

Flotation-Spectrophotometric Determination of Ag(I) at the 10^{-7} mol L⁻¹ Level Using Iodide and Ferroin as an Ion-associate

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A simple and cost effective method for separation and preconcentration of Ag(I) at the 10^{-7} mol L⁻¹ level in the environmental and mineral samples is present. The method is based on the flotation of Ag(I)-iodide complex as an ion-associate with ferroin in pH of 4 from a large volume of an aqueous solution (500 mL) using *n*-heptane. The floated layer was then dissolved in dimethylsulfoxide (DMSO) for the subsequent spectrophotometric determination. Beer's law was obeyed over a range of 2.0×10^{-7} - 4.0×10^{-6} mol L⁻¹ with the apparent molar absorptivity of 2.67×10^5 L mol⁻¹ cm⁻¹. The detection limit ($n = 5$) was 4×10^{-8} mol L⁻¹, and RSD ($n = 5$) obtained for 2.0×10^{-6} mol L⁻¹ of Ag(I) was 2.2%. The interference effects of a number of elements was studied and found that only Hg²⁺ at low concentration, and Pb²⁺, Cd²⁺, Cu²⁺, and Fe³⁺ ions at moderately high concentrations were interfered. To overcome on these interference effects, the solution was treated with EDTA at a buffering pH of 4 and passed through a column containing Amberlite IR-120 ion-exchanger resin, just before the flotation process. The proposed method was applied to determine of Ag(I) in a synthetic waste water, a photographic washing sample and a geological sample and the results was compared with those obtained from the flame atomic absorption spectrometry. The results were satisfactorily comparable with together, so that the applicability of the proposed method was confirmed in encountering with the real samples.

Key Words : Flotation-spectrophotometry, Ag(I) determination, Ferroin, Ion-associate

Introduction

Silver is an important metal in view of its high resistance to corrosion and antibacterial properties. The various compounds of this commercial metal are largely used in the medicinal and photographic industries. Despite of its well-known usefulness properties, the toxicity of silver is characterized by a severe pulmonary edema, hemorrhage, and necrosis of bone marrow, liver, and kidney.^{1,2} So, long-term human exposing to silver compounds or colloidal silver may cause argyria.³ Very low concentrations of silver are currently found in various complex samples, such as drinking water, soil, rock, coal fly ash, air, cigarettes, plants, sea water, etc.⁴ Silver in small quantities usually is discharged to environment from the industrial contaminates and photographic washing wastes. Therefore, in view of analytical point, when it is present in trace amounts in the complex matrix, development a sensitive, selective, high precise and economical method for its quantitative determination is very important. Although, this determination can be carried out by expensive analytical methods, such as inductively couple plasma atomic emission spectrometry,^{5,6} inductively couple plasma mass spectrometry,⁷⁻⁹ and electrothermal atomic absorption spectrometry;¹⁰ but these methods are also suffering from many complicated processing steps and various type of inherent interferences.^{11,12} These drawbacks may be partly avoided using the enrichment processes, such as liquid-liquid and solid-phase extractions.¹³⁻¹⁷ These methods, in spite of the good feasibility, are suffering from troubles; for instance, liquid-liquid extraction procedures are

usually harmful to environment, and solid-phase methods are frequently recognized as time consuming with sometimes low reproducibility.

Recently, flotation-spectrophotometry is established as a preconcentration method in which trace amounts of elements in various complex materials can be enriched in a few times.¹⁸⁻²⁴ In such treatment, when a sparingly soluble species containing the analyte is formed, by using a light organic solvent, it is floated at the interface of aqueous/organic layers.²⁵⁻³¹ These procedures are suitable especially in treatment with large volume of the solution sample and cause to achieve a high enrichment factor. In addition, the organic phase can be usually reused without any pretreatment process. Thus, in comparison with the conventional solvent extraction methods, there is not such environmental contamination problem.

In the present work, the determination of trace amount of Ag(I) in aquatic samples was performed by a simple flotation-spectrophotometric method in which the anionic silver-iodide complex is strongly associated with ferroin as a cationic dye reagent.

