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Preconcentration of Silver with the Ion-pair of 1,10-Phenanthroline and Tetraphenylborate on Naphthalene

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A solid ion-pair material produced from 1,10-phenanthroline and tetraphenylborate on naphthalene provides a simple, rapid, economical and fairly selective means for the preconcentration of silver from a large volume of the aqueous samples (about 200-fold concentration can be easily achieved). Silver is quantitatively adsorbed on this material in the pH range 2.0 ~ 11.0 in HCl medium and in the concentration range of 1 ~ 8 N HNO_3 medium at a flow rate of 1 ml/min. The solid mass from the column is dissolved out with 5 ml of dimethylformamide (DMF) and measured by an atomic absorption spectrophotometer at 328.1 nm. Beer's law is obeyed over the concentration range 0.5 ~ 10 μg of silver in 5 ml of the DMF solution. Seven replicate analyses of a sample solution containing 2 μg of silver gave a mean absorbance of 0.140 with a relative standard deviation of 1.2%. The sensitivity for 1% absorption is 0.013 μg/ml (0.060 μg/ml for the direct atomic absorption spectrophotometric method from the aqueous solution). Various parameters have been evaluated and the method has been employed for the trace determination of silver in various standard materials.

INTRODUCTION

Several preconcentration techniques for trace-element analysis of aqueous samples have been proposed by various authors. Liquid-liquid extraction is one of the most widely used techniques, owing to its simplicity and applicability to both trace and macro amounts of metal ions, however, it cannot be employed directly for the extraction of metal ions which form complexes with the reagent at a high temperature[1]. Although this difficulty can be overcome by using molten naphthalene as an extractant[2], but it is inconvenient since the operation is carried out at a high temperature and cannot be employed for the thermally unstable metal chelates. The method, solid-liquid separation after adsorption of metal chelates on microcrystalline naphthalene, is very convenient, rapid,

economical and can be applied to many types of the metal complexes and is especially useful for metal complexes which have low solubility in the non-aqueous organic solvents[3]. The only difficulty is the filtration of small amounts of naphthalene, which may result an error in the analysis.

In the present communication, a chromatographic method has been developed for the selective preconcentration of silver from a large volume of the aqueous phase by using 1,10-phenanthroline-tetraphenylborate-naphthalene as an adsorbent. The adsorbed metal in the column is not eluted even on washing with water but can be dissolved out along with naphthalene using a suitable solvent like dimethylformamide and can be determined directly by atomic absorption spectrophotometrically[4–7].

Although some methods have been developed by using various adsorbents like thiol cotton[8], siland glass beads[9], resin[10], cellulose and a few metal oxides and hydroxides but the proposed method is more economical (only 0.2 g of the adsorbent is used), rapid (the solid mass is dissolved out with a small volume of the solvent instead of eluation) and sensitive (more than 200–fold concentration can be achieved easily). Various parameters have been evaluated and the method has been employed to the determination of silver in standard materials.

EXPERIMENTAL

Apparatus

A Hitach model 170–50 atomic absorption spectrophotometer and a Hitach-Horiba M-7E pH meter were used. A hollow-cathode lamp for silver was obtained from Hitachi Ltd., Japan. A glass tube of 60 mm in length and 6 mm internal diameter was used as a chromatographic column. It was fitted with cotton wool and then filled with suitable amount of naphthalene loaded with 1, 10-Phenanthroline and tetraphenylborate.

Reagents

Silver nitrate solution was prepared from 1000 ppm standard atomic absorption solution in double distilled water. Buffer solutions were prepared by mixing 1M acetic acid and 1M ammonium acetate solution, and 1M aqueous ammonia and 1M ammonium acetate solution in a suitable ratio.

Naphthalene, 1,10-phenanthroline (Phen), sodium tetraphenyl-borate (TPB), DMF and all other reagents were of analytical-reagent grade.

Preparation of loaded 1,10-phenanthroline-tetrapheneylborate-naphthalene mixture

A 20% solution of naphthalene in acetone (100 ml) was transferred to 0.1 N hydrochloric acid (700 ml) of 1,10-phenanthroline (4.1 g) which was being stirred on a hot-stirrer at room temperature. Then 100 ml of

aqueous solution of TPB (6%) were added to it slowly. The mixture was stirred for about 3 ~ 4 hr for the complete coprecipitation of the naphthalene-Phen-TPB mixture. This was stored in a brown bottle for a long storage which was a slurry of the adsorbent in water and slurry packed in the column after washing with water for use.

