STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLVIII, 1, 2003

FLAME ATOMIC EMISSION DETERMINATION OF STRONTIUM IN FLOTATION TAILINGS USING THE METHANE-AIR FLAME AS EXCITATION SOURCE

LADISLAU KÉKEDY-NAGY, TIBERIU FRENȚIU, ANA-MARIA RUSU, MICHAELA PONTA and EMIL A. CORDOŞ

Universitatea "Babeş-Bolyai", Facultatea de Chimie şi Inginerie Chimică
3400 Cluj-Napoca, Arany J. 11, România

ABSTRACT. The strontium content of flotation tailings has been determined by flame atomic emission spectroscopy using the methane-air flame. It was studied and optimized the flame and instrumental parameters (flame composition, the observation height in the flame) on the emission of strontium. The best results were obtained with the strontium line of 460.7 nm at the observation height of 7 mm, with the flame composition of 1.12 (relative stoichiometric units, (RSU)). The effect of Na, K, Mg, Ca, Al, ClO_4^-, SO_4^{2-}, and PO_4^{3-} on the emission of strontium was studied too. The calibration curve was linear in the 0.1 - 10 mg L^{-1} range, the detection limit of 0.030 ± 0.022 mg.L^{-1} was obtained in the presence of 200 mg L^{-1} of Cs. The strontium content of flotation tailings has been determined in the presence of 100 mg L^{-1} $HClO_4$ using the calibration curve and the standard addition method. With background correction results agree between these two methods.

INTRODUCTION

Strontium is the 21st in the rank of the element-abundance in the Earth crust, having of magma origin. Its dispersion into the environment is due to the erosion of the volcanic rocks (crashing and subsequent dissolution) giving rise of the weather factors. Therefore these types of rocks (granite, andezite and others) are considered as primary strontium source in the environment, the degree of its loading is determined by the dissolution rate of the different strontium compounds. The mobility of the strontium in the environment as a water-soluble salt is high, being ensured mainly by the natural waters (ground waters, rivers, oceanic streams, etc.).

The mean Sr content of the surface waters is of 80 μg L^{-1} and of the seawater of 80 mg L^{-1}, respectively [1]. The human technological activities as mining for metal processing contribute significantly to the release and the mobilization of strontium in the environment. Huge amounts of rocks are

displaced and processed annually, the flotation tailing wastes are stored open air as heaps for long time, usually close to the processing factories. These tailings act as long term point-pollution sources, the soil, the ground waters and the streams are primarily polluted. Strontium, among the other elements, enters the ecosystem, moves from an ecological trophic layer into the other, accumulates in living organisms, throughout the food chain, which has humans at its top. Therefore it is important to know the degree of pollution produced by the source in order to assess the environment loading and to evaluate the risk for health. Strontium is retained by soils (the mean Sr-content being of 280 mg kg^{-1}) and by the living organisms (biosorption). From biological point of view it is not considered as essential element for life, its compounds generally are non-toxic, not hazardous to health [2]. However sometimes it exhibits toxic effect for low order organisms, young humans and animals when their calcium intake is low, the Ca/Sr intake ratio is also low [3,4]. Plants accumulate more strontium, humans and animals less, 99% of the strontium being accumulated in the bones. The daily human strontium intake is attained with vegetables and drinking water.

Flame atomic emission spectrometry (FAES) is a simple method, largely used for the determination of strontium in samples of different origin, as: biological materials [5, 6, 7], aluminum alloys [8], rocks and brine [9], minerals [10]. As excitation sources the C_2H_2-air, C_2H_2-N_2O flames have been used. The optimal flame conditions for the quantification of strontium in these flames were established, the detection limits being of order of 10^{-3}-10^{-4} μg L^{-1} using the most sensitive atomic resonance line of 406.8 nm [11]. Strontium yields different refractory compounds (chemical interference) in the flame as: SrO and SrOH, spinell-type mixed oxides with Ca, Al, Mg, Si, etc. [12]. Refractory compounds are formed with the SO_4^{2-} and PO_4^{3-} ions too [13]. The depressing effect of the interferents on the emission signal could be minimized by using the hotter C_2H_2-N_2O flame [14]; by adding either 1-5 % La or 0.1 M EDTA or 2% quinolin-8-ol (as releasing agent) [14, 15]; ascorbic acid - K citrate (as matrix modifier) to the sample [16]. The releasing agents are effective only in the hot flames. Strontium ionizes partially in the acetylene flames, this phenomenon can be suppressed by adding either K, Rb or Cs salts to the sample in excess [11]. The cooler flames, as propane-butane-air (PB-A) and the natural gas-air (NG-A) flames are seldom used, often in low performance commercial flame-photometers, designated for routine analysis. The methane-air flame (M-A) has similar properties with the PB-A and NG-A flames, exhibiting lower temperature and burning velocity than the C_2H_2 ones. To our best knowledge the behaviour of strontium in the M-A flame was not reported. The aim of this work is to study the behaviour of strontium in the M-A flame, to optimize the flame and instrumental parameters and the determination of strontium in flotation tailing wastes, respectively.

