

# Differential Pulse Polarographic Determination of Trace Antimony in Standard Biological Samples after Preconcentration Using 2-Nitroso-1-naphthol-4-sulfonic Acid

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**ABSTRACT:** A highly selective, sensitive, rapid and economical differential pulse polarographic method has been developed for the determination of trace amounts of antimony in various standard alloys and biological samples after adsorption of its 2-nitroso-1-naphthol-4-sulfonic acid - tetradecyldimethylbenzylammonium chloride on microcrystalline naphthalene in the pH range of 7.5-11.0. After filtration, the solid mass is shaken with 8-10 ml of 1 M hydrochloric acid (with preconcentration factor of 10) and antimony is determined by differential pulse polarography (DPP). Antimony can alternatively be quantitatively adsorbed on 2-nitroso-1-naphthol-4-sulfonic acid- tetradecyldimethylbenzylammonium-naphthalene adsorbent packed in a column (with preconcentration factor of 30) and determined similarly. In this case, 1.5 µg of antimony can be cocentrated in a column from 300 ml of aqueous sample, where its cocentration is as low as 5 ng/ml. Characterization of the electroactive process included an examination of the degree of reversibility. The results show that the irreversibility of antimony. Various parameters such as the effect of pH, volume of aqueous phase, HCl concentration, reagent concentration, naphthalene concentration, shaking time and interference of a number of metal ions on the determination of antimony have been studied in detail to optimize the conditions for determination in standard alloys and standard biological samples.

**KEY WORDS:** Differential pulse polarography, Antimony determination, Standard alloys, Standard biological samples, 2-nitroso-1-naphthol-4-sulfonic acid

## INTRODUCTION

The reagent 2-nitroso-1-naphthol-4-sulfonic acid (nitroso-S salt) was introduced by Hoffman [1] for the qualitative and later by Wise and Brandt [2] for the quantitative determination of cobalt. This reagent reacts

with many metal ions and forms water-soluble, colored chelate complexes and has been applied widely in the liquid-liquid extraction spectrophotometric determination of metals in materials[3]. The most common techniques

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available for the preconcentration of metals from aqueous samples are the solvent extraction, and column methods using various adsorbents such as thiol cotton[4], activated carbon[5], adsorption resins[6-7], green tea leaves [8], chelating resins [9], cellulose [10], and polythioether[11]. Although some of these adsorbents are fairly effective their methods of preparation are time consuming and cumbersome. Solvent extraction is a simple and convenient technique for separating and concentrating metal ions, but it cannot be applied directly to metal ions which form stable complexes with the chelating agents only at elevated temperature. This difficulty can be overcome by using naphthalene as the extractant [12] for thermally stable metal chelates [13]. Solid-liquid separation after adsorption of metal chelates on microcrystalline naphthalene is more rapid and convenient and can be applied to many types of metal complexes [14-16]. The preconcentration of metal ions is also possible by passing their aqueous solutions over nitroso -S- tetradecyldimethylbenzylammonium-naphthalene adsorbent taken in a column. The microcrystalline naphthalene method is rapid but the column method gives a better preconcentration factor [17-19].

Direct polarographic determination of metals after extraction of their metal complexes into organic solvents has been reported [20-24]. Unfortunately, electrochemical methods for direct determination of reducible substances require the solvents with a fairly high dielectric constant in order to obtain well defined polarograms. Therefore, the organic phases after extraction has to be mixed with a suitable solvent of high dielectric constant[25-26]. The main disadvantage of this method is that sensitivity is lost and the preconcentration factor is considerably lowered. Hence, the dual aim of preconcentration and direct determination of a metal is unachievable. For the direct determination of metal ions after extraction of their metal complexes into molten naphthalene and dissolution of the product in an organic solvent such as dimethylformamide [27], an inert gas normally  $N_2$  has to be passed for at least 10-15 min to remove the dissolved oxygen, again making the method more time consuming and less reproducible owing to the partial evaporation of the organic solvent.

