

## Synthesis of Nano-Pore Size Ag(I)-Imprinted Polymer for the Extraction and Preconcentration of Silver Ions Followed by Its Determination with Flame Atomic Absorption Spectrometry and Spectrophotometry Using Localized Surface Plasmon Resonance Peak of Silver Nanoparticles

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Silver ion imprinted polymer (IIP) was synthesized in the presence of Ag(I)-*N,N'*-bis(salicylidene) ethylenediamine (salen) complex using 4-vinylpyridine as the functional monomer, ethylene glycol dimethacrylate (EGDMA) as the crosslinker, and 2,2-azobis(isobutyronitrile) (AIBN) as the initiator. The Ag(I)-imprinted polymer (IIP) particles were characterized by SEM (scanning electron microscope), FTIR (Fourier transform infrared spectroscopy) and BET/BJH (Brunauer-Emmett-Teller/Barrett-Joyner-Halenda) analysis. The imprinted Ag(I) ions were completely removed by leaching the IIP with thiourea (0.5 mol L<sup>-1</sup>). The polymer was employed as a selective sorbent for extraction and separation of the trace amounts of the Ag(I) ions. The preconcentrated ion was determined via the flame atomic absorption spectrometry (FAAS) or it was reduced to silver nanoparticles and quantified by spectrophotometry based on its localized surface plasmon resonance peak (LSPRP). The figures of merit of both methods were compared. Under the optimized conditions, a sample volume of 80 mL resulted in an enhancement factor of 312. The detection limit (3S<sub>b</sub>/m) and the relative standard deviation (n = 10) at 10 µg L<sup>-1</sup> level for FAAS were found to be 0.06 µg L<sup>-1</sup>, 2.9%, whereas for the LSPRP method they were 0.5 µg L<sup>-1</sup> and 10.3%, respectively. The methods were successfully applied to the determination of silver in radiology film, hair, nails, and water samples.

**Keywords:** silver, solid phase extraction, ion imprinted polymer, silver nanoparticles, localized surface plasmon resonance peak, flame atomic absorption spectrometry

### Introduction

Silver is a precious metal used by humans for thousands of years. It is widely used in photography, electrical equipments, mirrors, medical and dental equipments, jewelry and artwork, pharmaceutical preparations, manufacturing of fungicides, and disinfection of water.<sup>1,2</sup> Silver, a mildly toxic element, plays no known natural biological role in humans, but in large doses, silver and its compounds can be absorbed into the circulatory system and become deposited in various body tissues leading to argyria which results in a blue-grayish pigmentation of the skin, eyes and mucous membranes.<sup>3</sup> However, it is well recognized that silver is a toxic element to many aquatic organisms even at low concentrations.<sup>4</sup> Thus, the determination of the trace amounts of silver in water and

the environmental samples is of great importance. Up to now, various elemental analysis techniques have been applied for the determination of silver ions in different matrices including inductively coupled plasma optical emission spectrometry (ICP OES),<sup>5</sup> inductively coupled plasma mass spectrometry (ICP-MS),<sup>6</sup> and flame and electrothermal atomic absorption spectrometry (FAAS and ETAAS).<sup>7-10</sup> Among these techniques, FAAS is the most frequent chosen one because of its speed and ease of operation, but its major drawbacks for the direct measurement of trace amounts of silver ions are interfering matrix components as well as insufficient detection limit.<sup>11</sup> The spectrophotometric method is also a relatively inexpensive and easily operated technique, however, it lacks the required selectivity and sensitivity for the trace metal determination. Thus, for the ultratrace determination of silver by the FAAS or the spectrophotometric method, a selective separation and preconcentration step is required.

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Different separation and enrichment methods have been used prior to the determination of silver ions including liquid-liquid microextraction,<sup>12</sup> cloud point extraction (CPE),<sup>7</sup> floatation<sup>13,14</sup> and solid phase extraction (SPE).<sup>15-19</sup> Among these methods, SPE has gained rapid acceptance because of its simplicity, flexibility, high enrichment factors, high recovery, low consumption of reagents, as well as being relatively free of hazardous solvents.<sup>20-23</sup> A very important focus in studies on SPE is the use of new sorbents with high selectivity, chemical and mechanical stability and sensitivity. Among different sorbents used in SPE methods, recently new materials named ion-imprinted polymers (IIPs) have attracted great attention.<sup>24-27</sup> IIPs are synthetic polymers with a predetermined selectivity for a given target ion. The selectivity of the sorbent is due to the three dimensional structure (3D) of the complex which is based on the coordination geometry and coordination number of the ions which is consequently correlated to the charges and sizes of the ions. These sorbents are synthesized in a process in which a functional monomer and a crosslinker are typically polymerized in the presence of a template ion. The subsequent removal of the template ion leaves a predetermined arrangement of ligands and a tailored binding pocket.<sup>28</sup> The resulting imprinted polymer is capable of selective sorption of the template ion. IIPs have been widely applied in solid phase extraction of metal ions.<sup>29-34</sup> But, according to our literature survey, there is only one published paper dealing with the synthesis and the use of the IIP for the selective extraction of silver ions.<sup>35</sup>

Another ongoing field in analytical chemistry is sensing colorimetric approaches based on nanoparticles (NPs) aggregation (colorimetric assays). One of the most important characteristics of metal NPs such as Au and Ag is an absorption band which is the results of the resonant of the incident photon frequency with the collective oscillation of the conduction electrons and is called the localized surface plasmon resonance (LSPR).<sup>36</sup> As a result of this phenomenon strong absorption band(s) with extremely large molar extinction coefficients or increased scattering intensity of the radiation occurs at certain wavelengths for the metal NPs.<sup>37</sup> LSPR of the NPs is mainly related to the NP size, shape, composition, interparticle distance, and dielectric constant (refractive index) of the surrounding medium.<sup>38-40</sup> In recent decades, sensing colorimetric approaches based on NPs aggregation have received considerable attention.<sup>41-43</sup> This is because of their excellent analytical performance exhibited in terms of selectivity and sensitivity, as well as their extreme simplicity and low cost since this kind of assay does not require any expensive or complex instrumentation. However, to the best of our knowledge the spectrophotometric method based on LSPR

had not been used for quantification of low concentration of silver.