EXPERIMENTAL

INSTRUMENTATION

The measurements were carried out with a HEATH-701 (Heath Co., Benton Harbor, MI, USA) spectrophotometer. The instrumentation and operation conditions are provided in Table I.

Table I

Instrumentation and operating conditions

Equipment	Characteristics
Flame	Premixed methane – air Fuel: 99 % purity methane from pipe, flow rate 44 – 56 L h^{-1}, depending on flame composition Oxidant: compressed air, flow rate 500 L h^{-1}
Burner	Mecker-type, made of brass, 50 mm long, 4 x 20 holes, laboratory made
Sample introduction and desolvation system	Concentric pneumatic nebulizer, 150 mL cylindrical glass spray chamber (AAS –1, Carl Zeiss Jena, Germany) provided with a laboratory made 1 mm cylindrical impactor placed at 5 mm from the nebulizer head. Liquid aspiration mode: natural, flow rate 3,5 mL min^{-1}, 11% nebulization efficiency
Optics	scanning monochromator, Czerny-Turner mount, spectral range 190-1000 nm, 350 mm focal length, 1180 grooves mm^{-1} blazed at 250 nm, bandpass 0.2 nm at slitwidth 0.1 mm (HEATH EU-700, Heath Co., Benton Harbor, MI, USA)
Photodetection	1P28A (RCA, USA) photomultiplier supplied with -700 V from an HEATH EU - 700 - 30 (Heath Co., Benton Harbor, MI, USA) power supply
Data acquisition system	Strip chart recorder K-201 (Carl Zeiss Jena, Germany)

REAGENTS

Stock standard solutions (1000 mg L^{-1}) were prepared by dissolving the appropriate amounts of metals (Mg and Al (Specpure, Johson Matthey Chemicals Limited, England)) and compounds ($CaCO_3$, $SrCO_3$ (Specpure, Johnson Matthey Chemicals Limited, England) in corresponding acid. KCl, NaCl (analytical grade, Reactivul, Bucureşti, Romania), CsCl, HCl, H_2SO_4, $HClO_4$ and H_3PO_4 (analytical grade, Merck, Darmstadt, Germany)) were dissolved and diluted with double distilled water, respectively. For further dilutions double distilled water was used in all cases.

SAMPLING AND SAMPLE HANDLING

The solid samples were collected from the flotation tailings heap, situated in the city Deva area (Hunedoara county), Romania. The samples were taken with metallic hoe from different selected places and sites of the heap, at depths of 20 and 40 centimeters, respectively. After removal of the vegetable (leaves, roots etc.) and other foreign matters, the samples were air dried at room temperature, grounded, homogenized, sieved through 120-mesh sieve and stored in airtight plastic bags. The samples were digested using the method proposed by M. van Avendonk, R. Scogerboe [17], namely: ~ 2 grams of solid was weighed from each sample in 100 mL glass beaker and 20 mL of conc. $HClO_4$ was added at room temperature. The beakers were heated on the sand bath to dryness and the residue was treated two times with 3 mL of conc. $HClO_4$ and evaporated to dryness. To the final evaporation residue 20 mL of HNO_3 2% was added, the suspension was filtered in 100 mL of volumetric flask and filled with HNO_3 2% to sign.

PROCEDURE

The behaviour of strontium in the M-A flame was studied up to h = 18 mm over the burner head (1-mm steps), at three different flame compositions: 0.88; 1.00; 1.12 (expressed in relative stoichiometric units, RSU). Four replicate measurements were made. The mean, the standard deviation, the S/N and the signal-to-background (S/B) ratio were calculated for each h and flame composition investigated. It was tested the homogeneity of the means (at a significance level of 0.05) too. The burner was held parallel to the optical axis of the spectrophotometer. The slit width of the monochromator was of 0.1 mm, unless stated otherwise. The sensitivity of the strip chart recorder was different in different spectral domains, considering the intensity of the emission lines and the background observed. For a given set of determinations the sensitivity was kept constant.

