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Determination of Trace Amounts of Cobalt by Flame Atomic Absorption Spectrometry after Solid-Liquid Extraction and Preconcentration with Use of Nitroso-R Salt

MOHAMMAD ALI TAHER

Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, Iran
E-mail: ma_taher@yahoo.com; taher@arg3.uk.ac.ir

Cobalt was quantitatively retained by disodium 1-nitroso-2-naphthol-3,6-disulfonate (nitroso-R salt) and tetradecyldimethylbenzylammonium chloride on microcrystalline naphthalene in the pH range 3.6–8.2 from large volumes of aqueous solutions of various alloys and biological samples. After filtration, a solid mass consisting of the cobalt complex and naphthalene was dissolved with 5 mL of dimethylformamide and the metal was determined by flame atomic absorption spectrometry (FAAS). The cobalt complex could alternatively be quantitatively adsorbed on tetradecyldimethylbenzylammonium-naphthalene adsorbent packed in a column and determined similarly. In this case, 0.50 μg of cobalt can be concentrated in a column from 500 mL of aqueous sample, where its concentration is as low as 1.0 ppb. Eight repliate determinations of 1.0 ppm of cobalt gave a mean absorbance of 0.050 with a relative standard deviation of 1.9%. The sensitivity for 1% absorption was 88 ppb. Various parameters, such as the effect of the pH, the volume of the aqueous phase and the interference of a number of metal ions on the determination of cobalt, have been studied in detail to optimize the conditions for the determination of cobalt in various alloys and biological samples.

Key Words: Determination of trace cobalt; Solid-liquid extraction of cobalt; Flame atomic absorption spectrometry; Alloys and biological samples.

INTRODUCTION

Disodium 1-nitroso-2-naphthol-3,6-disulfonate (nitroso-R salt) was introduced in 1921 by Van Klooster for the detection of cobalt[1], and was then subsequently used by various investigators for the determination of small quantities of this metal in plant and animal tissues[2–7], soils[8–10], grasses[11, 12], steels and carbides[13]. Preliminary experiments indicated that metal ions also react with this reagent and form a coloured water-soluble anionic complex. This anionic complex in the presence of the tetradecyldimethylbenzylammonium cation forms a coloured water-insoluble ion-associated complex, which can be easily adsorbed on microcrystalline naphthalene.

Although solvent extraction is a simple and convenient technique for separating and concentrating metal ions, 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[14] for thermally stable metal chelates[15]. Solid-liquid separation after the adsorption of metal chelates on microcrystalline naphthalene is more rapid and convenient, and can be applied to many types of metal complexes[16, 17]. The only drawback is in filtration and drying. A survey of the literature revealed that various adsorbents, such as thiol cotton[18], silanized glass beads[19], C_{18}-bonded silica gel[20], amberlite XAD-4 resin[21], cellulose[22], silicagel[23], green tea leaves[24] and polythioether foam[25] have been tried for the preconcentration of metal ions. Although some of these adsorbents are fairly effective, their preparation methods are lengthy and involve rigid control of the conditions. Because 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), the procedure is time consuming.

This paper describes an efficient method for the preconcentration of cobalt from a large volume of aqueous solutions of various standard reference materials with 1-nitroso-2-naphthol-3,6-disulfonate-TDBA-naphthalene adsorbent. The method is economical (all reagents are low cost compared with many other reagents used recently[26–28]), rapid (the metal complex simply adsorbs on to microcrystalline naphthalene) and sensitive (the solid mass can be dissolved in 2–5 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 (Co-1-nitroso-2-naphthol-3,6-disulfonate-TDBA-naphthalene), can be easily dissolved with a suitable organic solvent, such as dimethylformamide and the metal content can be determined by atomic absorption spectrometry. Various parameters evaluated and the optimized conditions utilized for the trace determination of cobalt in alloys and biological samples.

EXPERIMENTAL

A Shimadzu AA 670 flame atomic absorption spectrophotometer was used in the following conditions: wavelength: 240.7 nm, lamp current: 6.0 mA, slit width: 0.2 mm, burner height: 6.0 mm, acetylene flow: 2.2 L min^{-1}, air flow: 8.0 L min^{-1}. A Beckman pH-meter was employed for pH measurements. A funnel-tipped glass tube (60 × 6 mm) was used as a column for preconcentration. It was plugged with polypropylene fibres and then filled with the adsorbent to a height of 1.0–1.2 cm after slightly pressing with a flat glass rod. All glassware and column were washed with a mixture of concentrated sulfuric acid and concentrated nitric acid (1 + 1) before use.

