



# Modification of chloromethylated polystyrene with 2-mercaptobenzothiazole for application as a new sorbent for preconcentration and determination of $\text{Ag}^+$ from different matrices

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## ABSTRACT

Chloromethylated polystyrene polymer (CMSP) modified with 2-mercaptobenzothiazole (MBT) has been developed for the selective separation and/or preconcentration of silver. The modified polymer (CMS-MBT) was characterized by elemental analysis and IR spectra. Batch and column modes were applied. The newly designed polymer quantitatively sorbed  $\text{Ag}^+$  at pH 2 when the flow rate is  $5 \text{ ml min}^{-1}$ . The maximum sorption capacity was  $0.493 \text{ mmol g}^{-1}$  while the preconcentration factor was 250 for  $\text{Ag}^+$ . The detection limit was  $8 \text{ ng ml}^{-1}$ . The desorption was effective with  $5 \text{ ml of } 2 \text{ mol l}^{-1} \text{ HNO}_3$  prior to detection using AAS. The modified polymer was highly ion-selective in nature even in the presence of large concentrations of electrolytes or organic media, with a preconcentrating ability for  $\text{Ag}^+$ . The utility of the modified polymer to synthetic and drugs samples showed RSD values of  $<3\%$  reflecting its accuracy and reproducibility.

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## 1. Introduction

Although atomic absorption spectrometry (AAS) [1,2] and inductively coupled plasma-atomic emission spectrometry (ICP-AES) [3–6] are among the most widely used methods for trace metal determination, they may be insufficient due to the matrix interferences and the very low concentration of metal ions. Therefore, a separation/preconcentration step is required. The traditional separation and preconcentration methods for metal ions include liquid–liquid extraction, co-precipitation, ion exchange, etc. These methods often require a large amount of organic solvents; some of which are harmful to health and cause problems. Recently, several methods have been used for pretreatment of the samples. Solid phase extraction (SPE) [7–12] is one of them. Its advantage is visible [13] which includes: (i) the fast, simple and direct application in very small sample amounts without loss; (ii) low risk of contamination; (iii) time and cost saving. So, SPE has been widely used for the isolation and concentration of target analytes, and the clean-up of samples (removal of matrix interferences) in pharmaceutical, clinical, environmental and food chemistry [14]. A number of solid phase extractors have been developed and tested for the removal and recovery of  $\text{Ag(I)}$  (e.g., activated carbon [15], cellulose nitrate membrane [16] and chelating resins [17]). Large improvements have been achieved in the last few years

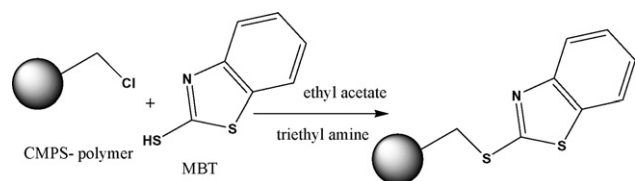
through the development of several chelating resins. The selectivity for a specific metal ion depends on what kind of complexing agent is introduced into the polymeric chain. According to the theory of hard and soft acids and bases (HSAB) defined by Pearson, metal ions will have a preference for complexing with ligands that have more or less electronegative donor atoms. Chelating agents with nitrogen and sulfur groups are highly efficient for the selective sorption of precious metal ions. Chelating resins with amine, mercaptan and thiourea groups are widely used in extraction, separation and recovery of precious metals in hydrometallurgical field.

The choice of sorbent is therefore a key point in SPE, because it can control the selectivity, affinity and capacity [18,19]. Chelating and modified polymers have found widespread applications in the separation and preconcentration of metal ions from various sources and have some advantages over SPE as higher preconcentration factor, higher selectivity, higher stability, better efficiency, and great simplicity in handling and transfer [20,21].

The increasing use of silver compounds and silver containing products in industry and medicine has resulted in an increase of environmental silver content [22,23]. Silver occurs as an impurity in copper, zinc, arsenic and antimony ores and occurs in environment through industrial waters [24]. Low-level exposure to silver compounds is widespread due to the use of soluble silver compounds to disinfect drinking water. On the other hand, recent information about the interaction of silver with essential nutrients, especially selenium, copper, Vitamins E and B12, has focused attention on its potential toxicity [25,26].