RESULTS AND DISCUSSIONTHE EMISSION SPECTRUM OF STRONTIUM, DETERMINATION OF THE ANALYTICAL EMISSION LINE

The emission spectrum of strontium in the M-A flame was determined first in the 200 - 800 nm spectral domain. It was registered the flame spectrum alone and its spectrum in the presence of a strontium of 100 mg L^{-1} in the flame. Using spectral table [18] it was identified, surprisingly, ionic lines with wavelengths of 407.7 nm and 421.5 nm, taking account of the relatively low temperature of the M-A flame. In addition it was also identified the strong atomic line of 460.7 nm and the molecular bands in the 375 –392 nm, 595 – 626 nm and 640 – 720 nm spectral domain, belonging to refractory SrO and $Sr(OH)_2$. The most intensive bandhead was located at 606 nm.

OPTIMIZATION OF THE FLAME AND INSTRUMENTAL PARAMETERS

The aim is to get that value for the flame composition and observation height h for whose the S/N ratio is maximal. The composition of the flame was kept constant, at 1.12 RSU. The concentration of the working calibration solutions was different, depending on the line intensity measured. The analytical signal, intensity (I, in a.u.), was measured at 407.7 nm, 421.5 nm, 460.7 and 606 nm and the background intensity (in the presence of strontium), at the base of the atomic emission line studied, at 461.5 nm. The variation of the line intensities versus observation height over the burner head is represented in Fig.1.

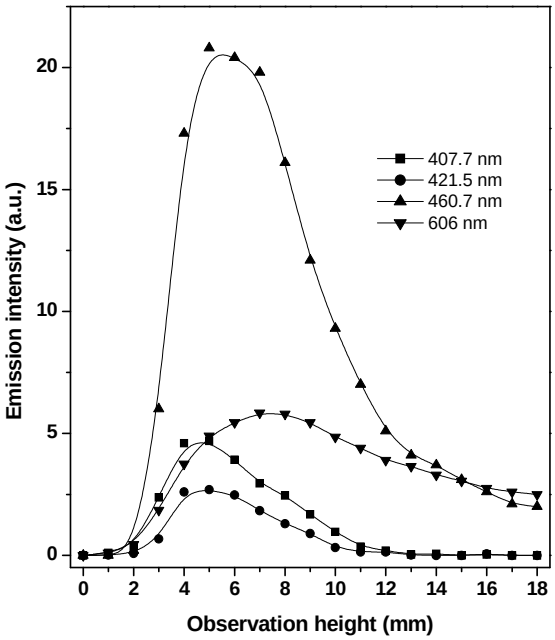

Fig. 1. The intensity of different strontium lines (not in scale) versus observation height

For the quantitative estimation of the results at different wavelengths only the maximal value of the analytical signal for each line was selected (I_{max}). It was calculated the relative intensity for each line (I_{rel}) considering the sensitivity of the chart recorder and the concentration of the working standard used. The reference line was the weakest one. The S/B ratio was determined in the same way. The results are summarized in Table II.

The ionic lines are weak, being excited by radicals in the primary reaction zone of the flame. The most intensive line is the atomic line of 460.7 nm, being excited in the interconal reaction zone of the flame, observed at 7 mm over the burner head. The maximum of molecular emission appears at the same height, their emission are less influenced by excitation conditions in the flame. The

influence of the flame composition and of observation height on the analytical signal only for the most sensitive line was investigated further, using three flame compositions (0.88, 1.00, 1.12 RSU), at the concentration level of 10 mg L^{-1} Sr. The data were processed by ing the MicroCal Origin™ Software package, version 6.0 (MicroCal Software Inc., MA, USA) and plotted as 2D contour map (Fig.2).