All reagents were of analytical reagent grade. A standard cobalt solution was prepared from cobalt(II) chloride in distilled water and standardized complexometrically.[29] A 2 ppm solution of cobalt was prepared by appropriate dilution of the standard solution. Buffer solutions of pH 3–6, pH 6–8 and pH 8–11 were prepared by mixing an appropriate ratio of 0.5 M acetic acid and 0.5 M ammonium acetate, 0.1 M disodium hydrogen phosphate and 0.1 M potassium dihydrogen phosphate, 0.5 M aqueous ammonia and 0.5 M ammonium acetate, respectively. A 1% solution of tetradecyldimethylbenzylammonium chloride (TDBA) and 0.1% 1-nitroso-2-naphthol-3,6-disulfonate acid (nitroso-R) was 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 to study the interference of anions and cations, respectively.

Preparation of a nitroso-R-TDBA-naphthalene adsorbent

A solution of naphthalene was prepared by dissolving 20 g in 40 mL of acetone on a hot-plate stirrer at approximately 35°C. It was transferred into a beaker containing 1500 mL of distilled water and 0.9 g of nitroso-R salt in a fast stream with continuous stirring at room temperature. $TDBA^+Cl^-$ (2.4 g, 0.0062 mol) was dissolved in 500 mL of distilled water by warming on a hot-plate. It was mixed with the above mentioned solution of naphthalene-acetone-nitroso-R salt in water. A yellow naphthalene material coprecipitated with TDBA and nitroso-R was stirred for about 2 h, and was 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 a slurry was stored in a brown bottle for subsequent use.

General procedure for the column method

An aliquot of cobalt solution containing 0.5–25 μg of cobalt was taken in a 25 mL beaker. The pH of this solution was adjusted to 6 with the addition of 2 mL of a buffer solution and diluted to about 15 mL with distilled water. After a column loaded with the nitroso-R-TDBA-naphthalene adsorbent was conditioned to pH 6 with 2–3 mL of buffer, the metal solution was passed through the column at a flow rate of 1 mL min^{-1}. The packing was washed with a small volume of water and then aspirated strongly for a few minutes, while pushing down the naphthalene material with a flat glass rod to eliminate any excess of water attached to the naphthalene. The solid mass, consisting of the metal complex along with naphthalene, was dissolved out in the column with 5 mL of dimethylformamide. The solution was aspirated into an air-acetylene flame and the absorbance was measured at 240.7 nm against a reagent blank. The absorbances for standard amounts of cobalt were measured and a calibration curve was constructed against a reagent blank prepared in a similar manner.

General procedure for microcrystalline naphthalene

An aliquot of cobalt solution (containing 0.5–25 μg) was placed in 100 mL of an Erlenmeyer flask with tight-fitting stopper. Then, 1 mL of a 0.1% reagent (nitroso-R) was added to it, and the mixture was diluted to 30–40 mL with water. After the pH was adjusted to 6 with 2 mL of the buffer, 2 mL of a 1% TDBA solution was added. 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 thus formed, consisting of naphthalene and the metal complex, was separated by filtration on Whatman filter paper (No.

1041). The residue was dried in the folds of a filter paper and transferred to an Erlenmeyer flask. The solid mass consisting of the metal complex along with naphthalene was dissolved with 5 mL of dimethylformamide. The solution was aspirated into an air-acetylene flame and the absorbance was measured at 240.7 nm against a reagent blank solution prepared in the same way. A calibration graph was prepared by taking various known amounts of cobalt under the conditions given above.

RESULTS AND DISCUSSION

Reaction conditions

These were established by using 5.0 μg of cobalt. The adsorption of cobalt on this absorbent was found to be maximum in the pH range 3.6–8.2. In a subsequent study, the pH was maintained at pH 6. The addition of 0.5–5.0 mL of the buffer (pH 6) did not affect the retention of cobalt, and the use of 2.0 mL was recommended. Cobalt was quantitatively adsorbed over the range 0.5–5.0 mL of the reagent. Therefore, 1.0 mL of the reagent is recommended based on the present study.

Various amounts of naphthalene (20% solution of naphthalene in acetone) were added to the sample solutions while keeping the other variables constant. It was observed that the signal height remained constant with the addition of 1.0–5.0 mL of a 20% naphthalene solution. Therefore, 2.0 mL of a 20% naphthalene solution was used in subsequent studies. The effect of the shaking time on the adsorption indicated that the signal height remained constant over a range of 0.5–8.0 min. Therefore, 1.0 min of shaking time was maintained in the present work.