The aim of this study is three fold: (i) synthesise of an ion imprinted polymer based on the complex of silver with salen (*N,N'*-bis(salicylidene)ethylenediamine) and considering its capability in separation and preconcentration of silver from samples with complex matrices; (ii) determination of the extracted and preconcentrated silver with the LSPR spectrophotometry as a new method for quantification of silver and with FAAS and (iii) comparing the analytical performance of FAAS and LSPR spectrophotometry.

## Experimental

### Apparatus

The measurements were done with an Analytik Jena atomic absorption spectrometer (model 330, Germany) using a silver hollow cathode lamp and an air-acetylene flame or with an Avantes photodiode array spectrophotometer (model AvaSpec-2048, The Netherlands) with a source model of Ava Light-DH-S-BAL equipped with a microcell of 70  $\mu\text{L}$  capacity and a 1 cm path length. The FAAS was operated under conditions recommended by the manufacturer, i.e., the wavelength of 328.1 nm, slit width 1.2 nm and the lamp current of 4.0 mA. The samples were introduced to FAAS using a single line flow injection system consisting a peristaltic pump (Ismatic, MS-REGLO/8-100, Switzerland) with silicone rubber tubing, and a rotary injection valve (Rheodyne, USA) with a loop of 200  $\mu\text{L}$  capacity. The pH measurements were done with a Metrohm 691 pH meter (Switzerland) using a combined glass calomel electrode. A Haiddolph heater stirrer (model MR 3200, Germany) was used for the polymer synthesis and a centrifuge (Shand Teb Aria, Iran) was used for the phase separation.

### Standard solutions and reagents

All chemicals used throughout this study were of highest purity available and were at least of analytical reagent grade. 4-vinylpyridine (4-VP), ethylene glycol dimethacrylate (EGDMA), thiourea, chloroform, acetonitrile, ammonia solution (25 wt.%), polyvinylpyrrolidone (PVP), sodium tetrahydroborate ( $\text{NaBH}_4$ ) and silver nitrate were purchased from the Merck Company (Germany). 2,2'-azobisisobutyronitrile (AIBN) was purchased from the ACROS Company (USA) and *N,N'*-bis(salicylidene)ethylenediamine (salen) with the formula of  $\text{C}_{16}\text{N}_2\text{O}_2\text{H}_{16}$  was synthesized and purified as illustrated elsewhere.<sup>44,45</sup> Double distilled water was used during the study. A stock solution of 1000  $\text{mg L}^{-1}$  of silver was prepared by dissolving

an appropriate amount of silver nitrate in 1% nitric acid solution. Working solutions were prepared daily from the stock solution by serial dilutions with double distilled water. The glassware used was kept in 10% nitric acid overnight and was subsequently rinsed several times with double distilled water before use.

#### Synthesis of silver ion imprinted polymer

The ion imprinted polymer was prepared by the thermal polymerization. In the initial experiment, it was proved by Job's method that Ag(I) forms a 1:1 complex with the *N,N'*-bis(salicylidene)ethylenediamine (salen). Then, the complex of Ag(I) with salen was prepared by the slow addition of 1 mmol of silver nitrate to 15 mL mixture of chloroform/acetonitrile (1:1) containing 1 mmol of salen. The mixture was then stirred for 45 min to ensure the formation of the complex. Then, 8 mmol of 4-vinylpyridine monomer was added and stirred for another 60 min until the reaction of 4-vinylpyridine and silver complex was completed. Afterward, 32 mmol of ethylene glycol dimethacrylate (EGDMA) as the crosslinker and 50 mg of AIBN as the initiator were added to the mixture. The mixture was cooled to 0 °C, purged with N<sub>2</sub> for 15 min, sealed and thermally polymerized in a water bath. The temperature was slowly raised from the ambient temperature to 55 °C and was maintained at 55 °C for 24 h. The resulting polymer was thoroughly washed with the mixture of deionized water and ethanol (3:1), dried, ground and was sieved to obtain the silver ion imprinted polymer particles. The Ag(I) ions were removed from the synthesized IIP particles upon the treatment with 50 mL of thiourea solution (0.5 mol L<sup>-1</sup>) for 1 h and the silver content was determined by flame atomic absorption spectrometry. The removal process was continued until no silver was detected. The polymer particles were then washed thoroughly with water and were dried in an oven at 55 °C for further use. Control polymer (CP) was prepared by using the same procedure but in the absence of silver ions.

#### Real sample preparation

##### Water samples

Water samples were filtered through a 0.45 μm Millipore filter (USA) and then treated according to the given procedure.

