Article

FAAS Determination of Ag(I) in Water, Anode Slime, Rock and Cream Samples by Solid Phase Extraction Method based on Sepabeads SP207/5-(*p*-Dimethylaminobenzylidene) Rhodanine Combination

Emre Yavuz, Şerife Tokalıoğlu* and Serkan Şahan

Chemistry Department, Faculty of Science, Erciyes University, TR-38039, Kayseri, Turkey

Um método simples e confiável para separação/pré-concentração de Ag(I) utilizando o reagente 5-(*p*-dimetilaminobenzilideno) rodanina e o adsorvente Sepabeads SP207 seguido de sua determinação por espectrometria de absorção atômica com chama (FAAS) foi desenvolvido. As condições ideais do método para a separação/preconcentração de Ag(I) foram estabelecidas em pH 4,0 com fator de preconcentração de 200. Os limites de detecção e quantificação do método foram 0,13 e 0,44 µg L^{-1}, respectivamente. Os valores de desvio padrão relativo e capacidade de adsorção foram de 1,0% e 5,40 mg g^{-1}, respectivamente. A recuperação de Ag(I) em pH 4,0 com 50 mg de resina foi quantitativa e sem interferências causadas por cátions de metais alcalinos e alcalino-terrosos, em concentrações de até 10000 µg mL^{-1}, com exceção de K$^+$. A exatidão do método foi avaliada analisando-se o material de referência certificado TMDA-70 água de lago e por experimentos de adição e recuperação. O método foi aplicado na determinação de Ag(I) em amostras de água da torneira, água mineral, água de mar, lama anódica, rocha e creme.

A simple and reliable method for separation/preconcentration of Ag(I) by using 5-(*p*-dimethylaminobenzylidene) rhodanine reagent and Sepabeads SP207 adsorbent prior to its determination by flame atomic absorption spectrometry (FAAS) was developed. The optimum pH of the method for separation/preconcentration of Ag(I) was found to be 4.0. The preconcentration factor was 200. The limits of detection and quantification of the method were 0.13 and 0.44 µg L^{-1}, respectively. Relative standard deviation and adsorption capacity were 1.0% and 5.40 mg g^{-1}, respectively. The recovery of Ag(I) at pH 4.0 with 50 mg resin was quantitative without interferences caused by alkaline and alkaline earth cations, presenting concentrations of up to 10000 µg mL^{-1}, except for K$^+$. The accuracy of the method was checked by analysing TMDA-70 lake water certified reference material and by addition-recovery experiments. The method was applied for the determination of Ag(I) in tap water, mineral water, sea water, anode slime, rock and cream samples.

Keywords: Ag(I), 5-(*p*-dimethylaminobenzylidene) rhodanine, sepabeads SP207, FAAS

Introduction

Silver is an important element that is widely used in human life. Because of its bacteriostatic properties, silver compounds are often used in filters and other equipments to purify swimming pool and drinking waters, and used in the processing of foods, drugs, and beverages. In many countries, silver impregnated filters are used for drinking water preparation. In mammals, silver usually interacts competitively with essential nutrients, especially with selenium, copper, Vitamin E and Vitamin B12.[1]

Silver is a metal of commercial importance for use in high strength and corrosion resistant alloys, and jewellery. Silver and its compounds have a variety of applications in electronics, photographic and imaging industry, mirrors, medicine, foods or clothing production and also as catalysts. Its compounds and alloys have been widely used in dental and pharmaceutical preparations, and in implanted prosthesis.[2,3] The increasing use of silver compounds and silver containing products in industry and medicine has resulted in an increase of the discharge in the environment of residues that contain this metal. Silver occurs as an impurity in copper, zinc, arsenic and antimony ores and occurs in the environment in industrial waters.[4] The recommendations of the World Health Organization (WHO) permit maximum

*e-mail: serifet@erciyes.edu.tr

concentrations of 0.1 mg L^{-1} of silver ions in drinking water disinfection, but the United States Environmental Protection Agency (US EPA) recommends 0.05 mg L^{-1} as the maximum.[5] The development of analytical methods for the silver determination in industrial and environmental samples is important for the monitoring of pollution levels of silver in several samples.