Experimental Section

Instrumentation. A Shimadzu model 160A spectrophotometer with a 10-mm quartz cell was used for the absorbance measurements of the ion-associate solutions. A Phillips model PU9400X flame AAS was also used to confirm the Ag(I) determination. A Corning model 125 pH meter was used for pH adjustment.

Reagents. All the reagents were of analytical grade, obtained from Merck, Germany and used without further purification. Deionized and double distilled water was used in all the experiments.

An approximately 0.1 mol L^{-1} AgNO_3 solution was prepared and standardized against 0.1 mol L^{-1} standard solution of sodium chloride by the Mohr method. A stock Ag(I) solution ($1.0 \times 10^{-3} \text{ mol L}^{-1}$ in 0.01 mol L^{-1} HNO_3) was made by suitable dilution of the standard solution and used for preparing the working solutions. Both the standard and stock solutions were stored in PTFE bottles. The buffer solutions required to adjust the pH of the aqueous phase were prepared by mixing 1 mol L^{-1} formic acid/sodium formate, acetic acid/sodium acetate and hydroxylammonium chloride/sodium hydroxide for the pH range of 2.5-3.5, 3.5-5.5 and 5.5-7.0, respectively. The solution of $6.25 \times 10^{-3} \text{ mol L}^{-1}$ ferroin was made by sequential dissolving of the appropriate amounts of FeSO_4 and 1,10-phenanthroline (phen) with the stoichiometric ratio of 1 : 3 in aliquot of fresh water and adjusting its pH to 5 by addition of adequate volumes of the acetic/acetate buffer. It was then diluted to a fixed volume.

Procedure. To aliquot of Ag(I) solution (500 mL) with a maximum concentration of $4 \times 10^{-6} \text{ mol L}^{-1}$, which was placed in a suitable flask, 7 mL 0.5 mol L^{-1} potassium iodide was added and its pH was adjusted to 5 by addition of 5 mL acetic/acetate buffer solution. The solution was transferred to a 1000-mL separating funnel and then 2.5 mL ferroin, 40 mL *n*-heptane were added, sequentially. The funnel was stoppered and vigorously shaken for 30 min, then left to rest for a few minutes. When the ion-associate was perfectly floated at the aqueous/organic interface, the upper organic and lower aqueous layers were discarded by slowly opening the stopcock of the funnel. The floated layer, which was completely separated by adhering to the inner walls of the funnel, was then dissolved in 5 mL dimethylsulphoxide (DMSO) for the subsequent spectrophotometric determination. The absorbance measurements were carried out against a reagent blank prepared in the same manner.

Results and Discussion

Optimization. The optimum conditions for precise determination of Ag(I) were achieved by studying certain experimental parameters, which influenced on the stability of the ion-associate and characterized the flotation process.

The effect of pH was examined by varying the pH of the solution in the range of 2.50-7.00, just before the organic phase addition. As shown in Figure 1, the absorbance measurements represent a maximum at pH of 4. Hence, this pH was chosen for the future studies. Evidently, the absorbance decreasing at the pHs less than 4 is due to the instability occurred for the ion-associate, which is subsequently attributed to the ferroin instability. On the other hand, the absorbance decreasing at higher pH values may be due to the tendency to form a more stable complex between Ag(I) and phen, Ag(phen)_2^+ , in turn of the silver iodide

