



## Off-line determination of trace silver in water samples and standard reference materials by cloud point extraction–atomic absorption spectrometry

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**Abstract.** An off-line method for the determination of trace silver in water samples and certified reference materials by cloud point extraction (CPE) followed by flame atomic absorption spectrometry (FAAS) has been worked out. Preconcentration of CPE was based on complex formation of silver with dithizone in the presence of non-ionic micelles of octylphenoxy polyethoxy ethanol (Triton X-114) at pH 4.0. Optimization was performed on the variables influencing complexation and phase separation. The detection limit of silver in certified samples was  $1.42 \text{ ng mL}^{-1}$ , the quantification limit was  $4.72 \text{ ng mL}^{-1}$ , and precision expressed as relative standard deviation was 2.2% ( $n = 3$ , for silver concentration of  $50 \text{ ng mL}^{-1}$ ). The method was applied for the determination of trace silver in certified reference materials with satisfactory results.

**Key words:** atomic spectroscopy, cloud point extraction, FAAS, Ag, water, standard reference material, Triton X-114, dithizone complex.

### INTRODUCTION

The widespread industrial applications of silver may result in its increased concentrations in aquatic ecosystems. Because of their bacteriostatic properties, silver compounds are often used in filters and other equipments to purify different types of water and in the processing of foods, drugs, and beverages. In many countries, silver-impregnated filters are used for drinking water preparation [1].

Silver is considered toxic for humans and the recommendations of the World Health Organization (WHO) permit maximal concentrations of  $0.1 \text{ mg L}^{-1}$  of silver ions in drinking water disinfection, but the United States Environmental Protection Agency (USEPA) recommends  $0.05 \text{ mg L}^{-1}$  as maximum [2].

Silver is distributed as a recycled element, with relatively low concentrations ( $<2 \text{ pM}$ ) in remote surface waters [3]. The interest in measuring trace and ultratrace amounts of silver in natural waters has increased due to

concerns over its toxicity to aquatic organisms. Furthermore, silver has long been used as a geochemical tracer of wastewater discharges in waters and, more recently, as a tracer of atmospheric contamination from fossil fuel combustion in oceanic waters [4]. The production and usage of engineered nanomaterials, like silver nanoparticles, is growing, possessing potential hazard to the environment [5] and enhancing eutrophication in aquatic ecosystems [6].

The toxicity of silver depends not only on its total concentration, but also on its speciation. It was found that nearly 85% of total dissolved ( $\leq 0.45 \text{ }\mu\text{m}$  filter) silver in San Francisco and Galveston estuarine waters is associated with colloids; and that colloidal matter is almost entirely composed of organic matter [7]. Dissolved silver speciation is expected to change markedly in estuaries, owing to changes in chloride concentration (as a proxy for salinity). Formation of the neutral chloro complex,  $\text{AgCl}^0$ , might increase bioaccumulation of silver [8]. Low concentrations of silver, combined with relatively high (mM) concentrations of alkali and alkaline earth ions, make direct determination of trace

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silver levels in waters very challenging. Consequently, it is essential to isolate silver from interferences and pre-concentrate it prior to instrumental analysis.

There are several literature reports dealing with the preconcentration of silver ions based on different methods, most of which employ solid phase extraction followed by flame atomic absorption spectrometry (FAAS) [9–16]. FAAS has been widely used for the determination of trace metal ions because of the relatively simple and inexpensive equipment. More recently multi-walled carbon nanotubes have been used as a packing material for the solid phase extraction procedure [17]. Other preconcentration methods of silver involve batch adsorption [18–20], flotation [21], and precipitation–dissolution [22]. In the recent years adsorption on a tungsten wire, followed by electrothermal atomic absorption spectrometry with a tungsten tube atomizer [23] and chemical vapour generation technique [24] were reported.

