

Solid phase extractive preconcentration of silver from aqueous samples

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Abstract *N,N*-dibutyl-*N*¹-benzoylthiourea (DBBT) impregnated onto a polymeric matrix, Amberlite XAD-16 was prepared. The separation and enrichment of Ag(I) from solution was investigated. Effective extraction conditions were optimized in column methods prior to determination by atomic absorption spectrometry. The optimum pH range for quantitative adsorption is 2–5. Quantitative recovery of Ag was achieved by stripping with 1 mol L⁻¹ thiourea in 1 mol L⁻¹ HCl. The sorption capacity of resin is 0.115 mmol Ag⁺ g⁻¹ resin. The relative standard deviation and detection limit was 3.1% for 1 μg Ag⁺ mL⁻¹ solution and 0.11 μg L⁻¹, respectively. The method was used for the determination of silver in geological water samples.

Keywords Benzoylthiourea · Preconcentration · Silver · Solid phase extraction

Introduction

Silver is a heavy metal that its content in environmental samples is increased with the increasing use of

silver compounds and silver-containing products in industry, medicine and commerce (Kolthoff and Elving 1966). Silver can be found into the environment via industrial waters because it is often present as an impurity in copper, arsenic and antimony ores (Soager 1984). Silver is a toxic element for microorganism or larval forms of aquatic animals (Bury et al. 1999; Meian 1991). Silver-impregnated filters are used for water purification and a concentration of up to 50–200 g Ag⁺ L⁻¹ (depending on the country) is permitted to control antimicrobial activity with no risk to human health (Gomez et al. 1995).

The determination of trace elements in low concentrations is very difficult and often carried out by atomic absorption spectrometry (AAS). The most widely used methods for metal preconcentration have been liquid–liquid extraction, ion-exchange and solid phase extraction (SPE). Solid phase extraction has some advantages over liquid–liquid extraction such as a higher preconcentration factor, better efficiency, greater reproducibility and greater simplicity in handling and transfer. A variety of materials such as polymeric resins (Saha et al. 2004), ion exchangers (Malla et al. 2002), modified silica (Zougagh et al. 2005), alumina (Soliman et al. 2006) and activated carbon (Yusof et al. 2007) have been used. Macroporous hydrophobic resins of the Amberlite XAD series are good supports for developing chelating matrices or impregnation. Amberlite XAD-2, XAD-4 and XAD-16 are polystyrene-divinylbenzene (PS-

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DVB) resins with a high hydrophobic character and no ion-exchange capacity. The broader range of pH stability of these resins increases the flexibility of the method, and they have no silanol groups (Bouvier et al. 1997).

Various chelating agents impregnated or chemically bound to Amberlite XAD-2 (Villaescusa et al. 1992), XAD-4 (Moon et al. 2006), XAD-7 (Saha et al. 2004), XAD-16 (Raju et al. 2005) as polymeric supports were used for preconcentration of several metal ions. Immobilized Amberlite XAD-16 resin has been used as a sorbent in the separation and preconcentration of metal ions including silver such as derivatized resorcinarene (Gok et al. 2007), 1-(2-pyridylazo) 2-naphthol (Narin et al. 2003), sodium tetraborate (Tokalioglu et al. 2002), thiocyanate (Tunceli and Turker 2000) and pyridine-2-carbaldehyde thiosemicarbazone (Baytak et al. 2006).

N,N-dialkylderivatives of benzoylthiourea are known to have strong tendencies to form complexes with metal ions particularly platinum group metals, transition metals and silver through the N–CS–NH–CO–Ph chelating group (Beyer et al. 1981; Schuster and König 1988). *N,N*-diethyl-*N'*-benzoylthiourea (DEBT) and *N,N*-dibutyl-*N'*-benzoylthiourea (DBBT) have been used for preconcentration of several transition metals (Merdivan et al. 2000), actinide ion (Merdivan et al. 2001) and some platinum group metals (Aygun et al. 1997; Philippeit and Angerer 2001). So, it was attractive to study the impregnation of DBBT ligand to polystyrene-divinylbenzene polymeric resin.

In this study, DBBT was impregnated onto Amberlite XAD-16 for selective uptake of silver from aqueous solutions. The structure of impregnated polymeric matrix was characterized by Fourier Transform Infrared Spectroscopy (FT-IR). The properties of impregnated resin for preconcentration and separation of Ag(I) from aqueous samples and recovery of silver (I) ion was examined in detail.

