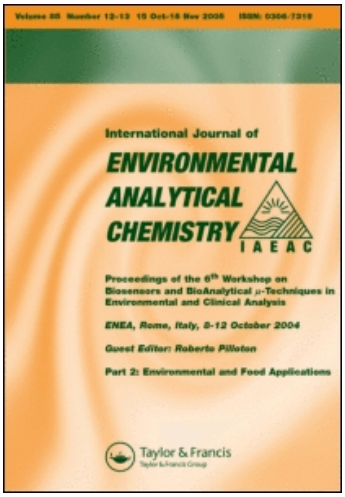

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Determination of Vanadium by Solid-Phase Spectrophotometry in a Continuous Flow System

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DETERMINATION OF VANADIUM BY SOLID-PHASE SPECTROPHOTOMETRY IN A CONTINUOUS FLOW SYSTEM

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A flow analysis method based on direct absorptiometric measurement in solid phase of the violet complex formed between V(V) and 5-Bromosalicylhydroxamic acid has been developed. The measurement is continuously performed at 555 nm, while the coloured species is being concentrated on-line on the beads of an anion exchanger packed into a flow-through cell. The sensing solid phase is regenerated after each measurement achieving a sampling frequency ranged between 10 to 15 h^{-1} depending on the working conditions. The sensitivity of the method depended on the sample volume injected, being the detection limit 0.024 and 0.014 $\mu g\ mL^{-1}$ for 2 and 5 mL, respectively. The method shows a good selectivity and has been applied to determination of V(V) in many different sample matrices namely mussel, oyster and toadstool tissues, petroleum crudes and water samples.

Keywords: Solid Phase Spectrophotometry-Flow Injection Analysis; vanadium; petroleum; mussels; oysters and water

INTRODUCTION

Vanadium's role in physiological systems includes participation in various enzyme systems as an inhibitor and a cofactor[1], catalysis of the oxidation of various amines[2] and normalisation of sugar levels. This element is present in superficial waters (200–300 μg/L) and is an essential element for all cell growth, but is toxic in high concentrations since transforms some metabolisms and behaves as a poison of central nervous system and can produce renal and hepatic damages.

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Solid-phase Spectrophotometry (SPS)[3–5], a methodology based on the direct measurement of the absorption of light by metal complexes or other species preconcentrated on an appropriate solid support, has been applied for the determination of vanadium[6,7] and it has been extended to flow analysis[8–10]. The systems using SPS integrated with flow injection analysis are flow-through sensors[11]. The integration of reaction, retention and detection steps offers an increase in the sensitivity of detection and a decrease in the dispersion, as well as an improvement on selectivity, compared with conventional methods in homogeneous solution. Many interferents can be avoided because of selective retention of the species of interest in the solid support [12] as well as the possibility of performing on-line sample treatments [13].

Hydroxamic acids have been widely used for spectrophotometric determination of vanadium via formation of coloured complexes providing methods very sensitive by using solvent extraction in most cases. Among them, 5-bromo-salicyl-hydroxamic acid has been used to determine vanadium by means of solvent extraction with a liquid anion-exchanger[14] as well as by SPS (batch mode) using Sephadex QAE anion exchanger resin as a solid support[7].

In this paper we have used Sephadex QAE A-25 ion exchanger placed in the flow cell to retain the 5-bromo-salicyl-hydroxamic acid-vanadium coloured complex. After each measurement, the sensor is regenerated by means of an appropriate eluent and hence rendered ready for subsequent analysis. In this way, we achieve a great improvement over the batch method previously reported: the here developed sensor system avoid any previous step of mixing reagents, adding the solid support and transferring it to the measurement cell. In addition, the sensitivity of the method is comparable to the previously reported, but with a very much lower consumption of sample, reagents and solid support.

EXPERIMENTAL

Reagents

All chemicals were of analytical-reagent grade.

