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Synthesis, characterization and application of a new chelating resin for on-line separation, preconcentration and determination of Ag(I) by flame atomic absorption spectrometry

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ABSTRACT

A simple and reliable on-line separation/preconcentration procedure was developed for the determination of trace levels of Ag(I) by flame atomic absorption spectrometry. Poly[N-(3-methyl-*1H*-indol-1-yl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propane sulfonic acid-co-divinylbenzene] was synthesized and characterized as a new chelating resin for the first time. Ag(I) was sorbed on the chelating resin, from which it could be eluted with 3 mol L^{-1} HCl and then introduced directly to the nebulizer-burner system for flame atomic absorption spectrometry. The parameters influential on the determination of Ag(I) ions such as the pH of the sample solution, amount of resin, eluent type, interfering ions and flow variables were studied. Under the optimum conditions, the calibration graph obtained was linear over the concentration range of 2–20 μg L^{-1}. The detection limit of the method (3 σ) was 0.3 μg L^{-1} while precision was 1.5% (n=25) at the level of 10 μg L^{-1} Ag(I). The limit of quantification for the method, based on 20 σ, was 2.0 μg L^{-1}. The enrichment factor was found to be 65 while the optimized sample volume was 13.6 mL. The accuracy of the method was performed by analyzing certified reference materials. The developed method was applied successfully for the determination of silver in different water samples with satisfactory results.

1. Introduction

Silver is a low-abundance element found in the earth's crust, and is one of the so-called noble metals. Great economical interest is associated with silver, and its widespread use for a variety of materials and applications is responsible for its dissemination in the environment [1]. Silver content in environmental samples has increased with the increasing use of silver compounds and silver-containing products in industry, medicine and in commerce [2].

Silver is a commercially important element that is widely used in everyday life. It is valued for its resistance to corrosion and for its use in alloys, medicine and jewelry. Because of its marked antibacterial properties, silver compounds are often used in dental and pharmaceutical preparations, implanted prostheses, electronic devices, photographic materials, mirrors, cloud seeding, filters and other equipment to purify water, and in the processing of foods, drugs, and beverages. In many countries, silver impregnated filters are used for drinking water preparation [3–5]. Also, silver is often presented as an impurity in Cu, Zn, As and Sb ores and thus it is possible for it to enter into the environment from industrial wastes [3,6].

Silver is most toxic to microorganisms or larval forms of aquatic animals. Silver-impregnated filters are used for water purification and a concentration of up to 50–200 μg L^{-1} silver (depending on country) is permitted to control antimicrobial activity with no risk to human health. Silver can enter into the environment via industrial waters and may pose a potential risk as a water pollutant [2,6]. On the other hand, recent information about the interaction of silver with essential nutrients, especially selenium, copper, vitamins E and B_{12}, has focused attention on its potential toxicity [7]. Consequently, the determination of trace amounts of silver is important for many areas of chemical analysis.

Analysis of trace metals is difficult because of both their low abundance levels in samples and the high complexity of sample matrices. Hence, preliminary concentration and matrix removal steps are frequently required to guarantee the accuracy and precision of the analytical results [8].

Among the on-line preconcentration techniques frequently used, flow injection micro-column based solid phase extraction offers many advantages, such as a relatively high preconcentration factor

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and sampling frequency, simplicity of phase separation and suitability for automation [9]. Several methods have been reported to adapt on-line solid phase extraction coupled with FAAS for the determination of silver. These methods include silica gel [10–13], alumina [4,14], fibers [15], knotted reactor (KR) [16], and lead diethyldithiocarbamate [5].

Chelating resins can be used in the concentration and selective separation of silver ions. Also, ion exchange resins can be used for silver ions, but chelating resins are preferred instead of ion exchange resins because of their selectivity [17–19]. Chelating resins have different functional groups as the matrix or support. The functional groups in these resins may include N, O, S and P donor atoms. Chelating resins are used widely in the separation, concentration or analytical preconcentration of metal ions [20].

In this study, a newly synthesized chelating resin, poly[N-(3-methyl-*1H*-indol-1-yl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propane sulfonic acid-co-divinylbenzene] (MMAD) was used for the first time, and the possibilities of its utilization in an on-line preconcentration system were investigated for the determination of silver. We equipped the on-line preconcentration system with a home-made time controller with five independent channels. To the best of our knowledge, an on-line preconcentration system combined with the (MMAD) resin has not been used before in the determination of Ag(I) by flame atomic absorption spectrometry (FAAS). The proposed method was applied for the determination of silver in various water samples.

2. Experimental

2.1. Instrument

A PerkinElmer (Norwalk, CT, USA) model AAnalyst 800 flame atomic absorption spectrometer equipped with a deuterium background correction system and an air-acetylene burner was used for the determination of silver. The wavelength of 328.1 nm, spectral bandwidth of 0.7 nm, acetylene flow rate of 1.4 L min^{-1}, and nebulizer flow rate of 10.0 mL min^{-1} were the conventional working parameters for the instrument. For measuring pH values in the aqueous phase, a Consort model C533 pH meter combined with a glass-electrode and also a magnetic stirrer (Chiltern) were used. The NMR spectra were recorded on a Bruker DPX 400. Chemical shifts are reported in parts per million relative to DMSO (^{1}H: $\delta=2.50$ ppm), DMSO (^{13}C: $\delta=40.6$ ppm). FT-IR Spectrometer, PerkinElmer Spectrum 400 (IR Microscopy and imaging) was used.

