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Solid-Phase Extraction of Silver in Geological Samples and its Determination by FAAS

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Abstract: A macroporous and a nonionic resin, Amberlite XAD-16 as a solid sorbent and N,N-diethyl-N′-benzoylthiourea (DEBT) as a chelating agent have been used for the selective separation and preconcentration of silver. Sorption of silver was studied in three ways: sorption on DEBT impregnated Amberlite XAD-16 by batch and column processes and sorption of Ag-DEBT complex on Amberlite XAD-16 by column process. Factors affecting the sorption and desorption of silver ion were investigated. The stripping of silver was achieved by using either sodium thiourea or sodium thiosulfate solution. The silver ion capacity of impregnated resin was found to be 11.22 mg Ag^+/g resin and 870 μg Ag^+/g resin for batch and column processes, respectively. It was 370 μg Ag^+/g resin for Ag-DEBT complex. The interference effects of possible co-existing metal ions and some electrolytes were investigated. The applicability of the proposed method was shown by analyzing the geological copper ore samples.

Keywords: DEBT, silver, preconcentration, impregnated resin, solid-phase extraction

INTRODUCTION

Platinum group elements (PGE's); Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Osmium (Os), Iridium (Ir), Platinum (Pt) together with Gold (Au) and

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Silver (Ag) are called precious metals (PM's). This term, "precious", reflects their economic value as well as their rare occurrences. The precious metals occur in geological and technological samples at trace and ultra-trace levels and in the materials with complex compositions (1).

The increasing use of silver compounds and silver containing preparations in industry and medicine has resulted in an increased silver content of environmental samples. Silver also enters the environment in industrial waters because it often occurs as an impurity in copper, zinc, arsenic, and antimony ores. In addition, low level exposure to silver compounds is widespread owing to soluble silver compounds where they were used to disinfect drinking water. Silver with a concentration of up to 20–200 μg/mL is permitted to control antimicrobial activity with no risk to human health (2). A sensitive and selective separation together with preconcentration is necessary for trace level determination of silver. Separation and preconcentration of metals are usually affected by methods such as extraction, precipitation, co-precipitation, sorption, and crystallization (3). Among the various preconcentration methods, solid phase extraction is one of the most effective methods because of its simplicity, rapidness, and ability to attain a high concentration factor. Until now, activated carbon (4, 5), modified silica gel (6–8), polymeric material (9–11), XAD resins (12–14), and chelating resins (15–17) have been used as solid phase material for separation and enrichment of silver ion in various matrices. Amberlite XAD-16 resin has been used as a sorbent in the separation and preconcentration of metal ions including silver after complexation with complexing agent such as diethyldithiocarbamate (18, 19), thiocyanate (12), chloro (20) and humic substances (21). Nowadays, mostly XAD-16 resin functionalized with chelating agents has been used as a sorbent (22–24). In literature, many attempts have been made in order to indicate the use of DEBT as a chelating agent, especially for PGE's with which forms highly stable complexes (25), and Amberlite XAD-16 as a sorbent for preconcentration of several metals, again especially for PGE's but not for Ag (25, 26). However, preconcentration of precious metals using DEBT impregnated Amberlite XAD-16 has not been studied yet. Therefore, in the first part of the study, the sorption behavior of silver with DEBT impregnated Amberlite XAD-16 by batch and column process was investigated. Then, the separation and preconcentration of silver after complexation with DEBT on Amberlite XAD-16 by column process was studied. Finally, the application of the proposed method to the geological samples was demonstrated.

EXPERIMENTAL

Chemicals and Reagents

All the reagents used were of analytical reagent grade. Deionized water from a Milli-Q water system was used throughout the study. The standard solutions of

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Ag were prepared by fresh daily dilution of 1000 μg/mL stock solution (High-Purity Standards) with 0.05 M HNO_3 (J.T. Baker, 70% w/w). For interference studies, 1000 μg/mL standard copper solution (Merck) was used. During batch process, NaOH (Acros, 50% w/w) was used for pH adjustments. For desorption studies, thiourea (Allied Chemical, 99.0%) and sodium thiosulfate (Bileşik Kimya Mekanik, extra pure) were used. Amberlite XAD-16 was initially purified and pretreated according to procedure described elsewhere (27). DEBT was synthesized according to the modified procedure in our laboratory using analytical reagent grade chemicals (25).