In the present paper, we have developed a simple, rapid and economical method for direct differential pulse polarographic determination of antimony after adsorption

of its nitroso - S - tetradecyldimethyl benzylammonium complex onto microcrystalline naphthalene and subsequent desorption by 8 ml of 1.0 M hydrochloric acid. After desorption of the metal complex with HCl from microcrystalline naphthalene, there is no need to remove naphthalene. The reagent Nitroso-S selected is very cheap, easily accessible and does not interfere with the polarographic estimation of this metal ion. Various operational parameters have been evaluated and it is found that the method is highly selective, rapid, economical and fairly sensitive. The procedure has been used for determination of trace amount of antimony in various standard alloys and standard biological samples.

## EXPERIMENTAL

### Apparatus and reagents

Polarograms were recorded with an Elico CL-90 polarograph equipped with three electrodes. It was outfitted with a model LR-108 X-Y recorder. Cyclic voltammograms were recorded with a cyclic voltammeter (model CV-27) outfitted with a X-Y-T recorder. All atomic absorption measurements were made using an atomic absorption spectrometer (Shimadzu AA 670). Funnel-tipped glass tube ( 60 mm × 6 mm ) was used as column for the preconcentration purposes. The column was plugged with polypropylene fibers and then filled with the adsorbent to a height of 1.0-1.2 cm after pressing lightly with a flat glass rod. A Beckman pH meter was employed for pH measurements.

All chemicals used were of analytical reagent grades. An antimony solution was prepared by dissolving an appropriate amount of antimony(III) chloride in glacial acetic acid and diluted with doubly distilled water and standardized by the established methods [28]. A 1% solution of tetradecyldimethylbenzylammonium chloride ( $TDBA^+ Cl^-$ ) and 0.1% 2-nitroso-1-naphthol-4-sulfonic acid (nitroso-S) was prepared in distilled water. A 20% solution of naphthalene in acetone and 1 M pyridine in 1 M HCl was used. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations, respectively. Buffer solution of pH ~10 was prepared by mixing of 0.5 M ammonia and 0.5 M ammonium acetate solutions in appropriate ratio.

**Preparation of nitroso-S-TDBA-naphthalene adsorbent**

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

**General procedure using microcrystalline naphthalene**

An aliquot of antimony solution (containing 3-3000 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) was added to it and the mixture was diluted to 30-40 ml with water. The pH was adjusted to 10 with 2 ml of the buffer (ammonia ammonium acetate solution) and then, 2 ml of 1% TDBA solution was added. The solution was mixed well and allowed to stand for 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 shaken vigorously with 8 ml of 1 M hydrochloric acid and transferred to the polarographic cell. After addition of 2 ml of 1 M pyridine chloride solution, the differential pulse polarogram was recorded in each case after the removal of dissolved oxygen by passing purified nitrogen gas for 8-10 min.

**General procedure by column method**

An aliquot of antimony solution containing 3-3000 µg of antimony was taken in 25 ml beaker. The pH of this solution was adjusted to 10 with the addition of 2 ml of a buffer solution (ammonia and ammonium acetate solutions) and diluted it to ~15 ml with distilled water. The column loaded with the adsorbent nitroso-S-TDBA-

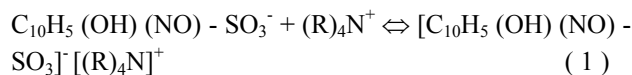
naphthalene was conditioned to pH 10 with 2-3 ml of buffer and then the metal solution was passed through the column at a flow rate of 1 ml/min. The packing was washed with a small volume of water. Desorption of metal was carried out by passing 8 ml of 1 M of HCl at flow rate of 1 ml/min and the solution was transferred to the polarographic cell. After the addition of 2 ml of 1 M pyridine chloride solution, the differential pulse polarogram was recorded in each case after the removal of dissolved oxygen by passing purified nitrogen gas for 8-10 min.

