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# Selective Flotation-Separation and Inductively Coupled Plasma-Atomic Emission Spectrometric Determination of Ultra Trace Amounts of Silver Ion Using Bis(2-mercaptoanil)acetylacetone

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**Abstract:** A rapid, selective and highly sensitive flotation method is developed for separation and enrichment of ultra trace amounts of $Ag^+$ ion from water samples. At pH 6.0 and using sodium dodecylsulfate as a foaming agent, $Ag^+$ was separated with bis(2-mercaptoanil)acetylacetone (BMAA) added to 1000 mL of aqueous solution. The proposed procedure of pre-concentration is applied prior to the determination of silver ion using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The influences of pH, concentration of BMAA, applicability of different surfactants and foreign ions on the separation efficiency were investigated. The pre-concentration factor of the method is 1000 and the detection limit is 0.045 $\mu g\ mL^{-1}$.

**Keywords:** Silver ion, ICP-AES determination, flotation-separation, bis(2-mercaptoanil)acetylacetone

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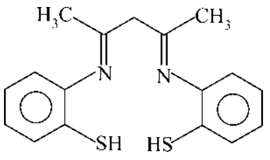
## INTRODUCTION

Silver is of great commercial importance due to its widespread use in photography, in the electronic industry, and in the field of medicine. The silver content of environmental samples is increased with increasing use of silver compounds (1, 2).

Silver can enter the environment *via* industrial waters because it is often present as an impurity in copper, zinc, arsenic, and antimony ores (3). Recent information about the interaction of silver with essential nutrients, especially Se, Cu, vitamin E, and vitamin $B_{12}$, has focused attention on potentially toxic nutrients (4, 5). Therefore, the design of reliable sensing methods for the highly sensitive and selective separation and determination of silver ion is still a challenging task.

Liquid–liquid extraction and separation of silver ion in the presence of classical (6–9) and macrocyclic ligands (10–15) are frequently reported in the literature. However, a serious limitation in traditional solvent extraction processes is that a large inventory of high purity solvents (and carriers) is required, especially when processing dilute solutions. An additional concern is the disposal of the solvent used, which creates a severe environmental problem.

Among different separation and preconcentration processes, flotation has the advantages of rapidity and simplicity, and it is suitable for the separation and pre-concentration of ions from highly dilute solutions (16–26). The necessary equipment for flotation pre-concentration is simple and inexpensive. The use of small amounts of a surfactant and tiny air bubbles required to perform a proper flotation process would not cause serious contamination risks, which could be manifested by the high blank values. One of the most important advantages of the flotation methods is the ability to analyze a larger volume of sample solutions and to obtain a greater pre-concentration factor. In recent years, flotation has also found use in the industrial recovery of gold and silver (23, 24). The objective of this work is to present the use of a new dithiol derivative bis(2-mercaptoanil)acetylacetone (BMAA, Scheme 1) as a very suitable reagent for the selective separation and pre-concentration of $Ag^+$ by flotation followed by ICP-AES determination in the float layer. The influences of several factors on the recovery were studied, and the optimum experimental conditions are presented.



***Scheme 1.*** Structure of BMAA.

## EXPERIMENTAL

### Apparatus

The flotation cell used (Fig. 1) was made by joining a sintered glass (porosity No. 4) funnel to a cylindrical glass tube of 4-cm inner diameter and 105 cm length. A hole was drilled in the funnel 1 cm above the sintered glass disk and fitted with a stopper for the sample removal by a syringe. A non-oil compressor was used for bubbling.

Traces of silver ion were determined by inductivity coupled plasma-atomic emission spectrometry (ICP-AES) using a Varian spectrometer model Varian Vista Pro, CCD Simultaneous, Springvale, Australia. The observation mode is radial-viewing, with an argon counter gas flow through the cone to eliminate the recombination zone on use of an echelle grating (94 grooves per mm) with a CaF2 prism cross-dispersion. The echellogramme is sampled by a segmented CCD, with each segment covering one of the 70