##### Hair and nail samples

The hair and nail samples were prepared as described elsewhere.<sup>46</sup> The samples were rinsed with acetone, chloroform and double distilled water, respectively, and were dried at 60 °C in an oven. 0.7 g of each dried

sample was then transferred to a 50 mL beaker, 12 mL of concentrated HNO<sub>3</sub> and 2 mL concentrated HClO<sub>4</sub> were added and the mixture was first heated at 100 °C for 45 min and then at 150 °C for another 45 min. After dissolution, the solution was cooled to 70 °C while 5 mL of 30% hydrogen peroxide was added. The mixture was heated to dryness, then 10.0 mL of 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> was added to the beaker and was heated for several minutes. After cooling to the ambient temperature, it was filtered; the filtrate was diluted to 100 mL and it was treated according to the given procedure.

#### Radiology film

The radiology film was cut into small pieces and 10 mL of nitric acid solution (6 mol L<sup>-1</sup>) was added to 0.1 g of it. The content was filtered and diluted to 500 mL with deionized water. 1 mL of this solution was further diluted to 250 mL and after the adjustment of pH at 4.0, it was treated according to the given procedure.

#### Reference material

2 mL of concentrated nitric acid was added to 100 mg of the certified reference material of reference copper concentrate (CCU-1b) and was heated near to dryness. Then, 20 mL of double distilled water was added to the residue. The mixture was filtered and transferred to a 50 mL flask, and was diluted to the mark upon the addition of distilled water. After that, 3 mL of this solution was diluted to 100 mL in a volumetric flask while the amount of silver was determined according to the given procedure.

#### Extraction procedure

80 mg of sorbent was added to an 80 mL of standard or sample solution containing not more than 2 μg of silver and the pH was adjusted to 4.0 using dilute nitric acid solution. The mixture was stirred for 20 min and the sorbent was separated by centrifugation and decantation of supernatant solution. Then, under sonic agitation, 250 μL of thiourea solution (0.5 mol L<sup>-1</sup>) at pH ca. 8 was added to the sorbent, the mixture was then stirred for 15 min until the silver was desorbed. The silver content in eluent was introduced to FAAS for quantification via single line flow injection system or it was reduced to NPs and measured by LSPR spectrophotometry as indicated in the next section.

#### Spectrophotometric determination of silver using LSPRP of NPs

For the spectrophotometric determination of silver based on LSPRP, first Ag<sup>+</sup> ions were converted to colloidal

silver nanoparticles with the size of 5-10 nm using the reducing agent of sodium tetrahydroborate ( $\text{NaBH}_4$ ) and stabilizer of polyvinylpyrrolidone (PVP) according to the given procedure in the literature,<sup>47</sup> i.e., 25  $\mu\text{L}$  of 2.0  $\text{g L}^{-1}$  PVP was transferred to a vial and 25  $\mu\text{L}$  of 0.02  $\text{mol L}^{-1}$  sodium tetrahydroborate was added, the solution was mixed and after a few seconds, 200  $\mu\text{L}$  of the eluent containing silver ions was added and the vial was kept in a water bath at 45 °C for 45 min. At this step, the silver nanoparticles were formed and the absorption of their LSPRP was measured at 396 nm.

## Results and Discussion

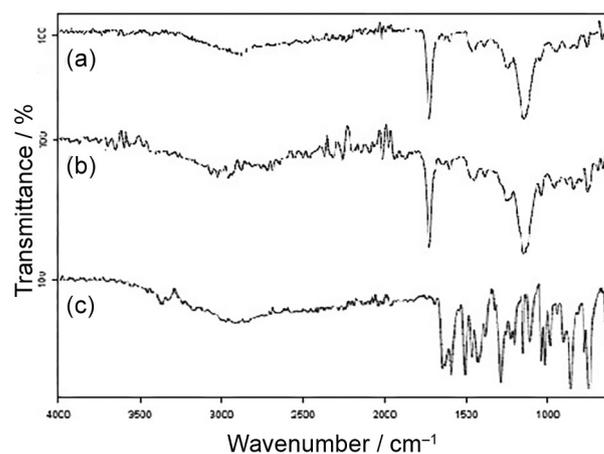
In order to synthesize a sorbent with high capacity and selectivity for silver ions, three different Ag(I)-ion imprinted polymers and the corresponding control polymers were synthesized using ethylene glycol dimethacrylate (EGDMA) as the crosslinker, *N,N'*-bis(salicylidene)ethylenediamine (salen) as the chelating agent and 4-vinylpyridine, styrene or methacrylic acid as the monomer. The synthetic conditions and the capability of resulting IIP for the sorption of silver are summarized in Table 1 indicating that the IIP<sub>1</sub> synthesized by 4-vinylpyridine as the monomer and EGDMA as the crosslinker have the highest capability for the retention of silver while the corresponding control polymer CP<sub>1</sub> has lost. This might be due to the presence of nitrogen heteroatom in the benzene ring of 4-vinylpyridine which in comparison with styrene, increases its affinity to the formation of a complex with silver ions. Similar behavior in the formation of a ternary complex and the improvement of polymer performance with 4-vinylpyridine as the monomer has been reported.<sup>48-50</sup> It should be noted that in the synthesis of IIP<sub>2</sub>, because of the reaction of methacrylic acid and EGDMA as the ester, the polymerization was not very good and the resulting IIP<sub>2</sub> was soft. Therefore, the IIP<sub>1</sub> was selected for further studies. In the synthesis of IIP<sub>2</sub>, the complex of silver ions with salen was formed and then it was polymerized in the presence of 4-vinylpyridine, EGDMA and AIBN. The

salen was then trapped in the polymer matrices offering imprinting cavities for the silver ions.