Several methods for the preconcentration of silver have been developed by using a micelle-mediated methodology [25–29]. Cloud point extraction (CPE) provides certain advantages such as low cost, safety, faster operation, no need for a large amount of organic solvents. The method has been used to separate and preconcentrate organic compounds [30–36] and metal ions [32–34,37–41]. When an aqueous solution of a non-ionic or amphoteric surfactant above their critical micellar concentration (CMC) is heated at a characteristic temperature, called cloud point temperature, the solution containing the surfactant becomes turbid and divided into a surfactant-rich phase (very small viscous volume) and the remaining larger volume (bulk amount) of the diluted aqueous solution with the surfactant concentration, which is approximately equal to its CMC. During the formation of the two phases, the insoluble hydrophobic complex can be entrapped in situ in the surfactant-rich phase. With CPE a high preconcentration factor can be obtained [42]. In comparison with the traditional organic liquid–liquid extraction, CPE requires a very small amount of relatively non-flammable and non-volatile surfactants. Various non-ionic surfactants such as Triton X-100, Triton X-114, PONPE 7.5, and Tween 80 and doubly ionic surfactants such as ammoniumethylsulphates, ammoniumpropylsulphates, ammoniumpropylsulphonates, phosphobetaine, and dimethylalkylphosphine oxides have been used [36]. CPE permits the design of extraction schemes that are of lower toxicity and high efficiency.

Silver was determined by CPE as a complex with dithizone (Dz) in strongly acidic solutions [29]. At low pH the AgHDz complex and at higher pH values Ag<sub>2</sub>Dz complex is formed [43]. Selective reaction of dithizone with silver in mild acidic conditions (acetate buffer) is noted in [44,45]. However, CPE preconcentration of silver with dithizone complexation in weak acidic solutions prior to AAS has not been reported previously.

As the natural water samples in previous studies were acidified to pH < 2 with sulphuric acid [29], the precipitation of colloidal matter (and humic substances) was possible and it was also likely that colloidal precipitates trapped silver species, making them unavailable to complex formation.

In the present paper, we report the results of selective CPE preconcentration of silver after the formation of a hydrophobic complex with dithizone at pH 4.0. Octylphenoxy polyethoxy ethanol (Triton X-114) was used as surfactant. The proposed method was applied for the determination of silver in certified reference materials.

## EXPERIMENTAL

### Instrumentation and chemical reagents

A Varian Spectra AA 220 FS, Varian (Victoria, Australia), flame atomic absorption spectrophotometer (FAAS) equipped with a Varian hollow cathode lamp as the radiation source was used for the determinations of silver. The optimum conditions for FAAS are given in Table 1. A thermostatted bath maintained at the desired temperature was used for cloud point preconcentration experiments and phase separation was assisted using a centrifuge. Speedwave MWS-3, Berghof (Eningen, Germany), was used as a microwave digestion system for solid reference material.

The non-ionic surfactant Triton X-114, Sigma (Missouri, USA), was used without further purification. The stock atomic spectroscopy standard solutions (1000 mg L<sup>-1</sup>), Fluka (Buchs, Switzerland), were used for Ag and other metals. Working standard solutions were obtained by appropriate dilutions. Dithizone, Merck (Darmstadt, Germany), 1 × 10<sup>-3</sup> mol L<sup>-1</sup> solution was prepared by dissolving an appropriate amount in tetrahydrofuran, Merck (Darmstadt, Germany). The solution was kept in a refrigerator (4 °C) until use. Acetic acid, Merck, and sodium acetate (Darmstadt, Germany) were used to prepare the buffer with a concentration of 100 mM. High-purity deionized water obtained by a MilliQ water purification system, Millipore (Bedford, USA), was used in all experiments. Certified reference materials CWW-TM-D, High Purity Standards (Charleston, USA); NWTM-15, LGC Standards (Middlesex, United Kingdom); DORM-2, National Research

**Table 1.** Operating parameters for silver analysis by FAAS

Parameter	
Wavelength, nm	328.1
Lamp current, mA	4.0
Acetylene flow rate, L min <sup>-1</sup>	2.0
Slit width, nm	0.5
Air flow rate, L min <sup>-1</sup>	13.5
Background correction	Deuterium

Council (Ontario, Canada); and DOLT-3, National Research Council (Ontario, Canada) were used to check the accuracy of the method.