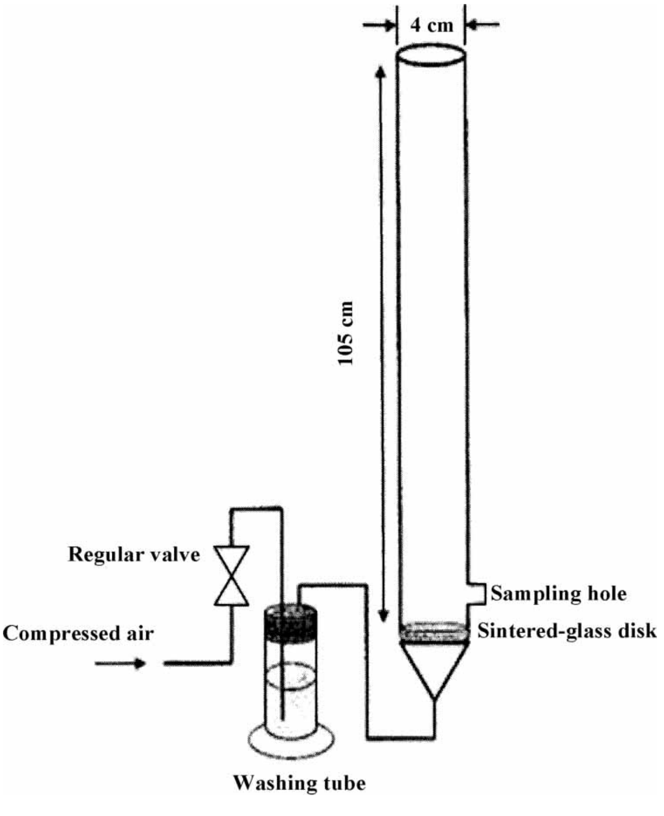


*Figure 1.* Schematic diagram of flotation system.

orders of the two-dimensional spectrum. The total number of pixels is ca. 70000 with a spectral resolution of 6.9 Ω (pico meter) at the Mo 202.032 nm emission line. The recommended instrumental characteristics and operating parameters are listed in Table 1. The pH reading was carried out with a Corning ion analyzer 250 pH/mV meter with a combined glass electrode.

## Reagents

All reagents used were of analytical reagent grade (Merck) except with the surfactants sodium dodecylsulfate (SDS), sodium oleate (SOL) and sodium stearate (SST), which were purchased from Fluka. Doubly distilled deionized water was used throughout. The stock solutions of $Ag^+$ ion (1 g $L^{-1}$) was prepared by dissolving an appropriate amount of $AgNO_3$ in water. Before each investigation, a series of standard solutions for the metal ion was prepared by appropriate dilution of the stock solution. Surfactant solutions used were 0.5% (by wt) in 95% ethanol. Solutions of $HNO_3$ (0.1 M) and KOH (20%w/w) were used for pH adjustments. Ionic strength was adjusted by a saturated solution of $KNO_3$.

## Preparation of BMAA

2-Aminothiophenol (2.5 g, 0.02 mol) was mixed with 100 mL of distilled ethanol in a 250 mL round bottom flask, while stirring with a magnetic

***Table 1.*** Instrumental and operating conditions for ICP-AES measurements

| Parameter | Type or amount |
|---|---|
| Frequency generator (MHz) | 40 |
| Plasma viewing mode | Radial |
| Viewing height (mm) | 8 |
| Injector i.d. (mm) | 2.5 |
| Optical mount | Echelle grating + cross-dispersion |
| Grating line number ($mm^{-1}$) | 95 |
| Focal length (cm) | 40 |
| Detector | CCD |
| Nebulizer | Concentric |
| Spray chamber | Cyclonic |
| RF power (kW) | 1.2 |
| Plasma gas flow rate (L $min^{-1}$) | 13.5 |
| Auxiliary gas flow rate (L $min^{-1}$) | 0.75 |
| Nebulizer pressure (kPa) | 200 |
| Rinse time (s) | 10 |
| Selected emission line (nm) | Ag (328.068) |

stirrer. Acetylacetone (1.01 g, 0.01 mol) dissolved in 50 mL distilled ethanol was added drop wise using a dropping funnel to the above solution. The contents were then refluxed for 2 h to get a red solution. On cooling, the red microcrystalline BMAA was precipitated out, collected by filtration, washed with ethanol, and dried in air. Elemental analysis (calculated): C, 64.83% (64.93%); H, 5.84% (5.77%); N, 9.05% (8.91%); S, 20.28% (20.39%).