**RESULTS AND DISCUSSION****Reversibility of antimony reduction process**

In the present work, the differential pulse polarograms for antimony, in pyridine-HCl-NaCl medium as supporting electrolyte, show half peak width of 80±2 mV, in both normal and reverse scan modes. Plot of the applied potential versus log [i/(i<sub>d</sub>-i)] from d.c.polarogram has a slope of -65±2 mV (r = 0.999 and N=5, where r is the correlation coefficient and N is the number of data points). The cyclic voltammogram of antimony reveals that antimony gives only cathodic wave. Hence, all these studies clearly establish the irreversibility of antimony under these conditions [29-30].

**Retention characteristics of nitroso - S - TDBA - naphthalene**

The TDBA chloride is a water soluble well known quaternary ammonium salt widely used as a counter-ion in anionic metal complexes in the solvent extraction of metals. The reagent 2-nitroso-1-naphthol-4-sulfonic acid has one sulfonic acid group capable of dissociation and thus it can form ion pairs (nitroso-S: TDBA = 1 : 1) with quaternary ammonium cations as follow:



The ion pair formed between the anionic nitroso-S and cationic TDBA<sup>+</sup> is easily coprecipitated with microcrystalline naphthalene. The ion-pair reaction between nitroso-S and several well known quaternary ammonium salts was therefore tried to develop new adsorbents. Preliminary results indicated that only TDBA<sup>+</sup> and cetyltrimethylammonium (CTMA<sup>+</sup>) can form ion-pair with nitroso-S. In the present study TDBA<sup>+</sup> as th

counter ion has been selected, since it is relatively cheaper than CTMA<sup>+</sup> and has excellent retention characteristics of metal ions.

### Reaction conditions

The reaction conditions were investigated with 100 µg of antimony. Adsorption was carried out at different pH, keeping other variables constant. It was found that the antimony complex was quantitatively adsorbed on naphthalene in the pH range 7.5-11.0 (Fig.1). Addition of 0.5-6 ml of buffer, did not have any effect on the adsorption, therefore, 2.0 ml of the ammonium acetate buffer was used in all the subsequent experiments. The reagent concentration was also varied. It was found that adsorption was quantitative for 0.5-5.0 ml of 0.1% reagent. Consequently 2.0 ml of reagent solution was used in subsequent studies. Various amounts of naphthalene was added to the sample solution keeping other variables constant, it was observed that the peak height remained constant with the addition of 1.0-4.0 ml of 20% naphthalene solution. Therefore, 2 ml of 20% naphthalene solution was used in subsequent studies. The effect of shaking time on the adsorption indicated that the peak height remained constant over the range of 0.5-8.0 min. Therefore, 1 min of shaking time was recommended in the present work.

In the case of column method, the flow rate was varied from 0.2 to 8 ml/min. It was found that a flow rate of 0.2-5.0 ml/min did not affect adsorption. A flow rate of 1 ml/min was recommended in all experiments.

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 100 ml (preconcentration factor of 10). However, for convenience, all the experiments were carried out with 40 ml of the aqueous phase.

In the case of column method, peak height was almost constant up to an aqueous phase volume of 300 ml. Therefore, a preconcentration factor of 30 can be achieved by the column.

Preliminary observations indicated that antimony complex was desorbed completely with 8-10 ml of 0.5-4.5 M hydrochloric acid. Therefore, 8-10 ml of 1.0 M hydrochloric acid was used in the present work.

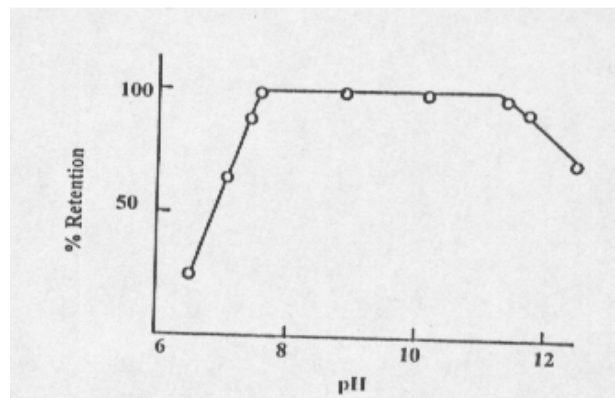


Fig. 1: Effect of pH of adsorption of antimony complex. Antimony, 100 µg in 10 ml of final solution (8 ml 1.0 M HCl & 2 ml of 1.0 M pyridinium chloride); reference, reagent blank. Instrumental setting: scan rate, 12 mV/sec; X=Y=100 mV/cm; sensitivity, 0.1 mA/V; drop time, 0.5 s.