Stock vanadium (V) solution 1000 $\mu g.mL^{-1}$, prepared by dissolution of the appropriate amount of NH_4VO_3 (Merck, Barcelona, Spain) in doubly distilled water. Working solutions were prepared daily by suitable dilution with bidistilled water.

5-Bromo-salicyl-hydroxamic acid (5BrSHA) solutions of various concentrations. The reagent was synthesised by the authors following the general procedure[15] for other hydroxamic acids. The solutions were prepared in doubly

distilled water containing the necessary amount of NaOH. Buffer solutions of pH 7.00, were made by dissolving 22.3 g of $Na_4P_2O_7$ (Panreac, Barcelona, Spain) in 500 mL of doubly distilled water containing HCl conc. solution.

Ion exchanger Sephadex QAE-A-25 (40–120 μm) (Aldrich, Madrid, Spain) in chloride form without previous pre-treatment.

Ascorbic acid, potassium fluoride and acetone (from Panreac) were also used.

Apparatus

The FI system comprised a GILSON MINIPULS 3 (Villiers-Le-Ber, France) peristaltic pump, three six-way rotary valves (RHEODYNE 50), one of which acted as a selecting valve, and PTFE connecting tube (0.8 mm inner diameter). The flow cell was a Hellma 138-OS with 50 μL inner volume and 1mm light path-length.

Ultraviolet and visible spectra and real-time data acquisition of flow injection peaks were obtained using a Perkin Elmer (Beaconsfield, Buckinghamshire, England) Lambda 2 UV-VIS Spectrophotometer. The instrument was interfaced to a 386 PC running Perkin-Elmer computerised spectroscopy software (PECSS.V4.1). The pH measurements were made with a Crison (Barcelona, Spain) pH-meter fitted with a glass saturated calomel electrode assembly and a temperature probe.

Procedure

The manifold used is shown in Figure 1. The carrier stream was splitted in two channels where the sample and the reagent were injected simultaneously by means of two rotary valves respectively. Before reaching the active retention-detection area, the two streams merged to form the coloured complex, which was being concentrated on the anion exchanger in the flow-through cell, while the attenuance was continuously monitored at the maximum absorption wavelength of the coloured species (555nm). When the signal was near to be constant, a desorbing solution was allowed to flow by switching the selecting valve. The next sample was injected when the recorder came back to its baseline.

Treatment of samples

Mussel and oyster tissues

The samples were dried in a forced-draft oven at 70° C to constant mass and then ground into a fine powder. A suitable aliquot was weighed (60.65 and 28.63 g

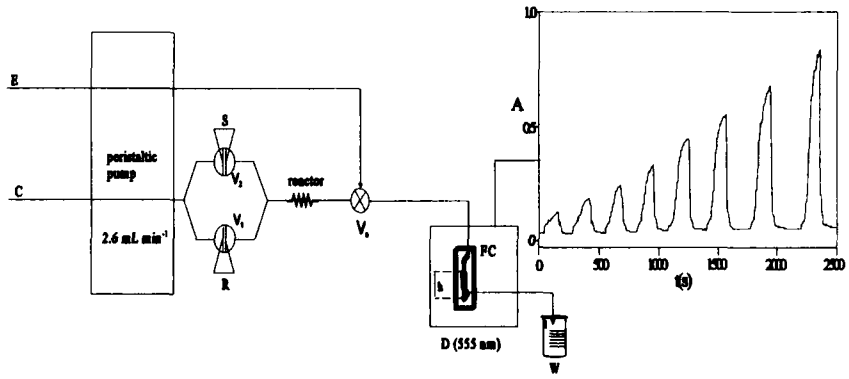

FIGURE 1 Scheme of flow-injection system. E: eluent, C: carrier, S: sample, R: reagent, V_1 and V_2: injection valves, V_s: selection valve, D: detector (spectrophotometer tuned at 555 nm), FC: flow cell housing the solid support, h: height of solid support in the flow cell, w: waste. Time development profile of signal is also shown. Vanadium concentration in samples increases from 0.15 to 2.5 μg mL^{-1} with a sample volume of 2 mL