Table II

The relative intensities of the strontium emission lines in the M-A flame

Wavelength (nm)	Emittent	h (mm)	I_{max}	I_{rel}	S / B
407.7	Sr **II**	5	23.5	1.74	0.45
421.5	Sr **II**	5	13.5	1.00	0.24
460.7	Sr **I**	7	20.8	1540.74	610.00
606.0	SrOH	7 - 8	11.8	86.66	106.30

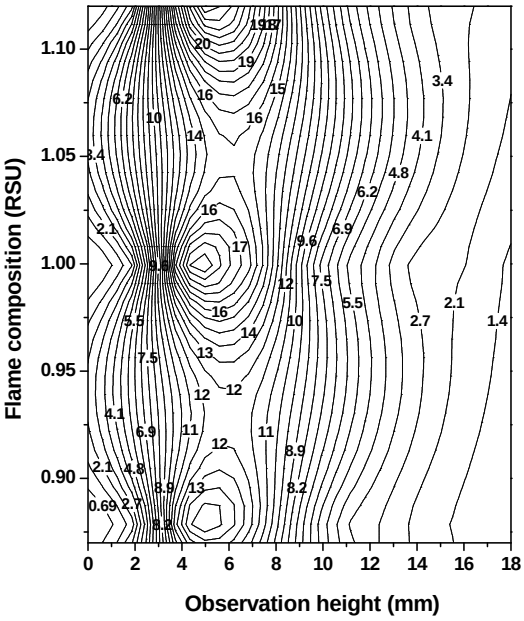

Fig. 2. The 2D contour map of the emission of the 460.7 nm strontium-line vs. observation height and flame composition relation. The data labels on the plot indicateindicate the grid matrix values

The results show that the analytical signal depend both of observation height and flame composition and increases significantly with the increase of the methane content in the flame. The emission maxims are located at observation heights between 5-7 mm. The standard deviation of all means were homogeneous, the magnitude of the S/N ratio being decided by the magnitude of the mean. In conclusion, the optimal conditions for the quantitative determination of strontium in the M-A flame are λ = 460.7 nm, h = 7 mm, flame composition 1.12 RSU.

THE INFLUENCE OF THE SPECTRAL BANDPASS OF THE MONOCHROMATOR ON THE ANALYTICAL SIGNAL, S/N AND S/B RATIO

A possibility to enhance the analytical signal consists in the extending the radiation energy reaching the photodetector, in broaden the spectral bandpass of the monochromator, in our case. It is determined, among others, by the width of the slit (SW) of the monochromator, which influences in different manner the amplitude and the fluctuations of the emission signal. Therefore the optimal value of SW can be determined for which the S/N ratio is maximum. The influence of the slitwidth on I, the S/N and S/B ratio was studied in the 0.1 – 1.5 mm domain, in steps of 0.1 mm, using a 1 mg L^{-1} strontium solution. The flame and instrumental parameters used were the optimal ones, determined earlier. The results show that the emission signal increases linearly with the spectral bandpass of the monochromator ($I = -0.0309 + 1.763SW$, $r^2 = 0.9883$) in the range of 0.1 – 1.1 mm. The standard deviation of the means increases slowly with the increase of SW but remains homogeneous in the entire SW domain. The maximum value of S/N was of 26 at the SW of 0.8 mm. The S/B ratio decreases continuously, its variation could be approximated best with a fifth order polinomial function. In conclusion, the slitwidth could be increased up to 0.8 mm without a significant decay of the S/N ratio.

INTERFERENCES

The effect of Na, K, Mg, Ca, Al, SO_4^{2-} and PO_4^{3-} on the emission signal of strontium of 5 mg L^{-1} was investigated, as possible inorganic interferents in the samples. The effect of $HClO_4$ was tested too, used as releasing agent. The experimental conditions were the optimal ones, determined previously. The background signal was measured at 461.5 nm, in the presence of working standard in the flame. The variation of the net analytical signal versus the concentration of the interferents is represented in Fig 3.

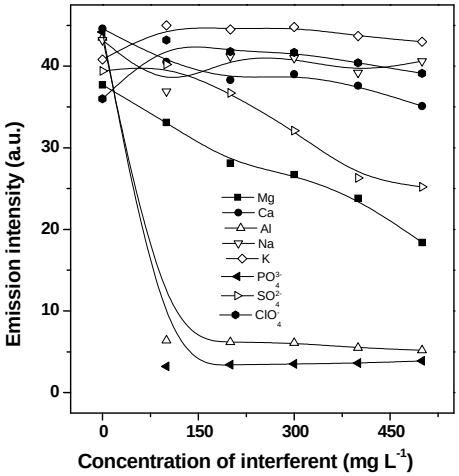

Figure 3. Influence of Na, K, Mg, Ca, Al, SO_4^{2-}, PO_4^{3-} and ClO_4^- on the emission signal of strontium of 5 mg L^{-1}

K acts as ionization suppresser, enhancing simultaneously the analyte and the flame background signal too. The influence of Na is lower, and is mainly due to the background enhancement. Calcium enhances the analytical signal in 20-fold excess too, acting as releasing agent by binding the free O and OH radicals of the flame and hindering the formation of the strontium (SrO, SrOH) compounds. Mg and Al decrease gradually the strontium emission signal by formation the thermally stabile mixed oxides. The SO_4^{2-} and PO_4^{3-} ions decrease drastically the strontium emission signal even at low concentrations. $HClO_4$ as matrix modifier, enhances the strontium emission signal with 19 %, without enhancing the flame background.