Flame atomic absorption spectrometry (FAAS) is widely used as a simple and fast instrumental technique. However, the sensitivity of FAAS for metal ions is relatively low and serious interferences are caused by concomitants.[6-9] Frequently, a preconcentration method has to be carried out before the determination of trace metals in environmental samples by FAAS. Interferences can be removed before analysis and the sensitivity of the method is enhanced.[10-12] The widely used techniques for separation and preconcentration of trace amounts of silver are traditional liquid-liquid extraction,[13] dispersive liquid-liquid microextraction,[5,14-16] coprecipitation,[17] cloud point extraction[18-21] and solid phase extraction (SPE).[1,4,22]

SPE has been widely used for the preconcentration of target analytes, and removal of matrix interferences in pharmaceutical, clinical, environmental and food chemistry. There are some advantages such as (*i*) the fast, simple and direct application in small sample amounts without losses; (*ii*) low risk of contamination; (*iii*) time and cost saving.[4] Different sorbents such as carbon nanotubes,[23] C$_{18}$ immobilized on silica,[24] biosorbent,[5] Amberlite XAD 16,[12] silica gel,[25] chitosan-based chelating resin,[1] magnetic nanoparticles[26] and chelating resin containing indole-methionine composite[27] have been used as a sorbent for preconcentrating silver ions.

Sepabeads SP207 (SP207) used in this study is a highly porous, styrene based adsorbent resin with bromine groups chemically bonded to the crosslinked polystyrene matrix. The bromination makes it superior to styrene-divinylbenzene polymers: strongly hydrophobic, high density and large capacity. This type of adsorbent is suitable for adsorption of very low concentrations of organic substances or highly hydrophilic substances. Its specific gravity, particle size, pore volume and specific surface area are 1.18 g mL^{-1}, 20-60 mesh, 1.3 mL g^{-1} and 650 m^2 g^{-1}, respectively.[28]

5-(*p*-Dimethylaminobenzylidene) rhodanine (PDR) is a derivative of rhodanine that is especially suitable as a sensitive and highly selective reagent for silver.[29] It forms slightly soluble red precipitate with Ag(I). The insoluble chelate formed by reaction of PDR with Ag(I) has the composition AgPDR. An atom of metal replaces H of the imino group and is bonded to S of the thioketo group. It is unlikely that four-membered rings are formed. Probably the structure is polymeric. The chemical structure of the AgPDR chelate is shown in Figure 1.[30]
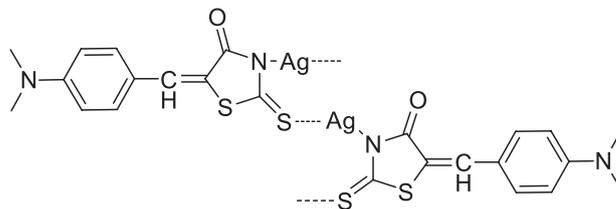
Figure 1. The molecular structure of the AgPDR complex.

In the present study, a solid phase extraction method prior to FAAS determination of Ag(I) in various samples (natural and mineral waters, anode slime, rock and cream) was described by using SP207 adsorbent and PDR reagent. The effect of various parameters affecting the recovery of Ag(I) (such as pH, amount of ligand, eluent type and concentration, sample and eluent flow rate, sample volume, effect of matrix components and adsorption capacity) was examined in detail. To our literature knowledge, the combination of PDR reagent and SP207 resin has not been used for the determination of silver trace ions.

Experimental

Instrument

A PerkinElmer AAnalyst 800 model flame atomic absorption spectrometer (Waltham, MA, USA) equipped with Ag hollow cathode lamp as the radiation source was used for absorbance measurements. The operating conditions were as follows: wavelength 328.1 nm, lamp current 4.0 mA and spectral resolution 0.7 nm. The acetylene and air flow rates were 2.0 and 17 L min^{-1}, respectively. The pH measurements were carried out by using WTW pH315i apparatus equipped with a combined pH electrode.

Reagents and solutions

All reagents used were of analytical grade without further purification. Distilled water was used throughout all the work. An ethanolic solution of 0.05% (m/v) PDR chelating reagent (Merck Darmstadt, Germany) was prepared by dissolving 0.05 g of PDR in warm ethanol and diluting to 100 mL with distilled water. Ag(I) stock solution (1000 mg L^{-1}) was purchased from Merck and Sepabeads SP207 from Sigma (St. Louis, MO, USA). Ag(I) working solutions were prepared by diluting from its stock solution. KSCN and Na$_2$S$_2$O$_3$ solutions at different concentrations

were prepared by dissolving appropriate amounts of KSCN (Merck) and $Na_2S_2O_3$ (Merck) by appropriate solvents. Buffer solutions were prepared using 1.0 mol L^{-1} phosphoric acid and sodium dihydrogen phosphate for pH 2.0, 1.0 mol L^{-1} acetic acid and sodium acetate for pH 3.0-6.0, 1.0 mol L^{-1} ammonium acetate for pH 7.0 and 1.0 mol L^{-1} ammonia and ammonium chloride solutions for pH 8.0 and 9.0.