### Flotation Procedure

A combined glass electrode was immersed into a 1-L beaker of the sample solution containing 54 μg of $Ag^+$ ion. After adding 2.0 mL of saturated $KNO_3$ solution and 0.5 mL 0.5% alcoholic solution of SDS, the pH of the medium was carefully adjusted to 6.0 with the KOH solution and then 10 mL of $5.0 \times 10^{-3}$ M BMAA in methanol and 2.0 mL of 0.1 M $NH_4NO_3$ were introduced into the mixture. After stirring for 20 min, the mixture was diluted to 1000 mL with distilled water. The content of the beaker was transferred into the flotation cell. It should be noted that the addition of 2 mL of 0.1 M $NH_4NO_3$ served to transfer quantitatively the contents of beaker into the flotation cell (16, 17, 20). An air stream (50 mL $min^{-1}$) was kept for 8–10 min to raise the foam layer to the water surface. Here, a foamy layer was obtained and the aqueous solution in the cell became clear. Then a glass pipette tube was immersed into the cell through the foam layer and the water sample was sucked off for ICP-AES measurements.

The flotation efficiency was calculated from $\%F = C_f/C_i \times 100$ (25), where $C_f$ and $C_i$ denote the float and initial concentrations of silver ion.

## RESULTS AND DISCUSSION

The existence of two donating nitrogen atoms and two-SH groups of soft character in the structure of Schiff's base BMAA was expected to increase both the stability and selectivity of its complexes with heavy metal ions over other cationic species. Our preliminary conductometric studies revealed that the ligand forms a highly stable and selective 1:1 $(Ag\text{-}BMAA)^+$ complex with silver ion, which is more or less insoluble in water, via forming a well-flocculated precipitate. Thus, we examined the applicability of BMAA as a very progressing reagent in the development of a rapid flotation method for the selective separation and enrichment of ultra trace amounts of $Ag^+$ ions from water samples. It should be noted that, over the entire pH range studied, the silver ion recovery by the flotation method was found to be negligible in the absence of BMAA as a very suitable complexing agent for $Ag^+$.

## Influence of Medium pH on Flotation Efficiency

Due to the pH dependent nature of all species involved in the flotation process (*i.e.*, metal ion, ligand, and surfactant), the pH of the test solution was expected to significantly influence the concentrating tendency and flotation efficiency of the proposed system. Thus, in a first step, the effect of varying the pH from 2.0 to 9.0 on the floatability of $5.0 \times 10^{-7}$ M of $Ag^+$ was investigated in the presence of $4.0 \times 10^{-5}$ M BMAA and 0.5 mL of a 0.5% SDS (by wt) solution ion in 95% ethanol (Fig. 2).

From the results shown in Fig. 2, it is obvious that the maximum flotation efficiency (~100%) is attained in a pH range of 6.0–6.5. However, the silver ion recovery is sharply decreased at lower pH values (*i.e.*, 2.0–5.5), most probably due to the protonation of both BMAA and dodecylsulfate anion in acidic media. On the other hand, the possible hydrolysis of the cation at pH $> 7.0$ will result in some diminished recovery of it. Thus, a pH of 6.0 was selected for further studies.

## Effect of BMAA Concentration on Flotation Efficiency

It is well documented that the relative amount of the complexing agent may largely influence the flotation separation processes (16–26). Thus, in this work the effect of BMAA concentration on the floatability of $5.0 \times 10^{-7}$ M of $Ag^+$ in the presence of 0.5 mL of 0.5t% SDS (by wt) solution in 90% ethanol at pH 6.0 was investigated and the results are shown in Fig. 3. As is

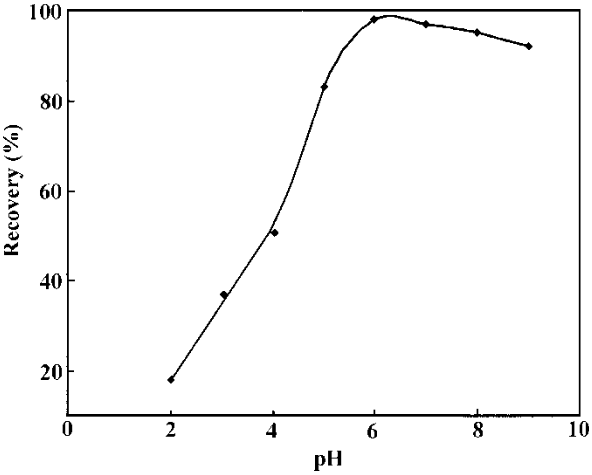


*Figure 2.* Effect of pH of test solution on the recovery of silver ion. The experimental conditions are given in the text.