CALIBRATION, DETERMINATION OF THE DETECTION LIMIT

For the determination of the detection limit the variation of the analytical signal versus concentration was studied. The calibration curves were plotted in the 0.1-100 mg L^{-1} strontium concentration range. Each calibration curve, covering only one order of magnitude of concentration, was established by using six standard solutions. Six replicate measurements were made at each concentration level. The homogeneity of the means and the linearity of the calibration curve was tested, it was calculated the equation of the regression line, the confidence limits, the coefficient of correlation (r^2), with the least squares method. The detection limit was calculated using the two step Neyman-Pearson model [19,20], for the fixed values of $(P_{10})_0 = 0.025$ and $(P_{11})_d = 0.975$. In order to extend the determination limit to lover concentrations 200 mg L^{-1} of Cs in final concentration was added to the diluted working Sr standards. The results are summarized in Table III.

Table III

The calibration data of strontium determination in the M-A flame

Nr.	Concentration range (mg/L)	Slitwidth (mm)	Equation of the calibration curve	r^2
(1)	100 – 10	0.1	$I = -1.54 + 0.66*C - 0.0023*C^2 - 7*10^{-7}*C^3$	0.9966
(2)	40 – 10	0.1	$I = 2.29 + 0.566*C$	0.9863
(3)	100 – 60	0.1	$I = 15.75 + 0.29*C$	0.9963
(4)	10 – 1	0.1	$I = 0.25 + 2.15*C$	0.9976
(5)	10 – 1	0.4	$I = -0.78 + 2.69*C$	0.9985
(6)	1 – 0.1	0.1	$I = -0.31 + 24.25*C$	0.9922
(7)[@]	1 – 0.1	0.1	$I = -1.1 + 24.95*C$	0.9972
(8)[@]	1 – 0.1	0.8	$I = -0.1 + 7.17*C$	0.9922

[@] 200 mg L^{-1} of Cs added

In the 10-100 mg L^{-1} domain the concentration-intensity relationship is not linear in the whole concentration range, it could be approximated best with a third-order polinom. (eq.(1)). Linear correlation exists only in narrower concentration domains (eq.(2) and (eq.3)), and at lower concentrations (eq.(4) - (eq.(8)). The presence of Cs enhances the sensitivity and the linearity of the calibration curve. The detection limit was calculated only in the 0.1- 1 mg L^{-1} concentration range, in the presence of Cs, being of 0.030 ± 0.022 mg L^{-1}.

DETERMINATION OF STRONTIUM IN SOLID SAMPLES

The calibration and the standard addition method have carried out for the strontium quantification in the flotation tailings, the later being used as reference method (absence of certified reference material). The determinations were performed with optimal instrumental parameters, determined previously. The measurements were carried out in the presence of 100 mg L^{-1} $HClO_4$, regardless of method used; the background signal being measured at 461.5 nm with the sample nebulized into the flame. In the case of standard addition method 100 µL of concentrated strontium standard was added to the 25 mL of sample. Three additions of standard were made, in 1mg L^{-1} concentration steps. It was calculated the regression line, the strontium content was determined from the intercept with the abscissa of the line. Comparing the calibration curves, the slope of calibration curves corresponding to the standard additions are significantly lover then of the calibration, fact, which suggests the existence of the chemical interference. The results of the determination of strontium content of flotation tailings are summarized in Table IV.