Column adsorption experiment

Off line column preconcentration system included a peristaltic pump with four channels (Masterflex L/S 7524-45, Cole Parmer, Vernon Hills, IL, USA) and four minicolumns (13 mm length and 3 mm i.d.). The resin amount used for each minicolumn was 50 mg. Small amounts of glass wool were inserted in each side of the minicolumn. By using this system, both sample and blank solutions were passed through different minicolumns at the same time.

Sample (tap, mineral and sea waters, cream, rock and anode slime) preparations

Tap water samples from a laboratory at the Erciyes University (Turkey), mineral water from a local market in Kayseri city (Turkey) and sea water from İzmir city (Turkey) were collected and they were filtered through a 0.45 μm membrane filter (except for tap water). Samples were acidified to pH 2.0 with concentrated HNO$_3$ in order to prevent adsorption of the metal ions on the flask walls. In the analysis of water samples, aliquots of 250 mL of tap water, 100 mL of mineral water and 50 mL of sea water were used. The pH value of the water samples was adjusted to 4.0 by using acetate buffer.

The anode slime from a copper plant in Organized Industrial District (Kayseri, Turkey) and rock sample from Yahyalı city (Turkey) were taken. Samples were ground and homogenized. Approximately 1.0 g of anode slime and 0.50 g of rock sample were weighed in a beaker of 100 mL, and 10 mL of aqua regia was added to the beaker and the mixtures were evaporated close to dryness. Then, 10 mL of aqua regia were added again to the residue and the mixtures were again evaporated close to dryness. The insoluble parts were filtered through a blue band filter paper by using distilled water.[31]

A cream sample was purchased from a pharmacy in Kayseri city (Turkey). A portion of 0.01 g of sample was weighed in a beaker. To decompose the sample, 10 mL of concentrated HNO$_3$ were added to the beaker. After evaporating close to dryness, 3 mL of concentrated H$_2$O$_2$

were used. The evaporation procedure was repeated and the residue was diluted to about 20 mL with distilled water.[31] The developed preconcentration procedure was applied. Silver(I) was determined by FAAS.

Preconcentration procedure

An aliquot of 2.0 mL of PDR (0.05%, m/v) reagent was added to model solutions of 20 mL containing 10 μg of Ag(I) ion. The pH value of the each solution was adjusted to 4.0 using buffer solution and they were passed through the pre-conditioning columns containing 50 mg of SP207 at a flow rate of 2.0 mL min^{-1}. The columns were washed with 5.0 mL of distilled water. The AgPDR complex adsorbed on each SP207 column was eluted with 5.0 mL of 1.0 mol L^{-1} HCl in acetone at a flow rate of 2.0 mL min^{-1}. The eluates were evaporated close to dryness on a hot plate and the residues were made up to 5.0 mL with 1.0 mol L^{-1} HCl. Silver(I) concentration was determined by FAAS. Blank analysis was performed adopting this same procedure.

Results and Discussion

Effect of pH

The effect of pH on the recovery of Ag(I) ions was investigated in the range of 2.0-9.0 by using buffer solutions. Results are presented in Figure 2. Quantitative recoveries (97-101%) for Ag(I) were obtained in the pH ranges of 4.0-9.0. Silver (I) is more stable at acidic pH values. When sample pH is higher than 7.0, Ag(I) may precipitate as silver hydroxide. So, pH 4.0 was selected for further experiments. Similar results were also found in other works.[4,32]
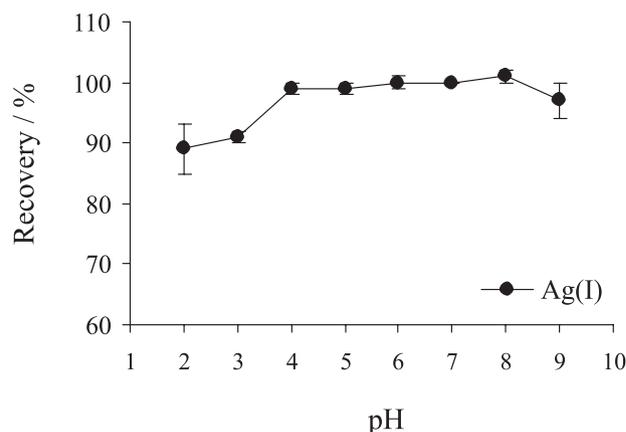
Figure 2. Effect of pH on the recovery of Ag(I). Experimental conditions: 0.5 μg mL^{-1} of Ag(I), 1.0 mg of PDR, 5.0 mL of 1.0 mol L^{-1} HCl in acetone, n=3.