Two real samples—one of which was supplied by Mineral Research and Exploration Institute, (MTA), Ankara, Turkey and the other one by Cyprus Mining Company, (CMC), Lefke, North Cyprus were analyzed to compare with the results of silver given.

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Apparatus and Instrumentation

100-mL DuPont polyethylene containers were used for the storage and preparation of the solutions. 5–50 μL, 25–250 μL, and 100–1000 μL adjustable micropipettes (Transferpette, Treff Lab) with disposable polyethylene tips were used in preparation of solutions. A magnetic stirrer was used for impregnation of DEBT. 50-mL Falcon tubes and a NÜVE SL 350 horizontal shaker were used for sorption/desorption optimizations in batch process. A Philips PU 9200 Atomic Absorption Spectrometer was used for the determination of silver ion.

Impregnation of DEBT on Amberlite XAD-16

0.1 g of Amberlite XAD-16 was stirred with 10 mL of 0.040 M DEBT in ethanol on a magnetic stirrer for 30 min. Then impregnated resins were filtered under vacuum and dried in air and under vacuum. The DEBT content of organic phases was determined by UV spectrophotometry. Similarly, 0.1 g resin was stirred with 10 mL of ethanol and the filtrate was used as blank. The amount of DEBT impregnated on Amberlite XAD-16 was found as 2.50 mmol/g resin.

Batch Process

The sorption behavior of silver on DEBT impregnated resin was investigated by batch process at relatively high concentrations (5 mg/L–500 mg/L Ag^+) at a constant volume of 10 mL. Critical parameters such as pH, stirring time, metal ion capacity, and agents suitable for desorption were studied. After sorption and desorption steps, metal ion concentrations in the filtrates were determined by FAAS.

Column Preparation

As columns, 12-mL syringe barrels (1.5 cm i.d., 7.8 cm height, PTFE, Supelco) were used. Disposable porous frits were placed at the bottom of the barrels and 1.0 g resin (unless otherwise stated), which was slurred in 50 mL water was uniformly placed in column. Resin was covered with cotton wool to prevent dispersion by the addition of sample solution. Tygon® tubing was used to connect the outlet tip of the syringe barrel to a Gilson Miniplus peristaltic pump. In order to adjust the desired flow rate, a calibration procedure, flow rate mL/min vs. rpm was carried out. This calibration was repeated for each column before the application. The column was cleaned by passing a 15-mL blank solution before sorption and desorption studies at a flow rate of 1 mL/min.

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Column Process by Impregnated Resin

Certain volume of 0.5 mg Ag^+/L of solutions were passed through the column containing 1.0 g impregnated resin at a flow rate of 0.5 mL/min at pH 1. Then, the sorbed metal ion was eluted with 0.1 M $Na_2S_2O_3$ aqueous solution at a flow rate of 0.3 mL/min. Then the metal ion in the effluent were determined by FAAS.

Sorption of Ag-DEBT Chelate on Amberlite XAD-16 by Column Process

Three different sample volumes, 10 mL, 50 mL, and 100 mL were used in column process. Silver chelate solution was prepared by using 0.5 μg Ag^+/mL solution and 3 mL of 2×10^{-3} M DEBT, which was in excess even when 100 mL Ag^+ solution was used. The chelate solutions at pH 1 were passed through a column containing 1.0 g of Amberlite XAD-16 at a flow rate of 0.5 mL/min. After that, the metal ion was eluted with 13 mL of 0.1 M $Na_2S_2O_3$ in water at a flow rate of 0.3 mL/min. Then the metal ion in the effluent were determined by FAAS.

