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Use of derivatised L-methionine for efficient extraction of Ag(I) by tracer technique

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ABSTRACT

N,*N*-Bis(2-pyridylmethyl) L-methionine (BPMM) have been found to have a strong affinity for silver(I) and is used for the selective and rapid extraction of silver ion from aqueous solution to chloroform (99.8%). The effect of Ag(I) concentration, pH, diverse ions, and temperature on such extraction is reported. The extraction of Ag(I) with BPMM ligand is maximum at pH 4.0. The change of enthalpy value of the extraction reaction of Ag(I) with BPMM in chloroform is -0.021 J mole^{-1}, indicating the extraction process as an exothermic one and so, low temperature is beneficial to the extraction process. The method has successfully been applied for the determination of silver in different samples. Radiotracer technique, using ^{110m}Ag(I) as a tracer, have been used for monitoring the concentration of silver ion.

Keywords: L-Methionine derivative; Extraction; Ag(I); tracer technique

1. Introduction

Recently derivatized amino acids having a tripodal ligand motif have attracted immense interest as it is used in the development of chiralty switch [1–3], to modeling the structure and function of zinc enzymes like carboxypeptidase [4], superoxide dismutase [5] and alkaline phosphatase [6], etc. Because of its rich chemistry and the wide area that remains uncovered, we are presently working on the synthesis of different derivatised chiral amino acids, their structural characterization, metal ion uptake properties and applications of these new series of ligands.

Inhalation exposure to silver leads to death, adverse cardiovascular or musculoskeletal effects and respiratory irritation. Acute inhalation of aerosol containing colloidal silver leads to ultrastructural damage and disruption of cell of tracheal epithelium. It also leads to abdominal and gastrointestinal pain [7–11]. Because of the hazardous nature, Ag(I) is an unwanted material in drinking water and food products. The reference dose, published by the United States Environmental Protection Agency in 1991, which recommends the estimated daily exposure that is unlikely to incur a appreciable risk of deleterious effects during a lifetime, is 5 μg/kg/d; meaning 5 μg of silver per kilo of weight per person each day – about 1 liter of 10 ppm colloidal silver per month for a 66 kg person [7]. Hence, there is always a need for a good separation method of Ag(I) from industrial and photographic wastes. Amongst various methods available in the literature, radiochemical techniques were used by several worker's, to determine silver ion concentration with the reagents like potassium 3-phenyl methyl dithiocarbazate [12], amberlite LA-2 [13], benzothiazole [14], NAA followed by extraction of silver with 1,2,3-benzothazole [15].

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Some ion exchangers have been reported for the separation of Ag(I). Grader et al. [16], have studies the adsorption properties of natural calcium cliptolite for Ag(I) ions. Akitimiti [17] employed radiotracer method to study the adsorption of Ag(I) on the fluoride. Distribution studies of Ag(I) was carried out by Varshney et al. [18], on the arsenophosphates of Sn(II) and Cr(III) using radiotracers. Several Ag(I) ion complexing ligands have been investigated such as crown ethers containing sulfur atom(s) in the cyclic structure [19–21], doubled armed [22], or multi-armed macrocycles [23]. In nitric acid medium, Ag(I) has been extracted by certain quinoline derivates [24]. Lee et al. [25] developed a method of silver extraction by an acyclic diazapolyether compound bearing dicarboxylate functional end groups. Kamata et al. [26] studied solvent extraction of silver using bis(o-butylxanthato)alkane derivatives. Salas et al. [27] studied the medium effect on the stoichiometry of the phase transfer extraction of silver(I) by calixarene amine derivatives. In the present work, we report selective and quantitative extraction of Ag(I) by *N*,*N*-bis(2-pyridylmethyl) L-methionine (BPMM) into chloroform using ^{110m}Ag(I) as a radiotracer. The effect of Ag(I) concentration, pH, diverse ions, and temperature on such extraction is reported. The method has successfully been applied for the determination of silver in different samples. Due to greater sensitivity, selectivity, precision, rapidity and least cost of the method, we have used radiotracer technique for monitoring the concentration of silver ion using ^{110m}Ag(I) as a tracer.