### Cloud point extraction procedure

For the cloud point extraction, aliquots of the cold solutions (10 mL) containing 50.0 ng mL<sup>-1</sup> Ag, Triton X-114 (0.2%, v/v), dithizone (1 × 10<sup>-3</sup> mol L<sup>-1</sup>), buffered at pH 4.0 with 100 mM acetate buffer, were kept for 15 min in the thermostatic bath at 45 °C. The separation of the phases was accelerated by centrifuging at 3500 rpm for 10 min. After cooling in an ice-bath, the surfactant-rich phase became viscous. The aqueous phase was separated with a syringe. Subsequently, to decrease the viscosity of the surfactant-rich phase, 1.0 mol L<sup>-1</sup> HNO<sub>3</sub> in methanol was added in order to make the final volume 0.5 mL. The preconcentrated solutions were introduced into the FAAS by conventional aspiration.

### Pretreatment of solid reference materials

To the weighed (0.35 g) solid reference samples the 5 mL of HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> (2:1) mixture was added. The samples were digested using a microwave oven with the temperature program presented in Table 2. After digestion, the clear solutions were separated and diluted to the final volume of 10 mL with water. All samples were analysed in triplicate.

## RESULTS AND DISCUSSION

### Effect of pH

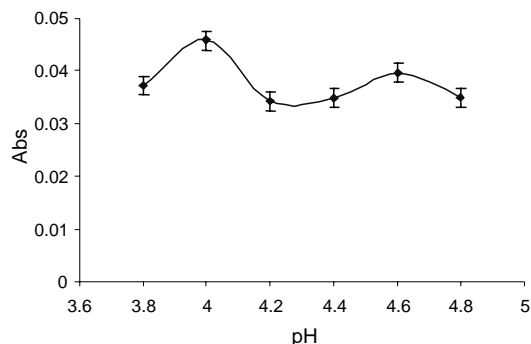
The formation of the metal chelate complex and its chemical stability are the two important factors for CPE. The pH plays a unique role in the metal chelate formation and subsequent extraction, and is proved to be a main parameter for CPE. The effect of the pH on the extraction of the Ag(I)-dithizone complex was studied and the results show that extraction was quantitative for silver in the pH range 3.8–4.8 (Fig. 1). Therefore, pH 4.0 was chosen for the subsequent work.

**Table 2.** Temperature program of the microwave digestion system

	Step			
	1	2	3	4
T, °C	140	160	165	100
Ta, min <sup>a</sup>	5	5	2	5
Time, min <sup>b</sup>	5	5	2	5

<sup>a</sup> Waiting time at the desired temperature.

<sup>b</sup> The time between two sequential temperatures.



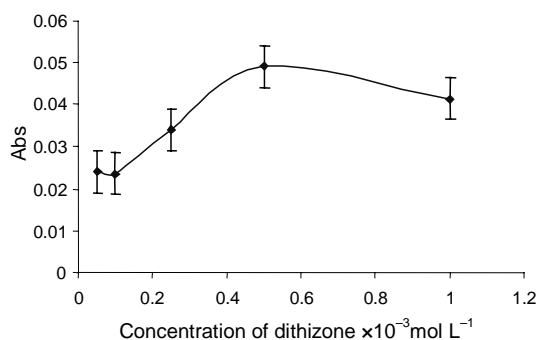
**Fig. 1.** Effect of the pH on the analytical signal of Ag. Conditions: 10 mL of cold aqueous solution, 50 ng mL<sup>-1</sup> Ag, 1 × 10<sup>-3</sup> mol L<sup>-1</sup> dithizone, 0.2% (v/v) Triton X-114 at 45 °C. Other conditions are described under experimental. Standard errors are indicated by error bars.

