Proc. Indian natn. Sci. Acad., **63**, A, No. 3, 1997, pp. 269-279.
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NONEXTRACTIVE, QUENCHOFLUORIMETRIC AND ULTRATRACE METHOD OF DETERMINATION OF VANADIUM IN SOME REAL AND ENVIRONMENTAL SAMPLES

BIJOLI KANTI PAL*, GOPINATH DEY AND DIPANKAR CHAKRABORTY

Analytical Chemistry Division, Department of Chemistry, Jadavpur University, Calcutta - 700 032, India

(Received 22 June 1996; Revised 8 Oct 1996; Accepted 28 Oct 1996)

A very simple, nonextractive, highly sensitive and selective quenchofluorimetric method for the rapid determination of vanadium in aqueous medium has been described. The method is based on the instantaneous quenching action by vanadium (*V*) upon the native fluorescence of bathophenanthrolinedisulphonate (4, 7-diphenyl-1, 10-phenanthrolinedisulphonate) solution [$\lambda_{ex(max)}$ = 288 nm; $\lambda_{em(max)}$ = 444.8nm] in the *p*H range of 3.8-4.8 at room temperature (25 ± 5) °C; sodium acetate-acetic acid buffer of *p*H 4.27 was used for convenience of later studies. The fluorescence intensity Vs vanadium (V) concentration calibration graph shows a rectilinear relationship for a wide range of 1 ppb - 1ppm [i.e., 1 ng/ml - 1μg/ml] vanadium (V). Only copper, nickel and cobalt interfere but it can easily be removed by a quick single-step cation-exchange separation process using Amberlite IR-120 resin. The results of analyses are in excellent agreement with their certified values.

Key Words: Vanadium Determination; Quenchofluorimetry; Bathophenanthrolinedisulphonate; Standard Alloys; Environmental Water Samples

Introduction

Vanadium is an ubiquitious element in nature, in soil, water and air. It is industrially important[1], biologically nutrient and toxicant[2-6], environmentally pollutant and occupationally health hazardous[7]. Vanadium poisoning causes nervous disturbances, paralysis of hind legs, breathing difficulties, convulsions, haemorrhagic enterities and finally death[8]. Toxicological studies reveal that V together with As and Zn is involved in lung-cancer.[9] All these make it prime necessity for accurate determination of vanadium at its trace and ultratrace levels.

Fluorimetry is one of the most powerful tools for trace and ultratrace level analysis techniques. Existing fluorimetric methods[10-16] for vanadium are few and of them, some are time consuming, tedious, being solvent extractive, poorly selective, insensitive and a few have no workable *p*H range and need rigidly fixed *p*H maintenance. To meet the demand for ultrasensitive-cum-semispecific fluoremetric method for vanadium assay, we have developed a nonextractive quenchofluorimetric method using natively intense fluorescent reagent, bathophenanthrolinedisulphonate. The high solubility of the reagent in water and the use of suitable buffer solution (sodium acetate-acetic acid buffer) make the method much simpler and yield higher

accuracy and reproducibility of results. The standard deviation and the relative standard deviation for 11 replicate determinations of 50pp[b] vanadium(V) were found to be ± 0.508 and 1.007% respectively.

Experimental

Apparatus

A Shimadzu Spectrofluorophotometer (Model RF-5000) with a video accessory was used to record the uncorrected spectra and to measure the fluorescence intensity. A digital *p*H-meter (Model *p*H 5651, Electronic Corporation of India Ltd.) was used for the measurement of *p*H. A Hanovia Fluorescence lamp (Model 11A, 240 V, 50 Hz, Arc tube, Hanovia Ltd., England) was employed for visual study of fluorescence intensity changes qualitatively.

Glass vessels were cleaned by soaking with acidified solutions of $KMnO_4$ or of $K_2Cr_2O_7$ followed by washing with concentrated HNO_3 and then several times with deionized water. Stock solutions and environmental water samples were kept in polypropylene bottles containing 1 ml concentrated HNO_3.

Reagents and Solutions

A stock solution (10^{-3}M) of the reagent, bathophenanthrolinedisulphonate (4,7-diphenyl-1, 10-phenanthrolinedisulphonate, $C_{24}H_{14}N_2Na_2O_6S_2$, $3H_2O$, M.W. 590.54) [Loba-chemie-Wein-Fischamend] was prepared by dissolving the requisite amount in distilled deionised water. From this stock solution, more dilute solutions were prepared as and when needed. The reagent solution is stable for more than a month if kept in refrigerator.