### Characterization studies

The synthesized IIP<sub>1</sub> was characterized by FTIR (Fourier transform infrared) spectroscopy, scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis. The infrared spectra of the salen, unleached and leached silver imprinted polymers using KBr method are described in Figure 1. The absorption bands of salen, the C–O stretching vibration at 1145  $\text{cm}^{-1}$ , the C=N stretching vibration at 1645  $\text{cm}^{-1}$  and the wide band of O–H stretching vibration around 3000  $\text{cm}^{-1}$ , are observed in both spectra indicating that the unleached and leached polymers have the same backbone and the salen is trapped in the polymer matrix. The decrease in the intensity of these absorption bands in the unleached ion imprinted polymer is the result of their interaction with silver ions.

The morphological characterization of the polymers (leached and unleached) was assessed by SEM. The corresponding SEM micrographs are depicted in Figures 2a



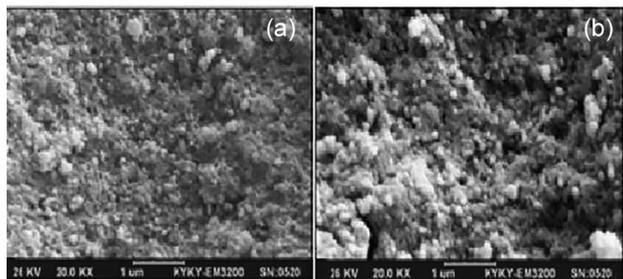
**Figure 1.** FTIR spectra of ion imprinted polymer before leaching (a), after leaching (b) and salen (c).

**Table 1.** Synthesized polymers with different monomers

No.	Silver / mmol	Salen / mmol	Monomer / mmol			EGDMA / mmol	AIBN / mg	Recovery /%
			Sty	MAA	VP			
IIP <sub>1</sub>	1	1	–	–	8	32	50	0.7 ± 60.2
CP <sub>1</sub>	–	1	–	–	8	32	50	30.9 ± 1.2
IIP <sub>2</sub>	1	1	–	14	–	32	50	31.5 ± 1.3
CP <sub>2</sub>	–	1	–	14	–	32	50	24.1 ± 0.9
IIP <sub>3</sub>	1	1	8	–	–	32	50	56.9 ± 0.5
CP <sub>3</sub>	–	1	8	–	–	32	50	32.2 ± 1.6

Sty: styrene; MAA: methacrylic acid; VP: 4-vinylpyridine; EGDMA: ethylene glycol dimethacrylate; AIBN: 2,2'-azobisisobutyronitrile.

and 2b and it seems that the porosity is increased after the removal of the silver ions.



**Figure 2.** SEM image of ion imprinted polymers before leaching (a) and after leaching (b).

The additional information about the surface areas, pore volumes and mean pores diameter of the imprinted polymer before and after leaching was obtained using BET and BJH analysis. The obtained parameters are summarized in Table 2 and Table S1 (see Supplementary Information). As it can be seen, the surface area is significantly increased after leaching. Pore size analysis shows an average pore diameter of < 10 nm. These data confirm the formation of polymer with nano-pore size and high surface area.

**Table 2.** Textural parameters of imprinted polymers based on BET/BJH analysis

Parameter	Imprinted polymer (before leaching)	Imprinted polymer (after leaching)
Surface area / (m <sup>2</sup> g <sup>-1</sup> )	129.28	186.38
V <sub>pores</sub> / (cm <sup>3</sup> g <sup>-1</sup> )	0.2978	0.3039
Mean pore diameter / nm	9.21	6.52

#### Optimization of the experimental variables

In order to find the best conditions for the extraction and determination of silver, the factors affecting the FAAS, spectrophotometry based on LSPRP measurement and the SPE method were optimized using one at a time method. For the sorption and desorption of the analyte by synthesized IIP sorbent, the optimization was performed by measurement of the extracted silver with FAAS only, whereas the analytical performance of the method and determination of silver in real samples was carried out with both of the determination techniques.

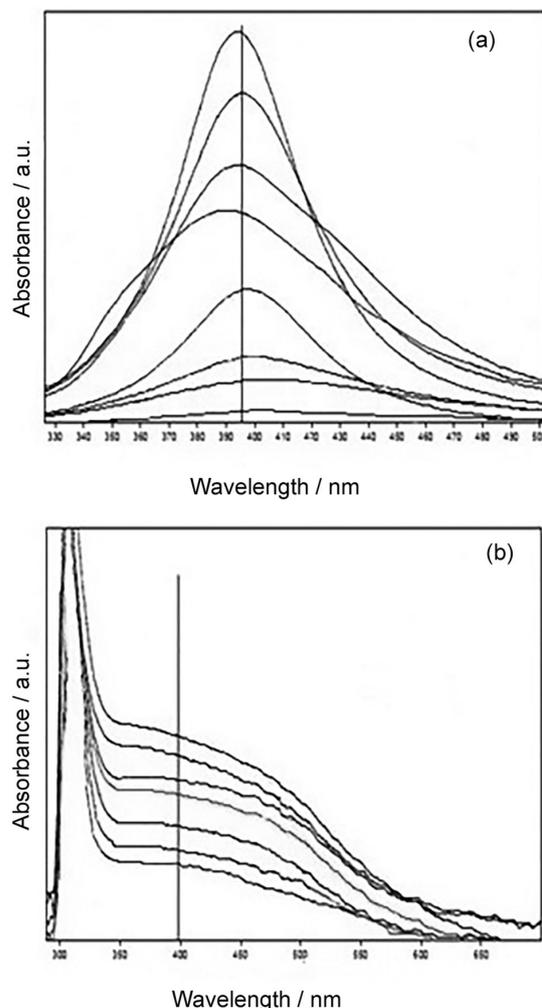
#### Optimization of FI-FAAS

A single line flow injection (FI) system connected directly to the nebulizer inlet tubing was used for the sample introduction to FAAS. The FAAS was operated

under conditions recommended by the manufacturer, but the effect of the sample flow rate (in the range of 3.0-7.0) and the volume of the injection loop (50.0-300 μL) were optimized by the injection of 0.5 mol L<sup>-1</sup> thiourea solution containing 4.0 mg L<sup>-1</sup> of Ag(I). It was found that with a flow rate of 5.0 mL min<sup>-1</sup> of the carrier and a sample loop of 200 μL the transient signal of the analyte was maximum and reproducible. Therefore, these conditions were selected for the FI system.

