A Spectrophotometric Determination of Chromium and Vanadium

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A very simple, selective and sensitive method is developed for the spectrophotometric determination of Cr^{VI} and/or V^V based on their reactions with perphenazine to instantaneously give a red colored product exhibiting a maximum absorbance at 526 nm. Following the recommended procedure, chromium and vanadium can be determined with linear calibration graphs up to 0.40 and 1.00 µg ml⁻¹ and detection limits of 3 and 5 ng ml⁻¹, respectively. The molar absorptivities are 1.87×10⁴ and 1.20×10⁴ l mol⁻¹ cm⁻¹ with Sandell sensitivity indexes of 2.8 and 4.2 ng cm⁻² for Cr and V, respectively. Analyses of mixtures of Cr^{VI} and V^V in the ratios of 1:100 to 100:1, following the recommended procedure gave recoveries of 97–102% with relative standard deviations of ≤1.4% for both Cr^{VI} and V^V. The total Cr and V was determined first; then, V was determined after addition of As^{III} to reduce Cr^{VI} that was calculated by the difference. Statistical treatment of the analytical results did not detect any systematic error and showed the high accuracy and precision of the method. The unique selectivity and sensitivity of the method allowed its direct application to the determination of Cr and V in complex matrices of certified reference materials and synthetic mixtures. The results obtained are in excellent agreements with the nominal values.

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Simultaneous determination of Cr^{VI} and V^V in complicated matrices is a very difficult task that was achieved using sophisticated and/or high cost instruments such as anodic-stripping voltammetry with ICP-MS detection,¹ ICP-AES,² NAA,³ HPLC,⁴ XRF,^{5,6} and AAS.^{7–10} However, the relatively high costs,^{1–10} high detection limits^{4–8} and poor recoveries and precisions^{1,9} are common disadvantages. Moreover, such methods must be combined with prior preconcentration, ion exchange and/or solvent extraction separation techniques.^{2–4,6} Therefore, the need for a simple, low cost, sensitive and highly selective method is clear.

On the other hand, numerous reagents were reported for the spectrophotometric determination of Cr and V.^{11–19} Methods based on the use of diphenylcarbazide^{11,15} and extraction with oxine^{11,16} are most popular and were adopted as standards^{11,17} for the determination of Cr^{VI} and V^V. However, the mutual interferences of these ions are very critical and their simultaneous spectrophotometric determination is difficult, so that prior separation or extraction techniques were frequently adopted to separate Cr and V from each other and also from other interfering ions, usually encountered in complicated matrices.^{11–17}

The present paper describes an extremely selective, sensitive and simple method for the direct determination of Cr^{VI} and/or V^V. The method is based on the reactions of these ions with perphenazine, 4-[3-(2-chloro-10*H*-phenothiazin-10-yl)propyl]-1-piperazine-ethanol hydrochloride, to give a red-colored product showing a maximum absorbance at 526 nm. The color developed instantaneously upon mixing the reagents and was stable for at least 30 min. The method is completely independent of the reaction conditions and was successfully

applied to the simultaneous determination of Cr and V over a wide range of matrices. Moreover, the *t*-test at the 95% confidence level could not detect any systematic error and showed the high accuracy and precision of the method.

Experimental

Apparatus

Absorbance measurements were made on a pre-calibrated Shimadzu UV-1601 (Kyoto, Japan) or a Speköl 11 (DDR, Germany) spectrophotometer using 10 or 50 mm cells, respectively. A circulating thermostated water bath was used for temperature control. pH measurements were made using a calibrated E.D.T. (Dover Kent, UK) pH-mV meter model GP 353 equipped with an E.D.T. combined glass electrode.

Reagents

Analytical grade reagents and de-ionized distilled water were used throughout. A stock solution of 0.10 mol l⁻¹ perphenazine hydrochloride, PP, was prepared by dissolving the reagent (Sigma, St. Louis, MO, USA) in 0.20 mol l⁻¹ phosphoric acid. This solution was stable for at least one month when stored in a bottle wrapped with an aluminum foil at 4°C.