dry material of mussel and oyster respectively) and placed in a cool furnace. The mineralization was carried out by heating slowly to 550°C for 2 h and holding at this temperature for 2 h. The samples were removed and cooled and the ashes were wet carefully with doubly distilled water, then adding 2 mL of 4 M NaOH solution. The crucible was covered with a watch glass, heated cautiously on a hot plate to boiling and finally let stand for a few minutes. Then, the solution was filtered through Whatman no. 42 paper over a 100 mL standard flask and the residues washed, diluting finally to volume after addition of 0.8 mL HCl conc. solution. In oyster samples, after neutralising with HCl, a precipitate with siliceous appearance was noticed so the samples were treated with 5 mL of HF in Teflon crucible before being brought up to 100 mL with bidistilled water.

Petroleum

A suitable weight of petroleum samples (from 5.82 to 35.69 g, depending on vanadium content) was treated in a Vycor vessel with sulphuric acid (1 mL for each gram of sample) in a sand-bath. Continuous agitation was maintained to avoid foam formation. Next, combustion of carbonaceous ash at 525±25°C was performed. The inorganic residue was treated with 1:1 HCl and heated to effect complete dissolution. After concentration, a few drops of nitric and sulphuric acids were added and the solution was heated gently until white fumes were formed and the small carbonaceous residue not ignited was destroyed. After, the Vycor vessel was washed carefully, the solution was heated to boiling and neu-

tralised and pH was fixed between 3 and 5 with sulphuric acid. Finally, the solution was diluted to 50 mL with doubly distilled water.

Water samples

Natural water was filtered through a 0.45 μm membrane filter (Millipore) and collected in a polyethylene container carefully cleaned with nitric acid and rinsed with bidistilled water. The samples were stored at 4°C until analysis. Analyses were performed with the least possible delay. The usual general precautions were taken to avoid contamination[16].

Toadstool tissue (amanita muscaria)

Firstly, all foreign matter, especially adhering soil, was removed from the sample by means of successive washings with distilled water, 0.1 M HCl and doubly distilled water (avoiding any excessively prolongate washing to prevent leaching). The sample was immediately dried into a forced-draft oven for 24 h at 70°C to prevent decomposition or weight loss by respiration and ground in a hand-mill. A suitable aliquot was weighed (2.7264 g dry material) and the mineralization was carried out by heating slowly to 450°C for 2 h as described for mussel tissues. The vanadium content was determined as described under *procedure*.

RESULTS AND DISCUSSION

Variables of the integrated retention-detection unit

The V(V)-5BrSHA complex was found to be retained in anion exchangers. Dowex type resins were disregarded because the strong retention of the reagent unables an easy regeneration after measurement. Two anion exchangers with dextran type matrix were tested (Sephadex QAE and Sephadex DEAE) and it was found that the coloured complex species was more easily sorbed in Sephadex QAE-A-25 providing higher signal. Moreover, the amount of solid support in the flow cell was studied, because the level it reaches in the cell is a key factor in this type of devices. It is always necessary to have a resin level achieving the light beam does not cross the solution but if the amount of resin is too high, a fraction of the coloured specie is retained above the irradiated zone, so decreasing the analytical response. The optimum level of solid support was found to be 17 mm which in working conditions was reached using 20 mg of resin.

Chemical variables

5BrSHA reacts with vanadium to form a violet colour complex in acidic medium in aqueous solution. The optimum pH of the carrier solution for the formation and fixation of the complex in the resin phase fell in the range 6.0–8.0 as can be seen in Figure 2. In this pH range the species fixed in the resin was negatively charged enabling the binding to the anionic exchanger. 5BrSHA was also retained in the resin phase but it showed no absorption in the visible region. A buffer solution of $HP_2O_7^{3-}/H_2P_2O_7^{=}$ 0.1 M at pH 7.0 was employed as carrier solution.