RESULTS AND DISCUSSION

IR Studies of Amberlite XAD-16, DEBT, Impregnated Resin, and Metal Chelates Retained on Resin

The impregnation of DEBT on to resin was confirmed by IR spectra of impregnated resin. The IR spectrum of Amberlite XAD-16 is available in literature (11). The characteristic absorption bands for N-H, C-H and amide

I (C═O), amide II and amide I at 3276, 3066–2936, 1656, 1537, and 1306 cm^{-1}, respectively appear only in the spectra of DEBT and impregnated resin. Some modifications of the characteristic normal modes of DEBT on resin were resulted when compared with the spectrum of the free reagent. Small shifts ($\sim$10 cm^{-1}) either positive or negative were observed upon impregnation.

The characteristic IR bands of -$N(CH_2CH_3)_2$ group, appearing at 2875 and 2885 cm^{-1} (ν CH_3) and 2936 cm^{-1} (ν CH_2) in the spectrum of the ligand, remain almost unchanged in the spectra of Ag-DEBT complex. As observed, only -$N(CH_2CH_3)_2$ group and aromatic ring displayed slight shifts upon complexation. The small change in the -$N(CH_2CH_3)_2$ band indicates that this group does not take part in coordination. In the aromatic ring upon the formation of the metal-ligand bond the C-H vibration is shifted to higher frequencies.

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Batch Process with Impregnated Resin

A series of experiments have been carried out in batch process. In order to investigate the pH effect, 10 mL of 20 mg/L of Ag^+ solutions in the pH range of 1–4 were stirred with samples of 0.1 g impregnated resin for 30 minutes. This range is intentionally investigated because DEBT has ability to form stable and selective complexes with noble metals in acidic or strongly acidic media. Schuster and co-workers suggested pH range as 0–4 in their studies related with liquid-liquid extraction of precious metals with DEBT (28). In Fig. 1, it can be seen that the maximum percent sorption is obtained at approximate pH 1. Therefore, for further sorption studies of silver, standard solutions were prepared by diluting standard stock solution with 0.05 M HNO_3.

Three different sets of 10 mL of 5, 50 and 150 mg/L of Ag^+ solutions in 0.05 M HNO_3 were stirred with samples of 0.1 g impregnated resin within time periods from 5 minutes to 1 hour. Referring to Fig. 2, twenty minutes of stirring is found to be good enough to achieve sorption equilibrium for silver ion.

Finally, in order to determine the resin capacity, samples of 0.1 g impregnated resin were stirred with 10 mL of silver ions in the concentration range of 5 to 500 mg/L in 0.05 M HNO_3 for 20 minutes. Silver ion capacity of the resin was calculated as 11.22 mg Ag^+/g resin (0.104 mmol Ag^+/g resin) (Figure 3).

Desorption was firstly tested using 0.1% thiourea (TU) (w/v) in 0.05 M HNO_3 as eluent. After 10 min stirring, 58% desorption was obtained. Approximately, 100% desorption was achieved for 20 min stirring. This showed that 0.1% TU in 0.05 M HNO_3 was dilute to achieve a fast and quantitative desorption. So, TU concentration was increased to 0.5% TU keeping acid concentration constant and after 10 min stirring a 100% desorption was obtained.

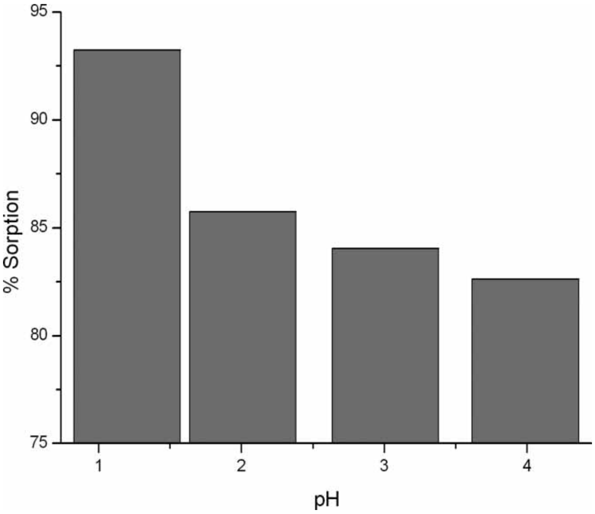

Figure 1. Effect of pH on silver sorption. Experimental conditions: Amount of resin: 0.1 g, amount of DEBT: 2.5 mmol/g resin, stirring time: 30 minutes.

