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Trace enrichment and determination of silver by immobilized DDTC microcolumn and flow injection atomic absorption spectrometry

S. Dadfarnia*, A.M. Haji Shabani, M. Gohari

Department of Chemistry, Yazd University, Yazd 89195-741, Iran

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Abstract

Flow injection (FI) system incorporating a microcolumn of immobilized diethyldithiocarbamate (DDTC) on surfactant-coated alumina was combined with atomic absorption spectrometry for on-line trace enrichment and determination of silver in different matrices. Silver was deposited on the microcolumn by processing a standard or solution of analyte at pH 3–4 on the column. Injection of 250 μl of ethanol then served to elute the retained species to atomic absorption spectrometry (AAS). A sample volume of 20 ml resulted in a pre-concentration factor of 125, and precision at the 20 $\mu g\,l^{-1}$ was 4% (R.S.D.). The procedure was applied to tap water, well water, rain water, sea water, radiology film, and lead concentrate samples. The accuracy was assessed through recovery experiments, independent analysis by furnace-AAS, and analysis of certified reference material.

Keywords: Silver determination; Immobilized diethyldithiocarbamate; On-line pre-concentration; Flow injection

1. Introduction

Silver is a metal of commercial importance. It is valued for its resistance to corrosion and for its use in alloys, medicine and jewelry [1]. Because of its marked antibacterial properties, its compounds and alloys have been widely used to disinfect the water used for drinking and recreational purpose, in dental and pharmaceutical preparation, and in implanted prosthesis [2,3]. It is also used in electronic devices, photographic material, mirrors, and cloud seeding [4,5]. Bowen [6] suggested that silver may pose a potential risk as a water pollutant because of the lack of recycling of mined silver. Therefore, determination of trace amounts of silver is important for many areas of chemical analysis.

Trace amount of silver in different media can be determined by expensive analytical methods such as inductively coupled plasma mass spectrometry [7,8], inductively coupled plasma atomic emission spectrometry [9] and electro thermal atomic absorption spectrometry [10].

However, flame atomic absorption spectrometry (FAAS) is the most frequent chosen technique, as shown by hundreds of paper published since the first reports on the trace determination of silver in 1959 [11]. Flame atomic absorption spectrometry is often accepted because of its speed and ease of operation, but it has the major drawback of low sensitivity for direct determination of silver in many matrices. Therefore, for ultra trace determination of silver a separation/pre-concentration step is required.

Several pre-concentration techniques such as solvent extraction [12], sorbent extraction [13], chromatography [14], precipitation [15], and donnan dialysis [16] have been used for trace enrichment and separation of silver. However, these manual batch procedures are labor, time and reagent consuming and required large volume of sample.

Flow injection (FI) separation and pre-concentration techniques have proved to be effective for enhancement of sensitivity of atomic spectrometry [17]. Since its introduction, flow injection analysis (FIA) has attracted increasing attention because of its high precision, high sampling rate and the possibility for on-line sample pretreatment. For determination of silver utilizing flame atomic absorption, different on-line sample processing system have been developed including solvent extraction [18,19], microcolumn sorbent ex-

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* Corresponding author. Tel.: +98-351-8212795; fax: +98-351-7250110.
E-mail address: sdadfarnia@yazduni.ac.ir (S. Dadfarnia).

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traction [20–22] precipitation [23,24] and co-precipitation [25–27].

Recently Pei and Fang [25] developed an on-line co-precipitation system for Ag determination. In this approach, silver was on-line co-precipitated with diethyldithiocarbamate (DDTC)–Iron (II) chelate in the presence of 1,10-phenanthroline. The precipitate was collected in a knotted reactor and was dissolved by isobutyl methyl ketone (IBMK) which was transported to FAAS for detection. An enrichment factor of 26 and a detection limit of 0.5 ng ml^{-1} were reported by authors. Mao et al. [26] used the same approach for determination of silver in geological sample, but they employed Cu-DDTC complex as coprecipitate carrier reagents. For a loading period of 30 s a detection limit of 0.6 μg l^{-1} was reported.