Vanadium Standard Solution

A stock solution of 1000ppm standard vanadium(V) was prepared by dissolving 0.2296gm of ammonium vanadate, NH_4VO_3 (Loba-Chemie) in 100 ml deionised water and subsequently standardised iodometrically with standard potassium iodate solution using carbon tetrachloride as an extractant.[17] More dilute solutions were prepared by appropriate dilution of aliquots from the stock solution with deionised water as and when required.

Buffer Solution

A 100ml buffer solution of pH 4.27 was prepared by mixing 30ml of 0.2M sodium acetate (E. Merck, Germany) and 70ml of 0.2M acetic acid (E. Merck,

Germany). A large number of solutions of inorganic ions and complexing agents were prepared from their Analar grade or equivalent grade water soluble salts. In case of insoluble substances, special dissolution methods were adopted[18]. Doubly distilled deionised water nonfluorescent to U.V. radiation was used throughout the study.

General Procedure

To a 10ml standard volumetric flask containing 0.01-0.1 μg or 0.1-1.0 μg or 1.0-10.0μg of vanadium(V) were added 0.3ml or 0.5ml or 2.0ml of 10^{-4} M reagent, bathophenanthrolinedisulphonate, respectively, and 1ml of *p*H 4.27 sodium acetate acetic acid buffer. The volume was then made up to the mark with deionised water and its fluorescence intensity was measured against a reagent blank at 444.8nm, using excitation at 288nm. The fluorescence quenching due to vanadium(V) is achieved by subtracting the relative fluorescence intensity of the vanadium-reagent system from that of the corresponding reagent blank system. The concentration of vanadium(V) in the unknown sample was determined with the help of a concurrently prepared calibration graph from standard vanadium(V) solution.

Results and Discussion

Spectral Characteristics

The uncorrected excitation and emission spectra of the reagent, bathophenanthrolinedisulphonate solution are shown in Fig. 1. The wavelength maximum of excitation and that of emission were found to occur at 288nm and 444.8nm, respectively.

Effect of pH

The effect of *p*H studies showed that the maximum and constant quenching occurred over the *p*H range 3.8-4.8 at room temperature (25±5)°C (Fig. 2).

Effect of Buffer

Sodium acetate-acetic acid buffer (*p*H 4.27) for a range of 1ml to 5ml for every 10ml total solution were without any adverse effect and consequently 1ml of the buffer was used throughout. (Fig. 3).

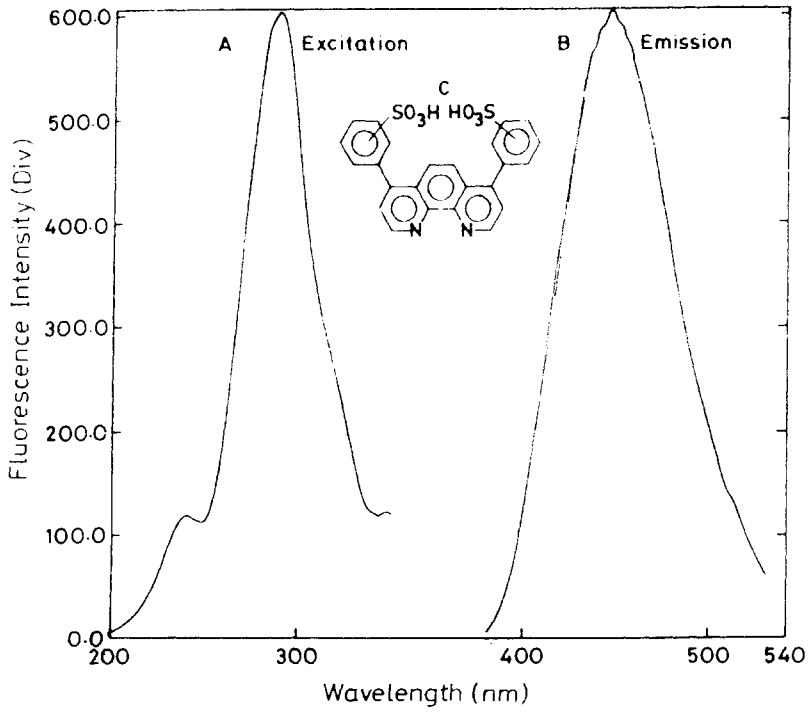

Fig. 1. Excitation (A) and Emission (B) spectra of Bathophenanthrolinedisulphonate (reagent) and structure of Bathophenanthrolinedisulphonate (C)