The flow system comprised a peristaltic pump with variable speed (Watson-Marlow Inc., Wilmington, MA, USA), a multichannel peristaltic pump (Ismatec SA, Glattbrugg, Switzerland) furnished with silicone tubes to deliver all solutions, and two three-way valves (Cole-Parmer Inc. Co., Illinois, USA) to select solution ways. The peristaltic pumps (PP) and valves (V) were controlled by a home-made five-channel time controller in which each channel can be set for 36 different timing periods with thumble switches. This unit was constructed in our instrumentation laboratory (at low cost) [21]. The flow system was constructed using fittings, unions and tees made of plastic and high density polyethylene (HDPE) materials. Resin (MMAD) packed into a minicolumn (glass, 3.5 cm in length and 0.3 cm i.d.) was used for the on-line separation/preconcentration of silver(I) ions.

2.2. Reagents and solutions

All the reagents used were of the highest available purity or at least analytical reagent grade (Merck, Darmstadt, Germany). Deionized water was used for the preparation of the solutions. 1000 mg L^{-1} Ag(I) was prepared by dissolving 40 mg of $AgNO_3$ with 2% (w/v) HNO_3 in a 25-mL volumetric flask. Standard solutions of silver were prepared by appropriate dilution of the stock solution with 0.1 mol L^{-1} HNO_3 just before use. The following solutions were used for the presented preconcentration procedure: HNO_3 solution for pH 1–2; CH_3COOH/NaOH for pH 3–5; CH_3COONH_4/CH_3COOH buffer for pH 6–7; NH_4Cl/NH_3 buffer for pH 8. A 3 mol L^{-1} hydrochloric acid solution was used as eluent throughout the experiments.

2,2'-Azobisisobutyronitrile (AIBN), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), methacryloyl chloride, and 3-methylindole (Merck, Darmstadt, Germany) were used without further purification. Divinylbenzene (DVB), N,N-dimethylformamide, diethylether, methanol, dichloromethane, triethylamine, acetonitrile, and benzene (Merck) were commercial products of analytical grade and used as received unless otherwise noted.

2.3. Synthesis of monomer and chelating resin

2.3.1. Synthesis of monomer

To a well-stirred solution of 3-methylindole (0.52 g, 4 mmol) in 10 mL CH_2Cl_2 and triethylamine (12 mmol) in 30 mL acetonitrile, was added methacryloyl chloride (0.52 g, 5 mmol) dropwise under cooling conditions in an ice bath (0–5 °C). After the complete addition of methacryloyl chloride, the reaction mixture was stirred for 22 h at room temperature, then filtered and evaporated with a rotavapor. A light yellow product was obtained and recrystallized from methanol as a yellow powder (yield: 80%). The reaction scheme of the monomer is shown in Fig. 1.

2.3.2. Synthesis of chelating resin

The preparation of poly[N-(3-methyl-*1H*-indol-1-yl)-2-methacrylamide-co-2-acrylamido-2-methyl propane sulfonic acid-co divinylbenzene] (MMAD) chelating resin was carried out with a radical initiator (AIBN) in a dimethylformamide solution. To a polymerization flask, were added the two appropriate monomers 2-methyl-1-(3-methyl-*1H*- indol-1-yl)prop-2-en-1-one (0.60 g, 3 mmol) and AMPS (0.23 g, 1 mmol), the crosslinking reagent DVB (0.52 g, 4.0 mmol), and the initiator AIBN (0.018 g, 0.1 mmol). The system was kept under N_2 for 3 h at 70 ± 1 °C.

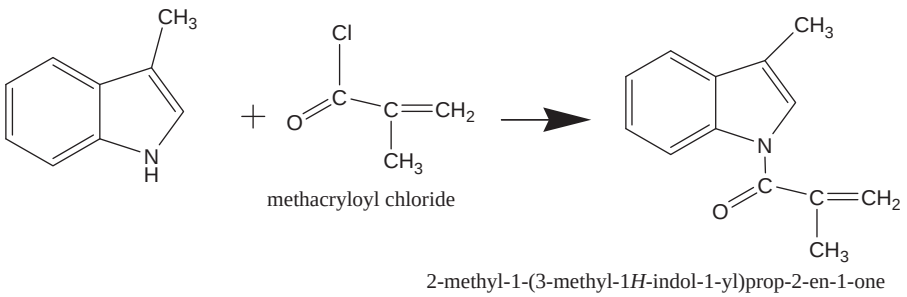

Fig. 1. Reaction scheme of 2-methyl-1-(3-methyl-1*H*-indol-1-yl)prop-2-en-1-one.

