Determination of Silver by Flame Atomic Absorption Spectrometry after Preconcentration on Naphthalene Modified with Dithizone

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A solid-phase extraction method for preconcentration of silver and consequent determination by atomic absorption spectrometry is described. The method is based on the adsorption of silver on naphthalene modified with dithizone in a column. The adsorbed silver is eluted from the column with a thiourea solution and determined by flame atomic absorption spectrometry. The adsorption conditions including pH, reagent concentration, eluent volume, flow rate and interfering ions were investigated. The calibration graph was linear in the range 10-1000 ng mL^{-1} of Ag in the initial solution with r = 0.9998. The limit of detection based on $3S_b$ was 3.9 ng mL^{-1}. The relative standard deviation for ten replicate measurements of 40 and 600 ng mL^{-1} of Ag was 4.4% and 0.9%, respectively. The method was applied to the determination of silver in mineral, radiology film and wound dressing samples.

Keywords: Solid-phase extraction; Naphthalene; Silver; Dithizone; Flame atomic absorption spectrometry.

INTRODUCTION

Silver compounds and alloys have been widely used in dental and pharmaceutical preparations because of their marked antibacterial properties.[1] Silver is also of commercial importance for use in high-strength and corrosion resistance alloys and jewelry. Silver is both vital and toxic for many biological systems and its content in environmental samples is increased with the increasing use of silver compounds and silver-containing products in industry and in medicine.[2] Silver can enter into the environment via industrial waters and might pose a potential risk as water pollutant. Thus, separation, pre-concentration and sensitive determination of silver ion is of increasing interest.[3]

A variety of methods including flame atomic absorption spectrometry,[4] electrothermal atomic absorption spectrometry (ETAAS),[5] inductively coupled plasma optical emission spectrometry (ICP-OES),[6] inductively coupled plasma mass spectroscopy (ICP-MS)[7] and stripping voltammetry[8] have been extensively used for trace element determination in different samples. Direct determination of trace amounts of metal ions in some samples by flame atomic absorption spectrometry (FAAS) is difficult because of low sensitivity. Thus, pre-concentration procedures are often required. Different techniques such as solvent extraction,[9] membrane filtration,[10] cloud point extraction[11] and solid phase extraction[12,13] have been used to enrich the analyte and separate it from the interferences. Solid phase extraction has frequently been applied to the preconcentration and determination of ultra-trace analytes in complex matrix samples by instrumental methods.[14,15] Various materials have been successfully used for the preconcentration and separation of heavy metal ions at trace levels including: activated carbon,[16] Amberlite XAD-16 resin,[1] benzil derivative of polyacrylohydrazide,[17] amidinothioureido-silica gel[18] and naphthalene.[19,20]

In this work a solid-phase extraction procedure for the determination of silver by flame atomic absorption spectrometry (FAAS) is described. Silver ions are adsorbed on dithizone-supported naphthalene, which is used as an adsorbent in a column. The silver ions are then eluted with thiourea solution and its silver content is determined by FAAS.

EXPERIMENTAL SECTION

Instrumentation

A Philips PU9100X flame atomic absorption spectrometer was used for the determination of silver. It was equipped with appropriate hallow cathode lamp and air-acetylene burner. The instrumental parameters were as follows: wavelength, 328.1 nm; lamp current, 5 mA; band

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pass, 0.5 nm. All pH measurements were made using a Metrohm digital pH meter with a combined glass electrode.

Reagents and Solutions

Double distilled water and analytical reagent-grade chemicals were used. A stock solution of 1000 µg mL^{-1} Ag$^+$ was prepared by dissolving 0.1575 g silver nitrate (Merck) in water and diluting to 100 mL in a volumetric flask. The working solutions were prepared by appropriate dilution of the stock solution. Solid dithizone (Fluka) was used as received.

The adsorbent solution was prepared by dissolving 20 g of naphthalene and 0.04 g of dithizone in 60 mL of acetone and heating on a hot-plate stirrer at 40 °C. This solution was transferred to 1000 mL of water while stirring the solution at room temperature. It was stirred for 12 h on a stirrer. This adsorbent slurry was stored in a dark bottle for further use.

General Procedure

The metal sorption studies on the solid-phase extraction were performed using a glass funnel (8 cm length and 0.7 cm i.d.) with a very fine bore as a pre-concentration column. It was filled with the naphthalene-dithizone adsorbent to a height of about 5 cm and slightly pressed in the column with a flat glass rod. 50 mL of the solution containing 10-1000 ng mL^{-1} of Ag$^+$ was passed through the column at a flow rate of 35 mL min^{-1}. The metal complex was eluted with 5 mL of 1% (w/v) thiourea solution and the silver content of the eluent was determined by FAAS and the recovery of silver ion was calculated. A blank solution was also run under the same analytical conditions without adding any silver ion.

