

## Fourth Derivative Spectrophotometric Determination of Trace Silver after Preconcentration with the Ion Pair of 2-Nitroso-1-naphthol-4-sulfonic Acid and Tetradecyldimethylbenzylammonium Chloride by Microcrystalline Naphthalene or Column Method

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Silver is quantitatively retained as 2-nitroso-1-naphthol-4-sulfonic acid (nitroso-S) and tetradecyldimethylbenzylammonium (TDBA) ion associated complex on microcrystalline naphthalene in the pH range 9.5–11.0 from large volumes of its aqueous solutions of various alloys and biological samples. After filtration, the solid mass consisting of metal complex and microcrystalline naphthalene was dissolved in dimethylformamide (DMF) and the metal determined by fourth derivative spectrophotometry. Silver can alternatively be quantitatively adsorbed on (nitroso-S)-(TDBA)-naphthalene adsorbent packed in a column at a flow rate of 1–2 ml min<sup>-1</sup> and determined similarly. The calibration curve is linear over the concentration range 0.2–30 µg ml<sup>-1</sup> of silver in dimethylformamide solution by measuring the distance  $d^4A/d\lambda^4$  between  $\lambda_1$  (606 nm) and  $\lambda_2$  (562 nm) with a correlation coefficient of 0.9994 and relative standard deviation of  $\pm 1.1\%$ . The analytical sensitivity is calculated to be  $0.198(d^4A/d\lambda^4)/\mu\text{g ml}^{-1}$  from the slope of the calibration curve. The detection limit is  $0.15 \mu\text{g ml}^{-1}$  for silver at the minimum instrumental settings (signal to noise ratio = 2). Various parameters

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such as the effect of pH, volume of aqueous phase and interference of a large number of metal ions on the determination of silver have been studied in detail to optimize the conditions for its determination in various complex samples.

*Key words:* derivative spectrophotometry, silver, preconcentration, 2-nitroso-1-naphthol-4-sulfonic acid, tetradecyldimethylbenzylammonium chloride, naphthalene.

## INTRODUCTION

The toxicity of silver is characterized by a severe pulmonary edema, hemorrhage, and necrosis of bone marrow, liver, and kidney.<sup>1-2</sup> Long-term human exposure to silver salts or colloidal silver may cause argyria.<sup>3</sup> Repeated exposure of animals to silver may produce anemia, cardiac enlargement, growth retardation and degenerative changes in the liver.<sup>4</sup> Very low concentrations of silver are present in various complex samples like drinking water (5 µg/l), soil, rock, coal fly ash, air, cigarettes, alloys, plants, sea water, *etc.*<sup>5</sup> Therefore, it is very important from the analytical point of view to develop sensitive, selective, rapid and economical methods for its quantitative determination even when present in trace amounts. NAA, AAS, graphite furnace-AAS, ICP-AES, ICP-MS may be used for the trace determination of metals in complex materials, but most these instruments are highly expensive, their day to day maintenance cost is high and are not free from various types of inherent interferences.<sup>6-9</sup> A survey of the literature reveals that silver may be determined spectrophotometrically using various complexing agents.<sup>10-17</sup> Although some of them are fairly sensitive, they have sometime limited selectivity and preconcentration factor as compared to the present method and a few of them are expensive too (Table I). 2-Nitroso-1-naphthol-4-sulfonic acid (abbr. nitroso-S) was introduced by Hoffman<sup>18</sup> as a qualitative analytical reagent for cobalt, copper and iron and applied to the colorimetric determination of cobalt by Wise and Brandt.<sup>19</sup> The reagent forms water-soluble chelate anion with

TABLE I

Some of the recent spectrophotometric methods for the determination of silver

Reagent	Characteristics <sup>a</sup>	Ref.
5-[4-(2-Methyl-3-hydroxy-5-hydroxy-methyl)pyridyl-en]rhodanine	$\epsilon$ : $1.5 \times 10^4$ . Linear range: 0.25–4.0. Reagent is expensive. Limited aqueous phase volume, Hg <sup>2+</sup> , Au <sup>3+</sup> , Pd <sup>2+</sup> , I <sup>-</sup> , Br <sup>-</sup> and S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> interfered. Silver determined in drug and ore samples.	10

TABLE I (cont.)