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Scheme 1. Synthesis of CMPS-MBT polymer.

Due to the very low concentration of most elements, including silver, in environmental samples, their separation and sensitive determination necessitate the use of a preconcentration or trace enrichment method [27,28].

In this work, a new modified polymer is prepared by reacting mercaptobenzothiazole (MBT) with chloromethylated polystyrene polymer and its sorption behavior towards  $\text{Ag}^+$  has been investigated in batch and column modes.

## 2. Experimental

### 2.1. Reagents

Commercial chloromethyl polystyrene copolymer (CMPS, MP-500A; Bayer Co., Germany) with divinyl benzene (2% DVB; specific surface area (BET)  $66 \text{ m}^2 \text{ g}^{-1}$  and  $46 \text{ meq Cl g}^{-1}$  resin) was used. 2-Mercaptobenzothiazole (MBT) and the nitrate salts of the metal ions (Aldrich) were used. The reaction was followed up in all experiments with the aid of FTIR spectral analysis.

### 2.2. Apparatus

A Perkin–Elmer 2380 Atomic Absorption Spectrometer (USA) was used. The IR spectra were carried out on a Mattson 5000 FTIR Spectrophotometer ( $4000\text{--}400 \text{ cm}^{-1}$ ) as KBr. The UV–visible absorption measurements were performed on a Unicam 2001 UV–VIS Spectrophotometer using a 1 cm quartz cell. The pH values were measured using a pH-meter (Hanna Instruments, 8519, Italy) with an expanded scale and accuracy of  $\pm 0.01$ . It was standardized with  $0.05 \text{ mol l}^{-1}$  potassium hydrogen phthalate (pH 4.01) and a standard tablet (pH 9.2) at  $25^\circ \text{C}$ .

### 2.3. Synthesis of CSP-MBT polymer

In a 100 ml round bottom flask, 1 g of chloromethylated polystyrene soaked in dry ethyl acetate (15 ml) was added to 0.5 g of 2-mercaptobenzothiazole. The slurry was stirred vigorously for 12 h at  $60^\circ \text{C}$  under reflux and the reaction mixture was filtered and washed with ethyl acetate. The liberating HCl was adsorbed by nitrogen site in 2-mercaptobenzothiazole to produce ammonium salt. To remove HCl from 2-mercaptobenzothiazole bonded CMPS-polymer, 1.5 ml of triethylamine diluted in distilled water (3 ml) was added to the residue. The slurry was stirred vigorously for 2 h. The residue was then washed several times with distilled water and filtered. The resulting residue was washed with acetonitrile (50 ml), filtered and dried at  $40^\circ \text{C}$  overnight and characterized by FTIR spectra and pH-metric measurements. The suggested structure of the prepared CMPS-MBT polymer is shown in Scheme 1.

### 2.4. Separation procedures

#### 2.4.1. Batch method

100 ml sample solution containing  $25 \mu\text{g ml}^{-1}$  of  $\text{Ag}^+$  was transferred to a glass stoppered bottle (250 ml) and 50 mg of the modified polymer were added after adjusting its pH to the optimum value. The mixture was then shaken for 30 min with mechanical

stirrer. After filtration, the modified polymer was washed with double distilled water, and the sorbed metal ion was eluted with 5 ml of a suitable concentration of  $\text{HNO}_3$  and the resulting solution was adjusted to 100 ml and determined using AAS.

#### 2.4.2. Column method

The modified polymer (0.5 g) was first swollen for 24 h, packed in a glass column ( $40 \text{ mm} \times 6 \text{ mm}$ ), treated with 20 ml of  $1 \text{ mol l}^{-1}$   $\text{HNO}_3$  at the optimum flow rate and washed with double distilled water until the modified polymer became free from acid. A 100 ml of  $50 \mu\text{g ml}^{-1}$  metal ion solution buffered at the optimum pH, was passed through the column at the optimum flow rate. After sorption step, the column was washed with 100 ml of double distilled water to remove any uncomplexed metal ions from the modified polymer bed. The stripping of metals from the modified polymer was carried out by suitable eluting agent ( $\text{HNO}_3$ ). The eluted solution was collected in a 100 ml calibrated flask and analyzed.