Stock standard solutions of 1000 µg ml⁻¹ of Cr^{VI} or V^V were prepared from potassium chromate and ammonium metavanadate, respectively.¹¹ Working standard solutions were daily prepared from their respective stocks by appropriate dilutions.

The following working solutions were used: 20.0 mmol l⁻¹ of PP, 10.0 mol l⁻¹ of H₃PO₄, 2.0 mol l⁻¹ of H₂SO₄, 50.0 mmol l⁻¹ of potassium permanganate, 10.0 mmol l⁻¹ of oxalic acid, 20.0 mg ml⁻¹ of As^{III} and 2.0 or 4.0 µg ml⁻¹ of Cr^{VI} or V^V, respectively. Also, a 5% solution of NH₄OH and a 0.02 mol l⁻¹

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Table 1 Tolerance limits in the determination of 0.20 or 0.30 $\mu\text{g ml}^{-1}$ of chromium or vanadium, respectively^a

Tolerance limit/ $\mu\text{g ml}^{-1}$	Chromium (VI)	Interfering ion	Vanadium (V)
≥ 2500	<i>o</i> -phenanthroline, 5-sulfosalicylic acid, triethanolamine, Al^{III} , As^{V} , Be^{II} , Cd^{II} , Ce^{III} , Cu^{II} , Fe^{III} , K^+ , Li^+ , Mg^{II} , Na^+ , NH_4^+ , Ni^{II} , Sr^{II} , Sb^{V} , Ti^{IV} , Zn^{II} , $\text{B}_4\text{O}_7^{2-}$, Br^- , CH_3COO^- , Cl^- , ClO_4^- , CDTA, EDTA, F^- , NO_3^- , SO_4^{2-}		
1000	phthalic acid, Hg^{II} , Mn^{II} , Sn^{IV} , UO_2^{2+} , $\text{CINH}_3\text{NH}_2^{\text{b}}$, $\text{CINH}_3\text{OH}^{\text{b}}$		
500	acetylacetone, citric acid, oxalic acid, tartaric acid, Cr^{III} , $\text{S}_2\text{O}_6^{2-}$		
300	Co^{II} , La^{III} , Pb^{II} , Mo^{VI} , Nb^{V} , Th^{IV} , Ti^{IV} , Zr^{IV} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_5^{2-}$		
40	Bi^{III} , Ce^{IV} , Ir^{III} , Mn^{VII} , Rh^{III} , IO_3^- , N_3^- , SCN^-		Cr^{VI} , Mn^{VII}
5	As^{III}		
1	Ag^{I} , Au^{III} , Ir^{IV} , Pd^{II} , Pt^{IV} , Re^{VII} , Rh^{IV} , Ti^{III} , W^{VI}		
0.05	NH_2NH_2 , Fe^{II} , I^- , $\text{S}_2\text{O}_5^{2-}$		
	Au^{III} , Ce^{IV} , Ir^{IV} , Mn^{VII} , Os^{VIII} , Pd^{II} , Pt^{IV} , Rh^{IV} , Ru^{III} , Ti^{III} , IO_3^- , $\text{S}_2\text{O}_3^{2-}$		

a. Reaction conditions are as given in the procedure, without KMnO_4 addition or precipitation. b. With KMnO_4 oxidation, followed by addition of oxalate and subsequent precipitation in presence of Fe^{III} collector. c. In the presence of 1000 $\mu\text{g ml}^{-1}$ of As^{III} .

of FeCl_3 were used as a precipitant and collector, respectively.

Concentrated hydrofluoric, nitric and perchloric acids were used without dilution.

Homogenized and finely powdered certified reference materials from MINTEK, Council for Mineral Technology, Randburg, South Africa, were used as received.