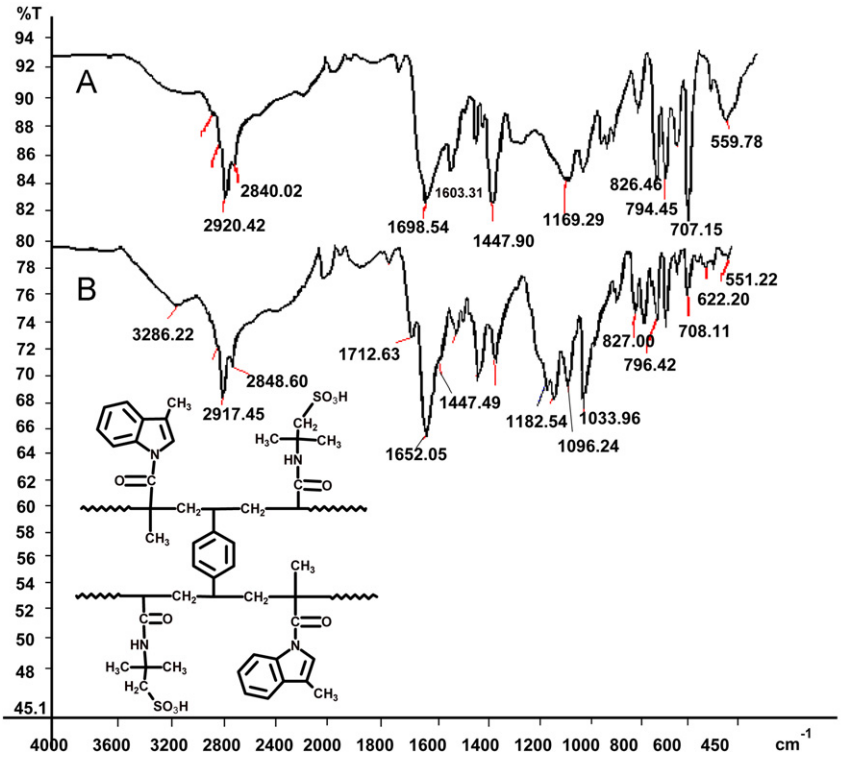

Fig. 2. Structure of the chelating resin (Poly[N-(3-methyl-*1H*-indol-1-yl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propane sulfonic acid-co-divinylbenzene]).

Subsequently, the resin was filtered and washed with abundant diethylether and dried under vacuum at 60 °C until a constant weight was obtained. The conversion of monomer to polymer resin was determined gravimetrically. The obtained chelating resin was 1.22 g.

2.4. Characterizations of monomer and chelating resin

2.4.1. 2-Methyl-1-(3-methyl-1H- indol-1-yl)prop-2-en-1-one

IR (ATR) (cm^{-1}): 2940, 2920, 2840 (aliphatic C–H), 1698 (C=O), 1603 (CH_2=C–), 1448 (aromatic, C=C), 1169 (C–O–C), 826, 794, 707 (aromatic C–H def. out-of-plane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (d, 1H, *J* 7.8 Hz, H-7), 7.32 (d, 1H, *J* 12 Hz, H-4), 7.08-7.02 (m, 2H, H-2, H-6), 6.98-6.94 (m, 1H, H-5), 5.94 (d, 1H_a, *J* 1.2, =C<u>H</u>), 5.53 (t, H_b, *J* 1.8, =C<u>H</u>), 2.74 (s, 3H, CH_3, in indole ring), 1.83 (s, 3H, CH_3). ^{13}C-NMR (400 MHz, $CDCl_3$) δ (ppm): 162.7 (1C, C=O), 138.0 (1C), 136.7 (1C), 128.3 (1C, C-8), 124.5 (2C, C-2, C-9), 123.0 (2C, C-5), 121.2 (1C, C-6), 118.6 (2C, C-4, C-7), 111.6 (1C, C-3), 31.1 (1C, CH_3, in indole ring), 18.71 (1C, CH_3).

2.4.2. Chelating resin

IR (ATR) (cm^{-1}): 3300–3190 (–NH), 2980, 2917, 2848 (aliphatic C–H), 1712 (C=O), 1652 (N–C=O), 1647 (aromatic, C=C), 1384 (C–N), 1196 (C–O–C), 1033 (–SO), 800 and 570 (aromatic C–H and C–C out of plane). ^{1}H-NMR (400 MHz, DMSO-d6) δ (ppm): 8.45 (s, 2H, NH), 7.94 (s, 4H, CH), 7.44 (d, 2H, *J* 7.7 Hz, H-7), 7.32 (d, 2H, *J* 8 Hz, H-4), 7.08 (s, 2H, H-2), 7.06–7.01 (m, 2H, H-6), 6.95–6.93 (m, 2H, H-5), 3.35 (s, 4H, CH_2), 3.11–3.05 (m, 2H, CH), 2.72 (s, 6H,CH_3), 2.50–2.48 (m, 2H, CH), 2.23 (d, *J* 1, 2H, OH, in sulfonic acid), 1.42 (s, 18H, CH_3), 1.23–1.15 (m, 12H, CH_2), 1.0–0.98 (m, 8H, CH_2). ^{13}C-NMR (400 MHz, DMSO-d6) δ (ppm): 172 (1C, CO), 164 (1C, CO), 136.6–109.6 (aromatic C), 60.6 (2C, CH_2SO_3H), 36.2 (6C, CH_3), 52.0–9.05 (aliphatic C). The structures of the monomer and the chelating resin and their FT-IR spectra are given Fig. 2.