## 3. Results and discussion

### 3.1. Characterization

The active groups of MBT in the modified polymer were investigated by recording the spectra of CMPS and CMPS-MBT. The IR spectrum of CMPS exhibits a characteristic band at  $701 \text{ cm}^{-1}$  which may be attributed to C–Cl band. The presence of a broad band at  $3400 \text{ cm}^{-1}$  is attributed to  $\nu(\text{OH})$  of water. Upon modification of CMPS with MBT (Scheme 1), the band at  $2600 \text{ cm}^{-1}$  in the IR spectrum of MBT, due to  $\nu(\text{SH})$  disappear. This proves that MBT is bonded to CMPS through sulfhydryl group. The broad band centered at  $1640 \text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  in MBT-CMPS is similar to that for MBT indicating that this group is not taking part in the bond formation.

The C, H and N content of MBT-CMPS was determined and the values (C = 68.20%; H = 5.23%; N = 4.80%) were compared with the calculated (C = 67.84%; H = 4.59%; N = 4.94%) to prove the modification of MBT-CMPS (97.16%). Water regain values were measured by recording the difference in weight of the modified polymer after its storage at  $100^\circ \text{C}$  for 48 h. The value found to be  $0.25 \text{ g g}^{-1}$  for MBT-CMPS. Comparison of the value with that of CMSP ( $0.12 \text{ g g}^{-1}$ ) indicates an appreciable improvement of the sorption capacity of the modified polymer [29].

### 3.2. Preliminary investigations

Batch and column preliminary experiments were carried out to investigate the quantitative sorption of  $\text{Ag}^+$  by CMPS and MBT-CMSP. It was found that, CMSP does not show any tendency for sorption of  $\text{Ag}^+$  ions. Alternatively, MBT-CMSP was found efficient. This is mostly due to the strong interaction between  $\text{Ag}^+$  and the loaded organic ligand through complex formation. The analytical variables (pH, sorption kinetics, temperature and matrix effect) have been studied in detail for batch and column techniques.

### 3.3. Batch technique

#### 3.3.1. Effect of pH

The effect of pH on the sorption of  $\text{Ag}^+$  has been investigated in the pH range 1–8 ( $\text{HNO}_3$  and NaOH were used to change the acidity of the medium).

The experiments were elaborated by shaking the solution containing  $\text{Ag}^+$  of variable pH with the modified polymer for sufficient equilibrium time. The pH was adjusted using suitable buffer solutions. From the data represented in Fig. 1, it could be concluded that, the maximum sorption efficiency of MBT-CMPS for  $\text{Ag}^+$  was

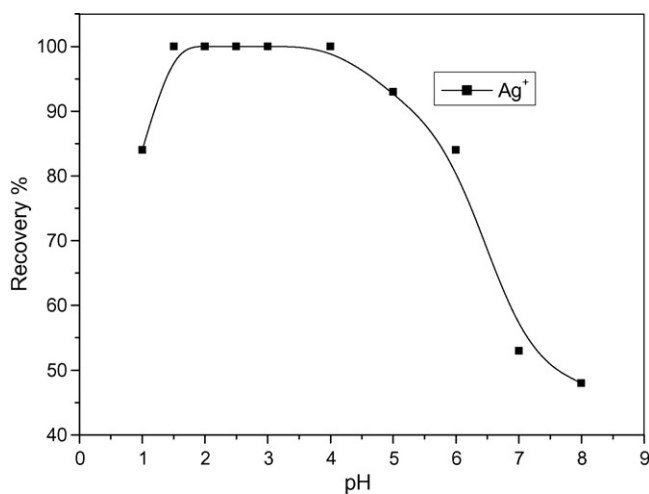


Fig. 1. Effect of pH on the recovery % of Ag(I) using 50 mg MTB-polymer and stirring time = 30 min at  $25 \pm 1^\circ\text{C}$ .

achieved at 1.5–4.0. As  $\text{Ag}^+$  is more stable at acidic pH values, pH 2.0 was chosen as the optimum pH for further studies.