Table IV

Results of analysis of flotation tailings samples (n = 4)

Sample cod number	Heap collection site and depth (cm)	Concentration (mg kg^{-1}, calibration)	Concentration (mg kg^{-1}, standard addition)
DHS 1	TOP, 40	7.0 ± 1.6	7.1 ± 1.9
DHS 2	TOP, 20	7.1 ± 1.6	8.9 ± 1.9
DHS 3	TOP, 40	6.2 ± 1.6	7.5 ± 1.9
DHS 4	BASE, 20	7.4 ± 1.6	6.9 ± 1.9
DHS 5	BASE, 20	8.3 ± 1.6	9.5 ± 1.9
DHS 6	BASE, 40	5.0 ± 1.6	5.5 ± 1.9

The results of the two methods agree, they are within the errors of the determinations. With the standard addition method the results are generally higher probably due to the chemical interference, but the means obtained with the two methods do not differ significantly ($t_{calc.}$= 0.8292 < t_{tab} = 2.97, for fixed value of $(P_{10})_0$ = 0.025). We can consider that both methods give acceptable results, the standard addition method offering better results, closer to the real strontium content. The strontium content of the tailing is low, lower than that admitted for soils (20 mg kg^{-1}), uniformly dispersed in different sites of the heap. The loading of the environment with strontium erasing from the heap is also low, it is not hazardous to health from this point of view.

In conclusion the strontium content of flotation tailings can be determined with acceptable precision in the presence of 0.01 N $HClO_4$, with the background correction, using the M-A flame. Due to the existence of chemical interference the standard addition method is recommended.

CONCLUSIONS

Strontium exhibits ionic, atomic and molecular spectrum in the M-A flame. The most intensive is the atomic line of 460.7 nm. The intensity of this line varies with the composition of the flame and observation height, the optimal observation height over the burner head is 7 mm, in fuel rich flame (RSU = 1.12). The presence of Mg, Al, SO_4^{2-}, and PO_4^{3-} decreases the emission of strontium. 0.01 N $HClO_4$ exhibits a good releasing effect. The intensity-concentration relationship is linear in the 0.1-10 mg L^{-1} range, the detection limit in the presence of 200 mg L^{-1} Cs is of 0.050 ± 0.022 mg L^{-1}. The strontium content of flotation tailings can be determined precisely in the presence of 0.01 N $HClO_4$ using background correction with the calibration or the standard addition method. Due to chemical interference the standard addition method is recommended. The strontium content of the heap is low, uniformly distributed, being not hazardous to health.

In final conclusion, M-A flame is a suitable excitation source with acceptable precision determination of strontium in flotation tailings using the calibration method and the standard addition method with the background correction.

REFERENCES

1. M. Anke, L.Angelow, Proc. VI. Internat. Tr.El.Symp., (Ed.I.Pais), Budapest, (1994)
2. S.C. Skoryna, *Tr.El.Med.,* 1986, **3**, 153
3. F.J. Dwyer, *Environ.Toxicol.Chem.*, 1992, **11**, 513
4. C.W. Weber, at al, *Poultry Sci.,*1972, **47,** 1318
5. A. Sanz-Medel, R. Rodriguez Roza, C. Perez Conde, *Analyst* (London), 1983, **108,** 204
6. H. Matusiewicz, *Anal.Chim.Acta*, 1982, 136215, 223
7. B.B. Razmilic, *At.Spectrosc*., 1986, **7,** 43
8. M. Brill, *Aluminium* (Duesseldorf), 1982, **58,** E189
9. H. Matusiewicz, *Spectroscopy*, 1986, **1,** 32
10. G. Schwedt, *LaborPraxis*, 1990, **14,** 620
11. E. Cordoş T. Frenţiu, M. Ponta, A. Rusu, A. Fodor, *Analiza prin spectrometria atomică* Institutul Naţional de Optoelectronică Bucureşti, 1989
12. W.W. Harrison, W.H. Wadlin, *Anal.Chem.*, 1969, **41,** 374.
13. C.B. Boss, G.M. Hieftje, *Anal.Chem*., 1979, **51**, 1897
14. W. Luecke, *J.Anal.At.Spectrom*., 1994, **9**, 105
15. J. Liang, Y. Ruan, *Guangpu-Shiyanshi*, 1993, **10,** 24
16. D.S.R.Murty, B.N. Tikoo, *At.Spectrosc.,* 1987, **8,** 79
17. M. van Avendonk, R. Scogerboe, Anal.Chem., 1981, **53,** 2349
18. R. Mavrodineanu, H. Boiteux, *Flame spectroscopy*, Wiley Interscience, New York, 1965.
19. C. Liteanu, I. Rică, *Statistical Theory and Methodology of Trace Analysis,* John Wiley, New York, 1980.
20. D.L. Massart, B.G.M. Vandeginste, S.N. Deming, Y. Michotte, L. Kaufman, *Chemometrics: a textbook,* Elsevier, New York, 1988.