5-[ <i>p</i> -(Dimethylamino)benzylidene]rhodanine	$\epsilon$ : $3.5 \times 10^4$ . Linear range: 10–40.0. Reagent is expensive. Poly(vinyl alcohol)-200 has to be added to improve $\epsilon$ , and colour developed in 15 min. Limited aqueous phase volume. A few metal ions interfered.	11
4,7-Dimethyl-2-thiol-2-thion-1,3,2-dioxophosphorinan (DOPh <sub>111</sub> )	Linear range: 1.0–18.0. The method involves the replacement of Cu <sup>2+</sup> from Cu(DOPh <sub>111</sub> ) <sub>2</sub> by silver and measuring the decrease in the absorbance of the Cu(DOPh <sub>111</sub> ) <sub>2</sub> toluene solution. F <sup>-</sup> , SCN <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> and Hg <sup>2+</sup> interfered seriously. Applied to some standard samples.	12
Dithizone	$\epsilon$ : $3.45 \times 10^4$ . Linear range: 0.1–6.0. Extracted into polyurethane and elution with Me <sub>2</sub> CO. Limited aqueous phase volume. Some metal ions interfered. Applied to glass analysis.	13
2-(8-Hydroxyquinolin-5-ylazo)benzoic acid	$\epsilon$ : $3.65 \times 10^4$ . Linear range: 0.05–0.65. Reagent is expensive. Several metal ions interfered and have to be separated as hydroxide. Applied to some geological samples.	14
2-Carboxybenzal-aldehyde thiosemicarbazone-octylmethyl-ammonium chloride	Linear range: 10–70. Method is time consuming, common metal ions interfered. Applied to ore samples.	15
4-(2-Hydroxy-4-substituted-azobenzene)-2-methylquinoline	Linear range: 2.5–23.0. Limited aqueous phase volume. Some metal ions interfered seriously. Applied to photographic fixing solutions.	16
Bromopyrogallol red-cetylpyridinium chloride	$\epsilon$ : $3.2 \times 10^3$ . Linear range: 2.15–8.6. Limited aqueous volume, a few metal ions interfered. Applied to silver amalgam and dental prothesis.	17
2-Nitroso-1-naphthol-4-sulfonic acid	$\epsilon$ : $6.47 \times 10^3$ . Linear range: 0.2–30. Preconcentration factor: 80, sensitivity: $0.198(d^4A/d\lambda^4) / \mu\text{g mL}^{-1}$ ; detection limit: $0.15 \mu\text{g mL}^{-1}$ , method is highly selective for silver; use of derivative spectrophotometry further increased the sensitivity and selectivity considerably; applied to standard alloys and biological samples.	Present method

<sup>a</sup> Remarks:  $\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ; linear range /  $\mu\text{g mL}^{-1}$ .

metal ions, but the high absorption of the reagent blank at the measurement wavelength makes the nitroso-S procedure more troublesome. Motomizu and Toei reported the extraction of Cu(II)-(nitroso-S) anion with TDBA cation<sup>20</sup> (TDBA, tetradecyldimethylbenzylammonium) and Fe(II)-(nitroso-S) anion with azo dye cation in chloroform.<sup>21</sup>

Preconcentration is the most important step for the determination of metal ions because of their low concentration in various materials. Solvent extraction is a simple and convenient technique for separating and concentrating metal ions from aqueous solutions, but it is sometimes tedious and the concentration factor is low due to mutual solubility of two phases. Certain materials such as thiol cotton, silanized glass beads, C<sub>18</sub>-bonded silica gel, Amberlite XAD-2 resin, cellulose, green tea leaves, polythioether foam and various metal oxides and hydroxides have also been used as adsorbents for preconcentration of metal ions. Some of them are quite effective, but their methods of preparation are lengthy and also involve rigid experimental conditions.<sup>22</sup> The desorption of the metal is carried out by a slow process of elution (probably the metal complex may be held by interior surfaces of the adsorbent and hence is not eluted easily), so the procedure is time consuming.

In the present communication, an efficient method for the preconcentration of silver from a large volume of its aqueous solutions of various standard reference materials using (nitroso-S)-TDBA-naphthalene adsorbent has been described. The method is economical (all reagents are cheap and only 0.3 g of the adsorbent and not much glassware are needed), rapid (the adsorbent is dissolved out of the column instead of being eluted), simple (the metal solution at a definite pH is passed over the adsorbent), sensitive (the adsorbent can be dissolved in 2–3 ml of an organic solvent, and the whole of the solution may be used for absorbance measurement) and highly selective. The solid mass, consisting of the metal ion associated complex and naphthalene can easily be dissolved out of the column with a suitable organic solvent such as dimethylformamide (DMF) and silver determined by fourth derivative spectrophotometry, which further enhances the selectivity and sensitivity of the method (Table I). Various parameters have been evaluated and the optimized conditions utilized for the trace determination of silver in standard alloys and biological samples. The method may also be employed for the determination of silver in various environmental samples.