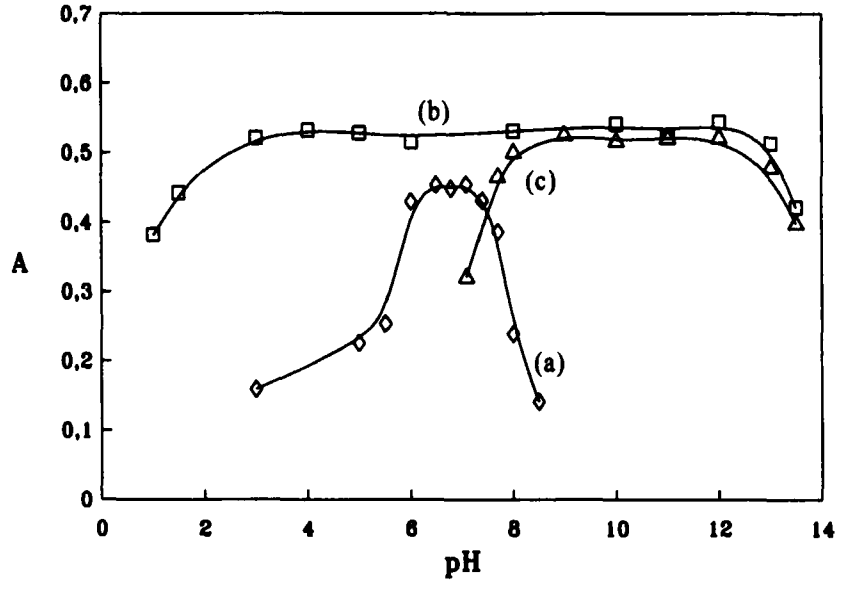

FIGURE 2 pH influence of (a) carrier solution, (b) sample and (c) reagent solution on analytical response. pH values were adjusted using HCl or NaOH. V inj. = 1 mL; [V] = 9.82×10^{-5} M (a) and (c) and 7.85. 10^{-5} M (b); [5BrSHA] = 8×10^{-4} M (a) and (c) and 3×10^{-3} M (b)

The influence of both pH and concentration of the reagent solution were also studied. The increase on concentration of the reagent from 2×10^{-4} to 3×10^{-3} M caused a great increase in the absorbance of the retained complex. Above this concentration the signal increased slightly, but 3×10^{-3} M was preferred for further experiences because the poor solubility of the reagent caused precipitation for more concentrated solutions. The signal was found to be constant in the range 8.0–13.0. For pH<8.0 a strong decrease in the analytical response was observed. Moreover at pH values below 7.0 reagent precipitation occurred. The pH of the

reagent solution was always maintained between 8–10 because stability of hydroxamic acids decreases in strongly basic medium.

In these working conditions the sample pH effect was evaluated. The signal was found to be independent of this variable in a wide range from 3.0 to 13.0 for 1 mL of sample volume, so we decided the sample not to be buffered that avoided any previous off-line sample treatment apart from dissolution. For higher volume of sample (2–5 mL) the absorbance values were constant in the pH ranges 3.6–12.0 (1 mL of sample) and 4.0–11.5 (5 mL of sample). Therefore, the optimum pH range is slightly shorter as the sample volume injected is increased, because the surrounding environment of the sensing zone provided by the carrier is changed when the sample pH is essentially different from the carrier solution pH, due to the high volume of the sample plug

Solid support regeneration

No sooner had the signal maximum been reached than the coloured species had to be quickly desorbed from the solid particles in order to make the system reusable. Several regenerating solutions were tested.

First, using a 1% ascorbic acid solution V(V) was reduced to V(III) and the desorption of the complex was achieved, but 5 BrSHA precipited on the resin due to the low pH value of the eluting solution and this gave rise problems in the stream circulation.

Then, surfactants, organic solvents and complexing agents were tested. The most effective desorbing solution was a strongly basic solution (pH=11.0) containing a large amount of electrolyte (2M NaF) and a 10 % of an organic solvent (acetone). This eluent solution acted both breaking down the V(V)-5BrSHA complex (due to the stability of V(V)-F^-complexes and the high concentration of F^-), so desorbing both V(V) and free reagent from the solid support. Moreover the strongly basic medium prevented reagent precipitation (which happened with acidic eluents).