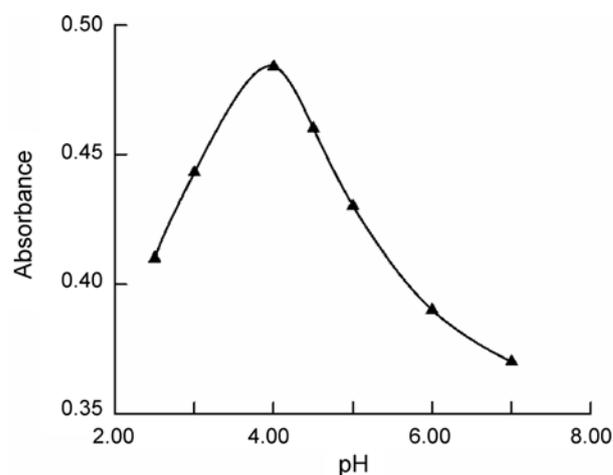


Figure 1. Effect of pH on the ion-associate formation in the flotation process at the conditions, where: $C_{\text{KI}} = 5.0 \times 10^{-3} \text{ mol L}^{-1}$, $C_{\text{Ferroin}} = 6.25 \times 10^{-5} \text{ mol L}^{-1}$, and $C_{\text{Ag}} = 2.0 \times 10^{-6} \text{ mol L}^{-1}$.

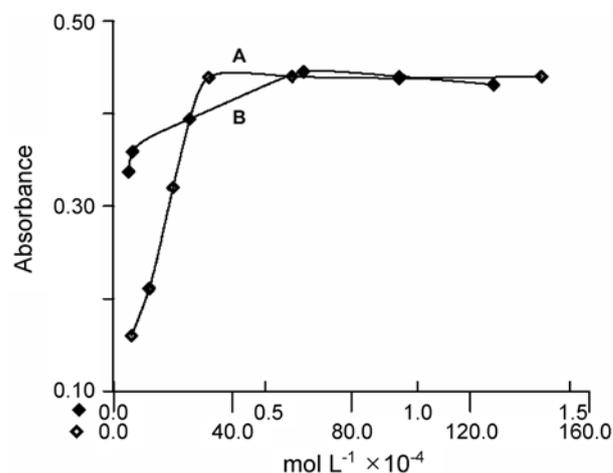


Figure 2. Curve A, Effect of iodide concentration on the determination of Ag(I) by the flotation method. The pH of the solution was adjusted to 4.00, $C_{\text{Ferroin}} = 6.25 \times 10^{-5} \text{ mol L}^{-1}$ and $C_{\text{Ag}} = 2.0 \times 10^{-6} \text{ mol L}^{-1}$ in all of the examinations, and curve B, effect of ferroin concentration at the similar conditions where the $C_{\text{KI}} = 5.0 \times 10^{-3} \text{ mol L}^{-1}$.

complex.

The effect of iodide concentration was studied over the range of 6.00×10^{-4} to $1.44 \times 10^{-2} \text{ mol L}^{-1}$. Curve A, in Figure 2, indicates a maximum absorbance occurs at the concentrations of iodide above $3.2 \times 10^{-3} \text{ mol L}^{-1}$. Since, by increasing the concentration of Ag(I) ions, it is necessary to use a high considerable amount of iodide, the flotation process was carried out at the presence of $5.0 \times 10^{-3} \text{ mol L}^{-1}$ iodide.

The effect of ferroin concentration on flotation of the ion-associate was also studied over the range of 5.00×10^{-6} to $1.25 \times 10^{-4} \text{ mol L}^{-1}$. As shown in curve B, Figure 2, a maximum absorbance was obtained at concentration of $6.25 \times 10^{-5} \text{ mol L}^{-1}$, which was used for further examination. Decreasing the absorbance at the lower concentrations of ferroin may be due to the decreasing of the

ion-associate concentration. Alternatively, the presence of excess amounts of ferroin causes to form the Ag(I)-phen complex, $\text{Ag}(\text{phen})_2^+$, and once again decrease the ion-associate formation. In addition, increasing the tendency to form ion-associate between the iodide and ferroin species, both in the blank and sample solutions and delaying the flotation process are the other effects of extra amount presentation of ferroin.

The flotation process was also examined by using several organic solvents including toluene, cyclohexane, *n*-hexane, and *n*-heptane. It was found that the absorbance depends on type of the organic phase. For example, at the optimum conditions the absorbance values for the flotation of $2.00 \times 10^{-6} \text{ mol L}^{-1} \text{ Ag(I)}$ using toluene, cyclohexane, *n*-hexane, and *n*-heptane were 0.267, 0.350, 0.257, and 0.486, respectively. By considering that separation between the phases was also achieved more quickly using *n*-heptane, it was chosen as the organic phase for the future examinations.