### 3.3.2. Determination of sorption capacity

The sorption capacity of MBT-CMPS for  $\text{Ag}^+$  was determined by shaking the solution containing excess  $\text{Ag}^+$  with 50 mg of the modified polymer under optimum conditions. The maximum sorption capacity for  $\text{Ag}^+$  with MBT-CMPS is  $0.493 \text{ mmol g}^{-1}$ .

### 3.3.3. Effect of the amount of polymer

The amount of polymer is an important parameter that affects the recovery of the metal ion. The quantitative sorption is not obtained by small amount of polymer than the optimum. On the other hand, excess amount of polymer prevents the elution of the quantitative sorbed metal ion by a small volume of eluent. For this reason, the used amount of polymer was optimized. To test the amount of polymer for a quantitative sorption of  $\text{Ag}^+$ , 25–500 mg was used. Quantitative recoveries of  $\text{Ag}^+$  were obtained in the range of 50–200 mg of the modified polymer. Thus, 50 mg of polymer has been used for subsequent experiments.

### 3.3.4. Stirring time

To determine the rate of sorption of  $\text{Ag}^+$  on the modified polymer, batch experiments were elaborated by shaking the solution containing  $\text{Ag}^+$  with 50 mg of the modified polymer at room temperature ( $25^\circ\text{C}$ ). Aliquots of 1 ml solution were taken for analysis at pre-determined intervals. The concentration of  $\text{Ag}^+$  in the supernatant solution was determined and its amount sorbed was calculated by mass balance. The sorption half-time ( $t_{1/2}$ ) defined as the time needed to reach 50% of the total sorption capacity was estimated from Fig. 2. From the data obtained, it was observed that the maximum sorption of  $\text{Ag}^+$  with polymer reached its equilibrium time after 28 min. However, the time required for 50% sorption of  $\text{Ag}^+$  was 10 min for the polymer.

### 3.3.5. Resin stability

The modified polymer (50 mg) was shaken with 100 ml of acidic or basic ( $1\text{--}6 \text{ mol l}^{-1}$  HCl and/or NaOH) or electrolytes ( $0.001\text{--}5 \text{ mol l}^{-1}$  NaCl, KCl and  $\text{NaNO}_3$ ) or organic solvent (ethanol, acetone and chloroform) solutions for 24 h, filtered and washed with doubly distilled water. It was found that, there was no change in its composition, which suggests a robust and stable nature of the modified polymer. The exchange capacity of  $\text{Ag}^+$  on the modified polymer was subjected to several sorption and desorption (batch) operations. The modified polymer (50 mg) was stirred with

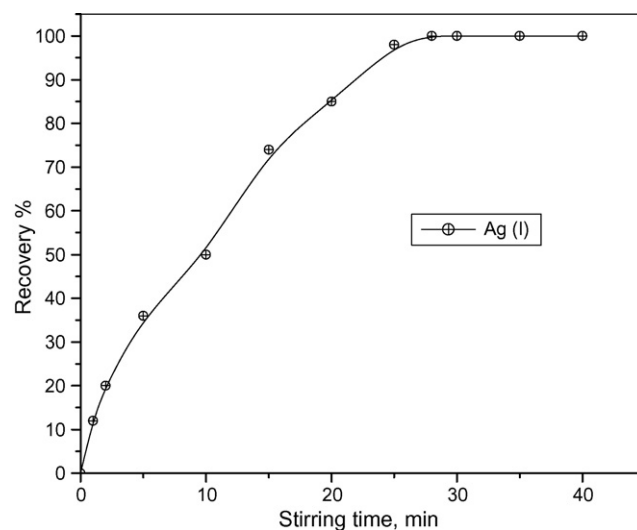


Fig. 2. Effect of stirring time on the recovery % of Ag(I) using 50 mg MTB-polymer, pH 2 at  $25 \pm 1^\circ\text{C}$ .

100 ml of  $25 \text{ mg l}^{-1}$  solution containing  $\text{Ag}^+$  for 1 h at room temperature. The polymer was separated and the  $\text{Ag}^+$  ions were desorbed using 5 ml of appropriate concentration of  $\text{HNO}_3$ . It was found that, the sorption capacity after 50 cycles for  $\text{Ag}^+$  varied by less than 2%. Therefore, the repeating of polymer is feasible. The capacity of the modified polymer stored for more than 1 year under ambient conditions has been found to be practically unchanged.