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Amberlite XAD-16 was chosen as solid support for impregnation, because it supplied fast sorption kinetics for silver. A stirring time as 5 min was sufficient for the sorption when 10 mL of Ag^+ solution was used. However, the advantage of fast kinetics is lost when concentration of Ag^+ becomes lower. This is the case with geological samples, especially when silver is present at trace levels and when larger sample volumes for

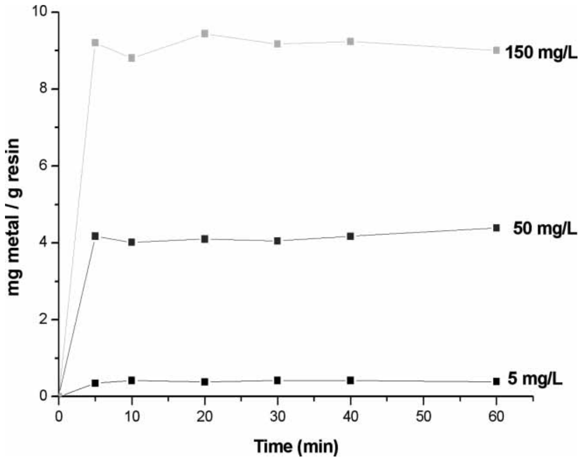

Figure 2. Effect of stirring time on silver sorption. Experimental conditions: Amount of resin: 0.1 g, amount of DEBT: 2.5 mmol/g resin.

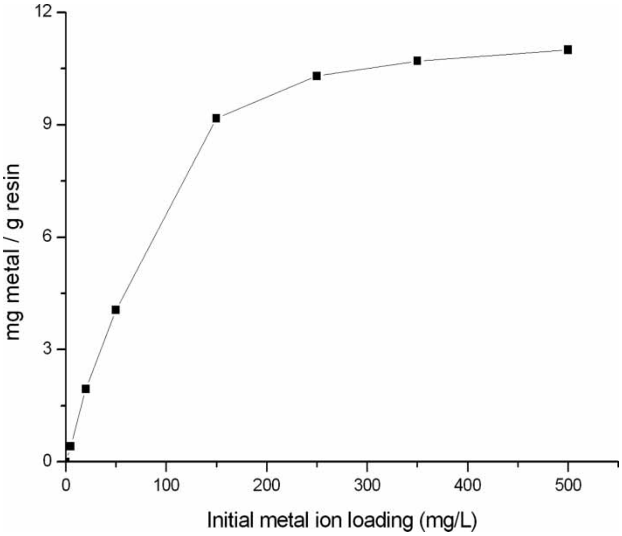

Figure 3. Silver ion capacity of resin. Experimental conditions: Amount of resin: 0.1 g, amount of DEBT: 2.5 mmol/g resin, stirring time: 20 minutes.

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preconcentration are required. Thus, solid phase extraction of silver in batch equilibrium process is expected to show slow kinetics for sorption. When a sample solution with Ag^+ concentration of 11 mg/L or less was studied in batch equilibrium, almost no change in Ag^+ concentration in supernatant liquid was observed even after one hour of stirring time.