## EXPERIMENTAL

### *Apparatus and Reagents*

A Shimadzu UV 160 spectrophotometer with a 1.0-cm quartz cell was used. A Beckman pH meter was employed for pH measurements. A funnel – tipped glass tu-

be (60 × 7 mm i.d.) was used as a column. The column was plugged with polypropylene fibers and slurry – packed with the naphthalene adsorbent to a height of ≈ 1.0–1.2 cm, pushing lightly with a flatted glass rod. All atomic absorption measurements were made with an atomic absorption spectrometer (Shimadzu AA 670). All glasswares were washed with mixture of concentrated sulfuric acid and nitric acid (1 + 1) before use.

All reagents were of analytical reagent grade. A standard silver solution was prepared from silver nitrate (Merck) in distilled water and standardized.<sup>23</sup> Buffer solutions of pH ≈ 10.5 was prepared by mixing an appropriate ratio of 0.5 M aqueous ammonia and 0.5 M ammonium acetate. A 1% solution of tetradecyldimethylbenzylammonium chloride (TDBA<sup>+</sup>Cl<sup>-</sup>) (Merck) and 0.1% 2-nitroso-1-naphthol-4-sulfonic acid (nitroso-S salt) (Fluka, Switzerland) were prepared in distilled water. A 20% solution of naphthalene was prepared in acetone. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations respectively.

#### *Preparation of (Nitroso-S)-TDBA-Naphthalene Adsorbent*

A solution of naphthalene was prepared by dissolving 20 g of it in 40 ml of acetone on a hot-plate stirrer at approximately 35 °C. It was transferred to a beaker containing 1500 ml of distilled water and 0.9 g of nitroso-S salt (0.0028 mole), in a fast stream with continuous stirring at room temperature. (TDBA<sup>+</sup>Cl<sup>-</sup>) (1.2 g, 0.0031 mole) was dissolved in 500 ml of distilled water by warming on a hot plate. It was mixed with the above solution of naphthalene-acetone-nitroso-S salt in water. The yellow naphthalene adsorbent coprecipitated with TDBA and nitroso-S was stirred for about 2 h and then allowed to stand for another 2 h at room temperature. The supernatant solution was decanted off and the residue was washed twice with distilled water. The adsorbent in the form of slurry was stored in a brown bottle for subsequent use.

#### *General Procedure for the Column Method*

An aliquot of silver solution containing 1.0–150 μg of silver was taken in a 50-ml beaker. The pH of this solution was adjusted to ≈ 10.5 with the addition of 2 ml buffer solution and diluted to about ≈ 30–40 ml with distilled water. The column loaded with the (nitroso-S)-TDBA-naphthalene adsorbent was conditioned to pH ≈ 10.5 with 2–3 ml of buffer and then the metal solution was passed through the column at a flow rate of 1–2 ml min<sup>-1</sup>. The packing was washed with a small volume of water and then aspirated strongly for a few minutes, pushing down the naphthalene material with a flat glass rod to eliminate the excess of water attached to naphthalene. The solid mass consisting of the metal complex along with naphthalene was dissolved out of the column with 5 ml of DMF. The fourth derivative spectrum of this solution was recorded from 550 to 650 nm against a reagent blank with Δλ = 9 nm.

#### *General Procedure for Microcrystalline Naphthalene Method*

An aliquot of silver solution (containing 1.0–150 μg) was placed in a 100 ml of an Erlenmeyer flask with tightly fitting stopper. Then, 1 ml of 0.1% of the reagent (nitroso-S) and 2 ml of 1% TDBA solutions were added to it. The mixture was diluted to

30–40 ml with water. The pH was adjusted to  $\approx 10.5$  with the addition of 2 ml of the buffer. The solution was mixed well and allowed to stand for a few seconds. Then, 2 ml of a 20% solution of naphthalene in acetone was added to it with continuous shaking. The solid mass so formed consisting of naphthalene and metal complex was separated by filtration on a Whatman filter paper (No. 1041). The residue was dried in the folds of a filter paper and transferred to the Erlenmeyer flask. The solid mass consisting of the metal complex along with naphthalene was dissolved in 5 ml of dimethylformamide (DMF). The fourth derivative absorption spectrum was recorded in the range 550 to 650 nm against a blank solution prepared in the same way.

## RESULTS AND DISCUSSIONS

### *Spectral Characteristics (Zero Order)*

The zero-order and fourth derivative spectra of the ion associated Ag-(nitroso-S)-TDBA-naphthalene in DMF against reagent blank prepared under the similar conditions are shown in Figure 1 and Figure 2, respectively. Derivatization leads to sharper zero-order bands and gives higher signals in the resulting spectra. The characteristics of derivative spectra, such as peak height and noise level, depend on the choice of parameters such as order of derivative, scan speed and integration time during the recording of the spectra. These parameters should be optimized to give a well-resolved peak (better resolution) *i.e.* to obtain good selectivity and higher sensitivity in a determination. Preliminary observations revealed that the best result were obtained from the fourth derivative with wavelength interval  $\Delta\lambda = 9$  nm. In the present work a peak-to-peak method between  $\lambda_1 = 606$  nm and  $\lambda_2 = 562$  nm was applied.