### 3.3.6. Choice of eluent

Choice of the most effective eluent for the quantitative stripping of the retained  $\text{Ag}^+$  on the polymer is of special interest. The metal sorbed on the polymer can be eluted with nitric acid into the aqueous phase (Fig. 3). The literature survey showed that, the technique used for determining the concentration of the analyte may be handicapped by the presence of a complex organic matrix that causes severe suppression of the analyte signal. So, the use of acid solution is analytically preferred. The data obtained indicate that, 5 ml of  $2.0 \text{ mol l}^{-1}$  of  $\text{HNO}_3$  afford a quantitative elution of  $\text{Ag}^+$  from the modified polymer. Subsequent elution of  $\text{Ag}^+$  was carried out with nitric acid solution taken the advantage that, nitrate

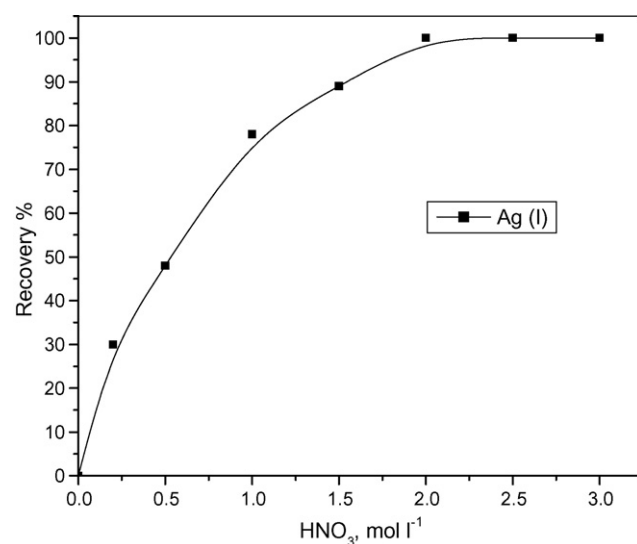


Fig. 3. Effect of  $\text{HNO}_3$  concentration (5 ml) on the recovery of Ag(I); MTB-polymer = 50 mg; stirring time = 10 min at  $25 \pm 1^\circ\text{C}$ .

**Table 1**  
Influence of interfering cations and anions on recovery percentage of  $5 \mu\text{g ml}^{-1}$  Ag(I) ion using MBT polymer and shaking for 30 min at  $25^\circ\text{C}$ .

Interfering ion	Concentration ( $\mu\text{g ml}^{-1}$ )	% Recovery
Na <sup>+</sup>	200	99.8
K <sup>+</sup>	200	99.6
Mg <sup>2+</sup>	200	99.3
Ca <sup>2+</sup>	200	99.4
Cu <sup>2+</sup>	200	99.0
Ni <sup>2+</sup>	200	99.1
Hg <sup>2+</sup>	200	97.8
NH <sub>4</sub> <sup>+</sup>	200	99.8
Acetate	200	100
Oxalate	200	99.2
Tartrate	200	99.1
Citrate	200	99.3
Thiourea	200	12.5
NO <sub>3</sub> <sup>+</sup>	200	99.9
F <sup>-</sup>	200	99.8
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	200	87.8
EDTA	200	99.2
SCN <sup>-</sup>	200	99.2
SO <sub>4</sub> <sup>2-</sup>	200	99.6

ion is an acceptable matrix for both AAS and spectrophotometric determination of the metal ions

### 3.3.7. Effect of interference

In an ambience of competitive reactions of the loaded chelating agent with various metallic species, a reduction of the sorption efficiency of the target metal species should be expected. The effect of interfering agents on the recovery was studied for several reasons: (1) to avoid their effect during application, (2) to suggest a selective eluent as predicted from its interfering effect, (3) to study the preferred positions of the different metal ions, and (4) to enhance the selectivity of the modified polymer. No effect on the recovery of Ag<sup>+</sup> was found for most common ions on MBT-CMPS such as: nitrate, acetate, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> ions (Table 1). However, the presence of thiosulphate and thiocyanate caused a remarkable suppression of Ag<sup>+</sup> sorption, while EDTA has no effect. Moreover, the presence of thiourea prevents the loading of Ag<sup>+</sup> on the polymer.