### Retention capacity of the adsorbent

The retention capacity of adsorbent was determined by a batch method. The experiment was performed by taking 500 µg of antimony, 2 ml of the buffer (pH ~10) and 40 ml of water in a beaker. This solution was transferred into a separatory funnel and then a suitable amount of the adsorbent nitroso-S-TDBA-naphthalene was added to it. The separatory funnel was vigorously shaken on a mechanical shaker for 5 min. The solid mass was separated by filtration on a Whatman filter paper (No. 1041) and antimony 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 know the mass of the adsorbent. The maximum amount of antimony retained was 4.5 mg/g of nitroso-S-salt, the adsorbent. It was also noted that the retention capacity depends on the amount of TDBA and nitroso-S supported on naphthalene. From the stoichiometry in the reaction 1, the molar ratio of nitroso-S and TDBA<sup>+</sup> is 1 : 1. From the observations on the preparation of the adsorbent, it was found that the use of nitroso-S (0.9 g ~0.0028 M) and TDBA<sup>+</sup> (1.2 g ~0.0031 M) slightly excess than nitroso-S and 20 g of naphthalene were enough for the complete retention of the metal ions.

### Calibration graph

A typical polarogram for antimony is given in Fig.2. A calibration graph for the determination of antimony was

prepared from the differential pulse polarograms obtained with different concentrations of antimony according to the general procedure under the optimum conditions developed above. Considering that it is possible to retain 1.5  $\mu\text{g}$  of antimony from 300 ml of solution passing through the column, the desorption with 10.0 ml of final solution gives a detection limit of 5 ng/ml for antimony. The linearity was maintained in the concentration range of 10 ng/ml to 10  $\mu\text{g}/\text{ml}$  antimony in first aqueous solution or 0.3-300  $\mu\text{g}/\text{ml}$  in final solution (Fig.3) with a correlation coefficient of 0.9996 and a relative standard deviation of  $\pm 0.95\%$ .

#### Effect of foreign ions

Various salts and metal ions were added individually to a solution containing 100  $\mu\text{g}$  of antimony and the general procedure was applied. The tolerance limit (error < 3%) is given in Table 1. Among most of the salts examined, did not interfere at the g-mg level, only EDTA

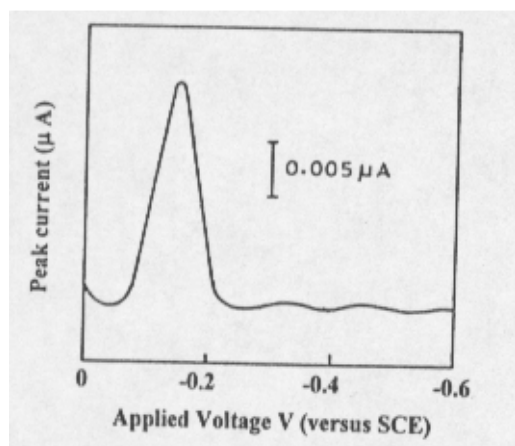


Fig. 2: A typical differential pulse polarogram of antimony. Experimental conditions and instrumental setting same as Fig. 1.