2. Experimental

2.1 Reagents and apparatus

All the chemicals used were of analytical reagent grade. A carrier solution containing 205 μg mL^{-1} of Ag(I) was prepared by dissolving $AgNO_3$ (SRL, India) in a 100 mL volumetric flask. The volume was made up to the mark after the addition of 0.5 mL concentrated HNO_3 and 1 mL of $^{110m}AgNO_3$ tracer. The radioisotope ^{110m}Ag(I) in the form of $AgNO_3$ was supplied by Board of Radiation and Isotope Technology; India. BPMM (compound 1) was prepared as reported by us earlier [3]. Stock solution of 1.02×10^{-3} μg mL^{-1} BPMM was prepared by dissolving 33.6 mg of BPMM in chloroform. Rock samples (G.S.I. Kolkata), chawanprash (DABUR), sulfadiazine (silverex) and photographic washings were used to establish the suitability of the new method. Three replicate measurements were performed for this purpose.

A single channel γ-ray spectrometer coupled with well type NaI(Tl) detector (ECIL, India) was used to measure radioactivity. Temperature (303–318 K) was monitored by using B.O.D INCUBATOR (YONA, India).The pH of the solutions were measured using SYSTRONICS pH meter (model 335).

2.2. Extraction procedure

A 1.0 mL volume of 205 μg mL^{-1} labeled silver(I) solution was taken in a separating funnel. 1.0 mL of 0.5 μg mL^{-1} KNO_3 solution was added for maintaining ionic strength of solution. The total volume of aqueous phase for all experiments was maintained at 5 mL. The pH of aqueous phase was adjusted to 4.0 using dilute HNO_3 solution. The aqueous phase was equilibrated with 5 mL BPMM solution in chloroform for 20 min. The phases were allowed to separate and the volumes were found to be practically equal. The activity of 1 mL aliquot of each phase was measured on a γ-ray spectrometer. The logarithm of distribution coefficient (*D*) was calculated as follows.

$$\mathrm{Log}D = \mathrm{Log}a_{\mathrm{Ag}}(\mathrm{Org.}) - \mathrm{Log}a_{\mathrm{Ag}}(\mathrm{Aq.}) \qquad \text{(i)}$$

where *a* is activity, (Org.) is organic phase and (Aq.) is aqueous phase.

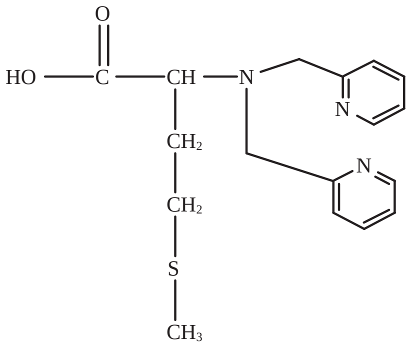
2.3. Substoichiometric method of extraction

A series of solutions containing increasing amount of labeled Ag(I) (from 20–200 μg) were taken in separating funnels. To this solution 5.0 mL of the reagent (BPMM) in chloroform was added. The pH of the solution was maintained at 4.0 with an aqueous phase volume of 5 mL. After separation, the activity of organic phase (1 mL) was measured.

3. Results and discussion

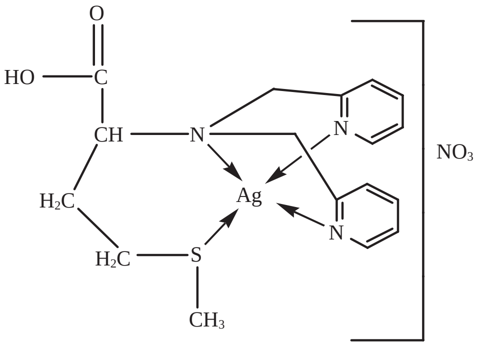
3.1. Effect of pH

Fig. 1 shows the extraction of Ag (I) by BPMM in chloroform in the pH range 1.0–8.0. It is observed that the extraction of Ag(I) with BPMM gradually increases with pH and becomes maximum at pH 4.0, and then decreases with pH. Hence, all the extractions were carried out at pH 4.0. This can be explained on the basis of Soft Hard Acid Base (SHAB) Principle. Ag(I), being soft acid prefers N and S donor centers of BPMM (as shown in compound 2) excluding the possibility of O-coordination, which remains as un-dissociated carboxylic acid at pH 4.0. The structure of the chelated Ag(I) complex has been verified by density functional theory (DFT) and is beyond the scope of this communication. Plausible mechanism can be described as an intimate ion-pair extraction.