Sample preparation

Transfer an accurate weight (0.5 – 1.0 g) of the certified ore to a 150 ml Teflon beaker, moisten with water and add a mixture of 20 ml HF, 5 ml HClO_4 and 5 ml HNO_3 .²⁰ Warm the beaker slowly on a hot plate until complete dissolution is achieved; then increase the temperature to about 200°C to evaporate the excess acid. Cool the sample and dissolve the salt in 10 ml of 2.0 mol l^{-1} sulfuric acid by warming. Filter off, wash the residue with two 5 ml portions of water, combine the filtrate and washings, add 1.0 ml of the working permanganate solution and boil gently for 5 min. If necessary, add more permanganate to keep the solution purple during boiling. Cool to about 60°C, add oxalic acid drop-wise to reduce the excess permanganate and after complete decolorization add 0.1 ml excess of oxalic acid. Add 2.5 ml of the collector solution to samples that might not contain enough Fe^{III} . Adjust the pH of the resulting solution to 10.3 ± 0.1 using the working NH_4OH solution, allow for coagulation and filter off the formed precipitate. Wash the precipitate with three 5 ml portions of water, collect the filtrate and washings, render the solution acidic to pH 2.0 ± 0.1 using sulfuric acid and make up with water in a 50 ml calibrated flask. Run a blank for this step to avoid any possible introduction of traces of Cr and/or V by the used reagents.

Determination of vanadium and/or chromium

To a 20 ml test tube equipped with a quick fit stopper, transfer a portion of the sample or the working standard solution and dilute with water to 7.5 ml. Add 2.0 ml of the working phosphoric acid, shake, add 0.5 ml of the PP working solution, mix well and transfer a portion of the reacting solution to the 50 mm spectrophotometric cell. Record the maximum absorbance of the resulting colored species at 526 nm, against water as reference.

To another portion of the unknown test solution, add 0.50 ml of As^{III} solution, dilute with water to 7.5 ml, add 2.0 ml of the working phosphoric acid solution, shake, set aside in the thermostated water bath at 60°C for 5 min and proceed as described above. Vanadium is determined directly from the similarly prepared calibration graph using the working standard

V^{V} solution, while Cr concentration is determined by subtraction.

Results and Discussion

Effects of reaction variables

In acidic media, oxidizing agents readily react with perphenazine to give a red-colored species that is believed to be a radical cation.^{21–23} The intensity and stability of the red oxidation product depends on the nature and concentration of the acid used; therefore, sulfuric, hydrochloric phosphoric and acetic acids were tested. Maximum color intensity and stability were obtained in sulfuric and phosphoric acid media; however, phosphoric acid was used to provide enhanced selectivity for the proposed method. The red oxidation product exhibited a maximum absorbance at 525 – 527 nm; therefore, 526 nm was used in the subsequent experiments. The color developed instantaneously, just upon mixing the reagents, and gave a constant absorbance for at least 30 min.

Absorbance values increased with phosphoric acid concentrations up to 1.0 mol l^{-1} and remained almost constant up to 4.0 mol l^{-1} with both Cr^{VI} and V^{V} . Further increase in acid concentration resulted in a slight decrease in absorbance values. Therefore, a phosphoric acid concentration of 2.0 mol l^{-1} was adopted in the recommended procedure.

Absorbances increased with perphenazine concentrations up to 0.3 mmol l^{-1} for both Cr^{VI} and V^{V} . Then the absorbances remained almost constant up to 3.0 mmol l^{-1} . Therefore, 1.0 mmol l^{-1} of PP was adopted in the recommended procedure.

Added salts, up to 1.0 mol l^{-1} of sodium chloride, sodium sulfate or sodium nitrate, had almost no effect on the color intensity or stability. Also, the method is not sensitive to changing the order of adding the reagents or to changes in temperature up to 40°C; however, at higher temperatures a noticeable decrease in absorbance was recorded. This may be attributed to the disproportionation of the red radical at elevated temperatures.

The effects of foreign ions were investigated in the determination of 0.2 or 0.3 $\mu\text{g ml}^{-1}$ of Cr^{VI} or V^{V} , respectively. The tolerance limit was defined as the maximum concentration of foreign ion that produced a change of 5% in the respective absorbance values. Apart from its simplicity and sensitivity, the most interesting feature of the developed method is its high selectivity towards the cations of the S- and P-block elements and those of the transition elements, as shown in Table 1.