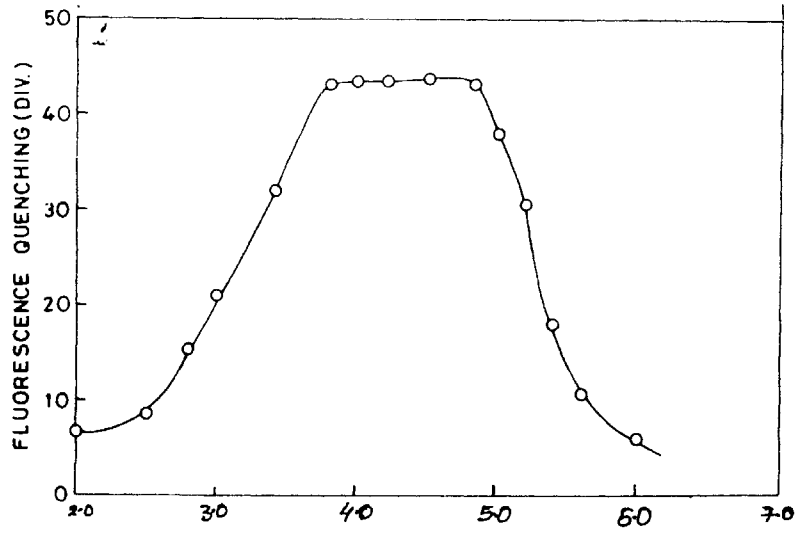

Fig. 2. Effect of pH on the Fluorescence Quenching intensity of V(V)-reagent System.

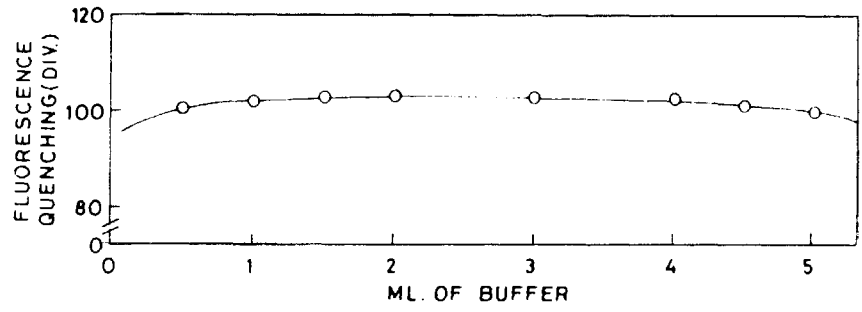

Fig. 3. Effect of Buffer on the Fluorescence Quenching Intensity of V(V) reagent System.

Effect of Time

The maximum quenching was reached immediately after making up the volume and remained constant for 24 hrs. Longer time periods were not studied. (Fig. 4)

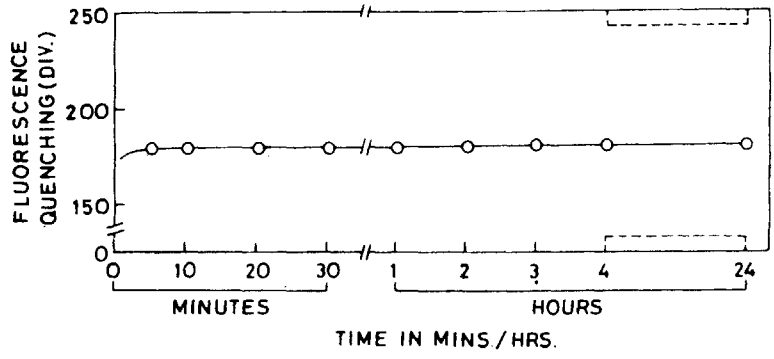

Fig. 4. Effect of time on the Fluorescence Quenching Intensity of V(V) - reagent System.

Effect of Metal Concentration (Calibration graph)

The study of the effect of metal concentration showed that the fluorescence intensity Vs vanadium(V) concentration calibration graph was rectilinear over a total range of 1 ppb - 1 ppm, vanadium(V). For the convenience of fluorescence

intensity measurements, it was distributed into three vanadium(V) concentration ranges (1-10 ppb, 10 - 100 ppb and 0.1 - 1.0 ppm). The fluorescence intensity Vs vanadium(V) concentration calibration graphs for these three ranges as displayed in the video display of the spectrofluorophotometer are reproduced in (Fig. 5).