Materials and methods

Reagents and chemicals

The stock metal ion solutions were prepared by dissolving analytical reagent-grade metal nitrates, chlorides or sulfates in doubly deionized water. Stock

solution of Ag⁺ was prepared by dissolving an appropriate amount of AgNO₃ (Merck) in deionized water. 1 mol L⁻¹ thiourea solutions was prepared by dissolving 7.6g of the reagent in 100mL by 1 mol L⁻¹ HCl. DBBT was prepared and purified according to the method in the literature (Schuster and König 1988). Potassium bromide (Merck, for spectroscopy) was used for the preparation of pressed discs for the Fourier Transform Infrared (FTIR) spectrometer. All other reagents and solvents used were of analytical reagent grade. The water used throughout the study had been deionized by means of a Millipore Milli-Q system.

The Amberlite XAD-16 resin (styrene–divinylbenzene copolymer, surface area: 800m² g⁻¹, pore diameter: 10nm and bead size: 20–60 mesh) was supplied by Sigma. The ethanolic solutions of DBBT were used as impregnation solution. Amberlite XAD-16 was purified with 4M HCl solution, after elimination of chlorides by washing with distilled water, with an ethanol–water (1:1) solution and finally with water again. Then, the resin was dried in vacuum oven at 60°C and stored in a polyethylene bottle.

Apparatus

FT-IR spectra of Amberlite XAD-16, DBBT, XAD-16-DBBT were recorded with a Perkin Elmer Spectrum BX Fourier Transform IR spectrometer using KBr discs in the range of 4000–700cm⁻¹, 30 co-added interferograms were scanned at 2cm⁻¹ resolution. pH measurements were made on a Lab WTW model digital pH-meter. For solid phase experiments a Varian cartridge (plastic container, 0.8cm × 6.2cm) equipped with 20mm polypropylene frits was used. GBC model atomic absorption spectrometer equipped with single element hollow cathode lamp and air–acetylene burner was used for the determination of silver contents of all the solutions at 328.1nm.

Preparation of solid phase by impregnation

The Amberlite XAD-16 resin was purified with 4M HCl solution, after elimination of chlorides by washing with distilled water, with methanol–water (1:1) solution and finally with water again. Then the resin was dried in vacuum oven at 60°C and stored in a polyethylene bottle. 1g of dry Amberlite XAD-16 was placed in %1 DBBT ethanolic solution and stirred

for 24h. The resin was separated by filtration through a sintered glass funnel and was washed with a water to remove the solvent. The resin was used as an air-dried product. The amount of DBBT attached to the polymer was found to be 0.306mmol g^{-1} .

Preparation of column

0.1g DBBT impregnated onto Amberlite XAD-16 was firstly wetted with 2.5mL methanol and stirred for 10min, then 25mL of doubly deionized water was added and stirred for 10min again. Lastly, the mixture is transferred to the polyethylene column and 10mL of methanol:water (10:90) is passed through the column. 10mL of doubly deionized water was added on the column. Before passing metal solution, column was washed with 5mL of suitable pH solution. Tygon® tubing was used to connect the outlet tip of the syringe barrel to a Watson Marlow peristaltic pump. In order to adjust the desired flow rate, a calibration procedure; flow rate mL min^{-1} vs. rpm was carried out. This calibration was repeated for each column before the application. Column was cleaned by passing a 15mL blank solution before sorption and desorption studies at a flow rate of 1mL min^{-1} .

Column process

A 100mL of Ag^+ sample solution was taken at pH 1–4 and passed through the above column at a flow rate of 1mL min^{-1} . Then, the Ag^+ ion was stripped from the column by 5mL of 1mol L^{-1} thiourea in 1mol L^{-1} HCl. After sorption and desorption steps, Ag^+ ion concentrations in the filtrates were determined by FAAS.