#### Optimization of spectrophotometric determination of silver based on LSPRP

The LSPRP of different concentrations of silver nanoparticles synthesized in water and thiourea (0.5 mol L<sup>-1</sup>) at pH 8.0 described in Figure 3a indicates that in aqueous solution the maximum absorption of the plasmon peak of silver NPs is at 396.0 nm which is in agreement with the literature value,<sup>48</sup> but the shape of the peak is changed in



**Figure 3.** The LSPRP of different concentration of silver nanoparticles synthesized in water (a) and thiourea solution (b).

the thiourea solution (Figure 3b). This might be due to the interaction of the thiol group with silver ions causing a change in the size and shape of the resulted NPS and consequently the LSPR. However, in this study the wavelength of 396.0 nm was selected for the quantification of the silver.

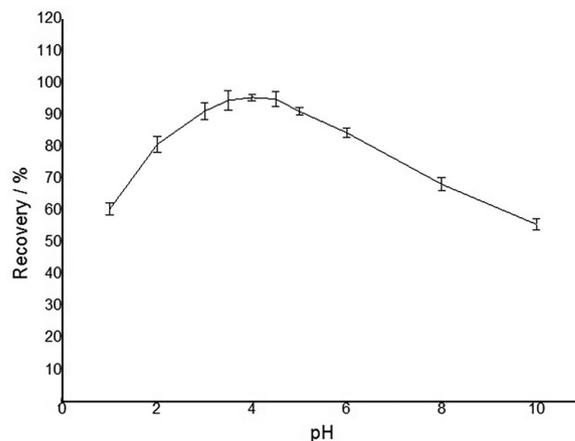
Silver nanoparticles were synthesized from a solution of 4.0 mg L<sup>-1</sup> of silver in thiourea matrix (0.5 mol L<sup>-1</sup>) at pH of ca. 8.0, a condition similar to eluent used for the desorption of the analyte from the IIP sorbent using sodium tetraborohydrate as the reducing agent and PVP as the stabilizer. In order to have minimum dilution of eluent, 25 µL volume of each of the reducing agent and the stabilizer were selected and the effect of their concentration on the surface plasmon peak intensity was investigated in the range of 0.006-0.06 mol L<sup>-1</sup> and 0.4-4.0 g L<sup>-1</sup> of sodium tetraborohydrate and PVP, respectively. The maximum intensity was obtained with 0.02 mol L<sup>-1</sup> of sodium tetraborohydrate and 2.0 g L<sup>-1</sup> of PVP.

The effect of time and temperature on the synthesis of silver NPs was also considered. Because of low volume of reactant, it was found that the synthetic rate of NPs was relatively slow and was completed after 45 min. The effect of temperature was studied by varying the temperature in the range of 30-60 °C and was found that the synthetic rate increases by an increase in temperature up to 45 °C and then remains constant. Thus, optimum time and temperature of 45 min and 45 °C were selected for this study, respectively.

#### Optimization of extraction conditions

The solution pH might affect the retention of silver ions by the sorbent. To investigate this possibility, the extraction of silver from 40 mL sample solution containing 10 µg L<sup>-1</sup> of silver in the pH range of 1.0-10.0 was studied. The pH was adjusted by diluted nitric acid or ammonia solution. The results demonstrated in Figure 4 show that the recovery of silver was maximum and constant in the pH range of 3.0-5.0. The decrease in absorbance at pH greater than 5.0 is probably due to the precipitation of silver as silver hydroxide or competition of ammonia with ligand in the formation of a complex with silver, whereas the signal decrease at pH < 3.0 might be due to the protonation of ligand and the incomplete complexation and retention of silver by the sorbent. Therefore, in order to achieve the maximum efficiency for the silver retention, a pH of 4.0 was selected for the subsequent studies.

The capability of 400 µL of different eluents on desorption of the silver from the sorbent was studied. The result (Table 3) shows that thiourea is the most suitable eluent for desorption of silver due to the strong interaction



**Figure 4.** Effect of sample solution pH on the extraction recovery of silver. Conditions: sample volume 40.0 mL; extraction time 30 min; silver concentration 10 µg L<sup>-1</sup>.

between its thiol group and the analyte. The effect of the thiourea concentration on desorption of silver from IIP was studied by varying its concentration in the range of 0.1-1.0 mol L<sup>-1</sup>. It was found that the extraction recovery increases, with an increase in the thiourea concentration up to 0.5 mol L<sup>-1</sup> and then becomes constant at a higher concentration. Complexation capability of the thiourea is also dependent on the pH of the solution; hence the extraction recovery of the silver was studied using a thiourea solution with pH in the range of 1.0-12.0. The results showed that the extraction recovery was constant and maximum in the pH range of 7.0-9.0. Therefore, the thiourea solution with the pH of ca. 8.0 was chosen as the eluent. The effect of the eluent volume on the recovery of silver was also considered by varying the eluent volume in the range of 150-1000 µL. The results showed that 250 µL of thiourea solution is sufficient for the complete recovery of the retained silver. Thus, 250 µL of thiourea with a concentration of 0.5 mol L<sup>-1</sup> at pH of ca. 8 was selected as the eluent in the subsequent studies.

