rate, 2.5 mL min⁻¹; Sample loading time, 120 s; Eluent, THF 50% (v/v).

Table 3. Investigated parameters and selected values for the proposed method.

Parameter	Studied range	Optimum value
Sample flow rate (mL min ⁻¹)	0.5-5.0	2.5
Eluent flow rate (mL min ⁻¹)	2.0-10	7.0
Column length (cm)	0.5-5.0	3.0
Cotton wool dry weight (mg)	50-200	100
Reactor length (cm)	25-150	100
Loading time (s)	30-240	120

Interference study

The effect of diverse ions on the determination of 100 $\mu\text{g L}^{-1}$ silver was studied. The common ions at the usual concentrations found in natural water samples as well as those ions that may form complexes with dithizone were tested. The tolerance limits (error < 5%) are shown in Table 4. The major interferences were caused by Pd(II), Hg(II), and Cu(II). The concentrations of these ions in water samples are usually very low and have no adverse effect in the determination step by FAAS, but they can interfere in the preconcentration of Ag. However, the interferences of Hg(II) (0.5 $\mu\text{g mL}^{-1}$) and Cu(II) (0.5 $\mu\text{g mL}^{-1}$) were eliminated by adding EDTA (1 \times 10⁻³ mol L⁻¹). Pd(II) could not be masked by the investigated masking agents; hence it was removed by a prior solvent extraction step as a dimethylglyoximate complex.

Analytical performance of the method

The calibration graph was linear over the range of 4-220 $\mu\text{g L}^{-1}$ for 2 min of preconcentration time. The calibration graph obtained under the optimal chemical and flow conditions was as $A = 4.0101 \pm 5.4 \times 10^{-3}(\mu\text{g mL}^{-1}) + 0.044 \pm 1.4 \times 10^{-3}$, ($r = 0.9992$). The precision for 6 replicate measurements at 0.05 $\mu\text{g mL}^{-1}$ was 2.0% relative standard deviation. The limit of detection (LOD), defined as $C_{LOD} = 3S_b m^{-1}$,³⁸ (where S_b is the standard deviation of the blank ($n = 6$), m is the slope of the calibration curve), was found to be 0.7 $\mu\text{g L}^{-1}$ for 10 mL of sample solution. The calibration graph was also obtained with standard solutions of silver (in the concentration range of 0.4-6 $\mu\text{g mL}^{-1}$) without preconcentration as $A = 0.1049 \pm 0.51 \times 10^{-3}(\mu\text{g mL}^{-1}) - 0.004 \pm 0.60 \times 10^{-3}$, ($r = 0.9997$). The R.S.D.% and LOD were 0.8% ($n = 6$ at 2 $\mu\text{g mL}^{-1}$ silver) and 20 $\mu\text{g L}^{-1}$ ($n = 6$), respectively. The enhancement factor, calculated as the ratio of the slopes of calibration curves obtained with and without preconcentration, was found to be 38.

Table 4. Tolerance limits of diverse ions in the determination of 100 $\mu\text{g L}^{-1}$ of Ag.

Interferent-to-analyte ratio	Tested ions
Tested ions	Interferent-to-analyte ratio
Na ⁺	2000:1
K ⁺	2000:1
Mg ²⁺	2000:1
Ca ²⁺	2000:1
Pb ²⁺	40:1
Zn ²⁺	40:1
Ni ²⁺	50:1
Co ²⁺	40:1
Cd ²⁺	40:1
In ³⁺	30:1
Pd ²⁺	1:1
Hg ²⁺	< 10 : 1
Cu ²⁺	< 10 : 1
CH ₃ COO ⁻	30:1

Application

In order to investigate the applicability of the proposed method, it was applied to the determination of silver in different water samples collected from Zanjan city and province. The samples were filtered through a 0.45 μm pore size nylon filter to remove any suspended particulate matter and were stored in the refrigerator (5 °C) prior to preconcentration. Then 10 mL of each sample was preconcentrated and determined by the proposed method. The validation of the method was performed by recovery experiments for spiked samples. The results given in Table 5 show quantitative recovery for 3 replicate analysis.

Table 5. Determination and recovery of Ag in water samples.^a

Sample	Ag ($\mu\text{g L}^{-1}$)		Recovery (%)
	Added	Found	
Tap water	-	nd ^b	-
	10	10.3 (± 1.0)	103.0 (± 2.6)
	20	19.8 (± 0.6)	99.0 (± 2.3)
Rain water	-	nd	-
	10	9.7 (± 1.2)	97.0 (± 1.6)
	20	19.6 (± 0.9)	98.0 (± 1.8)
River water	-	nd	-
	10	10.2 (± 1.4)	102.0 (± 2.4)
	20	20.2 (± 0.7)	101.0 (± 1.9)
Sea water ^c	-	nd	-
	10	9.7 (± 1.1)	97.0 (± 2.0)
	20	19.8 (± 1.4)	99.0 (± 2.5)
Deionized water	10	10.1 (± 1.0)	101.0 (± 1.9)
	20	19.8 (± 1.2)	99.0 (± 2.4)

^a Values in the parentheses are standard deviations for triplicate analysis.

^b Not detected.

^c Caspian Sea water sample.

Conclusion

The results presented show the suitability of dithizone as a complexing reagent for on-line CPE/determination of silver, and are comparable with those reported for off-line determination of Ag.²⁹ Triton X-114 surfactant has a low CPT (23 °C); hence, its application provided reproducible signals by avoiding bubble formation in the FI system, which otherwise usually occurs when using Triton X-100 surfactant (CPT = 68 °C). The prevention of this requires the reduction of CPT by applying salting out agents. The developed FIAAS system provided good results in terms of accuracy and precision for rapid determination of silver in water samples. The FI system with a single pump in this method offered a mean time of analysis of 6 min, a sample throughput of 10 h⁻¹, and detection limit of 0.7 $\mu\text{g L}^{-1}$.

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