2.5. Column preparation

50 mg of the chelating resin was packed into a minicolumn. A slurry of the polymer beads was injected into the minicolumn with a syringe. The ends of the minicolumn were fitted with glass wool to retain the packing material. Before use, ethanol, a 3 mol L^{-1} nitric acid solution and deionized water were passed through the minicolumn at a flow rate of 2.5 mL min^{-1} in order to clean it. Washing with nitric acid and ethanol was necessary in order to prevent any metal and/or organic contamination. All the minicolumns prepared in this way showed good reproducibility. The resin bed was approximately 1 cm in length. The packed column was washed with blank solutions to condition the chelating resin. After each elution cycle, it was automatically pre-treated with deionized water and buffer solution, respectively.

2.6. On-line preconcentration system

The performance of the on-line preconcentration method was tested with model solutions before its application to real samples. The schematic diagram of the flow injection (FI) manifold and operational sequence for on-line separation and preconcentration system coupled with FAAS is illustrated in Fig. 3 [21]. In the preconcentration step, PP1 and V1 were active while PP2 and V2 were inactive, and the sample and/or standard solutions buffered properly with CH_3COOH/NaOH solution (pH 3) were continuously passed through the minicolumn (MC) for 3.4 min at a flow rate of 4 mL1 – min^{-1}. The silver (I) ions were retained in the minicolumn while the effluent was sent to the nebulizer-burner system of the spectrometer. All the wastes obtained from the on-line preconcentration manifold were directly introduced to the spectrometer. Afterwards, the minicolumn was washed with water in order to remove any matrix ions. At this period, PP1 and V2 were active while PP2 and V1 were inactive. Finally, in the elution step, the eluent (E), 3 mol L^{-1} HCl, was aspirated by the PP2 at a flow rate of 3.6 mL min^{-1}. During elution, PP1 was inactive. The released silver

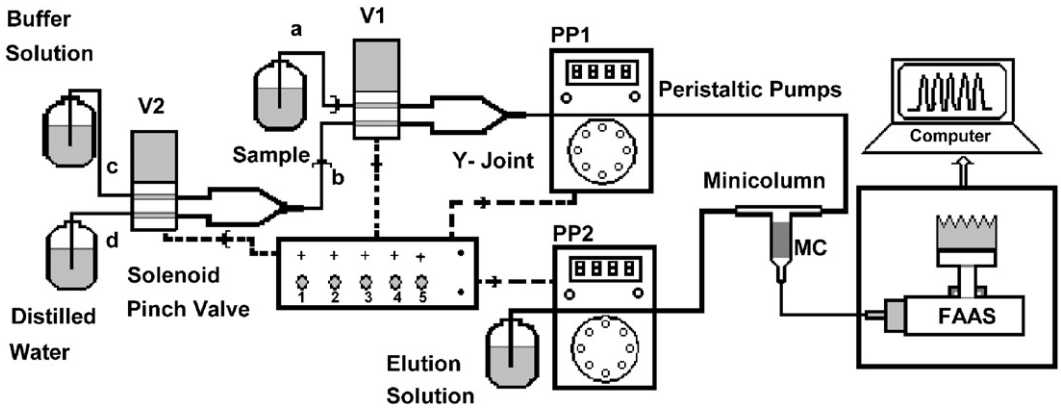

Fig. 3. Flow injection manifold and operational sequence for on-line separation and preconcentration system coupled with FAAS for the determination of Ag(I). PP1, PP2: peristaltic pumps; V1, V2: valves; E: eluent; MC: minicolumn; T: timer; S: sample; B: buffer solution; DW: distilled water; a, b, c, d: solution routes.

ions were directly transported to the nebulizer of the spectrometer. The signals were measured in the peak area mode using the instrument software. In the following step, the minicolumn was washed with water (PP1 and V2 were active, PP2 and V1 were inactive) to clean the resin. Afterwards, the buffer solution was pumped to the minicolumn to condition it before a new preconcentration cycle. During this period, PP1 and V2 were active while PP2 and V1 were inactive. The calibration curve was linear for Ag(I) concentrations in the range of 2–20 $\mu g\,L^{-1}$, with a regression coefficient of 0.9987. Real sample solutions were similarly subjected to the on-line procencentration procedure as described above.