**Table 3.** Extraction recovery of silver using different desorbing solutions. Conditions: sample volume 40.0 mL; extraction time 30 min; silver concentration 10 µg L<sup>-1</sup>

Desorbing solution	Recovery / %
Nitric acid / (2.0 mol L <sup>-1</sup> )	56.1 ± 2.9
Thiourea / (0.4 mol L <sup>-1</sup> )	95.1 ± 2.6
Sodium thiosulfate / (0.4 mol L <sup>-1</sup> )	81.9 ± 2.7
EDTA / (0.4 mol L <sup>-1</sup> )	33.9 ± 2.9
Methanol	13.0 ± 1.4
Ethanol	19.5 ± 2.5

The ionic strength of the solution can affect the efficiency of the extraction. So, the effect of the ionic strength of the solution on the extraction efficiency was studied by the

extraction of silver ions from the solutions in the range of 0.0-2.0 mol L<sup>-1</sup> of sodium nitrate. It was found that the extraction recovery is not affected by the ionic strength of the solution indicating that the method is suitable for the quantitative recovery of silver from high saline matrices.

The optimum extraction time is reduced to a minimum in order to achieve the equilibrium between the aqueous phase and the sorbent and is an important factor affecting the recovery of the analyte. The influence of the extraction time on its efficiency was studied in the range of 5-30 min under constant experimental conditions. It was observed that the sorption of silver to IIP sorbent increased with an increase in time up to 20 min and then become constant. So, an extraction time of 20 min was chosen for the subsequent studies. Another important factor affecting the extraction rate is desorption time of the analyte from the sorbent. Desorption time is defined as the contact time between the loaded sorbent and eluent for the complete elution of the analyte. Desorption time was studied in the range of 5-30 min and it was found that 15 min was sufficient for the quantitative recovery of the silver.

The mass of the sorbent is the other factor studied, also the mass was varied in the range of 10-200 mg and its effect on the extraction of 10 µg L<sup>-1</sup> of silver from 80 mL of solution was considered. The results showed that 80.0 mg of sorbent was sufficient for the quantitative recovery of the silver.

In SPE, the limit of the dilution is defined as the maximum volume of the solvent with a fixed amount of the analyte that a given amount of sorbent can quantitatively extract the analyte and show the capability of the proposed method for the enrichment of the low concentration of the analyte from the large sample volume. The effect of the sample volume on the extraction of 1.0 µg of silver from different aqueous volumes (20-120 mL) under optimum conditions was examined. The results showed that the recovery was quantitative (≥ 95%) up to 80 mL of the aqueous phase. Thus, the method has the capability of achieving the high concentration factor for the separation and determination of silver.

The quality of the sorbent is the other factor affecting the accuracy, precision and the performance of the SPE method. In this regard, capacity, selectivity, stability, and reusability of the sorbent should be considered. The capacity of the sorbent is the maximum amount of the analyte that can be retained by the sorbent under optimum conditions of the extraction. For this purpose, 25.0 mg of IIP sorbent was added to 50.0 mL solution of 15.0 mg L<sup>-1</sup> of silver under optimum conditions. After 60 min, the sorbent was separated and the remained concentration of silver in the solution was determined by means of FAAS. The

capacity of the IIP for the silver was determined through the differences in the amount of silver in the initial and final solutions. The capacity of the IIP for silver was found to be 18.9 mg g<sup>-1</sup> of the sorbent which indicates the high capacity of sorbent for silver ions. This is due to the proper selection of ligand and the synthetic process which resulted in a sorbent with high porosity and contact surface. The stability and reusability of the sorbent were studied by using the same sorbent in the repeated sorption and desorption process. It was found that the recovery of the silver was not significantly changed (95 ± 3.2%) after twenty cycles. The selectivity of the synthesized sorbent was considered through some interference studies. The interferences of co-existing ions in the extraction of 10 µg L<sup>-1</sup> of silver from 80 mL of sample solution were studied. A relative error of less than 5% was considered to be within the range of the experimental errors. The results are summarized in Table 4 and indicate that the silver recoveries were almost quantitative in the presence of the excessive amount of the possible interfering cations and anions. Thus, the sorbent offers high selectivity toward the extraction of silver which is due to the good tailoring of the pores in the polymer

**Table 4.** The effect of interfering ions on the extraction recovery of silver. Conditions: sample volume 40.0 mL; extraction time 30 min; silver concentration 10 µg L<sup>-1</sup>

Ion	Mol ratio / (ion/silver)	Recovery / % <sup>a</sup>
K <sup>+</sup>	4000	99.6 ± 2.6
Mg <sup>2+</sup>	4000	95.9 ± 2.7
Ca <sup>2+</sup>	1000	95.8 ± 2.1
Mn <sup>2+</sup>	1000	101.3 ± 2.5
Cd <sup>2+</sup>	1000	99.1 ± 1.4
Cu <sup>2+</sup>	4000	102.1 ± 1.9
Co <sup>2+</sup>	4000	95.3 ± 2.5
Al <sup>3+</sup>	4000	104.1 ± 2.9
Fe <sup>3+</sup>	4000	96.1 ± 2.4
Cr <sup>3+</sup>	1000	99.1 ± 1.6
Ba <sup>2+</sup>	1000	100.8 ± 2.4
Ni <sup>2+</sup>	4000	103.1 ± 2.2
Zn <sup>2+</sup>	1000	97.3 ± 1.9
Cs <sup>+</sup>	750	98.7 ± 0.9
Sr <sup>2+</sup>	750	99.1 ± 3.0
Pb <sup>2+</sup>	500	99.6 ± 2.2
Hg <sup>2+</sup>	500	99.9 ± 2.8
NH <sub>4</sub> <sup>+</sup>	1000	98.3 ± 2.5
CO <sub>3</sub> <sup>2-</sup>	1000	97.2 ± 1.7
NO <sub>2</sub> <sup>-</sup>	1000	96.9 ± 2.4

<sup>a</sup>Mean and standard deviation of three independent measurements.

matrix. Furthermore, in order to show that the observed selectivity is attributed to the sorbent, the amount of other ions remained in the binary mixture after the extraction was also determined and no significant change in the concentration of other ions was observed.