In order to investigate the volume of the aqueous phase, a number of the experiments were carried out in which the volume of the aqueous phase containing 0.1 mg Ag(I) was varied over the range of 50 to 700 mL. It was seen the flotation process can be carried out quantitatively, irrespective of the aqueous volume; however the reproducibility was made better by increasing the volume up to 500 mL.

Analytical Figures of Merit. Under the optimum conditions, a linear calibration curve was constructed for the spectrophotometric determination of Ag(I), over the range of 2.0×10^{-7} to $4.0 \times 10^{-6} \text{ mol L}^{-1}$ with a correlation coefficient (R^2) of 0.9978. The apparent molar absorptivity at the maximum wavelength of 513 nm for a path length of 1 cm, was $2.67 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ in which the aqueous phase volume was 500 mL. The RSD obtained for $2.0 \times 10^{-6} \text{ mol L}^{-1}$ of Ag(I) was 2.2% ($n = 5$) and the detection limit defined as the sample concentration giving a signal equal to the blank average signal ($n = 5$) plus three times the standard deviation of the blanks was found to be $4 \times 10^{-8} \text{ mol L}^{-1}$. When the measurements were directly carried out by flame atomic absorption spectrometry, a linear calibration curve with formula of: $A = 2.907 \times 10^4 [\text{Ag}] + 0.009$, was obtained for Ag(I) over the range of 1.0×10^{-6} to $3.0 \times 10^{-5} \text{ mol L}^{-1}$ at 328.1 nm with the correlation coefficient of 0.9995.

Complex Stoichiometry. Since direct construction of the ion-associate was not feasible in DMSO as a solvent, an excess amount of the complex was prepared by performance of the flotation process with moderately high concentration of the components. After flotation, separation and purification of the complex, it was decomposed by addition of 10 mL $0.1 \text{ mol L}^{-1} \text{ HCl}$. The released amounts of Ag(I) and iron(II) ions were determined directly by AAS method. The obtained results showed that the ratio of Ag(I) to iron(II) at the solution is 2 : 1, which denoted with the complex formula is $\text{Fe}(\text{phen})_3(\text{AgI}_2)_2$.

Effect of Foreign Ions. The flotation process was carried out on aliquot of 500-mL of a solution containing Ag(I) with concentration of $2.0 \times 10^{-6} \text{ mol L}^{-1}$ and various amounts of foreign ions as described in the procedure. As shown in

Table 1. Tolerance limits for foreign diverse ions in $3.19 \times 10^{-7} \text{ mol L}^{-1} \text{ Ag(I)}$ in a 500-mL solution

Mole ratio of interfering ion to Ag(I)	Ions
5000	$\text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}, \text{Cd}^{2+a}, \text{Co}^{2+}, \text{Cu}^{2+a}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+}, \text{Pb}^{2+a}, \text{Zn}^{2+}, \text{Al}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+a}, \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{SCN}^-, \text{ClO}_4^-, \text{CH}_3\text{COO}^-, \text{CO}_3^{2-}, \text{C}_2\text{O}_4^{2-}, \text{SO}_4^{2-}$
100	$\text{Pb}^{2+}, \text{Cu}^{2+}$
10	Fe^{3+}
1	Cd^{2+}

^aTolerated after masking with EDTA, in which 5 mL of 0.1 mol L^{-1} EDTA was added to the solution before the flotation process