General Procedure

A portion of the silver solution containing 0.5 ~ 10 μg of silver was taken in a 30 ml beaker and to it were added 20 ml of distilled water and 1.0 ml of the acetate buffer (pH 3.5). Before this solution was passed through the column loaded with naphthalene-Phen-TPB at flow rate of 1ml/min, it was conditioned to pH 3.5 by passing 3 ~ 4 ml of the buffer. The column was aspirated if necessary. It was washed with water and the metal complex along with naphthalene was dissolved out with 5 ml of DMF. This solution was aspirated into an air-acetylene flame and the absorbance measured at 328.1 nm against the reagent blank.

RESULTS AND DISCUSSION

Adsorption Characteristics of Phen-TPB

1,10-phenanthroline has two pyridine nitrogen atoms but only one is capable of reacting with hydrogen ion and thus acting as a monoacidic base because of the short distance of 2.5. A between them. The dissociation constant of monoacidic base is reported to be 5.0 or 4.95. Therefore, in acidic solution it behaves as follows:

$$(1, 10\text{–Phen}) + H^+ \rightarrow (1, 10\text{–Phen})\ H^+$$

In the presence of TPB^- ion,

$$(1, 10\text{–Phen})\ H^+ + TPB^- \rightarrow (1, 10\text{–Phen})\ H^+ \cdot (TPB)^-$$

The ion-pair formed from cationic (1,10-Phen) H^+ and anionic TPB^- is easily coprecipitated with microcrystalline naphthalene. This ion-pair adsorbent reacts with metal ions like Cu(I), Ag(I), Tl(I), Fe(II), Cs(I), Rb(I) to form water-insolube complexes. This adsorbent has the excellent adsorption characteristics towards metal ions in the column over the wide pH range of 0 ~ 11 and 1 ~ 8N HNO_3 solution.

Operating Conditions

All the measurements were carried out with the operating conditions given below: Wavelength 328.1 nm; slit setting 4(7A); current 8 mA; burner height from the top of the burner head 11 mm; acetylene flow 35 (pressure 0.5 kg/cm^2) and air flow 55 (pressure 2.1 kg/cm^2).

Effect of pH

The adsorption is maximum and constant on naphthalene- 1,10-

Phen–TPB in the wide pH range 2.0 ~ 11.0 and 1 ~ 8N NNO_3 aqueous medium (Fig. 1). In subsequent study, all measurements were carried out

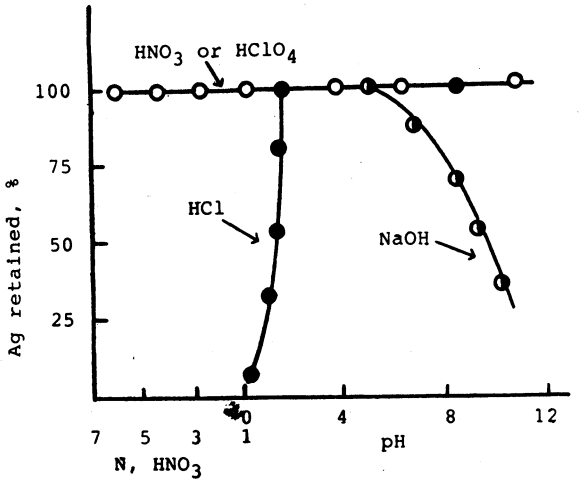

Fig. 1 Effect of pH: Ag: 2 μg; Wavelength: 328.1 nm; Reference: Reagent blank.

out at pH 3.5. Addition of 1.0–3.0 ml of the buffer (pH 3.5) caused virtually no variation in adsorption of silver, and use of 1.0 ml was recommended for convenience.

Effect of flow rate

The flow rate was varied from 0.5 ~ 7 ml/min. The flow rate did not affect the adsorption in 0.5 ~ 3.3 ml/min. A flow rate of 1 ml/min was recommended for convenience.

Adsorption capacity of the adsorbent

The adsorption capacity of the loaded ion pair-naphthalene mixture was determined by the batch method. The experiment was carried out by taking 1000 μg of silver, 1.0 ml of the buffer (pH 3.5), suitable amount of the loaded ion pair-naphthalene mixture in a 100 ml separatory funnel. The solution was diluted to 30 ml and shaken well for 20 min. The maximum amount of adsorption was found to be 4.65 mg/g of the adsorbent. The adsorption capacity of silver on naphthalene depends greatly on the molar ratio of 1,10-Phen to TPB. The experimental results showed that the adsorption capacity was the maximum when the molar ratio of 1,10-phen to TPB was at 1 : 1 which is also obvious from the equation.

Effect of volume of the aqueous phase

The effect of volume of the aqueous phase on the adsorption of silver in the column was studied by the general procedure. The adsorption

remained constant and maximum even when the volume of the aqueous phase did exceed 1300 ml.

Choice of Solvent

In the present work, DMF was used to dissolve the mixture due to the high absorbance. It was found that 3 ml of this solvent was enough for this purpose and 5 ml were recommended for safe side.