Effect of PDR amount

A PDR solution containing 0.05% m v^{-1} was used for evaluating the effect of PDR amount on the recovery of Ag(I). Different volumes of this solution were added to model solutions for testing the effects of reagent masses in the 0-1.25 mg range and their pH was adjusted to 4.0. The effect of reagent amount is shown in Figure 3. Recoveries of Ag(I) were 100 and 103% for reagent amounts of 1.0 and 1.25 mg, respectively. Without adding reagent, the recovery value was only 23% for Ag(I). For the subsequent experiments, the PDR amount was chosen as 1.0 mg (2 mL).
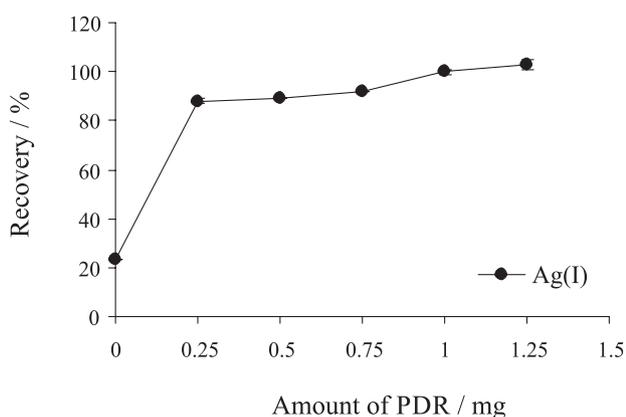
Figure 3. Effect of PDR amount (pH 4.0, 0.5 µg mL^{-1} of Ag(I), resin amount: 50 mg, eluent: 1.0 mol L^{-1} HCl in acetone, n=3).

Effect of type, concentration and volume of the eluent

Several eluents were examined to elute the retained AgPDR complex from the column. As eluent, 5.0 mL of HCl, HNO$_3$, HCl in acetone, HNO$_3$ in acetone, thiourea, KSCN and Na$_2$S$_2$O$_3$ solutions having different concentrations were investigated. As shown in Table 1, 1.0, 2.0 and 3.0 mol L^{-1} HCl in acetone were found to be the most effective eluents for quantitative recovery of Ag(I). Lower concentrations of the eluent were not effective for quantitative elution of the complex. Solutions containing 1.0 and 2.0 mol L^{-1} HNO$_3$, 1.0, 2.0 and 3.0 mol L^{-1} HNO$_3$ in acetone as eluent were also studied. Recovery values were ≤ 8%. The effect of 2.0, 3.0 and 4.0 mL of 1.0 mol L^{-1} HCl in acetone was tested. Recoveries for Ag(I) were 82, 89 and 100%, respectively. Thus, a volume of 5.0 mL of 1.0 mol L^{-1} HCl in acetone was selected for further studies.

Effect of sample and eluent flow rates

One of the most important parameters affecting both the retention efficiency of the analyte and the extraction

Table 1. Effect of eluent type (5 mL) on the recovery of Ag(I), pH 4.0

Eluent type	Recovery ± sd / %
1.0 mol L^{-1} HCl	66 ± 1
2.0 mol L^{-1} HCl	88 ± 1
0.1 mol L^{-1} HCl in acetone	85 ± 1
0.5 mol L^{-1} HCl in acetone	88 ± 2
1.0 mol L^{-1} HCl in acetone	100 ± 1
2.0 mol L^{-1} HCl in acetone	101 ± 1
3.0 mol L^{-1} HCl in acetone	100 ± 1
1.0 mol L^{-1} thiourea in 1.0 mol L^{-1} HCl	73 ± 3
0.1 mol L^{-1} thiourea in 2.0 mol L^{-1} HCl	38 ± 2
0.5 mol L^{-1} thiourea in 2.0 mol L^{-1} HCl	63 ± 5
1.0 mol L^{-1} thiourea in 2.0 mol L^{-1} HCl	73 ± 1
2.0 mol L^{-1} thiourea in 2.0 mol L^{-1} HCl	72 ± 2
1.0 mol L^{-1} KSCN	74 ± 1
1.0 mol L^{-1} KSCN in 1.0 mol L^{-1} HCl	87 ± 3
2.0 mol L^{-1} KSCN in 2.0 mol L^{-1} HCl	90 ± 2
0.1 mol L^{-1} Na$_2$S$_2$O$_3$	68 ± 2
0.5 mol L^{-1} Na$_2$S$_2$O$_3$	68 ± 2
1.0 mol L^{-1} Na$_2$S$_2$O$_3$	70 ± 1

Recovery ± sd: mean recovery ± standard deviation (n = 3).

time is the sample flow rate. For this purpose, the effects of sample and eluent flow rates were tested with a peristaltic pump. The effect of sample flow rates for 2.0, 3.0 and 4.0 mL min^{-1} and also the effect of eluent flow rates for 1.0, 2.0 and 3.0 mL min^{-1} were investigated under optimum experimental conditions (pH 4.0, eluent: 5.0 mL of 1.0 mol L^{-1} HCl in acetone, reagent amount: 1.0 mg). While the recovery for Ag(I) changed between 90 and 95% at the studied sample flow rates, recoveries for the eluent flow rates of 1.0-3.0 mL min^{-1} were found to be 90-97%. Thus, a flow rate of 2.0 mL min^{-1} was selected as optimum sample and eluent flow rates.