2.7. Application of the proposed method

The proposed method was successfully applied for the on-line determination of Ag(I) in various water samples. The water samples were collected in pre-washed polyethylene bottles. 2 mL of concentrated HNO_3 (65%, w/w) was added to 100 mL aliquots of each of the water samples and the proposed procedure was applied to these sample solutions. A 5-g portions of nut samples were dissolved in a mixture of 40 mL concentrated HNO_3 and 10 mL of concentrated H_2O_2 and then evaporated near to dryness, and the moist residue was completed to 50 mL with water by adjusting pH 3 with acetate buffer. Afterwards, the on-line preconcentration procedure was applied to these pretreatment sample solutions.

Analyses for blank samples were carried out in the same way. Then the on-line preconcentration procedure given above was applied to the samples. The determination of Ag(I) ions in the final solutions was performed by FAAS.

In order to ascertain the accuracy of the proposed procedure, the method was applied for the analysis of Ag(I) ions in the two certified reference materials (NCS DC 73349 bush branches and leaves and CWW-TM-D waste water). 10 mL aliquots of waste water standard sample were treated with 1 mL of HNO_3. A 2-g of NCS DC 73349 bush branch sample was dissolved in a mixture of 30 mL concentrated HNO_3 and 6 mL concentrated H_2O_2 and then evaporated near to dryness, and the moist residue was completed to 50 mL with water by adjusting pH 3 with the acetate buffer. Afterwards, the on-line preconcentration procedure was applied to these pretreatment sample solutions.

3. Results and discussion

The chemical and hydrodynamic conditions in the flow injection on-line separation/preconcentration system were optimized by applying the proposed procedure to model solutions involving 10 $\mu g\,L^{-1}$ silver in which the following important analytical parameters were tested individually and precisely.

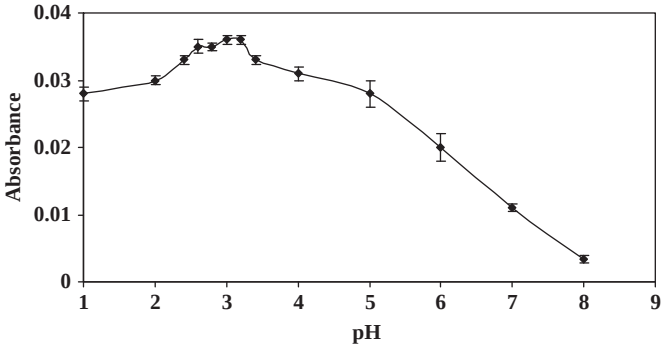

Fig. 4. Effect of pH on the absorbance of Ag(I).

3.1. Effect of pH

To find the optimal conditions for the on-line separation/preconcentration of trace silver, a careful examination of the effect of pH was carried out. The pH values, from 1 to 8, of the model solutions including 10 $\mu g\,L^{-1}$ silver were individually adjusted for each pH by using the relevant solutions (*see* Section 2.2. *Reagents and solutions*). The retention conditions of the analyte were optimized by evaluating the analytical signals monitored during the measurement with FAAS while changing the pH of the solutions that pass through the minicolumn in the flow system. The solutions were pumped through the minicolumn packed with the resin for a loading time of 3.4 min. As illustrated in Fig. 4, the absorbance of the analyte increases with increasing pH of the sample solution from 1 to 2.8 and then a significant decrease appears beyond pH 3.4, probably the concomitant ions may compete with the analyte ions for the binding sites of the resin. For pHs lower than 3, for competition between protons and the analyte for the adsorption sites may be responsible from the low anaytical signals. Considering these results, the acetate buffer of pH 3 was suggested since the solution provides a higher analytical signal. In the light of these results, the optimum pH of the flow system was chosen as 3.

3.2. Flow rates of sample and eluent

The flow rate of the sample solution establishes the contact time between the analyte and the chelating resin. At high sample flow

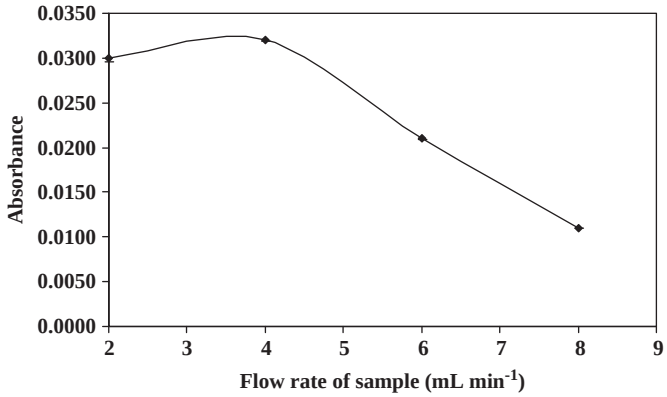

Fig. 5. Effect of flow rates of sample solution on Ag(I) signals.