## 3.4. Column technique

### 3.4.1. Effect of flow rate

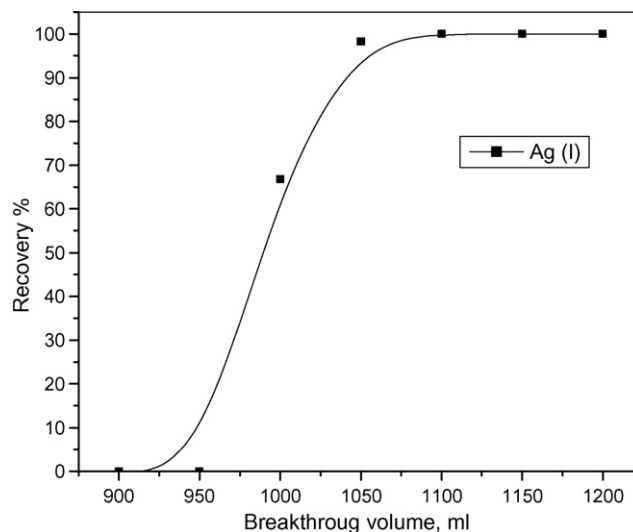
The effect of flow rate on the metal sorption was investigated by varying the flow rate ( $0.5\text{--}10 \text{ ml min}^{-1}$ ) under the optimum conditions. It was found that, the optimum flow rate for the maximum sorption capacity of Ag<sup>+</sup> was  $5 \text{ ml min}^{-1}$ . For flow rate greater than  $5 \text{ ml min}^{-1}$ , Ag<sup>+</sup> does not reach equilibrium. The faster sorption of Ag<sup>+</sup> with the modified polymer is taken as an indication for its higher reactivity.

### 3.4.2. Breakthrough capacity

It was used to evaluate the amount of Ag<sup>+</sup> sorbed per gram on the modified polymer under the operating conditions. In order to obtain a breakthrough capacity, a glass column was packed with 0.5 g of the modified polymer and  $50 \mu\text{g ml}^{-1}$  of Ag<sup>+</sup> solution at the optimum pH was passed through the column with the selected flow rate. The receiving effluent after 5 min was fractionalized into 5 ml portions and Ag<sup>+</sup> was determined. The breakthrough capacity presented in Fig. 4 indicates that, the column is exhausted with 53.17 mg Ag<sup>+</sup> per g polymer.

### 3.4.3. Column reuse

To test the long-term stability of the column containing the modified polymer, successive sorption and desorption cycles were subjected by passing the metal ion solution through the column



**Fig. 4.** Breakthrough volume of Ag(I) ion with flow rate  $5 \text{ ml min}^{-1}$  at  $25^\circ\text{C}$ .

at the optimum flow rate. The sorbed Ag<sup>+</sup> is then eluted with 5 ml of  $2.0 \text{ mol l}^{-1}$  HNO<sub>3</sub>. The procedure was carried out several times and the stability of the column was assessed by monitoring the change in the recoveries of the sorbed Ag<sup>+</sup>. The results of 50 sorption/desorption cycles indicated that, the recovery decreased by 2–3% for Ag<sup>+</sup>, which reflect good stability of the modified polymer.

### 3.4.4. Effect of volume and preconcentration factor

$0.1\text{--}1.5 \text{ L}$  aqueous solution containing  $10 \mu\text{g}$  of Ag<sup>+</sup> was passed through the modified polymer bed, eluted with 5 ml of the appropriate concentration of HNO<sub>3</sub> and determined. It was found that, Ag<sup>+</sup> could be removed quantitatively from volume up to 1250 ml, and then the recovery decreased remarkably. Therefore, using 5 ml of  $2.0 \text{ mol l}^{-1}$  HNO<sub>3</sub> as eluent, a practical maximum of 250-fold preconcentration factors for Ag<sup>+</sup> was obtained.

### 3.4.5. Detection limits of the metal ions

It means the lowest concentration of metal ion below which its quantitative sorption by the modified polymer is not perceptibly seen. It was investigated for Ag<sup>+</sup> at  $10^{-1}\text{--}10^{-3} \mu\text{g ml}^{-1}$  passed through the polymer bed at a suitable flow rate. The limit of detection (LOD) for Ag<sup>+</sup> is 8 ppb, showing a high sensitivity of the modified polymer in the preconcentration of trace analyte.