DDTC is a known classical complexing agent and is a dithiocarbamate which most commonly is used in spectrophotometric analysis. It form very strong complex with silver ion which is sparingly soluble in water. In this work the possibility of immobilization of DDTC on surfactant-coated alumina was considered, and a rapid on-line system for enrichment and determination of silver in different matrices by flame atomic absorption spectrometry incorporating a microcolumn of immobilized DDTC was designed.

2. Experimental

2.1. Instrumentation

An Instrumentation Laboratory AA spectrometer (Model 210 VGP, USA), furnished with a silver hollow-cathode lamp and air-acetylene flame was used for all measurements. The operating conditions were as follows: wavelength 328.1 nm, slit width 0.7 nm, lamp current 6.6 mA, burner height 4 mm. The absorbance time response was monitored on an *x*–*t* chart recorder (L-250) and quantitative analysis was based on measurement of the peak height of transient signals. A schematic diagram of flow injection system used is presented in Fig. 1. The manifold consists of peristaltic pump (Ismatec, Ms-4 REGL 018-100 Switzerland), rotary injection valve (Rheodyne, CA, USA) and microcolumn of DDTC immobilized on surfactant-coated alumina (PTFE tube 3 cm × 1.5 mm i.d.).

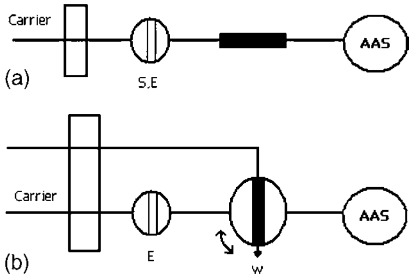


Fig. 1. Schematic diagram of the flow injection system. S, sample; E, eluent; W, waste; P, pump, flow rate 5 ml min^{-1}, eluent (ethanol 250 μl), and sample pH ∼3.

2.2. Reagents

Silver standard stock solution 1000 mg l^{-1} was prepared by dissolving 0.1578 g of $AgNO_3$ in 1 ml nitric acid in a 100 ml volumetric flask and diluting to mark with water. Working solutions were prepared daily from the stock solution by appropriate dilution with water.

Alumina (10–50 μm, γ type chromatography grade, Merck, Darmstadt, Germany) was purified by shaking with 5 mol l^{-1} nitric acid and washing three times with water. Sodium dodecyl sulfate (SDS) (Merck, Darmstadt, Germany) and sodium diethyldithiocarbamate (Merck, Darmstadt, Germany) were used without further purification. All other regents were of analytical grade and triply distilled, de-ionized was used throughout the experiments.

2.3. Immobilization of sodium diethyldithiocarbamate

Forty milliliter of a solution (pH ∼2) containing 100 mg sodium dodecyl sulfate was added to 1.5 g of alumina. This was mixed with a magnetic stirrer for 10 min. The supernatant was decanted and the SDS-coated alumina was washed thoroughly with several portions of water. Then, 20 ml of water and ∼0.1 g of sodium diethyldithiocarbamate was added, and the solution was shaken for 15 min. The mixture was then filtered through Millipore filter, washed, air-dried, and was kept in a closed bottle before use. It was stable for several weeks.

2.4. Preparation of microcolumn

Microcolumn was fabricated by using PTFE (Teflon) tubing (4 cm in length, internal diameter of 2.5 mm) and contained sodium diethyldithiocarbamate immobilized on surfactant-coated alumina (about 70 mg). The end of the tube was fitted with foam to retain the sorbent in the tube.

2.5. Preparation of radiology film

10 ml of aqueous nitric acid (6 M) was added to 0.12 g of radiology film. The mixture was filtered, and the solution was transferred to a 250 ml volumetric flask and was diluted to the mark with water. Then, 3 ml of the resultant solution was further diluted to 500 ml and the pH was adjusted to 3 by nitric acid solution (0.1 mol l^{-1}).

