

# PRECONCENTRATION OF TRACE VANADIUM WITH THE ION PAIR OF 2-NITROSO-1-NAPHTHOL-4-SULFONIC ACID AND TETRADECYLDIMETHYLBENZYL-AMMONIUM CHLORIDE ONTO MICROCRYSTALLINE NAPHTHALENE AND DETERMINATION BY DERIVATIVE SPECTROPHOTOMETRY

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**ABSTRACT:** Vanadium is quantitatively retained on 2-nitroso-1-naphthol-4-sulfonic acid tetradecyldimethylbenzylammonium chloride onto microcrystalline naphthalene in the pH range of 3.0-4.0 from a large volume of aqueous solutions of various alloys and synthetic samples. After filtration, the solid mass consisting of the vanadium complex and naphthalene was dissolved with 5.0 mL of dimethylformamide and the metal was determined by second derivative spectrophotometry. The detection limit is 40 ppb (signal to noise ratio = 2) and the calibration curve is linear over the concentration range of 0.08-20 ppm in dimethylformamide solution by measuring the distance  $d^2A/d\lambda^2$  between  $\lambda_1$  (575 nm) and  $\lambda_2$  (510 nm) with a correlation coefficient of 0.9995 and relative standard deviation of  $\pm 0.98\%$ . The effect of pH, volume of aqueous phase and interference of a large number of metal ions on the determination of vanadium was studied and the developed method is found to be highly selective and sensitive.

**KEY WORDS:** Vanadium, Microcrystalline naphthalene, Derivative spectrophotometry, 2-Nitroso-1-naphthol-4-sulfonic acid, Tetradecyldimethylbenzylammonium chloride, Alloys

## INTRODUCTION

Vanadium is one of the most important element which affects the physical properties of steel, alloys and high purity metals. It is widely distributed in earth's crust, its compounds can be highly toxic to

man and animals and cause environmental diseases when released in the atmosphere [1]. It has also been noted that the environmental background levels of vanadium have been slowly rising as a result of the

combustion of fossil fuels which have high vanadium content [2]. Vanadium is therefore, important not only because of the toxicity at high levels but also because it is an environmental pollutant [3]. Occupational exposure to vanadium has been observed in several industrial processes, for example, in iron and steel production, in the manufacture of pigments, printing inks and paints, in the glass industry and in the cleaning and repairing of oil fired boilers, particularly in electricity power stations [4-6]. Very low concentrations of vanadium are present in various matrices such as plants, soils and sea-water. 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 these instruments are highly expensive, high cost maintenance and not free from various types of inherent interferences [7-10].

2-Nitroso-1-naphthol-4-sulfonic acid (Nitroso-S) was introduced by *Hoffman* [11] as a qualitative analytical reagent for cobalt, copper and iron and applied to the colorimetric determination of cobalt by *Wise and Brandt* [12]. The reagent forms water-soluble chelate anions with 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 the Cu(II)-Nitroso-S anion with tetradecyldimethylbenzylammonium (TDBA) cation [13] and Fe(II)-Nitroso-S anion with azo dye cation in chloroform [14]. 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 [15] for thermally stable metal chelates [16]. 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 [17-19].

In this paper, an efficient method for the preconcentration of vanadium from a large volume of the

aqueous solutions of various standard reference materials with 2-nitroso-1-naphthol-4-sulfonic acid-TDBA-naphthalene adsorbent is described. The method is economical (all reagents are cheap compared with many other reagents used recently [20-27].), rapid (the metal complex simply to adsorb onto microcrystalline naphthalene) and sensitive (the solid mass can be dissolved in 3-5 mL of an organic solvent, and the whole of the solution may be used for the absorbance measurement). The solid mass, consisting of the metal ion associated complex and naphthalene, can easily be dissolved with a suitable organic solvent such as dimethylformamide (DMF) and the vanadium is determined by second derivative spectrophotometry. The metal can also be determined by directly aspirating the DMF solution into the flame of an AAS instrument, but the instrument is relatively expensive, and it is not free from matrix effects. Various parameters were evaluated and the optimized conditions were utilized for the trace determination of vanadium in various standard alloys and synthetic samples.