The developed method is based on the oxidation of PP with Cr^{VI} and/or V^{V} . Therefore, strong oxidizing or reducing species are expected to interfere by oxidation of PP or the reduction of Cr^{VI} and/or V^{V} , respectively. However, the steps of sample preparation, oxidation with KMnO_4 , addition of oxalate and the subsequent precipitation described in the recommended procedure successfully eliminated the effects of such oxidizing and/or reducing species, thus rendering the method highly selective for Cr and/or V. For example, as shown in Table 1, appreciable concentrations of many oxidizing and/or reducing species are tolerated to a great extent, *e.g.*, IO_3^- , Au^{III} , Ce^{IV} , Ir^{IV} , Mn^{VII} , Pt^{IV} , Rh^{IV} and Tl^{III} . Only Os^{VIII} and Ru^{III} interfered; however, the native elements of these interfering ions have extremely low natural abundance and are not attacked by acids;¹¹ therefore, they are not harmful for real samples' analysis following the recommended procedure and thus the method may be applied to a very wide range of matrices.

Reduction of chromium (VI) in presence of vanadium (V)

The developed method is based on the oxidation of perphenazine with Cr^{VI} and/or V^{V} . Thus for the analysis of real samples, Cr and V should be in the proper oxidation states suitable for the reaction.

Oxidation of the lower valence states of Cr and V is best achieved by boiling with excess permanganate in a sulfuric acidic medium,¹¹ as adopted in the procedure. However, for the simultaneous determination of Cr and V using the proposed method, it is essential to find a suitable reducing agent to eliminate the effects of the added excess Mn^{VII} and/or Cr^{VI} ions. Therefore, in the determination of $0.20 \mu\text{g ml}^{-1}$ chromium or $0.40 \mu\text{g ml}^{-1}$ vanadium, oxalate, azide and arsenous ions were tested as possible reductants at room temperature and also at 40, 60 and 80°C , respectively. At room temperature, all tested ions had very small effects, but pronounced effects were observed at higher temperatures. Namely, they were very effective against Mn^{VII} but they affected V^{V} and/or Cr^{VI} to varying degrees depending on the concentration and temperature, as shown in Figs. 1 A – C.

Azide ions, especially at high temperatures, affected the recoveries of both Cr^{VI} and V^{V} ; however, the effects were more pronounced with Cr^{VI} , Fig. 1A.

Oxalate ions up to $500 \mu\text{g ml}^{-1}$ and at temperatures $\leq 40^\circ\text{C}$, had negligible effects on Cr^{VI} and V^{V} determinations. However, at $60 - 80^\circ\text{C}$, low recoveries were recorded for both Cr^{VI} and V^{V} , especially at high oxalate concentrations, Fig. 1B. Therefore, the use of excessive amounts of azide or oxalate ions to reduce the unreacted Mn^{VII} ions from fairly hot solutions was avoided in the recommended procedure in order to avoid any possible loss of Cr^{VI} and/or V^{V} .

Arsenous ions, up to $2500 \mu\text{g ml}^{-1}$ had no effect on the determination of V^{V} , at temperatures up to 80°C . However, small concentrations of As^{III} at temperatures $\geq 40^\circ\text{C}$ can effectively reduce Cr^{VI} and can quantitatively eliminate its effects on the coloring reagent, Fig. 1C. Therefore, As^{III} ion was adopted as an effective reducing agent for Cr^{VI} in presence of V^{V} .