Effect of sample volume and preconcentration factor

The effect of sample volume was examined by passing through the column 25, 50, 100, 250, 500, 1000 and 1500 mL of model solutions containing 10 µg Ag(I). Results are shown in Figure 4. Recoveries for Ag(I) changed in the range of 95-102% for the sample volume ranges of 25-1000 mL. Considering that 5.0 mL of eluent were enough to elute the Ag(I) from SP207 column, a preconcentration factor (PF) of 200 was obtained.

Effect of matrix elements

The effect of the possible interfering ions on the recovery of Ag(I) was investigated. As can be seen in Table 2, the high concentrations of major matrix ions,
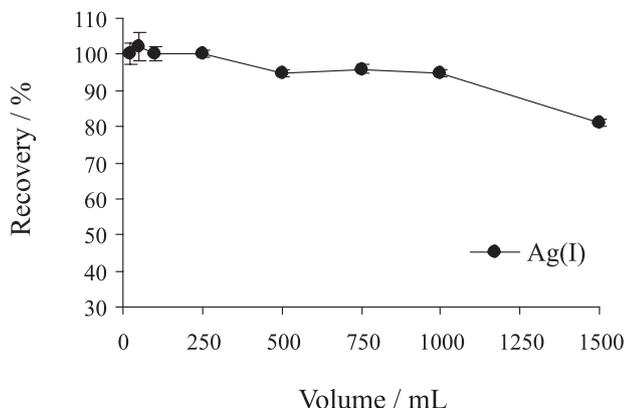
Figure 4. Effect of sample volume on the recovery of silver ion (0.5 µg mL^{-1} of Ag(I), PDR amount: 1.0 mg, resin amount: 50 mg, eluent: 1.0 mol L^{-1} HCl in acetone, n=3).

Table 2. Effect of matrix ions on the recovery of Ag(I) (pH 4.0, eluent: 5.0 mL of 1.0 mol L^{-1} HCl in acetone)

Ion	Concentration / (µg mL^{-1})	Salt	Recovery ± sd / %
Na$^+$	2500	NaNO$_3$	100 ± 4
	5000		101 ± 1
	10000		93 ± 1
Na$^+$	5000	NaCl	96 ± 1
	10000		75 ± 1
K$^+$	2500	KCl	100 ± 1
	5000		93 ± 2
	7500		89 ± 2
Mg^{2+}	2500	Mg(NO$_3$)$_2$.6H$_2$O	95 ± 1
	5000		100 ± 1
	10000		95 ± 2
Ca^{2+}	2500	Ca(NO$_3$)$_2$.6H$_2$O	100 ± 5
	5000		99 ± 1
	10000		99 ± 1
Cl$^-$	10000	NaCl	97 ± 5
SO$_4$$^{2-}$	250	Na$_2$SO$_4$	84 ± 6
PO$_4$$^{3-}$	250	Na$_3$PO$_4$	100 ± 0
CO$_3$$^{2-}$	250	Na$_2$CO$_3$	92 ±1
Cu^{2+}	10	Cu(NO$_3$)$_2$.5H$_2$O	96 ±1
Al^{3+}	10	Al(NO$_3$)$_3$.9H$_2$O	86 ± 2
Ni^{2+}	10	NiCl$_2$.6H$_2$O	89 ± 1
Co^{2+}	10	Co(NO$_3$)$_2$.6H$_2$O	89 ± 0
Fe^{3+}	5	Fe(NO$_3$)$_3$.9H$_2$O	87 ± 1
	10		75 ± 4
Mn^{2+}	10	Mn(NO$_3$)$_2$.4H$_2$O	95 ± 3
Pb^{2+}	5	Pb(NO$_3$)$_2$	102 ± 3
	10		75 ± 4
Cd^{2+}	10	Cd (NO$_3$)$_2$.4H$_2$O	91 ± 2
Cr^{3+}	10	Cr(NO$_3$)$_3$.9H$_2$O	94 ± 1
Zn^{2+}	50	Zn(NO$_3$)$_2$.6H$_2$O	97 ± 1
Au^{3+}	10	Au standard solution	89 ± 1
Pd^{2+}	10	Pd standard solution	64 ± 3
Hg^{2+}	10	Hg(NO$_3$)$_2$.H$_2$O	90 ± 2

Recovery ± sd: mean recovery ± standard deviation (n = 3).