FIA variables

The effect of the reaction coil length was examined and this variable did not have any influence on sensor response; thus, 50 cm (as short as possible) was the chosen length so being the dispersion minimum and the sampling rate higher. This result could be explained by a very fast formation of the complex in the transport system. Or, perhaps, because the complex formation could take place just in the solid phase due to the higher concentration of the reagent on the support, which

desplaces the reaction towards the formation of the V(V)-5BrSHA complex. In the absence of the solid phase, but using a flow-cell with a light path length of 10 mm, no signal could be observed, so confirming the above explanation.

The effect of the flow-rate was examined in the range between 1.5 –3.5 mL min^{-1}. Up to 2.6 mL min^{-1} the signal remained almost constant that indicates a rapid diffusion kinetic of the species of interest from the solution to the solid support. Flow-rates above this one gave rise to a decrease in the absorbance values so being 2.6 mL min^{-1} the optimum value selected.

The influence of sample volume was studied by inserting loops of different volumes between 1.0–5.0 mL. Much higher sensitivity was obtained by employing larger volume of sample solution, as a consequence of the greater amount of coloured complex retained in the same amount of active solid support, but more time was required for each determination and the sample throughput decreased. So, the selection of sample volume should reflect a consideration of both sensitivity and analysis speed. It is possible to select the most appropriate volume of sample taking into account the concentration of samples that are going to be analysed. We have chosen 2 and 5 mL of sample.

The variables studied are summarised in Table I.

TABLE I Selected values of the proposed sensor variables

Solid support	Sephadex QAE A-25
Amount of solid support	20 mg (17 mm height)
Carrier solution	($H_2Na_2P_2O_7$/$HNa_3P_2O_7$) 0.1 M at pH = 7.0
Reagent solution	3×10^{-3} M 5BrSHA solution at pH 9–10
pH of samples	3.6–12.0 (2 mLof sample)
	4.0–11.5 (5 mLof sample)
Flow-rate	2.6 mL min^{-1}
Sample volume	2 and 5 mL
Desorbing solution	$Na_4P_2O_7$ 0.1 M solution at pH 11.0 containing KF 2M and 10% acetone

Calibration graph

According to the proposed procedure, the calibration graph was established for both 2 and 5 mL sample volume with standard solutions of V(V). The calibration curve is reasonably linear in the concentration range of 0.15–2.5 and 0.05–1.2 μg mL^{-1} respectively. The analytical parameters are summarised in Table II.

TABLE II Analytical figures of merit

	Sample volume	
	2 mL	*5 mL*
Linear range ($\mu g\ mL^{-1}$)	0.15–2.5	0.05–1.2
slope ($\mu g^{-1}\ mL$)	3.54×10^{-1}	7.56×10^{-1}
Intercept	0.043	0.003
correlation coefficient (r)	0.9989	0.9992
relative standard deviation (% RSD), (n = 10)	2.23(1.0)[a]	1.15(1.0)[a]
limit of detection ($\mu g\ L^{-1}$)[b]	0.024	0.014
limit of quantification ($\mu g.L^{-1}$)[c]	0.081	0.048
sampling rate (h^{-1})[d]	15	10

a. Concentration ($\mu g\ mL^{-1}$) at which RSD was established
b. 3σ criterion[17]
c. 10σ criterion[18]
d. referred to the derivatisation/detection step

For 10 determinations, the relative standard deviations (%) were 2.23 and 1.15 for 2 and 5 mL respectively. The detection limit[17] was as low as 0.024 and 0.014 $\mu g\ mL^{-1}$ for 2 and 5 mL of sample respectively.