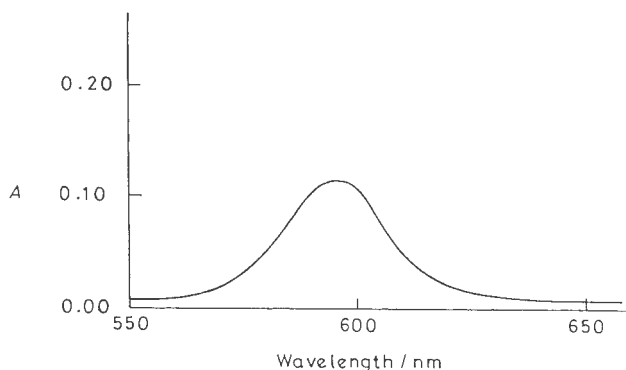


Figure 1. Zero order spectrum of naphthalene-Ag-(nitroso-S)-TDBA. Ag, 10  $\mu\text{g}$ ; buffer, 2 ml; pH, 10.5; solvent, 5 ml DMF; reference, reagent blank.

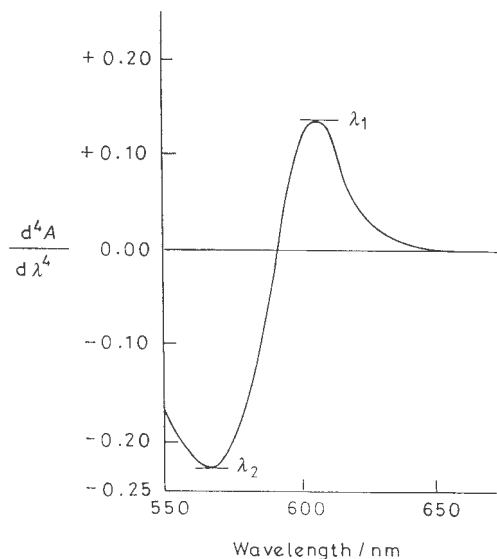


Figure 2. Fourth derivative spectra of naphthalene-Ag-(nitroso-S)-TDBA complex. For conditions, see Figure 1.

### Reaction Conditions

Reaction conditions were established with the use of 10  $\mu\text{g}$  of silver in each case. The adsorption of silver on this adsorbent was found to be maximum and constant in the pH range 9.5–11.0 (Figure 3). In subsequent study, the pH was maintained at  $\approx 10.5$ . Addition of 0.5–5.0 ml of the buffer (pH  $\approx$

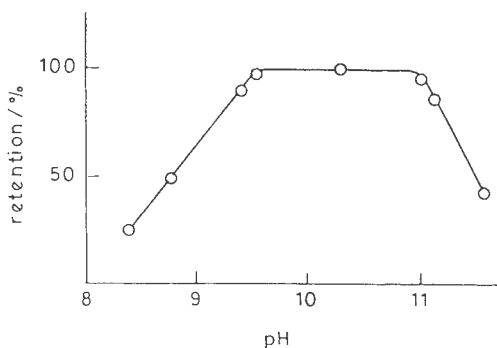


Figure 3. Absorption of  $\text{Ag}^+$  by the adsorbent as a function of pH. For conditions, see Figure 1.

10.5) did not affect the retention of silver and use of 2.0 ml was recommended. Silver was quantitatively adsorbed over the range 0.5–4.0 ml of the reagent and 1.0 ml of it was recommended in the present study.

Various amounts of naphthalene (20% solution of naphthalene in acetone) were added to the sample solutions keeping other variables constant. It was observed that the signal height remained constant with the addition of 1.0–4.0 ml of 20% naphthalene solution. Therefore, 2.0 ml of 20% naphthalene solution was used in the subsequent studies. The effect of shaking time on the adsorption indicated that the signal height remained constant over the range 0.5–7.0 min. Therefore 1.0 min of shaking time was maintained in the present work.

In the case of column method, the flow rate was varied from 0.2 to 8.0 ml min<sup>-1</sup>. It was found that a flow rate of 0.2–5.0 ml min<sup>-1</sup> did not affect the retention of the metal on this adsorbent. A flow rate of 1–2 ml min<sup>-1</sup> was recommended in all experiments. However, in case of larger volume of the sample solution, a flow rate of 5 ml min<sup>-1</sup> may be used.