Determination of chromium and/or vanadium

Calibration graphs, prepared following the recommended procedure, gave linear relationships ($r = 0.998$ and 0.999) between the absorbance and Cr^{VI} or V^{V} concentration up to 0.40 and $1.00 \mu\text{g ml}^{-1}$, respectively. The equations for calibrations are $A = 0.008 + 1.80[\text{Cr}^{\text{VI}}]$ and $A = 0.008 + 1.18[\text{V}^{\text{V}}]$, where $[\text{Cr}^{\text{VI}}]$ and $[\text{V}^{\text{V}}]$ are the respective concentrations in $\mu\text{g ml}^{-1}$. The small intercept may be attributed to the presence of a trace

Fig. 1 Effects of (A) azide, (B) oxalate and (C) arsenous ions concentrations on the recovery of Cr^{VI} and/or V^{V} at different temperatures. Except for the abscissa variable, other reaction conditions are as given in the recommended procedure; chromium (○, □, ◇, △) and vanadium (●, ■, ◆, ▲) at 25, 40, 60 and 80°C , respectively.

oxidizing impurity in the phosphoric acid used, as suggested by the manufacturer's specification sheet. The molar absorptivities are 1.87×10^4 and $1.20 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and the detection limits, calculated as three times the standard deviation of the blank,²⁴ are 3 and 5 ng ml^{-1} , with Sandell sensitivity indexes of 2.8 and 4.2 ng cm^{-2} for Cr and V, respectively.

In order to verify the possibility of simultaneously determining chromium and vanadium, several experiments were carried out to determine V^{V} in presence of varying amounts of Cr^{VI} , following the recommended procedure, wherein the addition of $1000 \mu\text{g ml}^{-1} \text{ As}^{\text{III}}$ effectively eliminated the interference of Cr^{VI} . For example, the determination of as little as $0.30 \mu\text{g ml}^{-1}$ of V^{V} , in the presence of 10 and $20 \mu\text{g ml}^{-1}$ of

Table 2 Determination of chromium and vanadium in certified ores and synthetic mixtures

No.	Sample composition ^a	Found $\pm$ S.D. / $\mu\text{g ml}^{-1}$ ($n=5$)	
		Chromium	Vanadium
SARM 2	SiO ₂ (63.63); Al ₂ O ₃ (17.34); Fe ₂ O ₃ (1.11); FeO (0.30); MgO (0.46); CaO (0.68); Na ₂ O (0.43); K ₂ O (15.35); P ₂ O ₅ (0.12); BaO (0.27); CO ₂ (0.09); Ce, 11.9; Cr, 12; Cu, 19; Eu, 0.30; Ga, 11; Mn, 80; Rb, 530; Sr, 62; Th, 1.0; Ti, 265; V, 10.	12.05 $\pm$ 0.05; $t = 2.24$	10.04 $\pm$ 0.10; $t = 0.89$
SARM 3	SiO ₂ (52.40); Al ₂ O ₃ (13.64); Fe ₂ O ₃ (8.78); FeO (1.13); MgO (0.28); CaO (3.22); Na ₂ O (8.37); K ₂ O (5.51); MnO (0.77); TiO ₂ (0.48); ZrO ₂ (1.49); SrO (0.54); Nb ₂ O ₅ (0.14); Cl (0.12); F (0.44); CO ₂ (0.17); Ba, 450; Cr, 10; Cu, 13; Eu, 1.2; Nd, 48; P, 260; Pb, 43; Rb, 190; Th, 66; U, 14; V, 81; Y, 22; Zn, 395.	10.12 $\pm$ 0.11; $t = 2.44$	80.93 $\pm$ 0.13; $t = 1.20$
Mixture 1	Matrix; ^b Cr, 0.10	0.103 $\pm$ 0.005; $t = 1.34$	—
Mixture 2	Matrix; ^b V, 0.10	—	0.102 $\pm$ 0.005; $t = 0.89$
Mixture 3	Matrix; ^b Cr, 0.30; V, 0.20	0.32 $\pm$ 0.03; $t = 1.49$	0.22 $\pm$ 0.04; $t = 1.12$
Mixture 4	Matrix; ^b Cr, 0.20; V, 1.00	0.21 $\pm$ 0.03; $t = 0.75$	0.99 $\pm$ 0.02; $t = 1.12$