However, in the case of the column method, the flow rate was varied from 0.3 to 8 mL min^{-1}. It was found that a flow rate of 0.3–5.0 mL min^{-1} did not affect the adsorption. A flow rate of 1 mL min^{-1} was recommended in all experiments.

The volume of the aqueous phase was varied over the range of 10–700 mL under the optimum conditions, while keeping all 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.

However, in the case of the column method, the peak height was almost constant up to an aqueous phase volume of 500 mL. Therefore, a preconcentration factor of 100 can be achieved by the column.

Retention capacity of the adsorbent

The retention capacity of the adsorbent was determined by a batch method. The experiment was performed by taking 500 μg of cobalt, 2 mL of a buffer solution (pH 6) and 40 mL of water in a beaker. After this solution was transferred into a separating funnel, a suitable amount of the nitroso-R-TDBA-naphthalene adsorbent was added. The separating funnel was shaken vigorously on a mechanical shaker for 5 min. The solid mass was separated by filtration and cobalt was determined from the filtrate by FAAS. 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 cobalt was retained with 3.9 mg g^{-1} of nitroso-R salt in the adsorbent. It was also noted that the retention capacity depends on the amount of TDBA and nitroso-R supported on naphthalene. The molar ratio of nitroso-R : $TDBA^+$ is 1 : 2 based on the observations of the preparation of the adsorbent; it was found that when using nitroso-R (0.9 g) and $TDBA^+$ (2.4 g), a slight excess of nitroso-R and 20 g of naphthalene was sufficient for complete retention of the metal ions.

Choice of solvent

A number of solvents were tried to dissolve the Co-nitroso-R-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 sensitive for spectrophotometric measurements. The solid material was found to be insoluble in ordinary organic solvents, such as toluene, 1,2-dichloroethane, hexane, nitrobenzene, isoamyl alcohol, *n*-amyl alcohol, ethylacetate, methylisobutylketone, chloroform and dioxane, but soluble in dimethyl sulfoxide, dimethylformamide, and propylene carbonate. Dimethylformamide was preferred due to its high solubility and stability. It was found that 3–5 mL of this solvent was sufficient to dissolve the mixture, thus enhancing the sensitivity of the method.

Calibration and sensitivity

Since it is possible to retain 0.20 μg of cobalt from 500 mL of solution passing through the column, the dissolution with 5.0 mL dimethylformamide gives a detection limit of 0.4 ppb for cobalt at the minimum instrumental settings. The linearity was maintained in the concentration range of 1.0 ppb to 2.5 ppm cobalt in aqueous solution or 0.10 to 5.0 ppm cobalt in final dimethylformamide solution with a correlation factor of 0.9995. Eight replicate determinations of 5.0 μg of cobalt in 5 mL dimethylformamide solution gave a mean absorbance of 0.050 with a relative standard deviation of 1.9%. The sensitivity for 1% absorption was 88 ppb.

Effect of diverse ions

Various salts and metal ions were added individually to a solution containing 5.0 μg of cobalt and the general procedure was applied. The tolerance limit was set as the diverse ion required to cause a ±3% error in the determination of cobalt. The obtained results are given in Table-1. Among the anions examined, large amounts of chloride, bromide, nitrate, acetate, carbonate and sulphate could be tolerated. Citrate, oxalate, orthophosphate, tartrate and EDTA interfered. Except for EDTA, a relatively small amount of these anions could be tolerated. Obviously, the stability constants of the Co-EDTA complex must be higher than that of the Co-nitroso-R complex. Of the metal ions examined, many did not interfere up to mg levels. Thus, the proposed method is selective and can be used to determine cobalt in standard alloys and biological samples without any prior separation.

TABLE-1
EFFECT OF DIVERSE SALTS AND METAL IONS

Salt or ion	Tolerance limit (mg)
$CH_3COONa{\cdot}3H_2O$, KNO_3	1000
K_2SO_4	190
KI	80
NH_4Cl, $Na_3PO_4{\cdot}12H_2O$, K_2CO_3	40
NaF	100
Sodium potassium tartrate	20
Thiourea, KSCN, $NaClO_4$	15
Sodium oxalate, $Na_2S_2O_3$	35
Trisodium citrate	10
Na_2EDTA	80
Mg(II)	150
Ca(II)	80
Cd(II), Sb(II), Pb(II)	40
Ti(IV), Fe(III)	25
Zn(II), Ag(I), Al(III)	15
Cr(VI), Cr(III)	10
Se(VI), Ga(III)	9
Mo(VI), U(VI), Ni(II), Cu(II)	8
Pd(II), Te(IV)	7
Os(VIII), Bi(III)	6.5
Rh(III), V(V)	6
Ru(III), Hg(II)	5