The volume of the aqueous phase was varied in the range of 10–700 ml under the optimum conditions, keeping other variables constant. It was observed that the signal height was almost constant up to 150 ml (preconcentration factor of 30) in case of microcrystalline method while it was 400 ml in the column method (preconcentration factor of 80). However, for convenience, all the experiments were carried out with 40 ml of the aqueous phase.

#### *Retention Capacity of the Adsorbent*

The retention capacity of the adsorbent was determined by a batch method. The experiment was performed by taking 5 mg of silver, 2 ml of buffer solution (pH ≈10.5) and 40 ml of water in a beaker. This solution was transferred into a separating funnel and then a suitable amount of the (nitroso-S)-TDBA-naphthalene adsorbent was added to it. The separating funnel was shaken vigorously on a mechanical shaker for 15 min. The solid mass was separated by filtration and silver was determined from the filtrate by AAS. The solid mass on the filter paper was dried in an oven, kept in a desiccator and then weighed to determine the mass of the adsorbent. The maximum amount of silver retained was 6.1 mg g<sup>-1</sup> of nitroso-S salt in the adsorbent. It was also noted that the retention capacity depends on the amount of TDBA and nitroso-S supported on naphthalene. The molar ratio of (nitroso-S) / TDBA<sup>+</sup> is 1:1 from the observations on the preparation of the adsorbent. It was found that with the use of nitroso-S (0.9 g) and TDBA<sup>+</sup> (1.2 g), a slight excess of nitroso-S and 20 g of naphthalene were sufficient for the complete retention of the metal ions.



### *Choice of Solvent*

A number of solvents were tried to dissolve the Ag-(nitroso-S)-TDBA-naphthalene. Since the solid mass was dissolved in a small volume (3–5 ml) of the solvent, it was essential to select a solvent in which the chelate is highly soluble and results in a high sensitivity for the spectrophotometry measurements. The solid material was found to be insoluble in ordinary organic solvents such as toluene, 1,2-dichloroethane, n-hexane, nitrobenzene, isoamyl alcohol, n-amyl alcohol, ethylacetate, methyl-isobutylketone, chloroform, and dioxane but soluble in dimethyl sulfoxide, dimethylformamide (DMF), and propylene carbonate. DMF was preferred due to the high solubility and stability of the metal complex in it. It was found that 2–3 ml of this solvent were sufficient to dissolve the mixture thus further enhancing the sensitivity of the method.

### *Calibration*

The calibration curve (Figure 4) for the determination of silver was prepared according to the general procedure under the optimum conditions developed above. The linearity was maintained in the concentration range 0.2–30  $\mu\text{g ml}^{-1}$  of silver with a correlation factor of 0.9994 and the relative standard deviation of  $\pm 1.1\%$ . The sensitivity was calculated to be 0.198 ( $d^4A/d\lambda^4$ ) /  $\mu\text{g ml}^{-1}$  from the slope of the calibration curve. The detection limit was 0.15  $\mu\text{g ml}^{-1}$  for silver at the minimum instrumental setting (signal to noise ratio = 2).

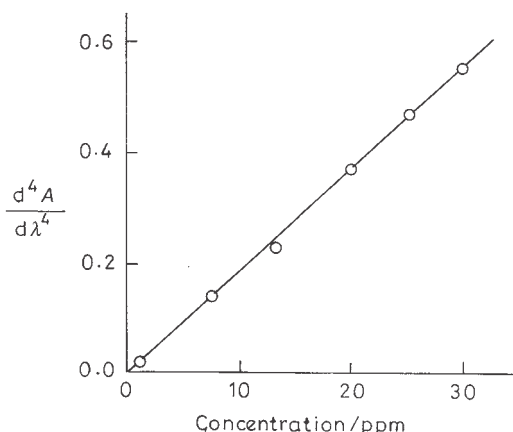


Figure 4. Calibration curve for silver by fourth derivative spectrophotometry from signal peak-to-peak measurements between  $\lambda_1$  and  $\lambda_2$ . For conditions see Figure 1.