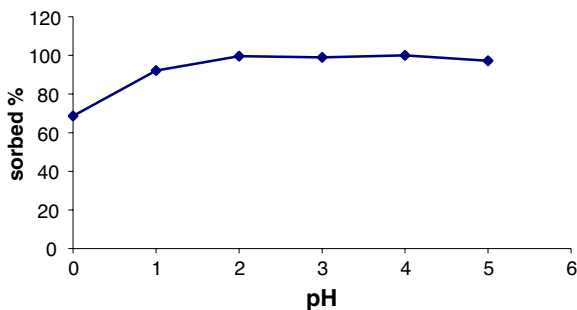


Fig. 1 Effect of pH on the sorption of Ag on DBBT/XAD-16 Ag

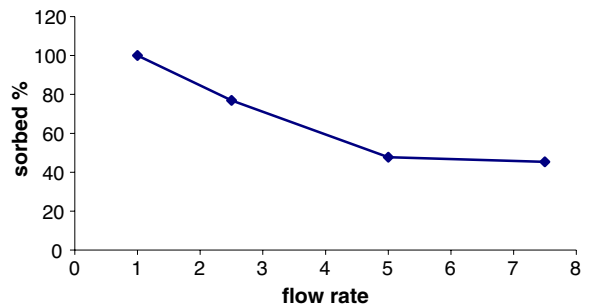


Fig. 2 Effect of flow rate on the sorption of Ag on DBBT/XAD-16

Sample preparation

Geological water samples collected from Salihli, Edremit, Kula region near İzmir, Turkey were filtered through a $0.45\mu\text{m}$ membrane filter, acidified to pH of about 1 with concentrated HNO_3 to storage for use. Before use, the pH values were adjusted to 2 with 0.1mol L^{-1} ammonia and 0.1mol L^{-1} HNO_3 .

Results and discussion

Characterization studies

Infrared spectrum of DBBT, Amberlite XAD-16 and DBBT impregnated Amberlite XAD-16 have been recorded. The IR absorption frequencies assignments for DBBT/XAD-16 resin show small modifications on the characteristic normal modes compared with the spectrum of the pure Amberlite XAD-16 as given before (Merdivan et al. 2001). The IR absorption frequencies assignments for DBBT molecule on DBBT/XAD-16 resin show similar modifications of the characteristics normal modes of DBBT compared with the spectrum of the free reagent as before (Merdivan et al. 2001).

Effect of pH and flow rate on metal sorption

An amount of 100mg of DBBT/XAD-16 was packed in the polypropylene column, and 100mL solution containing $1\mu\text{g Ag}^+ \text{mL}^{-1}$ of was passed at various pH values (0–5) (Fig. 1). The sorption experiments were carried out in triplicate. Sorption was quantitative (100%) in the pH range 1–5. For further studies, Ag^+ solutions at pH 2 or 4 were mostly preferred

Table 1 Tolerance limits for anions and cations on the sorption of silver on DBBT/XAD-16

	Anion ($\mu\text{g mL}^{-1}$)					Cation ($\mu\text{g mL}^{-1}$)				
	PO_4^{3-}	SO_4^{2-}	CO_3^{2-}	NO_3^{-1}	Cl^{-1}	Pt(II)	Pd(II)	Au(III)	Fe(III)	Cu(II)
Ag ($1 \mu\text{g mL}^{-1}$)	10,000	3,700	9,000	8,000	1,500	15	10	22	1,000	1,500

because real samples are mostly dissolved in acidic medium.

The contact between the metal ion in sample solution and the sorbent is depended on the flow rate of sample solution. Aliquots of 100mL of $1\mu\text{g mL}^{-1}$ solutions at pH 4 were separately passed at different flow rates ($1\text{--}7.5\text{mL min}^{-1}$) through the column having 0.1g of DBBT/XAD-16 (Fig. 2). Ag^+ ion was sorbed completely at a flow rate of 1mL min^{-1} with a good precision.

Sorption capacity of resin

In order to show the applicability of DBBT physically bound to XAD-16 for the preconcentration of trace metal ions, the sorption of Ag^+ was investigated using the column method. Increasing amounts of silver from

25 to $1250\mu\text{g}$ in 25mL of solution were added to 0.1g of loaded resin. Maximum sorption capacity was found as $0.115\text{mmol Ag}^+ \text{g}^{-1}$ resin. This indicates that DBBT/XAD-16 resin could be used as a sorbent for preconcentration of silver in the trace concentration range.

Reusability and stability of the resin

The reproducibility and reliability in analytical data on subsequent reusage was investigated by equilibrating 100mg resin with Ag^+ solution (100mL, $1\mu\text{g mL}^{-1}$) under optimized sorption conditions. After desorption and estimation, the results obtained on subsequent reusage of the same resin were reproducible with RSD values of $< 2.7\%$ up to 20 cycles, reflecting on its high mechanical stability and reusability nature.