Column Process with Impregnated Resin

Therefore, it was decided to use a column packed with impregnated solid extractant because passing the liquid sample through such a column provides intimate contact with the solid particles, and there are multiple equilibria as the sample passes through the column and comes into contact with fresh solid extractant particles. In the column process sorption and desorption steps were examined. However, it was realized that when excess volume of sample solutions were used during sorption it partially leached the impregnated DEBT which caused analyte losses. Percent sorption of silver ion (10 mL of 0.5 mg/L) on sorbent surface was examined at flow rates between 1.0–2.0 mL/min which resulted in a decreasing percent sorption from 98% to 70%. Considering the application of large sample volumes, 0.5 mL/min was accepted as optimum sample flow rate. The maximum sorption achieved when sample solutions were prepared in 0.05 M HNO_3 (pH $\sim$ 1). The large sample volumes resulted in poor desorption percentages as 84–70%, depending on the increasing flow rate varied from 0.3 to 1.0 mL/min and increasing sample volume, as 30 to 160 mL by increasing amount of sorbent used to 1.0 g for 0.5 mg Ag^+/L. Silver ion capacity of the impregnated resin was calculated as 870 μg Ag^+/g resin. Hence, a very low preconcentration factor could be achieved. In addition, the leaching effect reduced the life time of resin which could be used only for once. Another serious problem introduced by leaching of the impregnated ligand was the partial exhaustion of available chelating sites which caused irreproducible results of sorption percentages of metal ions (13). Consequently, further experiments for preconcentration of Ag^+ were carried out by preparing metal chelates by the addition of ligand to aqueous sample solution before introducing it into the Amberlite XAD-16 resin filled column.

Sorption of Metal Chelates on Amberlite XAD-16

With 3 mL of 2×10^{-3} M DEBT, up to 100 μg Ag^+ ion can be retained with 100% by column as Ag-DEBT complex at pH ~ 1. When 10 mL of 500 μg/mL Ag^+ solution as the metal complex was passed through the column, the decrease in retention to 74% was observed and the sorption capacity of column was found as 370 μg Ag^+/g resin.

In batch studies, thiourea seemed to be a good eluent for silver ions. However, in the analysis of silver in real samples supplied from CMC, the presence of copper might cause serious interference effect in the desorption step because of its high affinity to make complex with thiourea. Hence, other possible desorbing agents such as sodium cyanide, sodium thiocyanide, and sodium thiosulfate were tested to get the best desorption percentage. Sodium thiosulfate and sodium cyanide solutions gave the best recovery results. For later studies, $Na_2S_2O_3$ was preferred because of its low toxicity and also during desorption, (S-S) chelating groups of $Na_2S_2O_3$ provides a stronger complex formation as silver has a high affinity to (S-S) than (S-O) chelating group. It was found that recoveries of $\geq$95% to 88% with an error of $\pm$2% were achieved with 13 mL of 0.1 M $Na_2S_2O_3$ aqueous solution at 0.3 mL/min for 10 to 100 mL of silver sample solutions.

Interference Studies

The effect of various electrolytes like NaCl, $NaNO_3$, Na_2SO_4, Na_3PO_4, Na_2CO_3 on the sorption of silver (1 mg/L) as Ag-DEBT complex with Amberlite XAD-16 resin was studied. NaCl and Na_2SO_4 were tolerable up to 0.04 M, Na_3PO_4 up to 0.1 M and $NaNO_3$ and Na_2CO_3 up to 0.15 M.

In Table 1, a summary of metals that are mostly found in geological samples with the main metal ion, metals that form chelates with DEBT, and their pH ranges are given. According to Table 1, besides silver, copper is also expected to form chelates with DEBT at our working pH.

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Table 1. Summary of some metals in geological samples and metals forming chelates with DEBT and pH ranges

Metal ions co-existing in geological samples	Main metal ions forming chelate with DEBT (11)	pH for metal-DEBT chelates
Na^+, K^+	Au^{3+}	0–5[a]
Cu^{2+}, Ni^{2+}	Ag^+	0–4[a]
Pb^{2+}, Mn^{2+},	Pt^{2+}	1–7
Fe^{3+}, Zn^{2+}	Rh^{3+}	1–5
Al^{3+}, Cr^{3+}	Pd^{2+}	1–7[a]
	Ru^{3+}	1–3
	Ir^{3+}	2–7
	Cu^{2+}	0–7[a]
	Fe^{3+}	2–4[a]

[a] Complexation takes place at room temperature.