2.6. Preparation of reference lead concentrate CPB-1

Ten milliliter of concentrate nitric acid was added to 0.397 g of lead concentrate. The solution was heated to nearly dryness. The procedure was repeated several times, and after complete digestion of the sample, 25 ml water was added. The solution was filtered and diluted to 250 ml in a volumetric flask. One ml of this solution and 3 ml of EDTA (0.01 M) was added to 25 ml of water. The pH was adjusted to 3, and the solution was transferred to a 50 ml flask and was diluted to the mark with water.

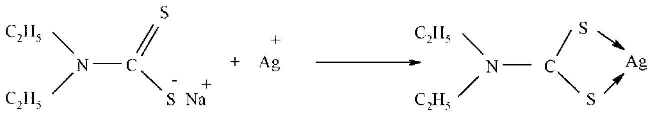
3. General procedure

The FI manifold used is presented in Fig. 1. The single line system (Fig. 1(a)) was used to study analyte breakthrough and to undertake initial method development studies. The two-line FI manifold (Fig. 1(b)) was used to process real samples and to obtain performance data. The carrier and eluent solution were water and ethanol (250 µl), respectively. The microcolumn was located in the sample loop of injection valve, so the sampling could be performed “off-line” and preventing matrix constituents entering the AAS. At the end of sampling the valve was switch “on-line” and the eluent was injected with the use of second valve to effect elution.

The pH of solution was adjusted to ∼3 with 1 M nitric acid, with reference to FI manifold (Fig. 1(a) and (b)), standard solution or samples were passed through the DDTC microcolumn (Fig. (1a) sample volume 250 µl; Fig. 1(b) volume-based sampling (e.g. 20 ml at flow rate of 5 ml min^{-1})) to effect the deposition of the analyte. The absorbed silver was then eluted by injection of ethanol (250 µl) and transported to flame atomic absorption spectrometer for quantization. (For the FI system in Fig. 1(b) the injection valve was switched to bring the microcolumn “on-line” prior to the injection of eluent.) The transient signal was monitored for quantitative analysis.

4. Results and discussion

According to the literature [27] the colorimetric reagent sodium diethyldithiocarbamat is relatively soluble in water and from sparingly water soluble silver complex as follows



This fact leaded to the development of some analytical method based on the co-precipitation of silver with either Fe [25] or Cu [26] DDTC ligand. On the other hand, Hiraide et al. [28] had previously proposed that water insoluble chelating sorbent could be trapped into the aggregate of sodium dodecyl sulfate alumina particles. We decided to consider the possibility of immobilization of DDTC on surfactant-coated alumina. It was found that when DDTC is added to the solution containing particles of alumina-coated SDS, the ligand trapped homogeneously on the hemi micelles or ad-micelles formed by SDS on the alumina surface in a manner similar to that demonstrated for some water insoluble organic ligands [29–33]. This changed the color of alumina from white to pale yellow. The chelating sorbent was then air-dried and was used for preparation of the microcolumn.

A possible concern was whether the column is stable in processing the large volume of sample. However, when the standard sample (40 µg l^{-1}) was processed with FI system, the variation of peak height with sampling volume was linear up to 100 ml (correlation coefficient 0.9992). This suggests that retention efficiency was constant within this volume interval, and the solubility of immobilized ligand in compare to free ligand is decreased.

4.1. *Effect of physical and chemical parameters*

As shown in previous studies concerned with modified alumina, microcolumn pre-concentration [29,31], the deposition/elution processes are influenced by FI parameters, such as carrier stream flow rate, nature and flow rate of eluent, sample pH, column length, etc. These variables were, therefore, critically studied to maximize recovery of silver. The efficiency of the precoentration/elution process was studied by comparing the peak area of the signals for the silver eluted from the microcolumn with that of the same amount of silver injected into the carrier stream flowing through an empty PTFE tube of the same dimensions as those of the immobilized DDTC microcolumn.

As shown in Fig. 2, when the pH of solution was varied from 1 to 7, the analyte deposition was found to be independent of sample pH. However, a further increase in pH caused a sharp decrease in analyte signal. The decrease in signal at pH > 7.5 is probably due to the precipitation of silver as silver hydroxide. Silver (I) is more stable at acidic pH. Thus, in order to achieve high efficiency and good selectivity, a pH of ∼3 was selected for subsequent work. It should be noted that although free DDTC is not very stable in acidic media, but when immobilized on surfactant-coated alumina is quite stable at pH 3.