Table 2 Determination of silver in synthetic and geological water samples

Composition of synthetic solution ($\mu\text{g}/100 \text{ mL}$, 0.1 g resin)	Concentration of Ag^+			
	Added ($\mu\text{g}/100 \text{ mL}$)	Found ^a ($\mu\text{g}/100 \text{ mL}$)	Ag^+ spiked (μg) real samples	Ag^+ found (μg) real samples
Cu (1,000), Fe (1,000)	100	98±10		
Pd (500), Au (500)	50	48±12		
Hg (500), Cu (500)	250	247±21		
Pt (500), Pd (500)	250	243±18		
Mineral water 1			0	ND
			100	99.7±0.5
Mineral water 2			0	ND
			100	97.6±0.4
Geothermal water 1			0	ND
			100	98.7±0.6
Geothermal water 2			0	ND
			100	98.4±0.3
Geothermal water 3			0	ND
			100	97.9±0.3
Geothermal water 4			0	ND
			100	98.8±0.5

ND Not detected

^a Average and standard deviation from triplicate run

Preconcentration factor

The preconcentration factor for silver on DBBT/XAD-16 resin was determined. Quantitative collection of silver was possible from a 1000mL solution of concentration 100ng mL^{-1} , with recovery up to 99%. The preconcentration factor of the resin for silver was 200.

Tolerance of diverse ions

Chloride, sulphate and phosphate anions are capable of forming complexes with several metal ions. Therefore, the efficiency of the chemically modified sorbent in binding metal ions must be checked for possible reduction in extraction. Hence, the effects of NaCl, NaNO_3 , Na_2SO_4 , Na_2CO_3 and Na_3PO_4 on the sorption of Ag on the DBBT/XAD-16 were studied using the recommended column method under optimum conditions for $1\mu\text{g Ag}^+ \text{mL}^{-1}$ solution (Table 1). It was observed that investigated ions were tolerated in the concentration range of 1,500 to 10,000 $\mu\text{g mL}^{-1}$. The effect of several cations was also investigated, and the results are summarized in Table 1 with the tolerance limits found for $1\mu\text{g Ag}^+ \text{mL}^{-1}$ solution.

Analytical figures of merit

The precision (relative standard deviation, RSD %) of the method was 3.1% for silver at a concentration of $1\mu\text{g mL}^{-1}$ for a ten series replicates. In order to check the accuracy of the proposed method, the recovery for 0.50 and $1.0\mu\text{g Ag}^+ \text{mL}^{-1}$ added to 100mL of water was measured. The recovery was found as $\geq 98\%$. The limit of detection (LOD) calculated based on $3s/s$ slope of 15 measurements of the blank sample, respectively, where s is the standard deviation of the blank solution was $0.11\mu\text{g Ag}^+ \text{mL}^{-1}$.

Applications

To check the ability of the proposed method for preconcentration and determination of silver, the resin was subjected to synthetic solutions and spiked geological water samples. The synthetic samples were prepared taking some metal ions based on their possible interference effects. The amount of sample used was always 100mL. The results in Table 2, indicate that an agreement between the amounts of spiked and detected by the proposed method.

Conclusions

DBBT could be immobilized on Amberlite XAD-16 resin yielding a sorbent of high capacity and good stability DBBT/XAD-16 resin has high mechanical and chemical strength. The resin can be used in acidic medium. The SPE method has a good potential for the separation of Ag(I) ion from co-existing electrolytes and most of transition metal ions. The method was applied for the determination of the investigated metal ions in spiked geological water samples and found accurate and precise.

References

- Aygun, R. S., Merdivan, M., & Kulcu, N. (1997). Determination of platinum, palladium and rhodium in Pt-catalysts by high performance thin layer chromatography using densitometry. *Microchim. Acta.*, *127*, 233–238.
- Baytak, S., Balaban, A., Turker, A. R., & Erk, B. (2006). Atomic absorption spectrometric determination of Fe(III) and Cr (III) in various samples after preconcentration by solid-phase extraction with pyridine-2-carbaldehyde thiosemicarbazone. *Journal of Analytical Chemistry*, *61*, 476–482.
- Beyer, L., Hoyer, E., Liebscher, J., & Hartmann, H. (1981). Formation of complexes with N-Acyl-thioureas. *Z. Chem.*, *21*, 81–91.
- Bouvier, E. S. P., Martin, D. M., Iraneta, P. C., Capparella, M., Cheng, Y. F., & Phillips, D. J. (1997). A novel polymeric reversed-phase sorbent for solid-phase extraction. *LC GC-Magazine of Sep. Sci.*, *15*, 152–158.
- Bury, N. R., Grosell, M., Grover, A. K., & Wood, C. M. (1999). ATP-dependent silver transport across the basolateral membrane of rainbow trout gills. *J. Toxic. Appl. Pharm.*, *159*, 1–8.
- Gok, C., Seyhan, S., & Merdivan, M. (2007). Separation and preconcentration of La^{3+} , Ce^{3+} and Y^{3+} using calix[4]resorcinarene impregnated on polymeric support. *Microchim. Acta*, *157*, 13–19.
- Gomez, M. M. G., Garcia, M. M. H., & Corvillo, M. A. P. (1995). Online preconcentration of silver on a sulfhydryl cotton micro column and determination by flow-injection atomic-absorption spectrometry. *Analyst*, *120*, 1911–1915.
- Kolthoff, I. M., & Elving, P. J. (1966). *Treatise on analytical chemistry*. New York: Interscience.
- Malla, M. E., Alvarez, M. B., & Batistoni, D. A. (2002). Evaluation of sorption and desorption characteristics of cadmium, lead and zinc on Amberlite IRC-718 iminodiacetate chelating ion exchanger. *Talanta*, *57*, 277–287.
- Meian, E. (1991). *Metals and their compounds in environment*. New York: VCH.
- Merdivan, M., Gungor, A., Savasci, S., & Aygun, R. S. (2000). Extraction of some transition metals with *N,N*-dibutyl-*N'*-benzoylthiourea into molten paraffin at 65°C . *Talanta*, *53*, 141–146.
- Merdivan, M., Duz, M. Z., & Hamamci, C. (2001). Sorption behaviour of uranium(VI) with *N,N*-dibutyl-