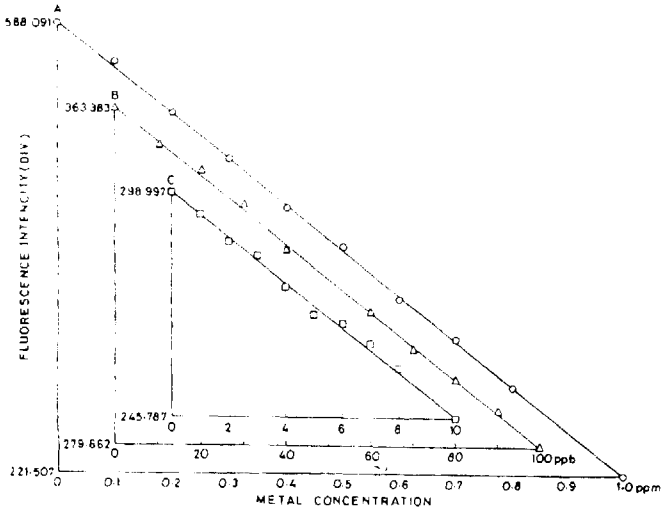

Fig. 5 Effect of vanadium (V) concentration on the Fluorescence Intensity of Bathophenanthrolinedisulphonate Calibration Graphs: (A) 0.1-1.0 ppm, V(V); (B) 10-100 ppb V(V); (C) 1-10 ppb, V(V).

Effect of Foreign Ions

The individual effect over 60 cations, anions and some common complexing agents were studied separately to investigate their adverse effect, if any, on the determination of 0.1 ppm of vanadium(V) by the proposed method. In case of any precipitation, the centrifuged solution was used for fluorescence measurement. No interference was encountered from 1000-fold excess each of tartrate, thiosulphate, perchlorate, thiocyanate, sulphate, phosphate, hydrogenperoxide, Na^+, K^+, Li^+, Ba^{2+}, Ca^{2+}, Sr^{2+}, La^{3+}, Se^{4+}, B^{3+}, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^-, HSO_3^-, HPO_4^-, and DMG. The amount mentioned above is not the tolerance limit, but the actual amount studied. However, some more ions whose tolerance limits have been studied are 500-fold excess of Al^{3+}, Th^{4+}, Zr^{4+}, Ce^{3+}, Ce^{4+}, I^- each; 200-fold excess of Tl^+, Tl^{3+}, U^{6+}, Ga^{3+}, As^{3+}, thiourea each; 100 fold excess of Bi^{3+} (in presence of tartarate), Be^{2+} each 50 fold excess of Sb^{3+} (in presence of tartarate), Mg^{2+}, Mn^{2+}, oxalate, ascorbic acid each; 20 fold excess of Sn^{4+}, Cr^{6+}, Ag^+, Pb^{2+}, Cd^{2+} (in presence of tartarate) Zn^{2+} (in presence of tartarate), Fe^{3+} (in presence of HF_2^-) each and 10-fold excess of Mo^{6+} (in presence of tartrate) and Hg^{2+} (in presence iodide/$S_2O_3^{2-}$). Only Cu^{2+}, Ni^{2+} and Co^{2+} interfere, the interference

of which were successfully removed by a quick single step ion-exchange separation process using Amberlite IR-120 cation exchange resin as described below:

Separation of Interfering Ions: One gram of a strong base cation exchange resin, amberlite IR-120 (Na^+ -form, 40 - 60 mesh) was placed in a small beaker and repeatedly washed with deionised water to remove fine particles. It was then immersed in 0.5 M ammonium acetate and kept over night so that it converted into ammonium form. Then, a small ;column (5cm × 1cm) was made with the resin supported over quartz wool in an all-glass column of specific id. (1 cm). The packed resin bed was washed with sufficient volume of 0.5 M ammonium acetate and through it the solution containing known amount of vanadium along with 100-folds excess of Cu^{2+}, Ni^{2+} and Co^{2+} was passed quantitatively at a flow rate of 1 ml/min. After passing the solution, the resin bed was washed thoroughly with deionised water and collected with the previous solution. The solution was then treated with 4-5 drops of 18 N H_2SO_4 and evaporated nearly to dryness. The cooled mass was diluted and neutralised with NaOH and its vanadium-content was determined fluorimetrically according to the usual procedure, with the help of a concurrently prepared calibration graph of standard vanadium solution, also absorbed in the similar resin bed in the same way under the same instrumental conditions. The results were quite satisfactory.