Study of interferences

The effect of potentially co-existing ions more usually present in the samples analysed as well as those ones which ussually react with hydroxamic acids was investigated. The tolerance level (greatest amount of foreign species, which caused an error not exceeding ±5% in the determination of vanadium) in the determination of 0.8 $\mu g\ mL^{-1}$ of vanadium was established using the proposed manifold and 5 mL of sample volume. The tolerance limits for the ions studied are shown in Table III. The sensor shows a noticeable tolerance at the presence of majority of cationic and anionic species tested, superior to those shown by the extracto-spectrophotometric method previously described[14]. Only Fe(III) interferes when it occurs in a 5:1 (Fe:V) rate or higher due to its reaction with 5BrSHA.

Analytical applications

There are several biological systems, which contain significant levels of vanadium and in which it is possible to determine the nature and function of their compounds. The *"amanita muscaria"* is an example of a biological system that holds a higher content of vanadium.

TABLE III Study of interferent species

Foreign species	*Tolerance ($\mu g.mL^{-1}$ interferent/$\mu g.mL^{-1}$ V(V))*
$SO_4^{=}$, Cl^-, NO_3^-,	> 10000
$CO_3^{=}$	1000
Mg(II)	750
Mo(VI)	500
F^-	250
Ca(II)	125
Mn(II), Ni(II), Co(II), W(VI), Cr(III)	100
Al(III)	25
Cu(II), Cd(II)	10
Fe(III)	5

The proposed method has been applied to the determination in toadstool, mussel and oyster tissues, petroleum crudes and waters. The determination of vanadium in mussels was performed using the standard calibration graph method, since no matrix effect was observed. *Amanita muscaria* and oyster tissues were analysed by the standard addition graph method since in this case a strong matrix effect was detected. The loss of sensitivity caused by this effect (evaluated by the slope's quotient between the standard addition calibration graph and the standard calibration graph) was 0.78 and 0.77 respectively. The results obtained in all cases were compared with those found by EAAS (reference method) and they were in excellent agreement (Table IV).

TABLE IV Determination of vanadium in biological and petroleum samples (in $\mu g.g^{-1}$)

Sample	*Proposed method*	*Reference method*	*Statistical comparison*	
	$\pm \sigma_m t_{s\,(0.05)}$	$\pm \sigma_m t_{s\,(0.05)}$	t_{exp} (t_{tab} = 2.776)	F_{exp} (F_{tab} = 39.00)
"Amanita Muscaria"	8.5 ± 0.3 [a]	8.3 ± 0.2 [b]	2.474 N.S.	1.73 N.S.
Mussels	0.42 ± 0.03	0.43 ± 0.02 [b]	0.813 N.S	1.69 N.S.
Oysters	1.16 ± 0.09 [a]	1.12 ± 0.02 [b]	1.906 N.S.	16.89 N.S.
Light Arabia	16.2 ± 0.4	15.7 ± 0.5 [ac]	3.346 S.	1.85 N.S.
Qatar Terrestrial	4.6 ± 0.2	4.4 ± 0.4 [c]	2.008 N.S.	3.12 N.S.
U-100	35 ± 1	35.4 ± 0.4 [c]	1.051 N.S.	8.86 N.S.
T-132	70 ± 1	70.2 ± 0.2 [c]	0.875 N.S.	1.57 N.S.

a. standard addition method
b. EAAS
c. ASTM method

The vanadium content in four petroleum samples of different origin, density and composition was analysed by the standard calibration graph method except in one sample (Arabian light) which showed matrix effect and then was analysed by standard addition calibration graph (Table IV). As a reference method, the ASTM procedure [19], based on tungstophosphovanadic acid formation and absorbance measurement at 436 nm, was employed but, in this case, a larger amount of sample than in the proposed method had to be used.

The statistical comparison study of precision and accuracy of the proposed method and the reference methods was made from F-criterion and the t-test, respectively. The results (Table IV) showed that both methods had the same precision and accuracy except Arabian light sample in which the t-test was significative, despite the difference between the two results was less than 5% (3.2%). The statistically significant difference can be justified by the repeatability of the measurements obtained by the two procedures (variation coefficients were around 1% in both cases).