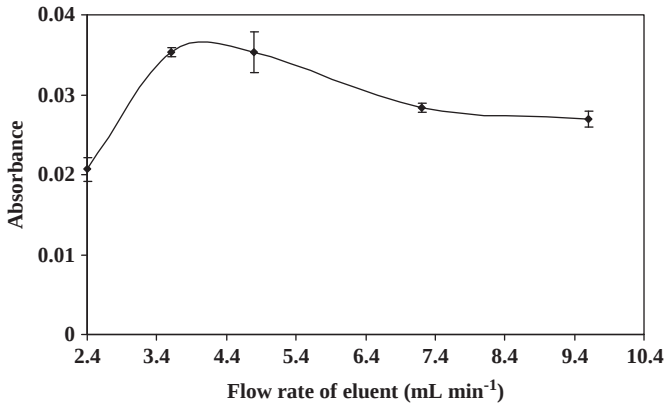

Fig. 6. Effect of flow rate of the eluent on Ag(I) signals.

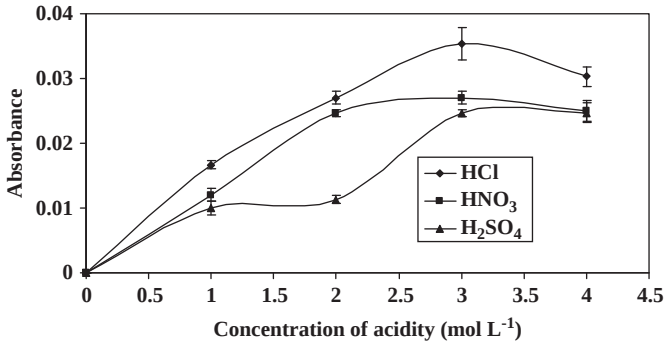

Fig. 7. Effect of acid concentration on Ag(I) signals.

Table 1
Effect of foreign ions in the determination of 10 μg L^{-1} Ag(I) using the on-line preconcentration system.

Ions	Added as	Concentration (mg L^{-1})	Recovery (%)
Na^{+} [a]	$NaNO_3$	750	95 ± 2
K^{+}	KNO_3	500	100 ± 1
Ca^{2+}	$Ca(NO_3)_2.4H_2O$	250	96 ± 1
Mg^{2+}	$Mg(NO_3)_2.6H_2O$	250	98 ± 2
Zn^{2+}	$Zn(NO_3)_2$	10	98 ± 1
Fe^{3+}	$Fe(NO_3)_3.6H_2O$	10	100 ± 1
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	10	98 ± 2
Al^{3+}	$Al(NO_3)_3.9H_2O$	10	99 ± 1
Cu^{2+}	$Cu(NO_3)_2.4H_2O$	10	100 ± 1
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	10	95 ± 1
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	10	95 ± 1
SO_4^{2-}	Na_2SO_4	1000	98 ± 1
$H_2PO_4^{-}$	$NaH_2PO_4.2H_2O$	1000	100 ± 2

[a] Mean ± s.

rates, Ag(I) ions could probably not equilibrate properly with the resin (50 mg) due to the increase in velocity of the ions, which reduces the contact time between the two phases. In contrast, low flow rates decrease the sample throughput, resulting in long analysis times. For this reason, the effect of the flow rates of the sample solution on the quantitative adsorption of silver(I) ions was considered by varying the flow rates from 2 to 10 mL min^{-1} while keeping the amount of analyte constant (10 μg Ag(I) L^{-1}). The results are illustrated in Fig. 5. The sample flow rate was maximum at around 4 mL−min^{-1}. Consequently, the optimum flow rate of sample solution was chosen to be 4 mL min^{-1} in subsequent experiments as a compromise between efficiency and stability.

The eluent flow rate is another important parameter for stripping the analyte off the column. In order to get as high an analytical signal as possible, the eluent flow rates were scanned. The scanning was carried out from 1.2 to 9.6 mL min^{-1} at pH 3 by using 50 mg of the resin. The results obtained are shown in Fig. 6. The optimum flow rate was selected to be 3.6 mL min^{-1} for subsequent studies in order to match the elution and the nebulization flow rates.

3.3. Effects of eluent type

The desorption of the retained silver ions from the minicolumn was tested using HCl, HNO_3, and H_2SO_4 solutions. The results obtained are shown in Fig. 7, from which it is clear that the 3 mol L^{-1} HCl solution is the best eluent. Increasing HCl concentration from 3 to 4 mol L^{-1} did not give any improvement in the silver signals. Therefore, a 3 mol L^{-1} HCl solution was chosen as eluent for stripping off Ag(I) from the column in subsequent experiments.

3.4. Effect of foreign ions

The effect of interferences on the determination of silver was investigated using the optimized on-line preconcentration procedure. Metal ions naturally and/or artificially occurring in water were added individually to model solutions containing 10 μg L^{-1} Ag(I) and then the proposed procedure was applied. The effect of each species was considered as interference when the analytical signal in the presence of the species resulted in an absorbance change or variation of more than ±5%. The results are shown in Table 1. The results indicate that various substances commonly present in water samples do not interfere in the analysis of silver(I) under experimental conditions.