Analysis of cobalt in standard alloys and steel samples

The proposed method was applied to the determination of cobalt in Nippo Keikinzoku Kogyo (NNK) CRM No. 916 and No. 920 aluminum alloy and Japanese standards of iron and steel (JSS) CRM 651–7 and 653–7 stainless steel. A 0.1 g sample of the standard aluminium alloy or steel was completely dissolved in 6–14 mL of hydrochloric acid (1 + 1) by heating on a water-bath; then, 1 mL of 30% (v/v) hydrogen peroxide was added. The excess 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. An aliquot (1–2 mL) of this sample was taken into a 20 mL beaker and the general procedure was applied. The results are given in Table-2. These results are in agreement with the certified values.

TABLE-2
ANALYSIS OF COBALT IN STANDARD ALLOYS

Sample	Composition (%)	Concentration (%)	
		Certified value	Found*
JSS 651-7 stainless steel	C, 0.047; Si, 0.072; P, 0.028; Cr, 18.60; S, 0.0063; Mo, 0.84; Al, 0.002; N, 0.0312; Cu, 0.082; Mn, 1.72; Ni, 9.20	0.22	0.214 ± 0.007[a]
JSS 653-7 stainless steel	C, 0.068; Si, 0.63; Cr, 22.53; Cu, 0.030; Mn, 1.72; Ni, 13.91; N, 0.0276	0.35	0.342 ± 0.009[b]
NKK No. 916 aluminum alloy	Si, 0.41; Fe, 0.54; Mg, 0.10; Cr, 0.05; Zn, 0.30; Ti, 0.10; Sn, 0.05; Pb, 0.04; Sb, 0.01; B, 0.0006; Zr, 0.05; Bi, 0.03; Cu, 0.27; Mn, 0.11; Ni, 0.06; V, 0.02	0.03	0.029 ± 0.002[a]
NKK No. 920 aluminum alloy	Si, 0.78; Fe, 0.72; Mg, 0.46; Cr, 0.27; Zn, 0.80; Ti, 0.15; Sn, 0.20; Pb, 0.10; Sb, 0.10; Bi, 0.06; Ga, 0.05; Ca, 0.03; Cu, 0.71; Mn, 0.20; Ni, 0.29; V, 0.15	0.10	0.103 ± 0.003[b]

*Average of five determinations, ± standard deviation

[a] Column method was applied

[b] Microcrystalline naphthalene method was applied.

Analysis of cobalt in biological samples

The accuracy and applicability of the proposed method have been applied to the determination of cobalt in National Institute for Environmental Studies (NIES) No. 1 pepperbush; NIES, No. 3 chlorella; NIES, No. 7 tea leaves. A 0.1 g sample was taken in a beaker and dissolved in concentrated nitric acid (*ca.* 5 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made 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 100 mL with distilled water. An aliquot (10–50 mL) of the sample solution was taken individually and cobalt was determined by the general procedure. The results are given in Table-3, which are in good agreement with the certified values.

TABLE-3
ANALYSIS OF COBALT IN BIOLOGICAL SAMPLES

Sample	Composition	Concentration (μg/g)	
		Certified value	Found[*+]
NIES, No. 1 pepperbush	K, 1.51 ± 0.06; Mn, 0.203 ± 0.107; Mg, 0.408 ± 0.020; Ca, 1.38 ± 0.07% Cd, 6.7 ± 0.5; Ni, 8.7 ± 0.6; Fe, 205 ± 17; Cu, 12 ± 1; Pb, 5.5 ± 0.8; Zn, 340 ± 20; Rb, 75 ± 4; Ba, 165 ± 10; Na, 106 ± 13; Sr, 36 ± 4; As, 2.3 ± 0.3; P, (1100); Cr, (1.3); Cs, (1.2); Tl, (0.13); Hg, (0.056) μg/g	23 ± 3	22 ± 1[b]
NIES, No. 3 chlorella	K, 1.24 ± 0.06; Ca, 0.49 ± 0.03; Fe, 0.185 ± 0.010; Mg, 0.33 ± 0.02; P, (1.7)% Zn, 20.5 ± 1.0; Sr, 40 ± 3; Cu, 3.5 ± 0.3; Mn, 69 ± 5; Cd, (0.026); Pb, (0.60); Sc, (0.013) μg/g	0.87 ± 0.05	0.89 ± 0.02[a]
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; Cu, 7.0; Mn, 7.00; Ni, 6.5 μg/g	0.12	0.117 ± 0.004[a]
NIES, No. 8 vehicle exhaust particulates	K, 0.115 ± 0.08; 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; 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	3.3 ± 0.3	3.2 ± 0.1[b]

[*] Average of five determinations, ± standard deviation.