Linearity, sensitivity and precision

With the optimum conditions described above, a calibration curve for silver was constructed at 328.1 nm. It was linear over the concentration range 0.5 ~ 12 μg of silver in 5 ml of DMF solution. Eight replicate analyses of 2 μg of silver gave a mean absorbance of 0.140 with a relative standard deviation of 1.2%. The sensitivity for 1% absorption is 0.013 μg/ml (0.060 μg/ml for direct AAS method from the aqueous solution). The preconcentration factor was 260.

Effect of diverse ions

Sample solutions containing 2 μg of silver and various amounts of different alkali metal salts or metal ions were prepared and the determination of silver was carried out by the general procedure. The tolerrance limit (error < 3%) is given in Table 1. Many of the salts can be

TABLE 1
EFFECT OF DIVERSE IONS

Salt or ion	Tolerance limit
$CH_3COONa\ 3H_2O$, NH_4Cl, Na_2SO_4, $NaClO_4\ H_2O$, NaCl, KNO_3, sodium tartrate, CH_3COONH_4, ammonium citrate, disodium EDTA	1. g*
KH_2PO_4	0.8 g*
$Na_2C_2O_4$, Na_2CO_3	0.5 g*
KI	25 mg
thiourea	10 mg
Ca(II), Zn(II), Cr(III), Cr(VI), Pb(II)	100 mg*
Zr(IV)	50 mg*
Fe(II)	50 mg*
Fe(III)	30 mg
Mn(II)	30 mg*
Al(III)	25 mg*
Cu(I), Cu(II), Cd(II), Pb(II), W(IV), V(V)	10 mg*
Ti(IV), Sn(II)	10 mg*
Co(II), Ni(II)	10 mg
Bi(III)	8 mg*
Hg(II), Pt(II)	5 mg*
La(III), Nb(III), Au(III), Sb(III), Cs(I), Ce(III)	2 mg*

*Maximum value tested. Ag: 2 μg, Wavelength: 328.1 nm, pH: 3.5, Adsorbent: (1,10-Phen–TPB–Naphthalene).

tolerated even up to mg-levels. Thiourea (10 mg) and KI (25 mg) would be tolerated. Metal ions can also be tolerated even over 2 ~ 100 mg amounts. Thus the present method is very selective and may be successfully applied for the determination of silver in various standard samples.

Determination of Silver in Alloys

The proposed method was applied to the determination of silver in the reference materials, lead-base alloy, tin-base alloy and zinc metal. The results are reasonably good agreement with those obtained by the certified values, as shown in Table 2. The analytical procedure were as

TABLE 2

ANALYSIS OF ALLOYS FOR SILVER

Sample	Silver certified, %	% Silver
N.B.S., SRM-127b lead-base alloy	0.01	0.0085±0.0002
N.B.S., SRM-54d tin-base alloy	0.0032	0.00307±0.00006
N.B.S., SRM-683 zinc metal	1.3 μg/g	1.28±0.02 μg/g
N.B.S., SRM-127b	(Cu: 0.011, Ni: 0.012, As: 0.01, Sn: 39.3, Sb: 0.43, Bi: 0.06, Ag: 0.01)	
N.B.S., SRM-54d	(Pb: 0.62, Sn: 88.57, Ni: 0.0027, Sb: 7.04, Bi: 0.044, Cu: 3.62, Fe: 0.027, As: 0.088, Ag: 0.0032)	
N.B.S., SRM-683	(Cu: 5.9, Pb: 11.1, Fe: 2.2, Cd: 1.1, Ti: (0.2), Sn: (0.02))	

follows: A mg-amount of the standard alloy was completely dissolved in aqua regia, concentrated sulfuric acid and hydrobromic acid. The solution was evaporated to dryness. The residue was dissolved in nitric acid, and then brought to standard volume with water. This sample was used for the procedure.

Conclusion

Solid-liquid separation after liquid-liquid extraction is especially useful for extracting metal complexes which are either formed at a high temperature or have low solubility in the non-aqueous organic solvents but inconvenient since carried out at a high temperature while the method of separation of metals after adsorption of their metal complexes onto microcrystalline naphthalene is convenient and sensitive but involves filtration which is a time-consuming process. The proposed technique is not only convenient but it is simple, rapid, sensitive and highly economical. The metal is preconcentrated on a very small amount of the

adsorbent (0.2 g) from a larger volume of the aqueous phase. The solid mass consisting of the metal complex and naphthalene can be dissolved in 3 ~ 5 ml of DMF, the whole of which can be taken for the absorbance measurement, making the technique highly sensitive. The method of preparation of the adsorbent is more easy as compared to the other adsorbents like thiol cotton, cellulose, amberlite XAD-resins and loaded glass bead. Since this reagent also reacts with some other metals too, therefore similar method may also be developed for their determination. The sensitivity of this method may be further improved by using other optical and electroanalytical techniques.

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