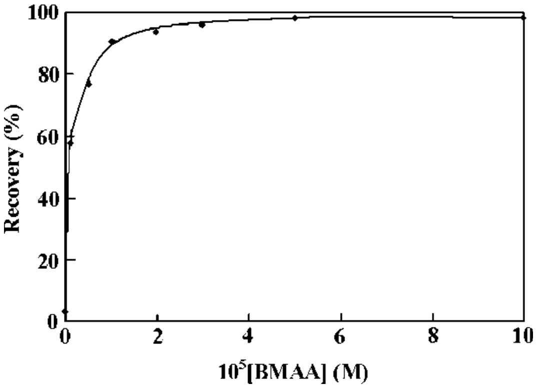


***Figure 3.*** Effect of BMAA concentration on the recovery of silver ion. The experimental conditions are given in the text.

obvious, complete flotation of $Ag^+$ was achieved at BMAA concentrations greater than $5.0 \times 10^{-5}$ M. Thus, for subsequent work, a BMAA concentration of $5.0 \times 10^{-5}$ M BMAA was selected. It is interesting to note that the presence of excess amounts of the ligand revealed no adverse effect on the flotation process. This is an advantageous point as the procedure could be applied to the analysis of $Ag^+$ in different real samples. As is seen from Fig. 3, the flotation efficiency of the system in the absence of BMAA is negligible.

## Choice of Surfactant

In an ion flotation process, a collector with a charge opposite to that of the ion to be floated is desirable. Since, in preliminary experiments it was found that silver exists as a complex cation $Ag(BMAA)^+$, in the proposed separation flotation process an anionic surfactant must be used as collector. It is worth mentioning that, in the case the of use of nonionic surfactants such as Triton X-100, although the surfactant foamed very well over the entire pH range and a copious white scum was formed at the top of the aqueous phase, the black $Ag(BMAA)^+$ complex was not separated by flotation and remained in water. These results further supported the existence of the silver-ligand complex in solution as a charged complex cation.

Thus, in further experiments, the influence of the nature of three different anionic surfactants, namely, sodium dodecylsulfate (SDS), sodium oleate (SOL) and sodium stearate (SST) on the flotation efficiency of $5.0 \times 10^{-7}$ M $Ag^+$ in the presence of $5.0 \times 10^{-5}$ M of BMAA and 0.5 mL of 0.5% of surfactants (by wt) in 90% ethanol was investigated at various pH values. The results are summarized in Table 2. As it is seen, over a pH

***Table 2.*** Applicability of diverse anionic surfactant for flotation $5.0 \times 10^{-7}$ M $Ag^+$ ion from aqueous solutions using 0.5 mL of 0.5% surfactant (by wt) and $5.0 \times 10^{-5}$ M BMAA

| | Recovery (%) | | | |
|---|---|---|---|---|
| pH | 4.0 | 5.0 | 6.0 | 7.0 |
| SDS | 44.6 | 85.4 | 99.3 | 97.9 |
| SOL | 58.1 | 74.3 | 93.5 | 98.2 |
| SST | 34.6 | 56.4 | 89.1 | 93.7 |

range of 6.0–7.0, the recovery by the proposed flotation method was in the range of 89.1 to 99.3% in the case of all three anionic surfactants used. Based on the results obtained in this section, SDS was selected as the most appropriate surfactant, which is also relatively cheap and advantageous for routine industrial use.

## Effect of Foreign Ions

The selectivity of the flotation system for the separation of $Ag^+$ ion over several potential interfering cations $M^{2+}$ ($M^{2+} = Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, and $Hg^{2+}$), present initially at $[M^{2+}]/[Ag^+] \geq 100$ in the feed solution. The tolerance limit was taken as the concentration of the foreign ion that caused an error of not more than 5% in the determination of the analytes. The results obtained from interference studies are summarized in Table 3. As is obvious, while the flotation recovery of silver ion in all cation mixtures examined is quantitative, the selected investigated elements which are usually present as main elements or traces in natural waters will remain in the test solution and have no adverse effect on the silver ion separation, pre-concentration, and determination, under the recommended conditions.

## Detection Limit

To determine the standard deviation of the method, 10 blanks were floated by the recommended procedure and then the concentration of silver ion was determined by ICP-AES. The detection limit of the method (DL) was estimated as three times the standard deviation ($S_b$) of the blank. The value of DL for silver was 0.045 $\mu g\, mL^{-1}$. The pre-concentration factor of the proposed flotation method is about 1000.