[+] Standard addition method was applied.

[a] Column method was applied.

[b] Microcrystalline naphthalene method was applied.

NIES: National Institute of Environmental Studies reference materials.

NIES, No. 1, No. 3 and No. 8 (Values in parentheses were approximate and not certified).

Conclusion

A simple, economical and highly selective adsorbent has been generated simply by mixing aqueous solutions of nitroso-R salt and TDBA$^+$ Cl$^-$ with an acetone solution of naphthalene for preconcentration of cobalt from a large volume of an aqueous solution of alloys and biological samples. Since nitroso-R reacts with many metal ions, a similar procedure may also be developed for other metal ions. It is not possible to develop selective methods for metal ions using microcrystalline naphthalene or a column method, since many metal-nitroso-R complexes absorb at close wavelengths. However, by using derivative spectrophotometry, this problem can be easily solved. Cobalt may also be determined by directly aspirating the dimethylformamide solution of the metal complex after preconcentration into the flame of the atomic absorption photometry or by pulse polarography. Although adsorption onto microcrystalline naphthalene is more rapid, the preconcentration factor is comparatively lower than in the column method.

REFERENCES

1. H.S. Van Klooster, *J. Am. Chem. Soc.*, **43**, 746 (1921).
2. H.R. Marston and D.W. Dewey, *Aust. J. Exp. Biol. Med. Sci.*, **18**, 343 (1940).
3. K.J. McNaught, *Analyst*, **67**, 97 (1942).
4. ———, *Analyst*, **64**, 23 (1939).
5. J.W.H. Lugg and S.W. Josland, *Aust. S. Exp. Biol. Med. Sci.*, **14**, 319 (1939).
6. F.J. Stare and C.A. Elvehjem, *J. Biol. Chem.*, **99**, 473 (1933).
7. R.Q. Parks, S.L. Hood, C. Hurwitz, and G.H. Ellins, *Ind. Eng. Chem. Anal. Ed.*, **15**, 527 (1943).
8. E.B. Kidson, H.Q. Askew and J.K. Dixon, *N.Z.J. Sc. Technol.*, **18**, 601 (1936).
9. H.T. Macpherson and J. Stewart, *Biochem. J.*, **32**, 763 (1938).
10. K.J. McNaught, *N.Z. J. Sci. Technol.*, **18**, 601 (1936).
11. E.B. Kidson and H.O. Askew, *N.Z. J. Sci. Technol.*, **21B**, 178 (1940).
12. L.I. Butler and H.D. Allen, *J. Assoc. Off. Agric. Chem.*, **25**, 567 (1942).
13. F.W. Haywood and A.A.R. Wood, *J. Soc. Chem. Ind.*, **62**, 37 (1942).
14. A. Wasey, R.K. Bansal, B.K. Puri and A.L.J. Rao, *Talanta*, **31**, 205 (1984).
15. M. Satake, G. Kano, S. Usami and B.K. Puri, *Indian J. Chem.*, **27A**, 268 (1988).
16. M.A. Taher, S. Puri, R.K. Bansal and B.K. Puri, *Talanta*, **45**, 411 (1997).
17. M.A. Taher, B.K. Puri and R.K. Bansal, *Microchemical J.*, **58**, 21 (1998).
18. M.Q. Yu and G.Q. Liu, *Talanta* **30**, 265 (1983).
19. S. Taguchi, T. Yal, Y. Shimada and K. Goto, *Talanta*, **30**, 169 (1983).
20. H. Watanabe, K. Goto, S. Taguchi, J.W. Melaren, S.S. Berman and D.S. Russell, *Anal. Chem.*, **53**, 738 (1981).
21. Y. Saki and N. Mori, *Talanta*, **33**, 161 (1986).
22. P. Burba and P.G. Willmer, *Talanta*, **30**, 381 (1983).
23. M. Kubota, K. Matsumoto and K. Terada, *Anal. Sci.*, **3**, 45 (1987).
24. M. Kimura, H. Yamashita and J. Komada, *Bunseki Kagaku*, **35**, 400 (1986).
25. A.S. Khan and A. Chow, *Talanta*, **33**, 182 (1986).
26. M.J. Toral, P. Richter and L. Silva, *Talanta*, **40**, 1405 (1993).
27. M.A. Taher, *Quimica Analitica (Spain)*, **20**, 139 (2001).
28. ———, *Talanta*, **52**, 181 (2000).
29. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 5th Edn., Longmans, London (1989).

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