## EXPERIMENTAL

### *Apparatus and reagents*

A Shimadzu UV 160 spectrophotometer with a 1.0 cm quartz cell were used. A Beckman pH meter was employed for pH measurements. All glassware was washed with mixture of concentrated sulphuric acid and nitric acid (1+1) before used. All the reagents used were of analytical grades.  $\text{NH}_4\text{VO}_3$  was dissolved in a few mL of 1 M NaOH, acidified the solution with dilute HCl and then diluted to 1000 mL in standard flask and standardized by known methods [28]. A more dilute solution of vanadium (1 ppm) can be prepared by diluting the standard solution. A buffer solution of  $\text{pH} \approx 3.5$  was prepared by mixing of 0.5 M acetic acid and 0.5 M sodium acetate solutions in appropriate ratio. A 1% solution of tetradecyldimethylbenzylammonium chloride (TDBA) and 0.1% 2-nitroso-1-naphthol-4-sulfonic acid (Nitroso-S) were prepared in distilled water. A 20% solution of naphthalene was prepared in acetone. Solutions of alkali metal salts (1%) and various metal ions (0.1%) were used for studying the interference of anions and cations respectively.

### General procedure

An aliquot of vanadium solution (containing 0.4-100  $\mu\text{g}$ ) was placed in a 100 mL an Erlenmeyer flask with tightly fitting stopper. Then 1 mL of 0.1% of the reagent (Nitroso-S) was added and diluted to 30-40 mL with water. The pH was adjusted to  $\approx 3.5$  with 2 mL of the buffer 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 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 with 5.0 mL of dimethylformamide (DMF). The second derivative absorption spectra in the range 400 to 600 nm was recorded against a blank solution prepared in the same way. The signal was measured between  $\lambda_1 = 575$  nm and  $\lambda_2 = 510$  nm. A calibration graph was prepared by taking various known amounts of vanadium under the conditions given above.

## RESULTS AND DISCUSSION

### Spectrophotometric measurements

The zero order and second order derivative spectra of the complex are shown in Figs. 1 and 2 respectively. As can be seen, the higher wavelength peaks of the derivative spectra are more significant. Derivative 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 recording of the spectra. The optimum parameters were chosen from preliminary experiments. The best results were obtained from second derivative with wavelength interval ( $\Delta\lambda$ ) 9 nm. In the present work a peak to peak method between  $\lambda_1 = 575$  nm and  $\lambda_2 = 510$  nm was applied.

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

2-Nitroso-1-naphthol-4-sulfonic acid (Nitroso-S)

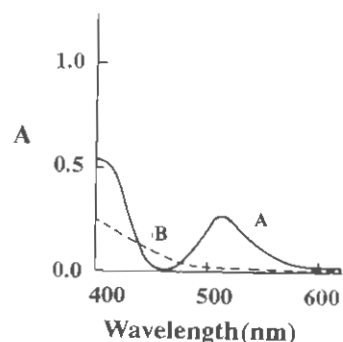


Fig. 1: Zero order spectrum of V-Nitroso-S-TDBA-naphthalene in DMF solution (A) and against reagent blank (B): V, 25  $\mu\text{g}$ ; pH, 3.5; and solvent, 5.0 mL of DMF.

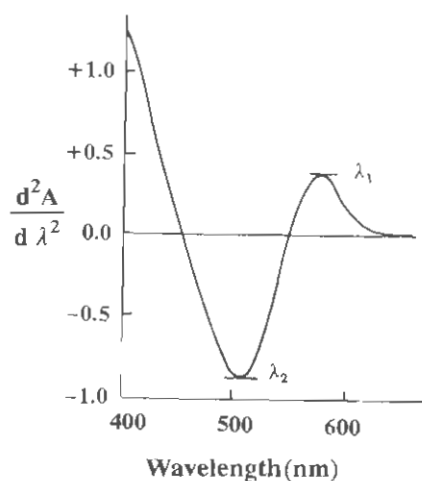
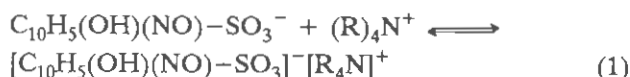


Fig. 2: Second order derivative spectrum of V-Nitroso-S-TDBA-naphthalene complex in DMF solution against blank: V, 25  $\mu\text{g}$ ; pH, 3.5; solvent, 5.0 mL of DMF; and  $\Delta\lambda$ , 9.

is applied as analytical reagent for V(V) and is formed V(V)-Nitroso-S complex. Tetradecyldimethylbenzylammonium (TDBA<sup>+</sup>) is applied as counter ion for adsorption of this metal complex to naphthalene and V(V)-Nitroso-S-TDBA-naphthalene is formed as solid phase which can be easily separated by filtration from aqueous solution. This solid is dissolved with 3-5 mL of dimethylformamide (DMF).

The TDBA chloride is water soluble well known quaternary ammonium salt widely used as 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

follows.