#### Analytical performance

The extraction and preconcentration of silver from 80 mL of sample solution under the optimum conditions was done by using synthesized ion imprinted polymer and the extracted silver was determined by FAAS and spectrophotometry based on LSPRP. Under the optimum conditions, with the FAAS measurement, the calibration graph exhibited linearity over the range of 0.4-25.0  $\mu\text{g L}^{-1}$  of silver with the regression equations of  $A = 0.0156C - 4 \times 10^{-5}$  and correlation coefficient of 0.9990; whereas with the LSPRP analysis, the linearity, regression equation, and the correlation coefficient were 3.0-30.0  $\mu\text{g L}^{-1}$ ,  $A = 0.0056C + 0.0122$  and 0.9906, respectively, (where A is the absorbance and C is the concentration of silver ( $\mu\text{g L}^{-1}$ ) in the initial solution. The preconcentration and enhancement factors defined as the ratio of the maximum volume of the initial solution (80 mL) to the final volume of extract (250  $\mu\text{L}$ ) and the ratio of the slope of calibration curves with and without preconcentration were found to be 320 and 312, respectively, using the FAAS measurement. The closeness of the enhancement and the preconcentration factors further indicate that the extraction and desorption of the silver ions are quantitative (> 98%).

The limits of the detection (LOD) and the quantification defined as the three and ten times of the ratio of the standard deviation of blank measurements to the slope of the calibration curve after preconcentration, were found to be 0.06 and 0.2  $\mu\text{g L}^{-1}$  for FAAS and 0.5 and 1.7  $\mu\text{g L}^{-1}$  for LSPRP, respectively. The relative standard deviation (RSD) of intraday and inter day for 10 replicate measurements at 10  $\mu\text{g L}^{-1}$  of silver was obtained to be 2.9% and 3.5% for FAAS and 10.3% and 11.4% for LSPRP, respectively. The figures of the merit of the FAAS measurement and spectrophotometric method based on LSPRP are presented in Table 5. The results indicate that although the sensitivity and reproducibility of LSPRP is lower

than the FAAS method, but combination of SPE with the spectrophotometric method based on LSPRP can be used as an alternative method to FAAS for the determination of the silver ions in various matrices.

#### Application

The accuracy of the recommended procedure was examined through the determination of silver in different water samples, radiology film, and biological samples including hair and nails. The reliability was checked by spiking the sample with two levels of silver and calculating the recovery. As the results of the Tables 6 and 7 shows, the recoveries of the spiked samples were good (94.7-102.0% for FAAS and 93.0-106.0% for LSPRP). The accuracy of the method was further considered by the application of the proposed method to the determination of silver in a certified reference alloy, CCU-1b, with silver concentration of  $178.0 \pm 2.0 \mu\text{g g}^{-1}$ . The amount of silver in CCU-1b found to were  $177.1 \pm 2.6 \mu\text{g g}^{-1}$  and  $174.2 \pm 10.1 \mu\text{g g}^{-1}$  using FAAS and LSPRP measurement, respectively, where the *t*-test indicates that at 95% confidence level there is no significant difference between the obtained values and the accepted ones. Thus, the procedure is capable to determine silver ions in the wide range of samples with complex matrices and the accuracy of both measurement methods are comparable.

#### Comparison of the proposed method with other methods

The analytical performance of the proposed extraction and FAAS measurement was compared with other reported SPE-FAAS for the determination of silver. The results summarized in Table 8 show that the enhancement factor, the sorbent capacity and the selectivity of the method are higher than other reported methods and the limit of detection is lower than most of them.

#### Conclusion

In this study, a novel ion imprinted polymer was synthesized for the selective extraction of silver from different matrices. The sorbent showed good thermal and mechanical stability, selectivity toward silver ions which can be reused in more than twenty cycles. It was shown that the preconcentrated silver ions can be reduced to silver nanoparticles and determine its concentration through the absorption of its localized surface plasmon peak. It was also demonstrated that combination of solid phase extraction (SPE) with spectrophotometry based on LSPRP can be used as an accurate and alternative method

**Table 5.** Comparison of analytical performance of FI-FAAS and LSPRP

Parameter	FI-FAAS	LSPRP
Correlation coefficient / $r^2$	0.9990	0.9906
Limit of detection / ( $\mu\text{g L}^{-1}$ )	0.06	0.5
Limit of quantification / ( $\mu\text{g L}^{-1}$ )	0.2	1.7
Dynamic range	0.4-25.0	3.0-30.0
RSD (10 $\mu\text{g L}^{-1}$ , n = 10) / %	2.9	10.3

**Table 6.** Determination of silver in water samples. Conditions: sample volume 40.0 mL; extraction time 30 min; silver concentration 10  $\mu\text{g L}^{-1}$ 