Applications

The present method was successfully applied to the determination of vanadium contents in a series of synthetic mixtures of various compositions having increasing complexities, in several standard alloys and steel samples and also in a number of environmental water samples both in spiked and unspiked conditions. The results of analyses in various types of samples are in excellent agreement with their certified values.

Determination of Vanadium in Synthetic Mixture

Synthetic inorganic mixtures of different compositions having increasing complexities were prepared. These were then subjected to the ion-exchange separation, the filtrate containing vanadium was collected along with appropriate washing and diluted identically to a known volume as described in the ion-exchange separation procedure. Then, from suitable aliquots, the vanadium(V) content was determined fluorimetrically as mentioned in the general procedure. Results are shown in Table I. Accurate recoveries were achieved in all solutions.

Table I
Analysis of Synthetic Mixtures

Sample No.	Composition of the mixture	Vanadium (V) content	Vanadium (V) found* μg/ml		Recovery
	μg/ml	μg/ml	Spiked	Unspiked	%
A	V^{5+} (0.1), As^{3+} (0.5), Th^{4+} (2), I^-(3), Cu^{2+} (0.5)	0.1	0.101	0.00	101
B	as in A, Ca^{2+}(1), Mg^{2+} (0.5), Mn^{2+} (0.5), SO_4^{2-} (10)	0.1	0.102	0.00	102
C	as in B, Se^{4+}(1), Zn^{2+} (0.5), Sr^{2+}(1); Citrate(0.5), Co^{+2}(1)	0.1	0.102	0.00	102
D	as in C, Zr^{4+}(1), U^{6+} (0.5), B^{3+}(1); tartrate(10), Ni^{2+}(1)	0.1	0.104	0.00	104
E	as in D, Na^+(2), Ce^{4+}(1), Bi^{3+}(0.2) SCN^- (4)	0.1	0.103	0.00	103

* Average of 5 replicate determinations.

Determination of Vanadium in Certified Reference Materials (CRM)

An accurately weighed 0.1g portion of the sample was dissolved in 4 ml of a mixture (1:1) of concentrated HCl-HNO_3 with heating and was then diluted to 100ml with deionised water. Suitable aliquots of this sample solution with and without vanadium(V) spiking were processed through the cation exchange resin, Amberlite IR-120, and the eluate containing vanadium was collected along with proper washings and diluted identically to a known volume as described in the ion-exchange separation procedure. From suitable aliquots of the above diluted solutions, the vanadium(V) content was determined fluorimetrically according to the general procedure. The results are shown in Table II.

Table II
Analysis of Certified Reference Materials (CRM)

Composition of CRM	Vanadium (V) content	Concentration of Vanadium (V) µg/ml		Recovery
%	%	added	Found[a]	%
BAS (64b)				
High Speed Steel				
T.C. = 0.90, Cr=4.55				
Mo = 4.95, V=1.99	1.99		2.10[b] + 0.004[d]	105
W = 4.05				
Carbon Steel 'U'				
No 163				
C = 1.20, Ni = 0.608		0.00	0.025[c] ± 0.002[d]	
S = 0.043, Cu = 0.05	Trace	0.05	0.078[c] ± 0.003[d]	112
V = trace,		0.10	0.126C ± 0.005d	104
Mn = 0.472, Si=0.18				
P = 0.005, Cr=0.03				
BAS (32a)				
Al - Bronze				
Al = 8.8, Mn=0.27		0.00	0.00[c] ± 0.004[d]	
Zn = 0.94, Cu = 85.9		0.05	0.052[c] ± 0.005[d]	104
Ni = 1.16, Fe = 2.69		0.10	0.101[c] ± 0.006[d]	101

[a] Mean value of 5 determination :
[b] Value in percentage;
[c] Value in ppm;
d The measure of precision is the standard deviation.

Determination of Vanadium in Environmental Water Samples

Aliquots (50 ml) of filtered environmental water were digested with 3 ml mixture (2:1) of Conc. HNO_3 - H_2SO_4 till the evolution of SO_3 fumes. After cooling, it was again treated with 2 ml conc. $HClO_4$ and heated again until SO_3 fumes were evolved. The resulting solution was cooled and filtered (if necessary). The filtrate was neutralised with dil. NH_4OH solution and made up to the mark with deionised water in a 50-ml volumetric flask. Suitable aliquots of this solution was then subjected to ion-exchange separation (Amberlite IR-120), as mentioned before and its vanadium content was determined fluorimetrically. The results are shown in Table III.