The ion pair formed between the anionic Nitroso-S and cationic TDBA<sup>+</sup> easily coprecipitated with microcrystalline naphthalene. The ion-pair reaction between Nitroso-S and several well known quaternary ammonium salts were 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 the counter ion has been selected, since it is relatively cheaper than CTMA<sup>+</sup> and has excellent retention characteristics for metal ions.

### Reaction conditions

These were established with the use of 25  $\mu\text{g}$  vanadium. The adsorption of vanadium on this adsorbent was found to be a maximum in the pH range 3.0-4.0 (Fig. 3). In subsequent studies, the pH was maintained at approximately 3.5. Addition of 0.5-5.0 mL of the buffer did not affect the retention of vanadium and the use of 2.0 mL is recommended. Various amounts of 0.1% reagent (Nitroso-S) were tried. Vanadium as V(V)-Nitroso-S-TDBA-naphthalene was quantitatively adsorbed over the range 0.4-4.0 mL of the reagent. Therefore, 1.0 mL of the reagent is recommended in the present study.

Various amounts of 1% counter ion of tetradecyl-dimethylbenzylammonium chloride (TDBA) were tried. It was observed that the signal height remained constant with the addition of 0.3-5.0 mL of the counter ion. Therefore, 2.0 mL of the counter ion was used in subsequent studies.

Various amounts of naphthalene (20% solution of

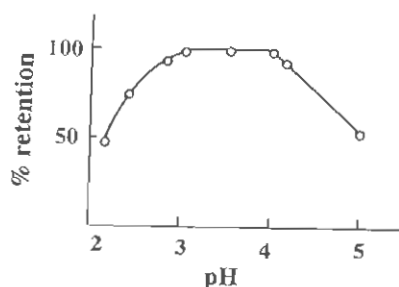


Fig. 3: Effect of pH on retention of vanadium: V, 25  $\mu\text{g}$ ; solvent, DMF;  $\Delta\lambda$ , 9; and reference, reagent blank.

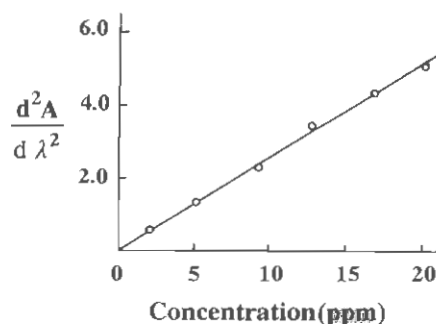


Fig. 4: Calibration curve for vanadium in DMF solution by second derivative spectrophotometry from signal peak to peak measurements between  $\lambda_1$  and  $\lambda_2$ . For conditions, see Fig. 2.

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 subsequent studies. The effect of shaking time on the adsorption indicated that the signal height remained constant over a range of 0.5-7.0 min. Therefore, 1.0 min of shaking time was maintained in the present work.

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

### Choice of solvent

A number of solvents were tried to dissolve the V-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, stable and also sensitive for UV-Vis 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. It was found that 2-3 mL of this solvent was sufficient

to dissolve the mixture thus enhancing the sensitivity of the method. As only a small volume (3-5 mL) of the solvent was used to dissolve the complex and naphthalene, therefore, it was essential to study the effect of water attached to naphthalene. It was noted that water decreased the absorbance by 12-15% and led to an error in the determination. Thus it was necessary to eliminate the water attached to the naphthalene and the residue was dried in the fields of a filter paper.

### Calibration

The calibration curve (Fig. 4) for the determination of vanadium was prepared according to the general procedure under the optimum conditions developed above.

The detection limit was 40 ppb for vanadium at the minimum instrumental settings (signal to noise ratio = 2). The linearity was maintained in the concentration range of 0.08-20 ppm vanadium with a correlation coefficient of 0.9995 ( $n=6$ ) and the relative standard deviation for  $5 \mu\text{g mL}^{-1}$  of vanadium was found to be 0.98% ( $n=6$ ).

### Effect of diverse ions

Various salts and metal ions were added individually to a solution containing 25  $\mu\text{g}$  of vanadium and the general procedure was applied. The tolerance limit (error <3%) is given in Table 1. 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 Fe(III) and Cu(II) which interfered but their lower amounts could be tolerated after masking Fe(III) with 2 mL of 5% NaF solution and Cu(II) with 0.2 g of thiourea and 0.1 g of  $\text{Na}_2\text{S}_2\text{O}_3$ , or both could be masked with EDTA. Thus the method developed above is fairly selective and sensitive and has been applied to the determination of vanadium in various complex materials.