### Effect of the dithizone concentration

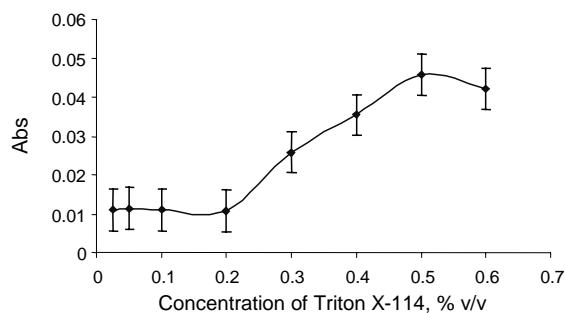
At the optimum pH, the complexation efficiency of Ag(I) with dithizone as a function of the concentration of the chelating agent was studied. A 10 mL solution containing 50 ng mL<sup>-1</sup> silver in 0.2% Triton X-114 buffered to pH 4.0 containing various amounts of dithizone was subjected to the cloud point preconcentration process. The signal increased up to a dithizone concentration of 0.5 × 10<sup>-3</sup> mol L<sup>-1</sup> and reached nearly quantitative extraction efficiency. The results are shown in Fig. 2.

### Effect of Triton X-114 concentration

An effective CPE would be that which maximizes the extraction efficiency through minimizing the phase volume ratio, thus increasing its concentrating ability. The variation of extraction efficiency within the Triton X-114 range 0.025–0.6% (v/v) was examined. Quantitative extraction was obtained when the Triton X-114 concentration was >0.5%. Figure 3 highlights the differences observed in the signals at different surfactant concentrations. With the increase of Triton X-114



**Fig. 2.** Effect of dithizone concentration on the analytical signal of Ag. Conditions: 100 mM acetate buffer pH 4.0; for other conditions see Fig. 1. Standard errors are indicated by error bars.



**Fig. 3.** Effect of Triton X-114 concentration on the analytical signal of Ag. Conditions:  $0.5 \times 10^{-3} \text{ mol L}^{-1}$  dithizone; for other conditions see Fig. 1. Standard errors are indicated by error bars.

concentration above 0.5%, the signals decrease because of the increment in the volumes and the viscosity of the surfactant phase. An amount of 0.5% (v/v) Triton X-114 was considered best in order to achieve the greatest analytical signal and thereby the highest extraction efficiency.

#### Effect of the equilibration temperature and centrifugation time

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which enabled the completion of the reaction and an efficient separation of the phases. It was found that  $45^\circ\text{C}$  was adequate for cloud point experiments. The dependence of extraction efficiency upon equilibration time was studied within a range of 5–30 min. An equilibration time of 15 min was chosen as the best to obtain quantitative extraction.

#### Interference effects

The effect of different cations and anions on the determination of  $50 \text{ ng mL}^{-1}$  silver ions by the proposed method was studied. An ion was considered interfering when it caused a variation greater than  $\pm 5\%$  in the absorption of the sample.

The results (Table 3) indicate that Ag(I) recoveries were almost quantitative in the presence of interfering cations.

**Table 3.** Effect of different ions on the preconcentration and determination of  $50 \text{ ng mL}^{-1}$  Ag

Ion	Ion/Ag(I), w/w	Recovery, %
Ni <sup>2+</sup>	100	94
Mn <sup>2+</sup>	100	93
Mg <sup>2+</sup>	1000	95
Cu <sup>2+</sup>	100	95
Cd <sup>2+</sup>	100	89
Zn <sup>2+</sup>	500	99
Pb <sup>2+</sup>	100	98
Mo <sup>2+</sup>	100	97
V <sup>5+</sup>	100	88
Hg <sup>2+</sup>	100	80
Se <sup>2+</sup>	100	89
Cr <sup>3+</sup>	50	90
Al <sup>3+</sup>	50	96
Ba <sup>2+</sup>	1000	80
NaCH <sub>3</sub> COO	1000	109
MgSO <sub>4</sub>	1000	109

#### Analytical figures of merit

Calibration graphs were obtained by preconcentrating 10 mL of sample in the presence of 0.5% Triton X-114 and  $0.5 \times 10^{-3} \text{ mol L}^{-1}$  dithizone in buffered solutions (pH 4.0). A linear relationship between the measured absorbance and silver concentration present in the solution was obtained. Table 4 summarizes the analytical characteristics of the optimized method, including linear range, limit of detection, reproducibility, and preconcentration and enhancement factor. The limit of detection was  $1.42 \text{ ng mL}^{-1}$ . The enhancement factor, defined as the ratio of the slope of the calibration graph for the CPE method to that of the slope of the calibration graph in micellar media without preconcentration, was 37.