TABLE II

Diverse salts and metal ions tolerance on the determination of 10  $\mu\text{g}$  of silver

Salt or ion	Tolerance limit / mg
$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ , $\text{KNO}_3$	1000
$\text{NH}_4\text{Cl}$ , $\text{KI}$ , $\text{KSCN}$ , thiourea	5.0
$\text{K}_2\text{CO}_3$	30
Sodium potassium tartrate	15
Trisodium citrate, sodium oxalate	10
$\text{Na}_2\text{EDTA}$	1.0
$\text{Mg}^{\text{II}}$ , $\text{Zr}^{\text{IV}}$ , $\text{Ta}^{\text{V}}$ , $\text{Tl}^{\text{I}}$	250
$\text{Ca}^{\text{II}}$ , $\text{Ba}^{\text{II}}$ , $\text{Sr}^{\text{II}}$	60
$\text{Pb}^{\text{II}}$ , $\text{Sb}^{\text{III}}$ , $\text{As}^{\text{III}}$ , $\text{Sn}^{\text{II}}$	50
$\text{Mn}^{\text{II}}$ , $\text{W}^{\text{VI}}$	7.0
$\text{Cd}^{\text{II}}$ , $\text{Ti}^{\text{IV}}$	6.5
$\text{Zn}^{\text{II}}$ , $\text{Sc}^{\text{III}}$	4.0
$\text{Cr}^{\text{VI}}$ , $\text{Al}^{\text{III}}$ , $\text{Se}^{\text{VI}}$	2.5
$\text{Cr}^{\text{III}}$ , $\text{U}^{\text{VI}}$ , $\text{Mo}^{\text{VI}}$	2.0
$\text{Ni}^{\text{II}}$ , $\text{Fe}^{\text{III}}$ , $\text{Ga}^{\text{III}}$ , $\text{Te}^{\text{IV}}$	1.7
$\text{Pd}^{\text{II}}$ , $\text{Co}^{\text{II}}$	1.0
$\text{Bi}^{\text{III}}$ , $\text{Ru}^{\text{III}}$	0.9
$\text{Rh}^{\text{III}}$ , $\text{Os}^{\text{VIII}}$	0.8
$\text{Hg}^{\text{II}}$ , $\text{V}^{\text{V}}$	0.6
$\text{Cu}^{\text{II}}$	0.25 <sup>a</sup>

<sup>a</sup> After masking with 0.5 mg  $\text{Na}_2\text{EDTA}$ .*Effect of Diverse Ions*

Various salts and metals ions were added individually to a solution containing 10  $\mu\text{g}$  of silver and the general procedure was applied. The tolerance limit (error < 3%) is given in Table II. Among the salts examined, many did not interfere at the gram or milligram level. Among the metal ions studied, most did not interfere at the milligram level, except  $\text{Cu}(\text{II})$ , but its lower amounts could be tolerated after masking with EDTA. In case of steel samples, iron may be removed by preextraction as its acetylacetonate complex into chloroform and silver determined in the aqueous phase.<sup>24</sup> Thus the method developed above is fairly selective and sensitive and it has been applied to the determination of silver in various complex materials.

*Analysis of Silver in Synthetic Samples*

A synthetic sample containing silver was prepared in 10 ml of concentrated hydrochloric acid and nitric acid (1 + 1) and the final volume was ma-

de to 100 ml with distilled water in a standard flask. An aliquot of the sample solution (40–100 ml) as prepared above was taken and silver was determined by the general procedure. The results are given in Table III.

TABLE III  
Analysis of silver in synthetic samples

Composition of synthetic sample $\mu\text{g g}^{-1}$	Expected value $\mu\text{g g}^{-1}$	Amount found by the present method <sup>a,b</sup> / $\mu\text{g g}^{-1}$
As, 4.0; Cd, 3.0; Cu, 0.60; Ca, 150; Fe, 6.0; Ni, 6.5; Mn 10.0; Hg, 8.0; Mg, 100; Pb, 25; Zn 3.5; Tl, 1.5	7.5	$7.39 \pm 0.10^d$
As, 4.0; Cd, 3.0; Cu, 0.60; Ca, 150; Fe, 6.0; Ni, 6.5; Mn 10.0; Hg, 8.0; Mg, 100; Pb, 25; Zn 3.5; Tl, 1.5	2.5	$2.46 \pm 0.04^c$
Ni, 15; Fe, 3.5; Zn, 6.5; Ca, 120; Mg, 65; Mn, 25; As, 3.5; Bi, 16; Mo, 6.5; Sb, 7.5; Hg, 15.0	3.5	$3.45 \pm 0.05^c$

<sup>a</sup> Average of five determinations,  $\pm$  standard deviation.

<sup>b</sup> After masking with 0.5 mg of  $\text{Na}_2\text{EDTA}$ .

<sup>c</sup> Column method was applied.

<sup>d</sup> Microcrystalline naphthalene was applied.

#### *Analysis of Silver in Standard Alloys and Steel Samples*

The proposed method was applied to the determination of silver in SRM 464 and SRM 467 low-alloy steels, SRM 127b solder (40Sn-60Pb) and SRM 54d tin-base alloys. A 0.1–0.5 g sample of the standard aluminum alloy was completely dissolved in 6–15 ml of hydrochloric acid (1 + 1) by heating on a water-bath and then 1 ml of 30% (vol. fraction) hydrogen peroxide was added to it. The excess of peroxide was decomposed by heating the sample on the water-bath. The solution was cooled, filtered if needed and diluted to 100 ml with distilled water in a standard flask.<sup>25</sup> An aliquot of this sample was taken in a beaker and the general procedure was applied. The results obtained are given in Table IV.