### Analysis of standard alloys

The proposed method has been applied to determination of vanadium in Nippon Keikinokogyo (NKK) CRM 916 aluminium alloy, NKK No. 920 aluminium alloy and NKK No. 1021 Al, Si, Cu, Zn, alloy. A 0.1 g sample of the standard alloy was completely dissolved in 4-5 mL of hydrochloric acid (1+1) by

Table 1: Effect of added salts and metal ions.

Salt or ion	Tolerance limit
$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ , $\text{KNO}_3$ , $\text{NH}_4\text{Cl}$	1 g
$\text{K}_2\text{SO}_4$	600 mg
Thiourea, NaF	300 mg
$\text{Na}_3\text{PO}_4$ , $\text{K}_2\text{CO}_3$	250 mg
KI	200 mg
$\text{Na}_2\text{S}_2\text{O}_3$	95 mg
Sodium potassium tartrate	25 mg
KSCN	20 mg
Trisodium citrate, sodium oxalate	19 mg
$\text{Na}_2\text{EDTA}$	100 $\mu\text{g}$
Mg(II)	150 mg
Ca(II)	70 mg
Pb(II), Sb(III)	10 mg
Cd(II), Mn(II), Ti(VI)	5 mg
Ag(I), Zn(II)	4 mg
Ni(II), Cr(VI), Al(III), Se(VI), Cr(III)	2 mg
Te(IV), U(VI)	1.5 mg
Ga(III), Pd(II)	1.0 mg
Fe(III)	1.0 mg <sup>a</sup>
Hg(II), Bi(III)	0.9 mg
Ru(III), Os(VIII), Co(II)	0.6 mg
Cu(II)	0.2 mg <sup>b</sup>

a) After masking with 2 mL of 5% NaF solution.

b) After masking with 0.2 g thiourea and 0.1 g  $\text{Na}_2\text{S}_2\text{O}_3$ .

heating on a water-bath and then 1 mL of 30% hydrogen peroxide was added to the solution. The excess of peroxide was decomposed by heating the solution on a water-bath. The solution was cooled and filtered if needed and the filtrate was diluted to 100 mL with doubly distilled water in a calibrated flask. An aliquot (1-2 mL) of this solution was taken and vanadium was determined by the general procedure (Table 2).

### Analysis of synthetic samples

A synthetic sample containing vanadium was prepared in 10 mL of concentrated hydrochloric acid (1+1). The solution was filtered if needed, and the volume was made to 100 mL in a standard flask. An aliquot of the sample (40-100 mL) solution was analyzed by the general procedure and the results are

Table 2: Analysis of vanadium in standard alloys

Sample	Composition %	Concentration %	
		Certified value	Found <sup>*+</sup>
NKK No. 916 aluminium alloy	Si, 0.41; Mg, 0.10; Cr, 0.05; Ni, 0.06; Zn, 0.30; Pb, 0.04; Sn, 0.05; Ti, 0.01; Zr, 0.05; Bi, 0.03; Co, 0.03; Sb, 0.01; Cu, 0.27; Mn, 0.11 B, 0.0006; Fe, 0.54	0.02	0.019±0.001
NKK No. 1021 Al, Si, Cu, Zn alloy	Pb, 0.18; Ni, 0.14; Zn, 1.76; Sn, 0.10; Mg, 0.29; Cr, 0.03; Ti, 0.04; Si, 5.56; Zr, 0.01; Bi, 0.01; Sb, 0.01; Ca, 0.004; Fe, 0.99; Cu, 2.72; Mn, 0.20	0.007	0.0068±0.0006
NKK No. 920 aluminium alloy	Co, 0.10; Ni, 0.29; Cr, 0.27; Si, 0.78; Ti, 0.15; Sn, 0.20; Pb, 0.10; Bi, 0.06; Ga, 0.05; Zn, 0.80; Sb, 0.10; Ca, 0.03; Mg, 0.46; Fe, 0.72; Cu, 0.71; Mn, 0.20	0.15	0.148±0.005

\* Average of five determinations, ± standard deviation

+ Standard addition method was applied

2 mL of 5% NaF solution, 0.1 g of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and 0.2 g thiourea were added as masking agents.

given in Table 3.

## CONCLUSION

A simple, economical and highly selective adsorbent has been generated simply by mixing the aqueous solutions of Nitroso-S salt and TDBA<sup>+</sup> Cl<sup>-</sup> with the acetone solution of naphthalene for the preconcentration of vanadium from the large volume of the aqueous solution of alloys and synthetic samples. Since Nitroso-S reacts with many metal ions, therefore, similar procedure may also be developed for other metal ions too. It is not possible to develop selective methods for metal ions using microcrystalline naphthalene since many metal-Nitroso-S complexes absorb at close wavelengths. However, with the use of derivative spectrophotometry this problem can be easily solved.