3.5. Analytical figures of merit

The characteristic data for the performance of the on-line preconcentration system under optimum conditions were studied. The flow injection system showed a linear response within the concentration range from 2 to 20 μg L^{-1} Ag(I) for 3.4 min of sample loading time. The calibration curves under the optimum flow conditions were obtained by using the least squares method, i.e., $A = 0.0012 + 3.308 \times C_{Ag}$, where A is the absorbance and C_{Ag} is the Ag(I) concentration in the standard solutions.

The enrichment factor is described as the ratio of the slope of the on-line calibration curve to the slope of the off-line calibration curve. By using this definition, the enrichment factor was found to be 65. The detection limit which is defined as the concentration that gives a response equivalent to three times the standard deviation of the blank solutions ($n=25$) was 0.3 μg L^{-1}. The precision for ($n=25$) replicate measurements was 1.5% (as relative standard deviation, RSD) at the 10 μg L^{-1} Ag(I) level.

Table 2
The determination of silver(I) in the standard reference materials by using the presented on-line preconcentration procedure.

Sample	Certified value	Found	Recovery (%)
CWW-TM-D waste water ($mg\ L^{-1}$, $n=3$)	0.25 ± 0.01	0.244 ± 0.002[a]	98 ± 1
NCS DC 73349 bush branches and leaves ($\mu g\ g^{-1}$, $n=5$)	0.049 ± 0.007	0.047 ± 0.004	96 ± 2

[a] Mean ± s.

Table 3
The determination of silver in the various water samples after the application of the presented procedure ($n=5$).

Water samples	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)
Moulding water	–	4.63 ± 0.04[a]	–
	3	7.63 ± 0.14	100 ± 2
	6	10.72 ± 0.21	101 ± 2
	12	16.30 ± 0.45	98 ± 3
Gelingüllü dam water	–	5.76 ± 0.15	–
	3	8.76 ± 0.08	100 ± 1
	6	11.67 ± 0.15	99 ± 1
	10	15.75 ± 0.22	100 ± 1
Dereköy 1679	–	3.75 ± 0.10	–
	3	6.67 ± 0.14	99 ± 2
	6	9.56 ± 0.15	98 ± 1
	12	15.59 ± 0.15	99 ± 1
Akdağ pit	–	7.02 ± 0.10	–
	3	9.86 ± 0.19	98 ± 2
	6	13.01 ± 0.21	100 ± 2
	10	16.97 ± 0.17	100 ± 1
Sorgun pit	–	6.28 ± 0.18	–
	3	9.22 ± 0.11	99 ± 1
	6	11.92 ± 0.22	97 ± 2
	10	16.41 ± 0.28	101 ± 2
Waste water (with boric acid)			
	–	3.15 ± 0.11	–
	3	6.08 ± 0.08	99 ± 1
	6	8.99 ± 0.16	98 ± 2
	10	12.97 ± 0.13	99 ± 1
Waste water (with H_2SO_4)	–	–[b]	–
	5	4.90 ± 0.04	98 ± 1
Dereköy Ayraklı	–	–	–
	5	4.87 ± 0.07	97 ± 2
Alacadağlar Çoban fountain	–	–	–
	5	4.93 ± 0.04	99 ± 1
Dereköy 1682	–	–	–
	5	4.99 ± 0.07	100 ± 2
Nut samples	Added ($\mu g\ g^{-1}$)	Found ($\mu g\ g^{-1}$)	
Walnut	–	0.035 ± 0.005	–
	0.03	0.062 ± 0.003	95 ± 1
	0.06	0.092 ± 0.004	97 ± 2
	0.10	0.128 ± 0.006	95 ± 2
Hazelnut	–	0.024 ± 0.003	–
	0.03	0.053 ± 0.001	98 ± 2
	0.06	0.083 ± 0.001	99 ± 1
	0.10	0.120 ± 0.007	97 ± 3
Nut	–	–	–
	0.03	0.029 ± 0.001	97 ± 3
	0.06	0.058 ± 0.002	97 ± 3
	0.10	0.096 ± 0.005	96 ± 1

[a] Mean ± s.
[b] Below the detection limit.

3.6. Accuracy and applications of the method

The accuracy of the developed method was tested by measuring the silver content in the two certified reference materials (CWW-TM-D waste water and NCS DC 73349 bush branches and leaves).

The silver contents established with the present procedure agreed very well with the certified values (Table 2). The results indicate that the developed procedure can be applied to the determination of silver(I) in the reference water samples.

The method was extended for the on-line determination of Ag(I) in various water samples. Preparation of the water samples for analysis was performed as described above in Section 2.7. The results are shown in Table 3. The proposed method was applied for the analysis of various water samples, with satisfactory results. The concentration of silver could not be determined due

Table 4
Comparison of the methods given in the literature for the separation, preconcentration and determination of silver(I) ion.