Sample	Amount of silver added / ( $\mu\text{g L}^{-1}$ )	Amount of silver found / ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>		Recovery / %	
		FI-FAAS	LSPR		
Rain water 1	–	ND	ND	–	–
	5	4.97 $\pm$ 0.1	4.9 $\pm$ 0.5	99.4	98.0
	15	15.3 $\pm$ 0.4	14.7 $\pm$ 1.4	102.0	98.0
Rain water 2	–	ND	ND	–	–
	5	5.1 $\pm$ 0.1	5.0 $\pm$ 0.5	102.0	100.0
	15	14.7 $\pm$ 0.3	15.3 $\pm$ 1.5	98.0	102.0
Well water 1	–	1.6 $\pm$ 0.1	ND	–	–
	5	6.5 $\pm$ 0.1	4.8 $\pm$ 0.4	98.0	96.0
	15	16.8 $\pm$ 0.4	14.9 $\pm$ 1.5	101.3	99.3
Well water 2	–	1.1 $\pm$ 0.1	ND	–	–
	5	5.9 $\pm$ 0.1	5.2 $\pm$ 0.5	96.0	104.0
	15	15.8 $\pm$ 0.3	14.6 $\pm$ 1.4	98.0	97.3
Tap water	–	2.0 $\pm$ 0.1	ND	–	–
	5	7.1 $\pm$ 0.1	5.3 $\pm$ 0.4	102.0	106.0
	15	16.7 $\pm$ 0.4	14.3 $\pm$ 1.4	98.0	95.3
Persian Gulf water	–	6.3 $\pm$ 0.1	5.4 $\pm$ 0.5	–	–
	5	11.2 $\pm$ 0.3	10.1 $\pm$ 0.9	98.0	94.0
	15	21.5 $\pm$ 0.4	19.9 $\pm$ 1.7	101.3	96.7

<sup>a</sup>Mean and standard deviation of three independent measurements; ND: not detected.

**Table 7.** Determination of silver in biological samples. Conditions: sample volume 40.0 mL; extraction time 30 min; silver concentration 10  $\mu\text{g L}^{-1}$ 

Sample	Amount of silver added / ( $\mu\text{g g}^{-1}$ )	Amount of silver found / ( $\mu\text{g g}^{-1}$ ) <sup>a</sup>		Recovery / %	
		FI-FAAS	LSPR		
Hair <sup>b</sup>	–	ND	ND	–	–
	0.1	0.096 $\pm$ 0.003	0.094 $\pm$ 0.010	96.0	94.0
	0.3	0.284 $\pm$ 0.006	0.286 $\pm$ 0.027	94.7	95.3
Hair <sup>c</sup>	–	ND	ND	–	–
	0.1	0.097 $\pm$ 0.003	0.099 $\pm$ 0.010	97.0	99.0
	0.3	0.291 $\pm$ 0.007	0.287 $\pm$ 0.003	97.0	95.7
Nail <sup>b</sup>	–	ND	ND	–	–
	0.1	0.096 $\pm$ 0.001	0.094 $\pm$ 0.010	96.0	94.0
	0.3	0.291 $\pm$ 0.006	0.287 $\pm$ 0.026	97.0	95.7
Nail <sup>c</sup>	–	0.009 $\pm$ 0.001	ND	–	–
	0.1	0.106 $\pm$ 0.003	0.095 $\pm$ 0.010	97.0	95.0
	0.3	0.296 $\pm$ 0.050	0.290 $\pm$ 0.020	95.7	96.7
Radiology film	–	17.2 $\pm$ 0.3 $\text{mg g}^{-1}$	16.9 $\pm$ 1.4 $\text{mg g}^{-1}$	–	–
	5	22.3 $\pm$ 0.5 $\text{mg g}^{-1}$	21.7 $\pm$ 2.1 $\text{mg g}^{-1}$	102.0	96.0

<sup>a</sup>Mean and standard deviation of three independent measurements; <sup>b</sup>healthy person; <sup>c</sup>patient with argyria; ND: not detected.

to FAAS for determination of trace amounts of silver in various matrices. Comparison of the proposed extraction and FAAS measurement with other reported SPE-FAAS revealed that the enhancement factor, the sorbent capacity

and the selectivity of the method are higher than other reported methods and the limit of detection is lower than most of them (Table 8).

**Table 8.** Comparison of analytical characteristics of the present method and some previously reported SPE-FAAS methods for the extraction and determination of silver

Sorbent	Sample	Sample volume / mL	PF	Capacity / (mg g <sup>-1</sup> )	RSD / %	LOD / (µg L <sup>-1</sup> )	Ref.
Octadecyl silica membrane disks modified by 1,3-bis(2-cyanobenzene) triazene	Natural water	1800	360	1.07	–	0.006	8
Moringa oleifera seeds	Natural water	14	35	–	3.8	0.22	9
Immobilized dithizone on surfactant-coated alumina	Natural water, radiology film	20	125	0.514	4.0	1.7	10
Immobilized dithizone on surfactant-coated alumina	River water	5	–	–	2.3	–	50
Silica gel modified with 2,4,6-trimercapholino-1,3,5-triazine	Natural water	130	130	0.38	3.03	–	51
Benzil derivative of polyacryloylhydrazide	Natural water	1000	100	–	5.3	–	52
Silver ion imprinted polymer	Natural water, hair, nail, radiology film, liver sample	80	312	18.9	2.9	0.06	CW

PF: preconcentration factor; RSD: relative standard deviation; LOD: limit of detection; CW: current work.

## Supplementary Information

Supplementary data of BET/BJT analysis before and after leaching are available free of charge at <http://jbc.sbg.org.br> as PDF file.

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