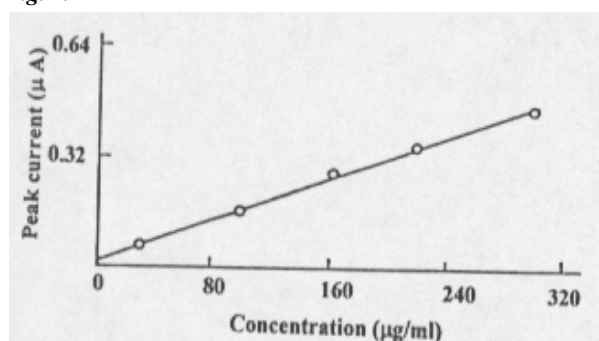


Fig. 3: Calibration curve for antimony. Experimental conditions and instrumental setting same as Fig. 2.

interfered seriously due to the higher formation constant of antimony-EDTA complexes than the nitroso-S. Among the metal ions as nitrate metals studied, many did not interfere even at the milligram level. Thus the method is highly selective without the use of masking agents. The proposed procedure has therefore been applied to the determination of antimony in standard alloys and biological samples without any prior separations.

#### Analysis of antimony in standard alloys

The proposed method was applied to the determination of antimony in Nippon Keikinokogyo (NKK) CRM 916, No. 920 Aluminum Alloy, NKK No.1021, Al, Si, Cu, Zn Alloy. A 0.1 g sample of the standard aluminum alloy was completely dissolved in 6-14 ml of hydrochloric acid (1 : 1) by heating on a water-bath and then 1 ml of 30% (V/V) hydrogen peroxide was added to it. The excess of peroxide was decomposed by heating the sample on a water-bath. The solution was cooled, filtered if needed and diluted to 100 ml with distilled water in a standard flask. An aliquot (1-2 ml) of this sample was taken in a 20-ml beaker and the general procedure was applied. The results obtained are given in Table 2. These results are in agreement with the certified values.

#### Analysis of antimony in standard biological samples

The accuracy and applicability of the proposed method has been applied to the determination of antimony in National Institute for Environmental Studies (NIES), No. 5 Human Hair and NIES, No.7 Tea Leaves. A 0.1 g sample was taken in a beaker and dissolved in concentrated nitric acid (~5 ml) with heating. The solution was cooled, diluted and filtered. The filtrate was diluted to 100 ml with water in a calibrated flask. NIES, No.8 Vehicle Exhaust Particulates (1 g) was dissolved in 18 ml of concentrated nitric acid, 18 ml of concentrated perchloric acid and 2 ml of concentrated hydrofluoric acid in a 100 ml Teflon beaker, evaporated to a small volume, filtered through a filter paper and made up to 100ml with distilled water. An aliquot (10-50 ml) of the sample solution was taken individually and antimony was determined according to the general procedure. The results are given in Table 3 which are in good agreement with the certified values.

Table 1: Effect of foreign salts and ions

Salt or ion	Tolerance limit
CH <sub>3</sub> COONa, H <sub>2</sub> O, KNO <sub>3</sub>	1 g
NaCl, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> CO <sub>3</sub>	200 mg
NaF	500 mg
NH <sub>4</sub> Br	150 mg
KI	100 mg
Sodium potassium tartrate	80 mg
KSCN	70 mg
Trisodium citrate	40 mg
Sodium oxalate	50 mg
Na <sub>2</sub> EDTA	50 µg
Mo(VI), Mn(II)	45 mg
Zn(II)	40 mg
Cr(III), Ti(VI)	20 mg
Se(VI), Ga(III), Al(III)	18 mg
U(VI), Te(IV)	4.5 mg
V(V), Bi(III), Rh(III), Ru(III), Os(VIII), Pb(II)	1.5 mg
Pd(II), Tl(I)	1.2 mg
Co(II), Sn(II), Cd(II)	0.8 mg
Ni(II), Cr(VI)	0.7 mg
Cu(II)	0.6 mg
Fe(III)	80 µg, 1.5 mg*