Table III
Analysis of Environmental Water Samples

Sample Source	Composition by AAS µg/ml	Concentration of Vanadium(V) µg/ml		Recovery
%		added	Found[a]	%
Tap Water (Garfa, Cal-75)			0.012 + 0.0017	
		0.050	0.063 ± 0.0015	102
		0.100	0.109 ± 0.009	97
Tubewell Water		-	0.009 ± 0.0012	
(Sonarpur,		0.050	0.059 ± 0.0300	100
24 Pgs(S))		0.100	0.107 ± 0.0020	98
Pond Water		-	0.005 ± 0.004	
Vill. Mathura		0.050	0.053 ± 0.004	96
Barasat.		0.100	0.106 ± 0.0012	101
24 Pgs(N)				
Factory Drain Water (Ordnance Factory)				
Collection	As^{3+}<0.01.Hg^{2+}<0.01	-	0.016 + 0.0015	
	Pb^{2+}<0.01, Cr^{3+}=0.09	0.050	0.065 + 0.0012	98
Site A	Ni^{2+}=0.20, Ag^{+}=0.02	0.100	0.119 + 0.0014	103
	Zn^{2+}=0.19, Na^{+}=56.0			
	Cu^{2+}=0.03, Cl - =108			
	SO_4^{2-} =25			
Collection	As^{3+}=0.01, Hg^{2+}=0.01	-	0.021 ± 0.0012	
	Pb^{2+}=0.01, Cr^{3+}=0.04	0.050	0.072 ± 0.0015	104
Site B	Ni^{2+}=0.18, Ag^{+}=0.08	0.100	0.120 ± 0.0013	95
	Zn^{2+}=0.19, Na^{+}=52.0			
	Cu^{2+}=0.02, Cl=105			
	SO_4^{2}=23			

[a]Mean + Standard Deviation (n = 5).

Acknowledgement

Two of the authors (G N D & D C) gratefully acknowledge the authorities of Jadavpur University for providing research facilities. The authors express their appreciation to Professor B K Mitra of this laboratory for his keen interest and some constructive suggestions. The service of COSIST (Chemistry) equipment, spectrofluorophotometer (Model RF 5000), is thankfully acknowledged.

References

1 A K De *Textbook of Inorganic Chemistry*, 7th edition, edited by Wiley Eastern Limited, India (1992) 630-634
2 L I Jr Hopkins and H E Mohr Newer Trace Elements in Nutrition *(Eds)* W Mertz and W E Comatzer) Marcel Decker New York and London, 1971 195-205
3 F Bernheim and M L C Bernheim *J Biol Chem* **127** (1939) 353
4 E J Underwood *Trace Elements in Human and Animal Nutrition*, Academic Press New York and London (1971) 416-424
5 G L Curran, D L Azarnoff and R E Bolinger *J Clin Nutr* **38** (1959) 1251-1255
6 E G Dimond, J Caravaca and a Benehimol *Am J Clin Nutr* **12** (1963) 49
7 D E Jackson *Pharmacol Exp Ther* **4** (1992) 1-10
8 T D Luckey and B Venugopal *Metal Toxicity in Mammals-1*, Plenum Press (1977) pp. 222
9 P Stocks *Br J Cancer* **14** (1960) 397-410
10 M Roman, F Garcia-Sanchez and A Gomez-hens *Quim anal* **28** (4-5) (1974) 191-197
11 F Garcia-Sanchez, A Navas M Santiago and F Grases *Talanta* **28** (11) (1981) 833-837
12 F Salinas, F Garcia-Sanchez and C Genestar *Microchem J* **27(1)** (1982) 26-31
13 F Grases, C Genestar and F Salinas *Anal Chim Acta* **148** (1983) 245-254
14 C Genestar, J J Gil and F Grases *Analysis* **12**(9) (1984) 462-466
15 W Li and S Zhou *Fenxi Huaxne* **18(4)** (1990) 305-309
16 N Jia and W Liu *Finxi Huaxue* **19(11)** (1991) 1314-1316
17 A I Vogel A Text Book of Quantitative Inorganic Analysis, 3rd Ed., The English Language Book Society and Longman, London 1969 p 381
18 B K Pal and B Chowdhury *Microchim Acta* **11** (1984) 121