Sample Preparation

Ore samples were dissolved according to the following procedure. 10 mL of concentrated nitric acid was added to 5 g of powdered ore sample in a beaker and boiled for 20 minutes. This procedure was repeated three times. The resulting solution was transferred to a 200-mL volumetric flask and diluted to the mark. Similarly, solutions of samples of radiology film and wound dressing were prepared.

RESULTS AND DISCUSSION

Dithizone (dipheylthiocarbazone) forms chelate complexes with a number of heavy metal ions in neutral, alkaline and acetic acid solutions. Dithizone was chosen as chelating agent and it was loaded on naphthalene and was used for pre-concentration of silver ions. In order to obtain quantitative recoveries for solid phase extraction of silver ion on

naphthalene-dithizone, the effect of various experimental parameters such as pH, sample volume, amounts of adsorbent and sorption capacity was optimized.

Effect of Variables

The preliminary investigation showed that the silver ion is retained by the sorbent more effectively in acidic media. Therefore the effect of nitric acid concentration on the recovery of silver ions was evaluated. Results shown in Fig. 1 demonstrated that maximum recovery (98.8%) was achieved at 0.1 mol L^{-1} of nitric acid. In subsequent studies concentration of nitric acid was maintained at 0.1 mol L^{-1}.

The eluent type is an important factor in the solid phase extraction. The effects of various solutions as eluents were investigated for the elution of adsorbed silver ions from column. Ammonia, thiosemicarbazid, sodium thiosulfate, potassium thiocyanate and thiourea were chosen for this purpose and their effect was studied. The highest recovery was obtained when using thiourea solution as an eluent. Thus, the effect of thiourea concentration in the range of 1-5% was evaluated. The results showed that the recovery of silver ions adsorbed was above 97% at all concenrations. Therefore, a 3% (w/v) of thiourea solution was selected for the elution of silver ions from the column.

The effect of volume of eluent on recovery of silver ions was studied by passing different volumes of 3% (w/v) of thiourea through the column. The results showed that the recovery increased to 97.5% with volume of eluent up to 5 mL, above which it remained constant. Thus, 5 mL of 3% (w/v) of thiourea was selected as optimized value.

The column packing height was varied from 2 to 8 cm by maintaining other optimum conditions. The recovery increased to 97% up to a height of 4 cm and it was constant above it. A column height of 5 cm was selected as opti-
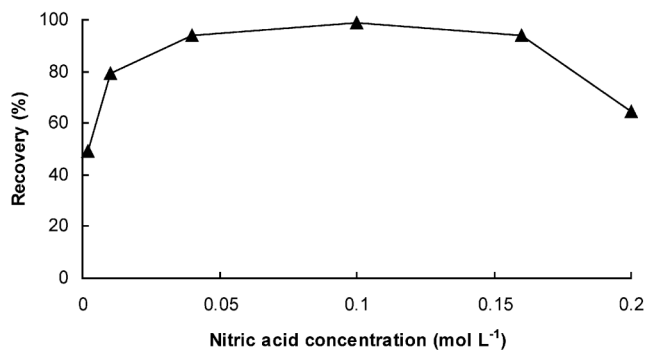

Fig. 1. Effect of nitric acid concentration on the recovery of 200 ng mL^{-1} of silver.

mized value.

The effect of amount of dithizone loaded on 20 g naphthalene was investigated in the range 0.002-0.2 g. The results showed that the recovery increased to 96% with dithizone amount up to 0.04 g and above that remained constant (Fig. 2). The optimum quantity of dithizone loaded on 20 g of naphthalene was fixed at 0.04 g.

The effect of sample flow rate was studied by passing identical samples with different flow rates ranging from 1.66 to 11.11 mL min^{-1} (Fig. 3). The optimized flow rate was selected as 2.5 mL min^{-1}.

The effect of sample volume on the recovery was investigated in order to explore the possibility of enriching low concentrations of silver ions from large volumes of sample. The amount of silver ion held constant (20 μg) while increasing sample volume from 25 to 250 mL. Maximum recovery of 98% was achieved when using 50-mL sample volume.

Reversibility of Column

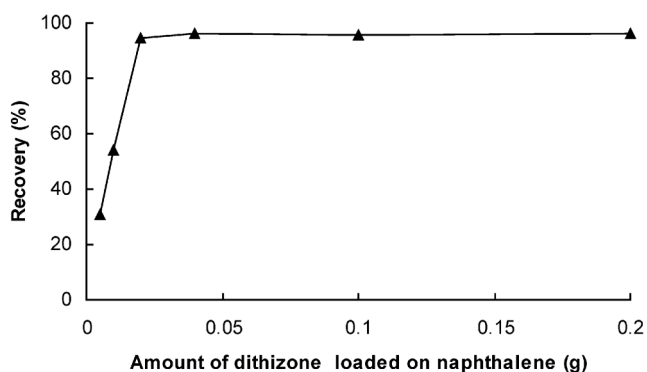Reversibility of column is one of the important char-