#### Application of the method to certified reference materials

In order to assess its applicability to certified reference materials with different matrices containing varying amounts of a variety of diverse ions, the method was applied to the separation and recovery of silver ions from different certified samples. Table 5 shows the

**Table 4.** Analytical characteristics of the optimized method

Parameter	Analytical feature
Linear range, $\text{ng mL}^{-1}$	5–50
Limit of detection, LOD, $\text{ng mL}^{-1\text{a}}$	1.42
Regression equation without CPE	$\text{Abs} = 4.84 \times 10^{-5} \text{ ng mL}^{-1} \text{ Ag}^+ - 0.00054$
Regression equation with CPE	$\text{Abs} = 1.80 \times 10^{-3} \text{ ng mL}^{-1} \text{ Ag}^+ + 0.0062$
Reproducibility, RSD, % <sup>b</sup> ; $n = 3$	2.2
Enhancement factor	37

<sup>a</sup> Determined as three times the standard deviation of the blank signal [41].

<sup>b</sup> Ag(I) concentration for which RSD was obtained was  $50.0 \text{ ng mL}^{-1}$ .

**Table 5.** Determination of Ag(I) in certified reference samples ( $n = 3$ )

Sample	Certified	Measured
CWW-TM-D	$1.0 \pm 0.005^a$	$0.96 \pm 0.09^a$
NWTM-15	$0.0118^a$	$0.010 \pm 0.002^a$
DORM-2	$0.041 \pm 0.013^b$	$0.038 \pm 0.011^b$
DOLT-3	$1.20 \pm 0.07^b$	$1.12 \pm 0.08^b$

<sup>a</sup>  $\mu\text{g mL}^{-1}$ , <sup>b</sup>  $\mu\text{g g}^{-1}$ .

results of the analysis of wastewater CWW-TM-D, spiked/fortified water NWTM-15, dogfish muscle (DORM-2), and dogfish liver (DOLT-3). Certified water samples (10 mL) were directly used for the pre-concentration of silver. The results indicated excellent performance of the applied method as the measured concentrations were close to the certified values.

## CONCLUSIONS

In this study, the use of a micellar system as an alternative method to other techniques of the separation and pre-concentration of Ag offered several advantages including low cost, high capacity with high recovery, and very good extraction efficiency. The results of the present study demonstrate the possibility of using the dithizone–Triton X-114 system for the pre-concentration of Ag(I) as a step prior to the determination at  $\text{ng mL}^{-1}$  level in water and other reference samples. Separation was efficient and selective, resulting in a good enrichment factor and a low limit of detection. The developed method can be used for the removal of the water as aimed. The accuracy of the method was checked by applying it to standard reference samples.

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**Hõbeda mikrokoguste *off-line*-määramine vees ja sertifitseeritud referentsmaterjalides sademe tekkepunkt-ekstraktsioonil ning aatomabsorptsioonspektroskoopilisel meetodil**

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On välja töötatud *off-line*-meetod hõbeda mikrokoguste määramiseks veeproovides ja sertifitseeritud referentsmaterjalides, mis põhineb sademe tekkepunkt-ekstraktsioonil ning järgneval aatomabsorptsioonspektromeetrilisel meetodil. Sademe tekkepunkt-ekstraktsiooniline eelkontsentreerimine põhineb hõbeda kompleksi moodustamisel ditisooniga mitteioonsete Triton X-114 mitsellide juuresolekul pH-väärtusel 4,0. Meetodit optimeeriti kompleksi moodustamist ja faaside eraldamist mõjutavate tegurite suhtes. Hõbeda avastamiskiir sertifitseeritud proovides oli  $1,42 \text{ ng mL}^{-1}$ , määramiskiir  $4,72 \text{ ng mL}^{-1}$  ja kordustäpsus väljendatuna standardhälbena 2,2% ( $n = 3$ , hõbeda kontsentratsioonil  $50 \text{ ng mL}^{-1}$ ). Hõbeda mikrokoguste määramisel sertifitseeritud referentsmaterjalides saadi rahuldavad tulemused.