## 3.5. Applications

### 3.5.1. Selective separation of Ag<sup>+</sup> from binary mixtures

In order to investigate the selective separation and determination of Ag<sup>+</sup> from its binary mixtures with diverse metal ions, an aliquot of aqueous solution (500 ml) containing 1 mg Ag<sup>+</sup> and 25 mg of another cation was taken and the recommended procedure was followed (column mode). The results summarized in Table 2 show that Ag<sup>+</sup> in the binary mixtures is selectively sorbed by the modified polymer up to 25 mg of the diverse ions.

### 3.5.2. Selective separation of Ag<sup>+</sup> from waste and medicinal samples

Trace quantities of Ag<sup>+</sup> present in photographic washings and medicinal sample; Argiderm P (Amoun Co., Egypt) were preconcentrated by column mode using this modified polymer. The sample was digested by treatment with HNO<sub>3</sub>. The concentration and the amount of silver present in the sample solution was determined using AAS. 1 ml of this solution was diluted to 25 ml using buffer with pH 3 and passed through the column containing 0.5 g of the

**Table 2**  
Separation of Ag(I) from binary mixtures.<sup>a</sup>

Diverse ion	Amount taken (mg)	Recovery % of Ag <sup>+</sup> ion
Na <sup>+</sup>	25	100.0 (0.07) <sup>b</sup>
Mg <sup>2+</sup>	25	99.5 (0.10)
Ca <sup>2+</sup>	25	99.4 (0.15)
Co <sup>2+</sup>	25	99.8 (1.10)
Ni <sup>2+</sup>	25	100.0 (1.48)
Cu <sup>2+</sup>	25	99.5 (1.90)
Zn <sup>2+</sup>	25	99.4 (1.92)
Pb <sup>2+</sup>	25	97.0 (1.68)
Cd <sup>2+</sup>	25	98.5 (1.73)

<sup>a</sup> Initial sample containing 1 mg Ag(I), 25 mg of diverse ions and 100 mg of the modified polymer in 500 ml water at pH 2.

<sup>b</sup> Values in parentheses are RSD's based on three replicate analyses.

**Table 3**  
Separation of Ag(I) from different samples.<sup>a</sup>

Sample	By AAS ( $\mu\text{g ml}^{-1}$ of stock solution)	Obtained value ( $\mu\text{g ml}^{-1}$ of stock solution)	% Recovery
Photographic washings	125.0	142.0	>100.00 (2.3) <sup>b</sup>
Argiderm P	98.0	97.50	99.48 (1.85)

<sup>a</sup> 25 ml of the diluted solution, 0.5 g of MBT polymer, pH 2 and flow rate = 5 ml min<sup>-1</sup>.

<sup>b</sup> Values in parentheses are RSD's based on three replicate analyses.

resin. Ag<sup>+</sup> was subsequently eluted by 5 ml of 2.0 M HNO<sub>3</sub> solution and determined by AAS.

Also, MBT-CMSP polymer is applicable for separation and estimation of silver present in natural samples. High percentage of Ag<sup>+</sup> has been extracted from different medicinal and waste sample (photographic washing) in similar type of experiment (Table 3). The results showed the utility of this polymer for preconcentration of Ag<sup>+</sup> before the analysis by AAS.

#### 4. Conclusions

The introduced modified polymer is found suitable and efficient for trace enrichment of Ag<sup>+</sup>. The proposed procedure is simple and fast for sorption and preconcentration of the metal ion without using organic solvents. In comparison with the other modified polymers, the main advantages of the polymer were: (1) higher preconcentration factor; (2) higher sorption capacity; (3) low matrix effect; (4) good precision; (5) strong stability in acidic medium; (6) quantitative sorption at a very low concentration of Ag<sup>+</sup> in samples having complicated and variable matrices; (7) recycling for 50 cycles, and (8) a short loading time ( $t_{1/2}$ ). From the economic point of view, the sorption capacity of the modified polymer, after its versatile use for 6 months and after being stored under ambient conditions, is practically unchanged.

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