#### *Analysis of Silver in Biological Samples*

The accuracy and applicability of the proposed method has been tested in the determination of silver in National Institute for Environmental Studies (NIES): No. 1, pepperbush; (NIES) No. 3, Chelorella; (NIES) No. 5, human hair and (NIES) No. 7, tea leaves. A 0.1–0.5 g sample was taken in a

TABLE IV  
Analysis of silver in standard alloys

Sample	Certified composition of the sample / %	Silver found <sup>a,b</sup> / %
SRM 464 Low-alloy steel	Ag, 0.0032; C, 0.54; Mn, 1.32; P, 0.017; S, 0.02; Si, 0.48; Cu, 0.094; Ni, 0.013; Cr, 0.078; B, 0.005; Pb, 0.02; Ge, 0.001; V, 0.29; Mo, 0.029; W, 0.022; Co, 0.028; Ti, 0.004; As, 0.018; Sn, 0.043; Al, 0.005; Nb, 0.037; Ta, 0.069; Zr, 0.01	0.0035±0.00005 <sup>c</sup>
SRM 467 Low-alloy steel	Ag, 0.0045; C, 0.11; Mn, 0.27; P, 0.033; S, 0.01; Si, 0.26; Cu, 0.067; Ni, 0.088; Cr, 0.036; B, 0.0002; Pb, 0.0006; Ge, 0.003; V, 0.041; Mo, 0.021; W, 0.20; Co, 0.07; Ti, 0.26; As, 0.14; Sn, 0.10; Al, 0.16; Nb, 0.29; Ta, 0.23; Zr, 0.94	0.0047±0.00007 <sup>c</sup>
SRM 127b Solder (40Sn-60Pb)	Ag, 0.01; Cu, 0.011; Ni, 0.012; As, 0.01; Sn, 39.3; Sb, 0.43; Bi, 0.06	0.00982±0.00015 <sup>c</sup>
SRM 54d Tin-base alloy	Ag, 0.0032; Pb, 0.62; Sn, 88.57; Sb, 7.04; Bi, 0.044, Cu, 3.62; Fe, 0.027; Ni, 0.0027	0.0034±0.00005 <sup>c</sup>

<sup>a</sup> Average of five determinations. ± standard deviation.

<sup>b</sup> After masking with 0.5 mg of Na<sub>2</sub>EDTA. In case of steel samples, FeIII was removed as acetylacetonate complex after extraction in to chloroform.

<sup>c</sup> Column method was applied.

beaker along with an appropriate amount of the silver from the standard sample and then dissolved in concentration nitric acid ( $\approx 10$  ml) with heating. The solution was cooled, diluted, filtered if needed and diluted to 100 ml with water in a calibrated flask.<sup>26</sup> An aliquot (10–50 ml) of the sample solution was taken individually and silver was determined by the general procedure. The results are given in Table V.

## CONCLUSION

A simple, economical and highly selective adsorbent was obtained simply by mixing aqueous solutions of nitroso-S salt and (TDBA<sup>+</sup>Cl<sup>-</sup>) with an acetone solution of naphthalene and applied for the preconcentration of silver from a large volume of the aqueous solutions of alloys, steel and biological samples. As nitroso-S salt reacts with several metal ions, it is not possible to develop selective spectrophotometric methods for them since many metal-(nitroso-S) complexes absorb at close wavelengths. However, with the use of derivative spectrophotometry this problem may be easily solved. The reagent is cheap and highly selective for silver and the use of fourth deriva-