a. The composition is given in (%), $\mu\text{g g}^{-1}$ for SARM 2 and 3 and in $\mu\text{g ml}^{-1}$ for synthetic mixtures 1–4. b. The Matrix consists of 100 $\mu\text{g ml}^{-1}$ of each of Al^{III}, B^{III}, Ba^{II}, Be^{II}, Ca^{II}, Cd^{II}, Co^{II}, Cu^{II}, Fe^{III}, Hg^{II}, K⁺, La^{III}, Mg^{II}, Mn^{II}, Na⁺, Ni^{II}, Sr^{II}, Th^{IV}, Ti^{IV}, U^{VI}, Zn^{II}, Zr^{IV}. These ions were added in the form of chloride or nitrate.

Cr^{VI}, required 1 and 5 min of contact between Cr^{VI} and As^{III} for complete reduction, respectively. The average recovery of vanadium was 99.7% with relative standard deviation (RSD) of $\leq 0.9\%$. Moreover, synthetic binary mixtures in the ratios of 1:100 to 100:1 of Cr^{VI} and V^V were also prepared. Upon analysis following the recommended procedure, they gave recoveries of 97–102 with RSD $\leq 1.4\%$ for both Cr and V. Moreover, the Student's t -test values were ≤ 1.2 . This shows the high accuracy and precision of the developed method and also shows that the t -test could not detect any systematic error in the developed method (the tabulated t -value for the 95% confidence level and $n = 5$ is 2.78).²⁴

Applications

The enhanced selectivity and sensitivity of the proposed method prompted us to simultaneously determine Cr and V in certified ores and complex synthetic mixtures.

The developed method can tolerate $\geq 2500 \mu\text{g ml}^{-1}$ Fe^{III}. However, it can withstand only $1.0 \mu\text{g ml}^{-1}$ Fe^{II}, due to its reducing effects on Cr^{VI} and V^V; a common feature for most methods based on the use of Cr^{VI} and/or V^V.^{11,13,14}

In the analysis step of vanadium, As^{III} was added to reduce Cr^{VI}. However, this led to a simultaneous partial reduction of Fe^{III} to Fe^{II} that seriously interfered with V^V determination. Therefore, a preliminary precipitation step at pH = 10.3 ± 0.1 was applied, to remove iron from the medium. Quantitative precipitation of Fe^{III}, as the hydroxide, may be achieved at pH ≥ 3 , in presence of a collector such as Al^{III}, Mn^{II}, La^{III},¹¹ or even Fe^{III} itself that was adopted in the procedure. Moreover, coprecipitations of V^V on Fe(OH)₃ and Mg(OH)₂ were reported from slightly neutral and strongly alkaline media, respectively.^{25,26} For the adopted precipitation step and in order to avoid the possible losses of V^V due to the presence of Fe^{III} and Mg^{II} in the studied complicated matrices, the effects of the different precipitation variables were investigated in presence of $100 \mu\text{g ml}^{-1}$ of both Fe^{III} and Mg^{II} in the pH range of 8–12. Ammonium hydroxide, rather than sodium hydroxide, was used as the precipitant in order to provide a relatively slow increase in pH, especially above 9. Chromium and vanadium gave quantitative recoveries after precipitation in the pH ranges of 8–12 and 9.9–10.8, respectively. Therefore, a pH of 10.3 ± 0.1 was adopted in the recommended procedure. Moreover,

collector concentrations in the precipitation vessel in the range of 10–300 $\mu\text{g ml}^{-1}$ of Fe^{III} had almost no effect on the recovery of Cr^{VI} and V^V. Therefore, a $100 \mu\text{g ml}^{-1}$ Fe^{III} was adopted in the procedure, especially for samples that might not contain enough concentration of collectors.

The implemented method was successfully applied to the simultaneous determination of Cr and V in two certified ores and four synthetic mixtures. Mixtures 1 and 2 were analyzed directly without the oxidation and precipitation steps; however, mixtures 3 and 4 were subjected to the precipitation step before analysis. The data obtained are in excellent agreements with the nominal values, as shown in Table 2. Moreover, the t -test values were ≤ 2.44 , showing that there are no statistically significant differences between the nominal values and the results obtained by the developed method, reflecting the high accuracy and precision of the method.