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The interference effect of copper on silver determination by the proposed method was examined. The average amount of analyte metal in the geological samples taken was calculated to be about 5 μg. The standard solutions in Ag/Cu mass ratios of 1:1, 1:10 and 1:50 were prepared in 0.05 M HNO_3 and 50 mL of each was percolated through the columns at a flow rate of 0.5 mL/min. Desorption was followed with 13 mL of 0.1 M $Na_2S_2O_3$ in water at a flow rate of 0.3 mL/min which were the optimum values obtained by previous experiments. The results are given in Table 2.

Although copper ion formed a complex with DEBT and retained on the resin, referring to Table 1, it was shown that no copper ions could be eluted with 13 mL of 0.1 M $Na_2S_2O_3$ eluent. When the amount of copper ions was increased to 250 μg, only 1.1% desorption was obtained which could be accepted as negligible (Table 2).

Analytical Figures of Merit

The detection limit and limit of quantitation for Ag^+ were determined employing the standard solutions giving absorbance signal slightly recognizable than blank

Table 2. Interference effect of copper during preconcentration and determination of silver

Amount of copper in sample solutions (μg)	5	50	250
% desorption of copper ions with 13 mL of 0.1 M $Na_2S_2O_3$ in water	0	0	1.1

Experimental conditions: Mass of resin; 1 g, amount of DEBT; 3 mL of 2×10^{-3} M, sample volume; 50 mL.

solution (0.05 M nitric acid with Ag^+ in appropriate concentration). The limit of detection (LOD) and the limit of quantitation (LOQ) were calculated based on 3s/slope and 10s/slope of 10 measurements of the blank sample, respectively, where s is the standard deviation of the blank solution. The results of the LOD, LOQ, and precision (RSD%) for the metal and in addition, its concentration that can be determined after preconcentration by the proposed method with the given preconcentration factor are shown in Table 3.

Analysis of Real Samples

In order to check the validity of the proposed method, two real samples; one of which was supplied by the Mineral Research and Exploration Institute, (MTA), Ankara, Turkey and the other one by the Cyprus Mining Company, (CMC), Lefke, North Cyprus and were decomposed by a microwave-assisted digestion technique described by Boch and coworkers (29). The results that were corrected for 88% desorption recovery value which was

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Table 3. Analytical figures of merit

Parameters	Silver
Sample volume	100 mL
Concentration of solution	0.30 mg/L
Detection limit (3s)	0.04 mg/L
Limit of quantitation	0.13 mg/L
Precision (RSD%)	4.44%
Number of replicates (N)	10
Concentration of solution preconcentrated by the proposed method	0.05 mg/L
Preconcentration factor	7.7

Table 4. Determination of Ag in geological samples

		Ag Concentration (mg/kg)	Corrected values (mg/kg) according to 88% desorption
MTA sample	Ag (found)[a]	29.7 ± 2.5	33.7 ± 2.5
	Ag (given)	37.5	37.5
CMC sample	Ag (found)[a]	17.9 ± 1.0	20.4 ± 1.0
	Ag (given)	24	24

[a] Values are given as mean ± standard deviation (SD) N = 3 (number of replicates).

found for 100 mL sample solution were also tabulated in Table 4. The corrected values were found to be in good agreement with the given values.

CONCLUSION

In literature, it is possible to find more sensitive but rather expensive and sophisticated determination methods for silver such as ICP-MS and NAA. However, the low cost and rapidness of FAAS make it available in most of the routine and research laboratories. By the proposed method, one can determine silver metal by preconcentrating at much lower concentrations in highly acidic mediums, by the use of specific chelating agent DEBT, as low as 0.05 $\mu g/mL$, compared to similar studies including preconcentration steps (12, 30). Therefore, this method was shown to be more sensitive than the other methods. In addition, it is highly selective for silver even in a highly interfering matrix of geological samples. Finally, the proposed method is inexpensive and can be widely applicable in most of the laboratories.

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