Method	Technique	DL ($\mu g\ L^{-1}$)	RSD (%)	Preconcentration factor	pH	Reference
SPE	FAAS	–	5.3	100	3	[2]
SPE	ICP-MS	700	–	50	5	[3]
SPE	FI-AAS	1.7	4	125	3-4	[4]
SPE	FI-FAAS	0.2	3.1	110	2	[5]
SPE	FI-FAAS	–	3.03	130	3.5	[7]
SPE	FAAS	6	–	360 (for sample volume: 1800 mL)	1–7	[22]
SPE	FAAS	–	2.04	300 (for sample volume: 300 mL)	3	[23]
SPE	FI-FAAS	0.3	1.5	65	3	This work

to its very low concentration. The recoveries for the additions of different amounts of Ag(I) varied from 95% to 101% (see Table 3). These results prove the validity of the proposed method. There was good agreement between added and the recovered amounts of the analyte.

4. Conclusions

A newly synthesized chelating resin, poly[N-(3-methyl-*1H*-indol-1-yl)-2-methacrylamide-co-2-acrylamido-2-methyl-1-propane sulfonic acid-co divinylbenzene] (MMAD) was for the first time used, and the possibilities of its utilization in an on-line preconcentration system for the determination of silver(I) ions by FAAS were successfully tested. Due to its high tolerance to interferences from the matrix, the proposed procedure was demonstrated to be promising for trace silver analysis. The relative standard deviation and preconcentration factor of the method were found to be satisfactory, i.e., 1.5% and 65, respectively. The elution was easily performed with 3 mol L^{-1} HCl. The method has a linear range from 2 to 20 $\mu g\ L^{-1}$ Ag(I). The advantages of this method are: low cost, simplicity, rapidity, studying in acidic medium required for Ag(I) separation/preconcentration. All processes are made automatically by the system itself which prevents contamination from the working ambient. The proposed method shows very good sensitivity and precision and has some significant advantages over the other preconcentration methods reported in the literature. A comparison of the described method with other preconcentration methods for silver is given in Table 4. As can be seen from Table 4, our results seem to be fairly comparable with the others.

References

[1] I.M. Dittert, D.L.G. Borges, B. Welz, A.J. Curtius, H. Becker-Ross, Microchim. Acta 167 (2009) 21–26.
[2] G. Absalan, M. Akhond, A.Z. Ghanizadeh, Z.A. Abedi, B. Tamami, Sep. Purif. Tech. 56 (2007) 231–236.
[3] R.K. Katarina, T. Takayanagi, M. Oshima, S. Motomizu, Anal. Chim. Acta 558 (2006) 246–253.
[4] S. Dadfarnia, A.M.H. Shabani, M. Gohari, Talanta 64 (2004) 682–687.
[5] C.K. Christou, A.N. Anthemidis, Talanta 78 (2009) 144–149.
[6] M. Akhond, G. Absalan, L. Sheikhian, M.M. Eskandari, H. Sharghi, Sep. Purif. Tech. 52 (2006) 53–59.
[7] T. Madrakian, A. Afkhami, M.A. Zolfigol, M. Solgi, J. Hazard. Mater. B128 (2006) 67–72.
[8] G. Yang, W. Fen, C. Lei, W. Xiao, H. Sun, J. Hazard. Mater. 162 (2009) 44–49.
[9] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, J. Anal. At. Spectrom. 17 (2002) 1330–1334.
[10] P. Liu, Z. Su, X Wu, Q. Pu, J. Anal. At. Spectrom. 17 (2002) 125–130.
[11] S. Zhang, Q. Pu, P. Liu, Q. Sun, Z. Su, Anal. Chim. Acta 452 (2002) 223–230.
[12] P. Liu, Q. Pu, Z. Su, Analyst 125 (2000) 147–150.
[13] Q. Pu, Q. Sun, Z. Hu, Z. Su, Analyst 123 (1998) 239–243.
[14] P.P. Coetzee, I. Taljaard, H. de Beer, Fresenius J. Anal. Chem. 336 (1990) 201–204.
[15] C.S. Gong, X.W. Guo, Z.X. Su, Yejin Fenxi 16 (1996) 9–15.
[16] S. Pei, Z. Fang, Anal. Chim. Acta 294 (1994) 185–193.
[17] Ş. Saçmacı, Ş. Kartal, Y. Yılmaz, M. Saçmacı, C. Soykan, Chem. Eng. J. 181–182 (2012) 746–753.
[18] S.L. Qi, Z.P. Wu, D.Z. Wu, W.T. Yang, R.G. Jin, Polymer 50 (3) (2009) 845–854.
[19] M.A.A. El-Ghaffar, M.H. Mohamed, K.Z. Elwakeel, Chem. Eng. J. 151 (1–3) (2009) 30–38.
[20] Z. Çelik, M. Gulfen, A.O. Aydın, J. Hazard. Mater. 174 (2010) 556–562.
[21] S. Şahan, Ş. Saçmacı, U. Şahin, A. Ülgen, Ş. Kartal, Talanta 80 (2010) 2127–2131.
[22] M.K. Rofouei, M. Payehghadr, M. Shamsipur, A. Ahmadalinezhad, J. Hazard. Mater. 168 (2009) 1184–1187.
[23] A. Safavi, N. Iranpoor, N. Saghir, Sep. Purif. Tech. 40 (2004) 303–308.