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References

1. J. R. Pretty, E. A. Blubaugh, J. A. Caruso, and T. M. Davidson, *Anal. Chem.*, **1994**, *66*, 1540.
2. S. Hirata, Y. Umezaki, and M. Ikeda, *Anal. Chem.*, **1986**, *58*, 2602.
3. R. R. Greenberg, R. Zeisler, H. M. Kingston, and T. M. Sullivan, *Fresenius' J. Anal. Chem.*, **1988**, *332*, 652.
4. Y. Wu and G. Schwedt, *Fresenius' J. Anal. Chem.*, **1987**, *329*, 39.
5. P. J. Potts, P. C. Webb, J. S. Watson, and D. W. Wright, *J. Anal. At. Spectrom.*, **1987**, *2*, 67.
6. J. Pascual, *Talanta*, **1987**, *34*, 1027.
7. C. M. Davidson, R. P. Thomas, S. E. McVey, R. Peralá, D. Littlejohn, and A. M. Ure, *Anal. Chim. Acta*, **1994**, *291*, 277.
8. E. Klaos and V. Odinet, *Talanta*, **1990**, *37*, 519.

9. G. Schlemmer and B. Welz, *Fresenius' J. Anal. Chem.*, **1987**, 328, 405.
10. M. Bettinelli, N. Pastorelli, and U. Baroni, *Anal. Chim. Acta*, **1986**, 185, 109.
11. Z. Marczenko, "*Separation and Spectrophotometric Determination of Elements*", 2nd ed., **1986**, Ellis Horwood, Chichester.
12. K. Ueno, T. Imamura, and K. L. Cheng, "*Handbook of Organic Analytical Reagents*", 2nd ed., **1992**, CRC press, Boca Raton.
13. M. J. C. Taylor and J. F. Van Staden, *Analyst* [London], **1994**, 119, 1263.
14. S. Ressalan, R. S. Chauhan, and D. N. Purohit, *Rev. Anal. Chem.*, **1997**, 16, 69.
15. B. E. Saltzman, *Anal. Chem.*, **1952**, 24, 1016.
16. N. A. Talvitie, *Anal. Chem.*, **1953**, 25, 604.
17. APHA-AWWA-WEF, "*Standard Methods for the Examination of Water and Wastewater*", 18th ed., **1992**, ed. A. E. Greenberg, L. S. Clesceri, and A. D. Eaton, American Public Health Association, Washington, D.C.
18. J. B. Raj and H. S. Gawda, *Analyst* [London], **1995**, 120, 1815.
19. A. T. Gowda and H. S. Gowda, *Anal. Chim. Acta*, **1988**, 209, 293.
20. J. C. Van Loon and R. R. Barefoot, "*Analytical Methods for Geochemical Exploration*", **1989**, Academic Press, San Diego, California.
21. C. Bodea and I. Silberg, in "*Advances in Heterocyclic Chemistry*", Vol. 9, **1968**, pp. 321-460, ed. A. R. Katritzky and A. J. Bulton, Academic Press, New York.
22. A. A. Mohamed, M. Iwatsuki, T. Fukasawa, and M. F. El-Shahat, *Analyst* [London], **1995**, 120, 2281.
23. J. Karpinska, B. Starczewska, and H. Puzanowska-Tarasiewicz, *Anal. Sci.*, **1996**, 12, 161.
24. J. C. Miller and J. N. Miller, "*Statistics for Analytical Chemistry*", 3rd ed., **1993**, Ellis Horwood, Chichester.
25. H. Naito and K. Sugawara, *Bull. Chem. Soc. Jpn.*, **1957**, 30, 799.
26. J. Rüter and G. Schwedt, *Fresenius' J. Anal. Chem.*, **1982**, 311, 112.