N, N-Bis(2-pyridylmethyl)L-methionine(BPMM)

(Compound 1)



Ag - BPMM complex (1:1)

(Compound 2) (pH = 4.0)

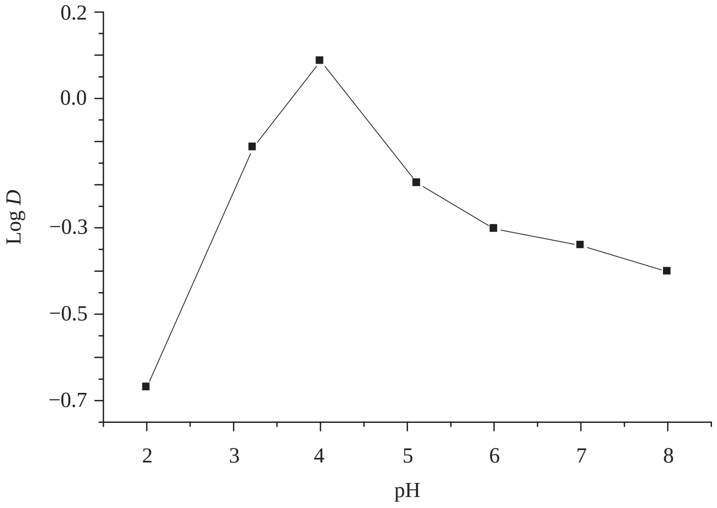


Fig. 1. Effect of pH on distribution coefficient of Ag (I) with 0.408 × 10^{-3} mol L^{-1} reagent (BPMM) into chloroform ($N = 3$).

3.2. *Effect of reagent concentration in organic phase*

The effect of the reagent concentration on the Ag(I) extraction from aqueous phase is illustrated in Fig. 2, which shows that there is a linear relationship between the two as given by the equation, $\text{Log } D = 2.98 + 0.805 \text{ Log[BPMM]}$.

3.3. *Composition of the extracted complex*

A plot of the activity against the concentration of labeled Ag (I) is shown in Fig. 3. As can be seen, the activity of the organic phase reached a saturation value at 110 µg of Ag(I)BPMM indicating a 1:1 stoichiometric ratio of silver to reagent ([BPMM] in $CHCl_3 = 11 \times 10^{-3}$ g L^{-1}). (Also confirmed by the elemental analysis of the extracted silver complex).

3.4. *Variation of the solvent*

Different solvents like 1-butanol, dichloromethane, toluene, chloroform, ethyl acetate, cyclohexane, carbon tetrachloride and cyclohexanol were used for the extraction studies. However it was found that the extraction of Ag(I) by BPMM was maximum with chloroform. The results are presented in Table 1.

3.5. *Influence of temperature*

The plot of log D vs. $1,000/\underline{T}$ ([BPMM] = 0.612 µg mL^{-1} in chloroform) (Fig. 4) clearly shows that the distribution ratio decreases with increase in temperature. A linear relationship is observed with an equation $\text{Log } D = -3.705 + 1204/T$. According to Van't Hoff equation; $d \log D/d(1/T) = -\Delta H^0/2.303R$, the change of enthalpy values of the extraction reaction of Ag(I) with BPMM in chloroform is −0.021 J $mole^{-1}$. This indicates