10000 µg mL^{-1} Na$^+$, 10000 µg mL^{-1} Mg^{2+}, 10000 µg mL^{-1} Ca^{2+}, 5000 µg mL^{-1} K$^+$ and 10000 µg mL^{-1} Cl$^-$, did not interfere with preconcentration of 0.5 µg mL^{-1} Ag(I). Some cations, especially 10 µg mL^{-1} Fe(III), Pb(II) and Pd(II) interfere with Ag(I) because of the probable formation of stable complexes with PDR. These results showed that the method had a good tolerance to matrix components and the presence of major and other matrix ions did not influence the determination of Ag(I) ion under optimized conditions.

Adsorption isotherms and adsorption capacity

The adsorption isotherm and adsorption capacity of the SP207 resin for Ag(I) were examined by using a column filled with 50 mg of SP207. The pH value of the model solutions of 20 mL including 5, 10, 30, 40 and 60 µg mL^{-1} Ag(I) was adjusted to 4.0 and the described preconcentration method was applied. The adsorption capacity of the resin was obtained by using the Langmuir equation[33,34] based on the following equation 1:

$$\frac{C}{n} = \frac{1}{n_m K} + \left(\frac{1}{n_m}\right)C \qquad (1)$$

where C (mg L^{-1}) is the concentration of Ag(I) in solution at equilibrium and n (mg g^{-1}) is the amount of adsorbed Ag(I) *per* g of resin at equilibrium (mg g^{-1}). A breakthrough curve was obtained by plotting the concentration (mg L^{-1}) *vs.* the mass of Ag(I) adsorbed *per* g of resin. The adsorption capacity (n$_m$) and the binding equilibrium constant (K) were obtained from the slope and the intercept of the regression plot obtained by the least squares method, respectively. The adsorption capacity of the resin for Ag(I) and binding equilibrium constant were found to be 5.40 mg g^{-1} and 0.162 L mg^{-1}, respectively.

Analytical figures of merit of the method

The linear working range for Ag(I) was from 0.05 to 10 µg mL^{-1} (Absorbance = 0.0542 [Ag] + 0.0039, r^2 = 0.9989). The precision of the method (as relative standard deviation, in %) for 0.5 µg mL^{-1} Ag(I) concentration was 1.0% (n = 10). The limits of detection (LOD) and of quantification (LOQ) of the described method for the determination of Ag(I) ion were studied by using blank solutions (n = 15) under the optimal experimental conditions (pH 4.0; eluent, 1.0 mol L^{-1} HCl in acetone; sample and eluent flow rates, 2.0 mL min^{-1}). LOD (3s/b) and LOQ (10s/b), where s is the blank standard deviation and b is the slope of calibration curve, were 0.13 and 0.44 µg L^{-1} for Ag(I) with 200-fold preconcentration factor, respectively.[35,36]

Analysis of real samples and evaluation of accuracy

To verify the applicability of the method, Ag(I) in certified reference material (TMDA-70, lake water) was determined by applying the developed method. The determined value was 10.8 ± 0.41 µg L^{-1} and it is in good agreement with the certified value (10.9 ± 0.13 µg L^{-1}). The percent relative error was -0.9%. The accuracy of the method for determination of Ag(I) in natural and mineral waters, anode slime, rock and cream samples was evaluated by spiking Ag(I) at various concentrations. Analytical results are presented in Tables 3 and 4. From the results, the method is suitable for the accurate and precise determination of Ag(I) at the µg L^{-1} level in several samples.

Table 3. Determination of Ag(I) in tap water, mineral water and sea water samples

Sample	Added / (µg L^{-1})	Found^a / (µg L^{-1})	Recovery / %
Tap water	–	4.4 ± 0.2	–
	20	24.9 ± 0.2	102
	40	43.3 ± 0.6	97
Mineral water	–	20.2 ± 0.4	–
	25	45.2 ± 1.8	100
	50	71.4 ± 0.4	102
Sea water	–	nd^b	–
	50	52.9 ± 1.6	106
	100	95.0 ± 1.8	95

^{a}Mean value ± standard deviation, n = 3; ^{b}not detected.

Table 4. Determination of Ag(I) in anode slide, rock and cream samples

Sample	Added / (µg g^{-1})	Found^a / (µg g^{-1})	Recovery / %
Anode slime	–	1.2 ± 0.1	–
	10	11.1 ± 0.3	99
Rock	–	1.1 ± 0.1	
	5	6.4 ± 0.3	106
Cream	–	1613 ± 46	
	250	1853 ± 55	96

^{a}Mean value ± standard deviation, n = 3.