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## REFERENCES

- [1] Lee, D. H. K., "Metallic Contaminants and Human Health", Academic Press, New York (1972).
- [2] Nelson, W. L., *Oil Gas J.*, **71**, 54(1973).
- [3] Vouk, V. W. and Piver, W. T., *Environ. Health Perspect.*, **47**, 201(1983).
- [4] Kiviluoto, M. P. L. and Pakarinen, A., *Int. Arch. Occup. Environ. Health*, **48**, 51(1981).

Table 3: Analysis of vanadium in synthetic samples

Composition of synthetic sample ( $\mu\text{g/g}$ )	Certified value ( $\mu\text{g/g}$ )	Amount found by the present method* ( $\mu\text{g/g}$ )
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; Pd, 7.5; Rh, 0.85; Ir, 5.5	6.5	$6.4 \pm 0.2^a$
Mn, 3.5; Pb, 2.0; Sb, 1.5; Ni, 6.0; Mo, 4.5; Mg, 75; Ca, 74; Cd, 7.5; Hg, 2.5; Bi, 8.0; Zn, 12; Al, 2.5; Pd, 7.5; Rh, 18.0; Ir, 15.0	25.0	$24.7 \pm 0.6$
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; Pd, 3.5; Rh, 17.5; Ir, 25.5	48.0	$47.8 \pm 0.5^b$

\* Average of five determinations,  $\pm$  standard deviation

a) After masking with 2 mL of 5% NaF solution, 0.2 g thiourea and 0.1 g  $\text{Na}_2\text{S}_2\text{O}_3$

b) After masking with 2 mL of 5% NaF solution

- [5] Gylseth, B., Leira, H., Steinnes, E. and Thomasen, Y., *Scan J. Work Environ. Health*, **5**, 188(1979).
- [6] Sabbioni, E. and Maroni, M., "A Study on Vanadium in Workers from Oil Fired Power Plants", Commission of the European Communities, Publication No. EUR. 9005, Luxembourg (1983).
- [7] Jackson, K. W. and Qiao, H., *Anal. Chem.*, **64**, 50R (1992).
- [8] Jackson, K. W. and Mahmood, T. M., *Anal. Chem.*, **66**, 252R(1994).
- [9] Kantipuly, C. J. and Westland, A. D., *Talanta*, **35**, 1(1988).
- [10] Ramesh, A., Krishnamacharayulu, J., Ravindranath, L. K. and Rao, S. B., *Analyst*, **117**, 1037(1992).
- [11] Hoffman, O., *Chem. Ber.*, **18**, 46(1885).
- [12] Wise, W. M. and Brandt, W. W., *Anal. Chem.*, **26**, 693(1954).
- [13] Motomizu, S. and Toei, K., *Bunseki Kagaku*, **27**, 213(1978).
- [14] Motomizu, S. and Toei, K., *Bunseki Kagaku*, **30**, 245(1981).
- [15] Wasey, A., Bansal, R. K., Puri, B. K. and Rao, A. L. J., *Talanta*, **31**, 205(1984).
- [16] Satake, M., Kano, G., Usami, S. and Puri, B. K., *Indian, J. Chem.*, **27A**, 265(1988).
- [17] Satake, M. and Mehra, M. C., *Microchem. J.*, **27**, 182(1982).
- [18] Satake, M., Matsumura, Y. and Mehra, M. C., *Mikrochim Acta*, **1**, 455(1980).
- [19] Lin, J. L., Satake, M. and Puri, B. K., *Analyst*, **110**, 1351(1985).
- [20] Taher, M. A. and Puri, B. K., *Talanta*, **43**, 247 (1996).
- [21] Taher, M. A. and Puri, B. K., *Ann. Chim. (Rome)*, **85**, 183(1995).
- [22] Barrera, A. B., Barrera, P. B. and Martinez, F. B.,

- Analyst*, **110**, 1313(1985).
- [23] Odashima, T., Kibuchi, T., Ohtani, W. and Ishii, H., *Analyst*, **111**, 1383(1986).
- [24] Sanchez, F. G., Lopez, M. J. and Gomez, T. C., *Talanta*, **197**, 275(1987).
- [25] Murillo, J. A. and Lemus, M., *Analyst*, **113**, 1439 (1988).
- [26] Jimenez, A. I., Jimenez, F. and Arias, J. J., *Analyst*, **114**, 93(1989).
- [27] Toral, M. I., Richter, P. and Silva, L., *Talanta*, **40**, 1405(1993).
- [28] Vogel, A. I., "A text Book of Quantitative Inorganic Analysis", 4th Ed., Longman, London (1978).