The effect of nature of eluent on desorption and measurement of analyte signal was considered. Different eluents, such as nitric acid (1–4 M); acetone; pure, diluted and acidified ethanol were examined. With pure ethanol, signal

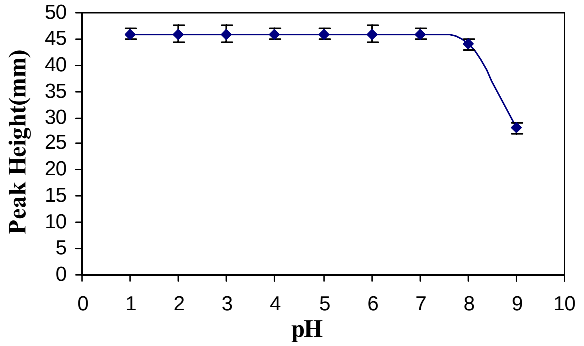


Fig. 2. Effect of pH on silver adsorption, Ag$^+$ solution (5 ml, 0.1 µg ml^{-1}, flow rate 5 ml min^{-1}), and eluent volume 250 µl.

enhancement was observed and was chosen as the most effective eluent. Ethanol was able to solubilize the complex; thereby, carry it to the spectrometer where the complex was destroyed and silver was measured. The efficiency of flow rate on analyte deposition on microcolumn was considered by varying the flow rate from 2 to 9 ml min^{-1}; while, keeping the amount of pre-concentrated silver constant at 1 μg. It was found that kinetic of exchange is very fast and independent of flow rate. However, higher flow rate was not examined due to the back pressure in the system. Analyte signal peak height was dependent on elution flow rate and a virtually linear increase in peak height response was observed and leveled off at a flow rate higher than the uptake of the nebulizer. The increase in peak height is due to starvation of the nebulizer at low flow rate. The eluent flow rate was chosen to match the recommended sample uptake of the atomic absorption spectrometry (3.5 ml min^{-1}).

The effect of the mass of packing material on efficiency of analyte deposition was considered and a column packed with ~0.07 g of sorbent (corresponding to a length of 3 cm of microcolumn) was found to be sufficient. A typical absorbance time response for the sequential injection of a standard solution (250 μl of 1 mg l^{-1} Ag) and ethanol (250 μl) is given in Fig. 3(c). For comparison, the equivalent transient signals for direct injection and pneumatic nebulization of sample (1 mg l^{-1} silver) are also included (Fig. 3(a and b)). The relatively sharp and narrow elution peak relative to signal for direct injection indicates that the dispersion characteristics are significantly modified as a result of microcolumn deposition/elution and a degree of pre-concentration is achieved. Furthermore, the relatively sharp elution peak is an indication of fast exchange kinetics for elution steps. On the basis of consideration of peak height of conventional nebulization and peak height of sequential injection with a microcolumn, a dispersion coefficient (16/30) of 0.53 was calculated. On the basis of consideration of the area for the respective signals of microcolumn elution peak (Fig. 3c) and direct injection (Fig. 3b), it is evident that a recovery of more than 99% was obtained with a single injection of eluent.

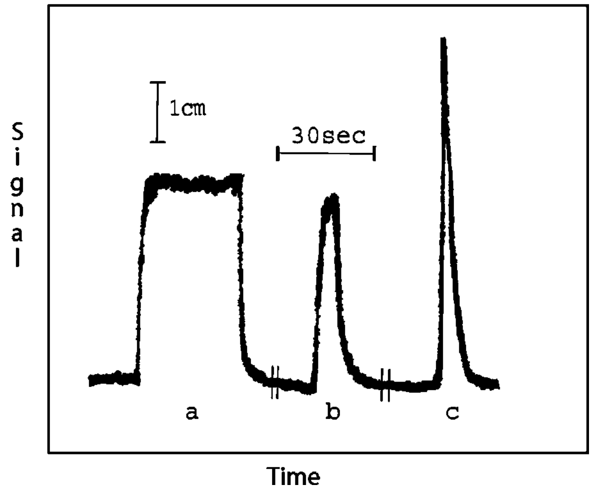


Fig. 3. Absorbance vs. time response for: (a) conventional nebulization of ethanolic silver solution (1 μg ml^{-1}); (b) direct injection of ethanolic solution of silver (250 μl 1 μg ml^{-1}); and (c) sequential injections of silver solution (250 μl, 1 μg ml^{-1} pH ~3) and ethanol (250 μl).