\* After masking with 2 ml of 5% triethanolamine solution

Table 2. Analysis of antimony in standard alloys

Sample	Composition%	Found <sup>*+</sup>
NKK No. 916 Aluminum Alloy	Si, 0.41; C, 0.41; Fe, 0.54; Mg, 0.10; Cr, 0.05; Sn, 0.05; Zn, 0.30; Ti, 0.10; Pb, 0.04; Sb, 0.01; B, 0.0006; Zr, 0.05; Co, 0.03; Mn, 0.11; Bi, 0.03; Ni, 0.06; V, 0.02; Cu, 0.27	0.0098 ± 0.0003 <sup>a, c</sup>
NKK No. 1021 Al, Si, Cu, Zn, Alloy	Pb, 0.18; Zn, 1.76; Si, 5.56; Sn, 0.10; Mg, 0.29; Ti, 0.04; Cr, 0.03; Fe, 0.99; Bi, 0.01; Zr, 0.01; Sb, 0.01; Ca, 0.004; Mn, 0.20; Ni, 0.14; V, 0.007; Cu, 2.72	0.0103 ± 0.0004 <sup>a, c</sup>
NKK No. 920 Aluminum Alloy	Cr, 0.27; Si, 0.78; Bi, 0.06; Ti, 0.15; Sn, 0.20; Ga, 0.05; Pb, 0.10; Fe, 0.72; Zn, 0.80; Ca, 0.03; Mg, 0.46; Sb, 0.10; Co, 0.10; Mn, 0.20; Ni, 0.29; V, 0.15; Cu, 0.71	0.098 ± 0.002 <sup>b</sup>

\* Average of five determinations, ± standard deviation

+ Standard addition method was applied.

<sup>a</sup> Column method was applied.<sup>b</sup> Microcrystalline naphthalene method was applied.<sup>c</sup> 2 ml of 5% triethanolamine solution was added as masking reagent.

Table 3: Analysis of antimony in biological samples

Sample	Composition	Found <sup>*+</sup>
NIES, No.5 Human Hair	Pb, 6.0; Cd, 0.20; K, 34; Rb, 0.19; Sb, 0.07; Zn, 169; Al, 240; Fe 225; Mg, 208; Hg, 4.4; Sc 0.05; Se 1.4; Na, 26; Sr, 2.3; Ti, 3.2; Ca, 728; Cr, 1.4; Ba, 2.2; Co, 0.10; Mn, 5.2; Cu, 16.3; Ni 1.8 µg/g	0.068 ± 0.003 <sup>a, c</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, 0.22; Co, 0.12; Mn, 7.00; Ni, 6.5; Cu, 7.0 µg/g	0.013 ± 0.001 <sup>a</sup>
NIES, NO. 8 Vehicle Exhaust Particulates	K, 0.115±0.008; Ca, 0.53±0.02; Mg, 0.101±0.005; Al, 0.33±0.02; Zn, 0.104±0.005; Na, 0.92±0.008% Sr, 89±3; Cu, 67±3; Co, 3.3±0.3; Ni, 18.5±1.5; Cd, 1.1±0.1; Pb, 219±9; As, 2.6±0.2; Cr, 25.5±1.5; V, 17±2; Sb, 6.0±0.4; Cs, (0.24); Rb, (4.6); Sc (0.055); La, (1.2); Br, (56); Ag, (0.2); Se (1.3); Mo, (6.4); Ce, (3.1); Th, (0.35); Sm, (0.20); Eu, (0.05); Lu, (0.02) µg/g	5.9±0.2 <sup>b</sup>

\* Average of five determinations, ±standard deviation

+ Standard addition method was applied.

<sup>a</sup> Column method was applied.<sup>b</sup> Microcrystalline naphthalene method was applied.<sup>c</sup> 2 ml of 5% triethanolamine solution was added as masking reagent.

NIES: National Institute of Environmental Studies reference materials.

NIES, No. 8 (Values in parentheses were approximate and not certified).

## CONCLUSIONS

It is difficult to obtain a well defined polarogram in the traditional analysis for metals after extraction of their complexes into an organic solvent owing to the low dielectric constant of the organic phase. Sensitivity is lost if it is mixed with another solvent of high dielectric constant. Another major disadvantage is the removal of dissolved oxygen, which is a tedious and time consuming process. Moreover, the reproducibility of the method is effected by the partial evaporation of organic solvent. The reported method has solved most of these problems and has been successfully tested for the determination of antimony in various standard alloys and standard biological samples. Column methods improve the preconcentration but are time consuming.

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