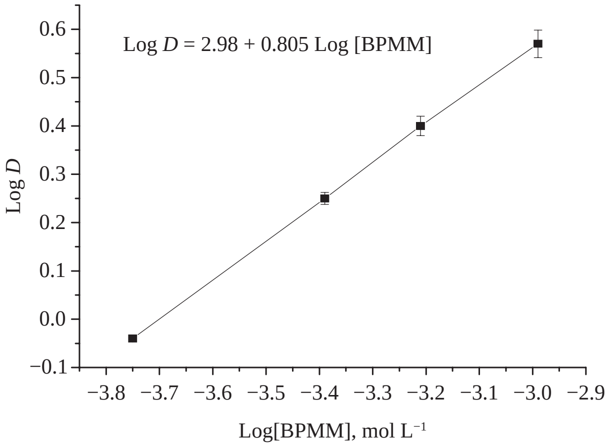


Fig. 2. Effect of variation of reagent concentration on distribution coefficient of Ag (I) into chloroform ($N = 3$).

that the extraction process is exothermic and low temperature is beneficial to the extraction process.

3.6. Effect of interfering ions

The possible chemical interferences were studies in the extraction of 100 µg Ag(I) in spike solution in presence of various foreign ions, if the activity of extracted silver in presence and in absence of foreign ions be 'a' and 'a^0' respectively, then the ratio a/a^0 value indicates the extraction efficiency and closer the ratio to 1, greater the extent of Ag(I) extraction. Results are shown in Table 2. It is clear from the table that 3–3.5-fold excess of the metal ions viz. Mg(II), Na(I), K(I), Cu(II), Al(III), Ni(II), Fe(III), Zn(II) give more than 90% recovery of Ag(I) ion from binary mixtures. Similarly, in presence of twofold excess of F^-, SO_4^{2-}, NO_3^- and OAc^-, more than 90% recovery of Ag(I) was observed from their binary mixtures. But in presence of 2.5-fold excess of cations like Hg(II), Cd(II) and Pb(II), extraction of silver was found to be reduced. Hence the present method needs the removal of such interfering ions by using suitable masking agents before it can applied for extraction of Ag(I).

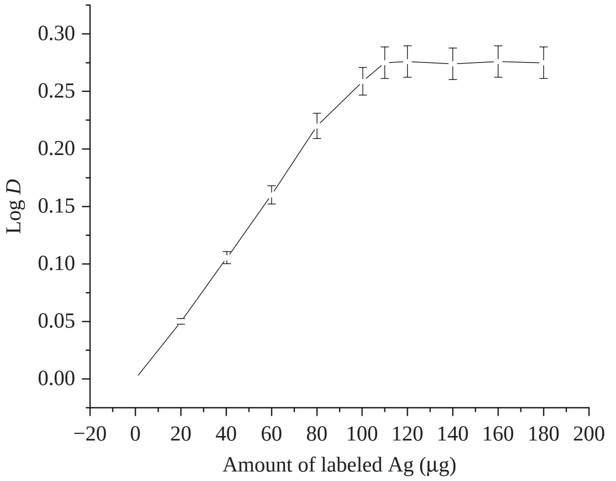


Fig. 3. Substoichiometric extraction of Ag (I) with BPMM into chloroform, ($N = 3$), [BPMM] = 11 µg mL^{-1}, volume of $CHCl_3$ = 10 mL.

Table 1
Studies on recovery (%) of Ag(I) from aqueous solution by different organic solvents (N = 3)

Solvent	% recovery of Ag(I)
Toluene	5.5 ± 0.05
Cyclohexane	8.8 ± 0.07
Carbon tetrachloride	9.2 ± 0.04
Cyclohexanol	20.6 ± 0.06
1-Butanol	30.0 ± 0.05
Ethyl acetate	45.4 ± 0.02
Dichloromethane	75.9 ± 0.03
Chloroform	99.8 ± 0.04

4. Analytical applications

The proposed method of extraction of silver by BPMM has been employed for the determination of silver in geological, medicinal and photographic washing samples. For these purpose two geological samples, gifted by geological survey of India, Kolkata, and few other samples (including medicinal samples) were collected from different areas in Burdwan district of West Bengal, India. The samples containing silver were brought into solution by usual method [28].A 0.5 g of the samples was digested with 10 mL concentrated HNO_3. Any acid left was removed and the residue was dissolved with 100 mL deionised distilled water.