Table 1
Effect of diverse ions in determination of silver (40 μg l^{-1})

Ions	Tolerance limit mole ratio of M^{n+}/Ag^{+}
Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}	1000[a]
Cr^{3+}, Cd^{2+}, Pb^{2+}, Ni^{2+}	1000[a]
As^{3+}, Co^{2+}, Mn^{2+}, Zn^{2+}	1000[a]
Sn^{2+}, Fe^{3+}	1000[a]
Cu^{2+}	1000[b]
V^{5+}	500
Mo^{6+}	100

[a] Maximum value tested.
[b] Masked with 0.01 g of thiourea.

4.2. Interference studies

The deposition efficiency of microcolumn in preconcentration of silver in presence of various foreign ions was examined and the results are shown in Table 1. A relative error of less than 5% was considered to be within the range of experimental error. With the exception of Cu, at the given level no significant interference was observed in the determination of silver at trace levels. Furthermore, the interference of Cu was removed by addition of thiourea at a level of twice of that of concentration of copper. Thus, the interference-free determination levels of present system indicate that high concentration of matrix salts, have minimal effect on Ag species relative to matrix ions.

5. Analytical performance

Twenty and 50 ml of standard solutions were proceed (in triplicate) at a sampling flow rate of 5 ml min^{-1} and the graph of a absorbance (as peak height) versus silver concentration were linear over the concentration range of 5–100 μg l^{-1} of silver. The equation of calibration graphs were $H = 0.777C–1.033$ and $H = 1.954C–1.348$ (where H is the peak height and C is the concentration) with correlation coefficient of 0.9998 and 0.9994, respectively. The calibration slopes increased proportionally with increasing pre-concentration volume, which indicate the retention/elution efficiency of the process is constant (100%).

A possible concern was whether high enrichment factors could be realized for natural waters and, particularly, salt-rich matrices such as sea water, where high concentration of humic acid, cations and anions might affect the active site and impair deposition efficiency of silver. However, when seawater (from Caspian Sea) was spiked at 20 μg l^{-1} and was processed with the FI system, the variation of signal peak height with sampling volume up to 20 ml was linear (correlation coefficient 0.9993) and was similar to that for processing silver standard solution. The relative standard deviation at 20 μg l^{-1} for 20 ml sampling volume was 4.0% ($n = 6$). The limit of detection defined as three times the standard deviation of the blank (3S) was 1.7 and 0.7 μg l^{-1} for 20 and 50 ml sampling volumes, respectively. An analytical throughput of 16 h^{-1} was achieved for 20 ml sampling volume.

The breakthrough capacity of immobilized DDTC microcolumn under the working conditions exceeded 514 μg of silver per gram of packing materials. This high value suggested high performance by the microcolumn even in the presence of competing ions. The capability of the FI system for quantification of silver at low level (μg l^{-1}) was investigated. The transient signals of Fig. 4 refer to processing of 20 ml silver standard solution (40 μg l^{-1}) (Fig. 4A) prior to elution. For comparison purposes, the signal of direct pneumatic nebulization of Ag (5 mg l^{-1}) is also given (Fig. 4B). Consideration of relative concentration and respective peak height responses for the two situations (Fig. 4A and B) enables a concentration factor of about 125 to be calculated (based on sample processing of 4 min). Extending the sample processing volume, however, results in improved method sensitivity. As mentioned before, in the present study a sampling volume up to 100 ml were investigated and the peak height response was found to vary linearly with volume.