TABLE V  
Analysis of silver in biological samples

Sample	Certified composition of the sample / $\mu\text{g g}^{-1}$ Silver added ( $\text{Ag}^\#$ ) <sup>c</sup> / $\mu\text{g}$	Silver found <sup>a,b</sup> $\mu\text{g}$
NIES, <sup>d</sup> No. 1 Pepperbush	K, 15100; Mn, 2030; Mg, 4080; Ca, 13800; Cd, 6.7; Ni, 8.7; Fe, 205; Co, 23; Pb, 5.5; Zn, 340; Rb, 75; Ba, 165; Na, 106; Sr, 36; As, 2.3; Cu, 12.0; Cr,(1.3); Cs, (1.2); P, (1100); Tl, (0.13); Hg, (0.056); $\text{Ag}^\#$ , 43	42±0.6 <sup>f</sup>
NIES, No. 3 Chlorella	K,12400; Ca, 4900; Fe, 1850; Mg, 3300; P, (17000); Zn, 20.5; Sr, 40.3; Cu, 3.5; Co, 0.87; Mn, 69.7; Cd, (0.026); Pb, (0.60); Sc, (0.013); $\text{Ag}^\#$ , 19	18.9±0.3 <sup>e</sup>
NIES, No. 5 Human hair	Pb, 6.0; Cd, 0.20; Cu, 16.3; Sb, 0.07; Zn, 169; Fe, 225; Mg, 208; Hg, 4.4; Al, 240; K, 34; Rb, 0.19; Se, 1.4; Na, 26; Sr, 2.3; Sc, 0.05; Ti, 3.2; Ca, 728; Ba, 2.2; Cr, 1.4; Ni, 1.8; $\text{Ag}^\#$ , 36	36.2±0.5 <sup>f</sup>
NIES, No. 7 Tea leaves	Pb, 0.80; Cd, 0.030; Sb, 0.014; Zn, 33; Cr, 0.15; Al, 775; Mg, 1530; Ba, 5.7; K, 18600; Sc, 0.011; Na, 15.5; Sr, 3.7; Ca, 3200; Cs, 0.221; Co, 0.12; Mn, 7.00; Cu, 7.0; Ni, 6.5; $\text{Ag}^\#$ , 18	17.8±0.3 <sup>e</sup>

<sup>a</sup> Average of five determinations,  $\pm$  standard deviation.

<sup>b</sup> After masking with 0.5 mg of  $\text{Na}_2\text{EDTA}$ .

<sup>c</sup> No silver was present in these standard samples. Therefore, silver was added. from the standard solution in each case.

<sup>d</sup> NIES: National Institute of Environmental Studies reference materials. NIES, No. 1, No. 3, No. 5, No. 7 (Values in parentheses were approximate and not certified).

<sup>e</sup> Column method was applied.

<sup>f</sup> Microcrystalline naphthalene method was applied.

tive spectrophotometry further increased the sensitivity and selectivity of the method. Silver may also be determined by directly aspirating the DMF solution of the metal complex after the preconcentration steps into the flame of an AAS. Although, AAS is a fairly selective technique, but its day-to-day maintenance cost is high and matrix effect is another major problem. Adsorption onto microcrystalline naphthalene method is more rapid, however its preconcentration factor is comparatively lower than the column method.

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## SAŽETAK

**Određivanje tragova srebra adsorbiranog na mikrokristalnom naftalenu ili na koloni nakon predkoncentracije s ionskim parom 2-nitrozo-1-naftol-4-sulfonska kiselina-tetradecildimetilbenzilamonij klorid, uporabom derivativne spektrofotometrije četvrtog reda**

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Srebro je kvantitativno adsorbirano na mikrokristalnom naftalenu, iz velikih volumena vodenih otopina različitih legura i bioloških uzoraka, u obliku kompleksa asociranih iona 2-nitrozo-1-naftol-4-sulfonske kiseline (nitroso-S) i tetradecildimetilbenzilamonijeva klorida (TDBA) u području pH od 9,5 do 11,0. Nakon filtracije, krutina sastavljena od metalnog kompleksa i mikrokristalnog naftalena otopljena je u dimetilformamidu (DMF) te je metal određen derivativnom spektrofotometrijom četvrtoga

reda. Srebro se može kvantitativno adsorbirati i u koloni punjenoj (nitroso-S)-TDBA-naftalenom kao adsorbensom, uz brzinu protoka otopine od  $1\text{--}2\text{ ml min}^{-1}$ , te odrediti gornjim postupkom. Kalibracijska je krivulja linearna za područje koncentracije srebra  $0,2\text{--}30\text{ }\mu\text{g ml}^{-1}$  u otopini dimetilformamida, a dobivena je mjerenjem udaljenosti između  $\lambda_1$  (606 nm) i  $\lambda_2$  (562 nm) na krivulji  $d^4A/d\lambda^4$ . Koeffcijent korelacije je 0,9994, a relativna standardna devijacija  $\pm 1,1\%$ . Iz nagiba kalibracijske krivulje izračunana je osjetljivost određivanja koja iznosi  $0,198(d^4A/d\lambda^4)/\mu\text{g ml}^{-1}$ . Granica detekcije (određivanja) srebra je  $0,15\text{ }\mu\text{g ml}^{-1}$ , pri čemu je minimalni instrumentalni odnos signal / šum iznosio 2. Da bi se što bolje optimalizirali uvjeti za određivanje srebra u različitim složenim sustavima, detaljno su analizirani efekti pH, volumena vodene faze te interferencije velikog broja metalnih iona.