The method was also applied to the determination of vanadium in tap water (Jaén, Spain). As in this water vanadium could not be detected, a study of recovery for three concentration levels (0.10, 0.20 and 0.40 $\mu g\ mL^{-1}$) was performed. The results found were satisfactory, obtaining a mean recovery percentage of 103.6%.

CONCLUSIONS

The here reported continuous flow method allows the determination of vanadium in a wide variety of real samples by measurement of the light absorption from a coloured complex retained on a solid support involving neither sophisticated nor expensive instrumentation (e.g. atomic optical techniques) but with acceptable sensitivity and selectivity. It clearly represents an improvement over the batch resin method[7] as the here proposed flow system is faster, simpler and cheaper. The following features should be outlined: a) it requires neither isolation of the ion exchanger from the solution nor equilibration steps; b) the measurement is performed at an only wavelength (in batch solid-phase spectrophometric methods two wavelengths are usually required); and c) the solid support is reusable being always packed into the cell. Moreover it is much more sensitive as demonstrated by the fact of showing a similar linear dynamic range (even wider) than the previous one but using a much smaller both sample (2–5 mL instead of 100–1000 mL) and reagent volumes.

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References

1. D.C. Crans, M. Shaia Gottlieb, J. Tawara, R.L. Bunch and L.A. Theisen, *Anal. Biochem.*, **88**, 53–64 (1990).
2. H.E. Stokinger, G.D. Clayton and F.E. Clayton (Eds), *Patty's Industrial Hygiene and Toxicology*, 3rd edn., Wiley-Intercience, Vol. 2A., New York, (1981).
3. K. Yoshimura and H. Waki, *Talanta*, **32**, 345–352 (1985).
4. K. Yoshimura, M. Ishii and T. Tarutani, Anal. Chem., **58**, 591–594 (1986).
5. A. Molina Díaz, M.J. Ayora Cañada and M.I. Pascual Reguera, *Spectrosc. Lett.* **31**, 503–520 (1998).
6. M. L. Fernández de Córdova, A. Molina Díaz, M.I. Pascual Reguera and L.F. Capitán Vallvey, *Talanta*, **42**, 1057–1065 (1995).
7. M.I. Pascual Reguera, A. Molina Díaz, N. Ramos Martos and L.F. Capitán Vallvey. *Anal. Lett.* **24**, 2245–2261 (1991).
8. R. M. Liu, D.J. Liu and A. L. Sun, *Talanta*, **40**, 381–384 (1993).
9. Z.Gong and Z. Zhang, *Anal. Chim. Acta*, **339**, 161–165 (1993).
10. M. Anmad and R. Narayanaswamy, *Sci. Total Environ.* **163**, 221–227 (1995).
11. M. Valcárcel and M.D. Luque De Castro, *Analyst*, **118**, 593–600 (1993).
12. P. Ortega Barrales, M.L. Fernández de Córdova and A. Molina Díaz, *Anal. Chim. Acta* **376**, 227–233 (1998).
13. M.J. Ayora Cañada, M.I. Pascual Reguera and A. Molina Díaz, *Anal. Chim. Acta* **375**, 71–80 (1998).
14. L.F. Capitán Vallvey, A. Molina Díaz and M.I. Pascual Reguera, *Analusis*, **17**, 280–284 (1989).
15. A.S. Bhaduri, Z., *Anal. Chem.*, **151**, 109–113 (1956).
16. American Public Health Association. American Water Works Association and Water Pollution Control Federation, *Standard Methods for the examination of water and wastewater*, 15th Ed, A.P.H.A, Washington D.C. (1981).
17. Analytical Chemistry Division, *Spectrochimica Acta Part B* 242–245 (1978).
18. ACS Commitee on Environmental Improvement, *Anal. Chem.* **52**, 2242–2249 (1980).
19. American Society For Testing and Materials "*Book of ASTM standards*" Part 23, (Philadelphia, 1975), Method D 1548–63.