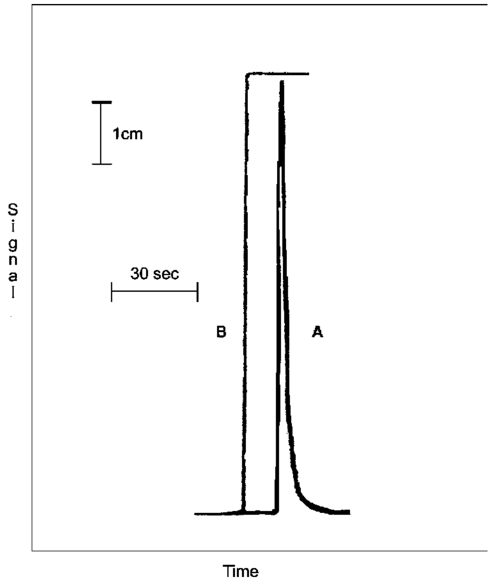


Fig. 4. Comparison of pre-concentration and direct nebulization: (A) Ag 0.04 μg ml^{-1}, 20 ml and (B) steady state response for direct nebulization of silver (5 μg ml^{-1}).

5.1. Applications

Procedure was applied to the determination of silver in tap water, well water, rain, and seawater. Reliability was checked by spiking the sample and comparing the results with data obtained by furnace atomic absorption analysis. The results given in Table 2 show that the recovery of spiked sample is good and there is satisfactory agreement between the results and data obtained by furnace atomic absorption analysis, suggesting that the FI–AAS procedure is suitable for the sample type examined. The suitability of the proposed method for determination of silver in radiology film was checked. The accuracy of the method was examined by recovery experiment and analysis using an independent technique (ET-AAS) on unpreconcentrated sample. The results are also given in Table 2. As presented, the average recovery is good and there is good agreement between the results and the data obtained by furnace atomic absorption.

Table 2
Determination of silver in water and radiology film samples

Sample	Silver (μg l$^{-1)}$		Recovery (%)	S.D.	Furnace AAS
	Added	Found[a]			
Tap water	0	<LOD	–	–	<LOD
	10	10	100	±0.35	–
Well water	0	<LOD	–	–	<LOD
	10	10.5	105	±0.42	–
Rain water	0	<LOD	–	–	<LOD
	10	10.3	103	±0.31	–
Sea water	0	<LOD	–	–	1.17 ± 0.06
	10	10.4	104	±0.16	–
Radiology film	0	10.24[b]	–	±0.17	10.5 ± 0.6[b]
	6.9[b]	16.83[b]	95.5	±0.42	–

Sample volume, 20 ml.

[a] Average of three determinations.

[b] Concentration is in mg l^{-1}.

Table 3
Determination of silver in lead concentrate

Sample	Accepted value (mg kg^{-1})	Determined value (mg kg^{-1})	
		FI–AAS[a]	Furnace[a]
Lead concentrate CPB-1	0.626 ± 0.006	0.64_5 ± 0.05	0.61_7 ± 0.07
Lead concentrate spiked at 0.630 ppm	–	1.30_4 ± 0.01	–

[a] Mean and standard deviation of three determinations.

Furthermore, the above procedure was applied for determination of silver in reference lead concentrate, and the accuracy of the method was assessed through recovery experiment and comparing the data with the accepted value. The results of this investigation together with the accepted value are also given in Table 3. It indicates the suitability of the method for this type of sample. Thus, the procedure is reliable for analysis of a wide range of sample.

6. Conclusion

It has been demonstrated that relatively soluble organic ligand can be immobilized on surfactant-coated alumina in a manner similar to water-insoluble chelating ligands

(29–33). Furthermore, the proposed FI system incorporating immobilized DTCC microcolumn permits effective on-line pre-concentration of silver and final determination by FAAS. In addition, it offers an alternative procedure to techniques such as GFAAS and ICP-AES for determination of silver at $\mu g\,l^{-1}$ level in different matrices. The main benefits of system were high tolerance to interference from the matrix ions in different sample, enhanced sensitivity of FAAS, low cost, simplicity and speed of analysis. In addition, the sorbent is stable for several weeks.

Future work will be directed at the assessment of the suitability of the immobilized microcolumn for the field sampling of silver.

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