Table 1, almost all of the cations and anions except that Hg^{2+} , Cd^{2+} , Cu^{2+} , Pb^{2+} , and Fe^{3+} are tolerated at the high concentrations. The interference effects of the first four ions may be due to form moderately stable complexes either with iodide or ferroin agents, whereas the interference of Fe^{3+} may be due to oxidize the iodide ions present in the medium. To overcome on these interference effects, they were removed from the solution just before the flotation process by treating it with aliquot of 10-mL of 0.01 mol L^{-1} EDTA at the buffering pH of 4, and then passing through a column containing Amberlite IR-120 as an anion-exchanger resin. Alternatively, at the absence of Hg^{2+} , it is not necessary to remove the last four metal ions from the solution by passing through the column, since they are essentially capable to form more stable complexes with EDTA in comparison with iodide ion. As pointed out in details of Table 1, they were masked and tolerated at high considerable ratios only by addition of the appropriate amount of EDTA just before the flotation process. It showed be considered, although the EDTA-Hg^{2+} is too stable, but the stability of HgI_4^{2-} is much greater than it, so the interference of Hg^{2+} could not be eliminated by the masking process and required to use from the first cited elimination method, if Hg^{2+} ions are present in the solution. Fortunately, Ag^+ and Hg^{2+} usually are not co-existing in the real samples and subsequently it is not considered as a serious interferent on the determination of Ag(I) in practical analysis of the real samples.³²

Sample Analysis. The applicability of the proposed method was investigated both for the environmental and geological samples. The slopes of the calibration graph prepared by the standard curve method for the water samples were found almost identical with that of the standard addition plot. Hence, the standard curve method was used in the determination of various samples. Initially a synthetic wastewater²⁹ was prepared and spiked to known amounts of Ag(I). The recovery of the spiked amounts was in the range of 95.3-104.7%, which is demonstrated that the proposed method is reliable (Table 2). Then analysis of Ag(I) in a photographic washing sample and a geological sample (obtained from Ghalah-Zari copper mine, situated in the south of Birjand), were examined similarly. To confirm the accuracy of the results obtained by this method, the measurements were carried out directly by AAS method. It

Table 2. Analytical data of Ag(I) in the synthetic waste water and real samples. The standard deviations are presented in the parentheses

sample	Spiked (mol L ⁻¹)	Measured (mol L ⁻¹)	
		This method	Flame-AAS
Synth. waste water	–	5.2×10^{-7}	– ^a
	5.00×10^{-7}	9.24×10^{-7}	9.37×10^{-7}
	5.00×10^{-6}	5.11×10^{-6}	5.17×10^{-6}
Photo. Washing	–	$1.42(\pm 0.03) \times 10^{-6}$	$1.32(\pm 0.05) \times 10^{-6}$
Geo. sample	–	$1.30(\pm 0.06) \times 10^{-6}$	$1.37(\pm 0.05) \times 10^{-6}$

^aCould not be measured by this method.

is worthwhile to discuss that the amount of the real samples, which were treated to prepare the analytical solutions, was so large in comparison with the flotation process. The concentrations of Ag(I) determined by the proposed method were in good agreement with those obtained by the AAS method. The RSD of this method, when applied to the above samples was in the range of 1.9 to 2.5%, whereas, the RSD of the AAS method was in the range of 2.4 to 3.2%. These results showed that the method is capable to determine of Ag(I) at the 10^{-7} mol L⁻¹ level in various type of complicated samples.

Conclusion

This work has demonstrated the ability of silver determination in the real samples with a good accuracy and selectivity. The AAS method, which is established as an accepted method for the determination of silver traces, exhibits insufficient sensitivity and poor detection limit for direct determination of, especially in the presence of some ions, such as Fe, Ni, Mg, Pb, Ca, Cu, and Na at high level, furthermore, the accuracy is endangered.³³ Although, the proposed method was also insecure at the presence of some metal ions, but they are easily can be eliminated by a simple treatment. The preconcentration factor for the proposed method is 100, which is a considerable factor and represents the applicability on treatment with the real samples containing trace amount of silver. In comparison with the extraction-spectrophotometric methods in which the organic solvents are usually harmful to environment, the organic solvent used in this method does not polluted and can be used repeatedly without any purification process. Consequently, this method can be carried out easily without any sophisticated devices, especially for the aquatic solutions.

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