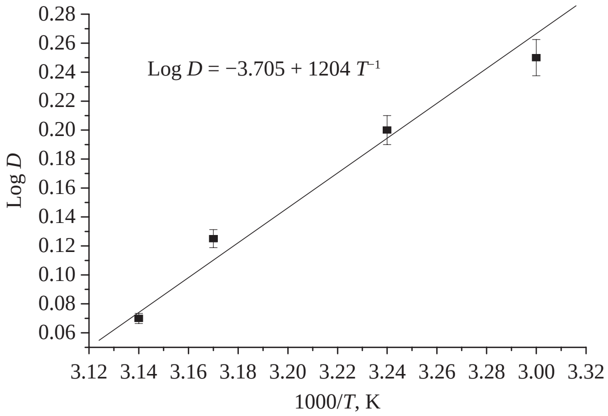


Fig. 4. Effect of temperature (303–318 K) on distribution ratio D; ([BPMM] in chloroform = 0.612 × 10^{-3} mol L^{-1}, at pH = 4.0) ($N = 3$).

Table 2
Studies on interferences by foreign ions. Amount of active silver = 100 μg; activity of extracted silver in presence and in absence of foreign ions have been designated as 'a' and 'a^0' respectively.

Diverse ions	Amount of diverse ion (μg)	a/a^0
Mg(II)	350	0.99
Na(II)	350	0.99
K(II)	350	0.99
Cu(II)	300	0.96
Al (III)	300	0.95
Ni(II)	300	0.95
Fe(II)	350	0.94
Zn(II)	300	0.92
Co(II)	300	0.94
Pb(II)	250	0.89
Cd(II)	250	0.82
Hg(II)	250	0.75
F^-	200	0.95
SO_4^{2-}	200	0.96
NO_3^-	200	0.98
OAc^-	200	0.93

4.5 mL aliquot of this sample solution was mixed with 0.5 mL labeled ^{110m}Ag (I) solution containing 10 μg mL^{-1} of Ag(I) ion. The volume of the solution was made 10 mL after adjusting to appropriate pH. This solution was subjected to silver extraction with the reagent solution. After equilibration 1 mL organic extract was collected, and radioactivity (C) determined. The experiment was repeated with the same aqueous solution containing only the labeled ^{110m}Ag (I) solution only, i.e. in absence of medicinal/geological solution and the radioactivity of the organic extract was again measured (C_0) and the amount of inactive Ag(I) present in each of the samples was computed from the relation:

$$W_{\text{inactive}} = \frac{C_0 - C}{C_0} W_{\text{active}} \qquad \text{(ii)}$$

From the results (Table 3), it may be concluded that there is a fair agreement between the observed data by the present method with that of the recommended value or the value obtained by some other methods.

5. Conclusions

The very high extraction efficiency of BPMM for Ag(I) is established. Only Hg(II), Cd(II) and Pb(II) interfere when present more than 2.5 times. The method is pH sensitive. As the extraction process is exothermic, low temperature favors the extraction. As our ligand, BPMM, is a pentadentate one, it uses N, N, N, S donor sites to bind soft Ag(I) ion, keeping –COOH functionality free. The ligand reacts instantaneously with Ag(I) to make a red colour precipitate extractable to chloroform, almost to the level of 99.8%. The method has successfully been applied to different geological, medicinal and photographic washing samples.

Table 3
Estimation of Ag(I) from geological, medicinal and photographic washing samples

Sample	Recommended value[a] /other method[b] (μg/g)	Amount of silver found (μg/g) ± σ
Rock sample (G.S.I. Kolkata)	600[a]	594 ± 2
Rock sample (G.S.I. Kolkata)	2700[a]	2680 ± 3
Chawanprash (DABUR)	66[b]	64 ± 1
Sulfadiazine (silverex)	1.5[b]	1.4 ± 1
Photographic washings	52.81[b]	49 ± 2

[a] Recommended by G.S.I Kolkata, [b] By flame atomic absorption spectroscopic method.

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