Comparison of the described method with other methods

A comparison of the present method with other off-line preconcentration methods for the determination of Ag(I) is given in Table 5. The main advantages of the developed method are as follows: comparable and/or higher preconcentration factor (200), lower limit of detection (0.13 µg L^{-1}), lower resin amount (50 mg), low matrix effect, good adsorption capacity (5.40 mg g^{-1}), acidic working pH, good precision (1.0%, as RSD), the use of a different eluent for elution (Table 5) and applicability for several types of samples.

Conclusions

The developed method is simple and reliable for separation and preconcentration of Ag(I) by using 5-(p-dimethylaminobenzylidene) rhodanine reagent and Sepabeads SP207 adsorbent. It was found that the

Table 5. Comparison of the optimum conditions of the present method with other methods reported in the literature for solid phase extraction of Ag(I) by FAAS

Ligand/Adsorbent	Sample	pH	AC / (mg g^{-1})	LOD / (µg L^{-1})	PF	RSD / %	Eluent	Sorbent mass / mg	Reference
2,4,6-Trimorpholino-1,3,5-triazin/Silica gel	spring water and tap water	3.5	0.384	–	130	3.03	0.05 mol L^{-1} Na$_2$S$_2$O$_3$	100	25
2-Mercaptobenzothiazole/Silica gel	lake water	3	0.343	–	300	2.04	0.005 mol L^{-1} Na$_2$S$_2$O$_3$	70	37
Dithizone/Naphthalene	ore, radiology film and wound dressing samples	1	0.029 mg/disk	3.9	10	0.9, 4.4	3% m v^{-1} thiourea	–	38
Mixed aza-thioether crowns/Octadecyl silica membrane disks	synthetic samples, rain, tap and spring water	5	0.917	0.10	200	1.6	2.0 mol L^{-1} Na$_2$S$_2$O$_3$	–	39
Di (n-propyl) thiuram disulfide/Silica gel	photographic waste and lake water	5.8	0.330	24	100	1.43	0.5 mol L^{-1} Na$_2$S$_2$O$_3$	200	40
Amidinothioureido/Silica gel	three national certified ores	0.1-6.0 mol L^{-1} HNO$_3$	10.36	1.1	–	1.2	5 % m v^{-1} thiourea	–	41
5-(p-Dimethylamino benzylidene) rhodanine/Sepabeads SP207	tap water, sea water, mineral water, anode slime, rock and cream	4.0	5.40	0.13	200	1.0	1 mol L^{-1} HCl in acetone	50	this work

AC: adsorption capacity; LOD: limit of detection; PF: preconcentration factor; RSD: relative standard deviation.

adsorption properties of the sorbent (50 mg) remained constant throughout the study (at least 100 cycles). The method is sensitive, selective and reproducible. The elution was easily performed with 5.0 mL of 1.0 mol L^{-1} HCl in acetone. The recovery of Ag(I) in the presence of the most common matrix elements was quite good. The developed method is suitable for quantitative Ag(I) determination in samples having variable matrices (tap water, sea water, mineral water, anode slime, rock and cream samples).

Supplementary Information

Supplementary information (adsorption isotherm) is available free of charge at http://jbcs.sbq.org.br as a PDF file.

References

1. Katarina, R. K.; Takayanagi, T.; Oshima, M.; Motomizu, S.; *Anal. Chim. Acta* **2006**, *558*, 246.

2. Rohani, T.; Taher, M. A.; *Talanta* **2010**, *80*, 1827.

3. Buhaceanu, R.; Sarghie, I.; Barsanescu, A.; Dulman, V.; Bunia, I.; *Cent. Eur. J. Chem.* **2009**, *7*, 827.

4. El-Menshawy, A. M.; Kenawy, I. M.; El-Asmy, A. A.; *J. Hazard. Mater.* **2010**, *173*, 523.

5. Araújo, C. S. T.; Alves, V. N.; Rezende, H. C.; Coelho, N. M. M.; *Microchem. J.* **2010**, *96*, 82.

6. Yuan, C.-G.; Liang, P.; Zhang, Y.-Y.; *Microchim. Acta* **2011**, *175*, 333.

7. Tokalıoğlu, Ş.; Ayhanöz, H.; *Food Chem.* **2011**, *127*, 359.

8. Tokalıoğlu, Ş.; Kartal, Ş.; Elçi, L.; *Bull. Korean Chem. Soc.* **2002**, *23,* 693.

9. Pourreza, N.; Zolgharnein, J.; Kiasat, A.R.; Dastyar, T.; *Talanta* **2010**, *81*, 773.

10. Rofouei, M. K.; Payehghadr, M.; Shamsipur, M.; Ahmadalinezhad, A.; *J. Hazard. Mater.* **2009**, *168*, 1184.

11. Lemos, V. A.; Baliza, P. X.; Santos, J. S.; Nunes, L. S.; de Jesus, A. A.; Rocha, M. E. A.; *Talanta* **2005**, *66*, 174.