***Table 3.*** Effect of various ions on the percentage removal of $5.0 \times 10^{-7}$ M $Ag^+$ in the presence of excess amounts of diverse ions from aqueous solutions using 0.5% surfactant (by wt) and $5.0 \times 10^{-5}$ M BMAA at pH 6.0

| Cation | $[M^{2+}]/[Ag^+]$ | Percent recovery of cation |
|---|---|---|
| Mixture 1 | | |
| $Ag^+$ | — | 98.7 |
| $Mg^{2+}$ | 5000 | 0.0 |
| $Ca^{2+}$ | 5000 | 0.0 |
| $Ba^{2+}$ | 2000 | 1.2 |
| Mixture 2 | | |
| $Ag^+$ | — | 96.3 |
| $Ni^{2+}$ | 300 | 0.0 |
| $Zn^{2+}$ | 300 | 2.1 |
| Mixture 3 | | |
| $Ag^+$ | — | 94.9 |
| $Cd^{2+}$ | 200 | 1.4 |
| $Co^{2+}$ | 200 | 0.0 |
| Mixture 4 | | |
| $Ag^+$ | — | 96.7 |
| $Pb^{2+}$ | 150 | 2.9 |
| $Cu^{2+}$ | 150 | 1.3 |
| $Hg^{2+}$ | 100 | 4.4 |

## Flotation Mechanism

There are in fact two main types of interactions involved in the process of flotation, namely physical and electrostatic interactions (21, 22, 26). The predominance of the electrostatic mechanism is mainly governed by such important factors as the size and charge of ionic species involved, the presence of electronegative atoms capable of forming hydrogen bonds in the ligand structure, and charged sites on the solid species and precipitates.

Based on the existence and observation of some experimental factors in the present work, it seems reasonable to assume the predominance of an electrostatic mechanism for the proposed flotation system. These factors include, the presence of $-SH$ and $-N{=}$groups in BMAA structure, which possess high tendencies for forming H-bonds with the surfactant, the inability of triton X-100 as a nonionic surfactant for flotation of the metal ion complexes involved and preliminary conductometric information about the 1:1 complexes of BMAA with silver ion.

***Table 4.*** Determination of silver in synthetic samples

| Sample | Composition (mg $L^{-1}$) | $Ag^+$ floated (mg $L^{-1}$) | Flotation recovery (%) |
|---|---|---|---|
| Synthetic sample 1 | $Ag^+$ (0.054), $Cu^{2+}$ (120), $Zn^{2+}$ (200), $Cd^{2+}$ (150), $Na^+$ (550), $Ca^{2+}$ (340) | 0.052 | 96.3 |
| Synthetic sample 2 | $Ag^+$ (0.054), $Co^{2+}$ (160), $Pb^{2+}$ (150), $Hg^{2+}$ (25), $Ba^{2+}$ (200), $K^+$ (500) | 0.051 | 94.5 |

## Application of the Method

The proposed flotation method was successfully applied to the quantitative recovery of traces of $Ag^+$ ion from tap water samples. It was also used for the analysis of silver ion in two synthetic samples. Here, immediately after the sampling, the samples were treated by a few milliliters of concentrated $HNO_3$ to prevent the possible hydrolytic precipitation of some mineral salts. The pH of the conserved sample had to be 2.5–3.0. The analytical results for the analysis of synthetic water samples are represented in Table 4. As it is seen, in the presence of very large excess of different alkali, alkaline earth, transition and heavy metal ions (up to 550 mg $L^{-1}$), very low concentrations of silver ion as 0.054 mg $L^{-1}$ can be separated and measured almost quantitatively.

## CONCLUSION

The proposed flotation method for the separation and determination of ultra trace amounts of $Ag^+$ ion from water samples using bis(2-mercaptoanil)acetylacetone is simple, highly sensitive, selective, reproducible, and rapid when compared with the previously reported flotation methods (23, 24). The time taken for the separation-concentration and determination of silver ion by ICP-AES in a 1000 mL aqueous sample is at the most 15 min. The detection limit of the method is 0.045 $\mu$g $mL^{-1}$, together with a pre-concentration factor of 1000. The method can be successfully applied to the separation, pre-concentration, and determination of silver in real samples.

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