- N'*-benzoylthiourea impregnated in amberlite XAD-16. *Talanta*, 55, 639–645.
- Moon, J. K., Han, Y. J., Jung, C. H., Lee, E. H., & Lee, B. C. (2006). Adsorption of rhenium and rhodium in nitric acid solution by amberlite XAD-4 impregnated with aliquat 336. *Korean Journal of Chemical Engineering*, 23, 303–308.
- Narin, I., Soylak, M., Kayakirilmaz, K., Elci, L., & Dogan, M. (2003). Preparation of a chelating resin by immobilizing 1-(2-pyridylazo) 2-naphthol on amberlite XAD-16 and its application of solid phase extraction of Ni(II), Cd(II), Co (II), Cu(II), Pb(II), and Cr(III) in natural water samples. *Analytical Letters*, 36, 641658.
- Philippeit, G., & Angerer, J. (2001). Determination of palladium in human urine by high-performance liquid chromatography and ultraviolet detection after ultraviolet photolysis and selective solid-phase extraction. *Journal of Chromatography B*, 760, 237–245.
- Raju, C. S. K., Srinivasan, S., & Subramanian, M. S. (2005). New multi-dentate ion-selective AXAD-16-MOPPA polymer for the preconcentration and sequential separation of U(VI), Th(IV) from rare earth matrix. *Separation Science and Technology*, 40, 22132230.
- Saha, B., Gill, R. J., Bailey, D. G., Kabay, N., & Arda, M. (2004). Sorption of Cr(VI) from aqueous solution by amberlite XAD-7 resin impregnated with Aliquat 336. *Reactive & Functional Polymers*, 60, 223–244.
- Schuster, M., & König, K. H. (1988). On the chromatography of metal-chelates. 18. Influence of the coordination sites on the chromatographic properties of *N,N*-dialkyl-*N'*-benzoylurea chelates. *Fresenius' Zeitschrift für Analytische Chemie*, 331, 383–386.
- Soager, R. (1984). *Metallic raw materials dictionary*. Zurich: Bank Tobel.
- Soliman, E. M., Saleh, M. B., & Ahmed, S. A. (2006). Alumina modified by dimethyl sulfoxide as a new selective solid phase extractor for separation and preconcentration of inorganic mercury(II). *Talanta*, 69, 55–60.
- Tokalioglu, S., Kartal, S., & Elci, L. (2002). Determination of some trace metals in waters by flame atomic absorption spectrometry after preconcentration on amberlite XAD-16 resin with sodium tetraborate. *Ann. Chim-Rome*, 92, 1119–1126.
- Tunceli, A., & Turker, A. R. (2000). Flame atomic absorption spectrometric determination of silver after preconcentration on amberlite XAD-16 resin from thiocyanate solution. *Talanta*, 5, 889–894.
- Villaescusa, I., Salvado, V., Depablo, J., Valiente, M., & Aguilar, M. (1992). Liquid solid extraction of gold(III) from aqueous chloride solutions by macroporous resins impregnated with triisobutyl phosphine sulfide. *Reactive Polymers*, 17, 69–73.
- Yusof, A. M., Rahman, M. M., & Wood, A. K. H. (2007). Adsorption of some toxic elements from water samples on modified activated carbon, activated carbon, and red soil using neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 271, 191–197.
- Zougagh, M., Pavon, J. M. C., & de Torres, A. G. (2005). Chelating sorbents based on silica gel and their application in atomic spectrometry. *Anal. Bioanal. Chem.*, 381, 1103–1113.