12. Ayata, S.; Kaynak, İ.; Merdivan, M.; *Environ. Monit. Assess.* **2009**, *153*, 333.

13. Camagong, C. T.; Honjo, T.; *Anal. Bioanal. Chem.* **2002**, *373*, 856.

14. Afzali, D.; Mohadesi, A. R.; Jahromi, B. B.; Falahnejad, M.; *Anal. Chim. Acta* **2011**, *684*, 54.

15. Liang, P.; Peng, L.; *Microchim. Acta* **2010**, *168*, 45.

16. Mohammadi, S. Z.; Afzali, D.; Taher, M. A.; Baghelani, Y. M.; *Talanta* **2009**, *80*, 875.

17. Mao, X.; Chen, H.; Liu, J.; *Microchem. J.* **1998**, *59*, 383.

18. Gao, Y.; Wu, P.; Li, W.; Xuan, Y.; Hou, X.; *Talanta* **2010,** *81,* 586.

19. Shemirani, F.; Kozani, R. R.; Assadi, Y.; *Microchim. Acta* **2007**, *157*, 81.

20. Manzoori, J. L.; Nezhad, G. K.; *Anal. Chim. Acta* **2003**, *484*, 155.

21. Manzoori, J. L.; Zadeh, H. A.; Amjadi, M.; *J. Hazard. Mater.* **2007**, *144*, 458.

22. Sabarudin, A.; Noguchi, O.; Oshima, M.; Higuchi, K.; Motomizu, S.; *Microchim. Acta* **2007**, *159*, 341.

23. Ding, Q.; Liang, P.; Song, F.; Xiang, A.; *Sep. Sci. Technol.* **2006**, *41*, 2723.

24. Dressler, V. L.; Pozebon, D.; Curtius, A. J.; *Anal. Chim. Acta* **2001**, *438*, 235.

25. Madrakian, T.; Afkhami, A.; Zolfigol, M. A.; Solgi, M.; *J. Hazard. Mater.* **2006**, *128*, 67.

26. Mashhadizadeh, M. H.; Karami, Z.; *J. Hazard. Mater.* **2011**, *190*, 1023.

27. Sahana, A.; Mandal, S.; Banerjee, A.; Guha, S.; Mukhopadhyay, S. K.; Das, D.; *J. Braz. Chem. Soc.* **2011**, *22*, 272.

28. http://www.sorbtech.com/, accessed in December 2012.

29. Pourreza, N.; Rastegarzadeh, S.; *Anal. Chim. Acta* **2001**, *437*, 273.

30. Sandell, E. B.; Onishi, H.; *Photometric Determination of Traces of Metals*, 4th ed.; John Wiley & Sons: New York, USA, 1978**.**

31. Çetin, T.; Tokalıoğlu, Ş.; Ülgen, A.; Şahan, S.; Özentürk, İ.; Soykan C.; *Talanta* **2013**, *in press*, doi.org/10.1016/j.talanta.2012.10.054.

32. Gao, Y.; Wu, P.; Li, W.; Xuan, Y.; Hou, X.; *Talanta* **2010**, *81*, 586.

33. Langmuir, I.; *J. Am. Chem. Soc.* **1918**, *40*, 1361.

34. Tokalıoğlu, Ş.; Arsav, S.; Delibaş, A.; Soykan, C.; *Anal. Chim. Acta* **2009**, *645*, 36.

35. Akl, M. A. A.; Kenawy, I. M. M.; Lasheen, R. R.; *Microchem. J.* **2004**, *78*, 143.

36. Turan, Ş.; Tokalıoğlu, Ş.; Şahan, A.; Soykan, C.; *React. Funct. Polym.* **2012**, *72*, 722.

37. Safavi, A.; Iranpoor, N.; Saghir, N.; *Sep. Purif. Technol.* **2004**, *40*, 303.

38. Fathi, M. R.; Pourreza, N.; Purweis, S.; *J. Chin. Chem. Soc.-Taip* **2009**, *56*, 725.

39. Shamsipur, M.; Javanbakht, M.; Ghasemi, Z.; Ganjali, M. R.; Lippolis, V.; Garau, A.; *Sep. Purif. Technol.* **2002**, *28*, 141.

40. Akhond, M.; Absalan, G.; Sheikhian, L.; Eskandari, M. M.; Sharghi, H.; *Sep. Purif. Technol.* **2006**, *52*, 53.

41. Zhang, S.; Pu, Q.; Liu, P.; Sun, Q.; Su, Z.; *Anal. Chim. Acta* **2002**, *452*, 223.