Fig. 2. Effect of amounts of ligand immobilized on naphthalene on the recovery of 200 ng mL^{-1} of silver.
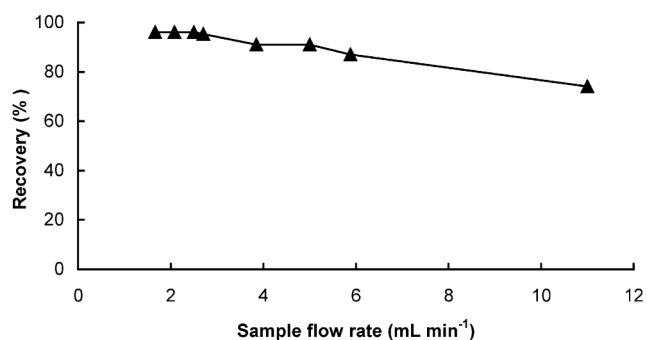

Fig. 3. Effect of sample flow rate on the recovery of 200 ng mL^{-1} of silver.

acters in solid phase extraction (SPE). Therefore, after passing sample solution through the column and regeneration of it by thiourea solution, the above procedure was repeated many times. The results showed that one column can be reused for 4-5 runs without loss of sensitivity.

Determination of the Adsorbent Capacity

For the determination of the adsorbent capacity, batch sorption procedures were applied. 1.0 g of the dry adsorbent was stirred with 50 mL of solution containing 30 μg mL^{-1} of silver ion and 0.1 M nitric acid in stoppered flask for 24 h. The remaining silver ion in the aqueous phase was determined by flame atomic absorption spectroscopy (FAAS) and the amount of Ag$^+$ ion loaded on the adsorbent phase was calculated by mass balance. Thus, adsorbent capacity of column was calculated as 29 μg Ag$^+$ per gram of dry adsorbent.

Analytical Performance

A linear calibration graph in the range of 10-1000 ng mL^{-1} of silver ion in the initial solution was obtained by applying the optimum conditions. The equation of the line is $A = 6 \times 10^{-4}$ C $+ 0.0102$ with regression coefficient of (r) 0.9998, where C is concentration of silver ion in ng mL^{-1} in the initial solution. The limit of detection (LOD) based on three times the standard deviation of the blank was 3.9 ng mL^{-1}.[21] The relative standard deviation (RSD) for 10 replicate measurements of 40 and 600 ng mL^{-1} of silver ion was 4.4% and 0.9%, respectively.

The Effect of Interfering Ions

The effect of various ions on the recovery of silver ion was investigated. 50 mL solutions containing 400 ng mL^{-1} of Ag$^+$ and each interferent at different weight ratios were subjected to general procedure. A given species was considered to interfere if it caused more than ± 5% variation in the FAAS signal. The results are presented in Table 1. As can be seen the effect of various ions are negligible; therefore Ag$^+$ can be determined quantitatively in real samples without interference from matrix of samples.

Application

In order to check the applicability of the proposed method it was applied to the pre-concentration and determination of silver in ore, radiology film and wound dressing samples. An aliquot of the prepared sample solutions was treated under the general procedure. The quantifica-

Table 1. Effect of interfering ions on the recovery of silver

Interfering ions	Interfering conc./Analyte conc.	Recovery (%)
Cr^{3+}, Mg^{2+}, K^+, Pb^{2+}, Bi^{3+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Ca^{2+}	1000	100
NO_3^-, CO_3^{2-}, SO_4^{2-}, Na^+, Mn^{2+}, CH_3COO^-	1000	99
Th(IV), Co^{2+}, Ba^{2+}	1000	98
NH_4^+	1000	97
Al^{3+}, Br^-, F^-	1000	95
Cd^{2+}	500	99
CN^-, HPO_4^{2-}	500	97
I^-	500	95
SCN^-, Zn^{2+}	100	98

Table 2. Determination of silver in real samples

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Ore	0	19.66	-
	200	218.00	99.2
	400	419.66	100.0
Radiology film	0	326.33	-
	80	409.66	104.0
	200	524.66	99.2
Wound dressing	0	68.00	-
	200	266.33	99.2
	400	469.66	100.4

tion of analytes was performed after pre-concentration using FAAS. In order to evaluate of procedure accuracy, standard addition method was used. The results are shown in Table 2. As can be seen in the Table silver can be determined in ore, radiology film and wound dressing samples with recoveries in the range of 99.2-104.0%.

CONCLUSION

In this research, a new simple and sensitive pre-concentration method for the determination of silver ion was presented. This simple method is based on the adsorption of silver ion on naphthalene-dithizone adsorbent, followed by elution by thiourea and subsequent determination by FAAS. The prepared sorbent is very economical and the method is highly selective for the determination of trace amounts of silver by flame atomic absorption spectrometry. The detection limits achieved for silver ions is as good as or better than some of the previously reported methods.[8,10,18]

A pre-concentration factor of 10 is achieved using the optimum conditions.

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