



Direct determination of gallium in bauxite employing ICP OES using the reference element technique for interference elimination[☆]

Fernanda A. de Santana, José T.P. Barbosa, Geraldo D. Matos,
Maria G.A. Korn, Sergio L.C. Ferreira^{*}

Universidade Federal da Bahia, Grupo de Pesquisa em Química e Quimiometria, CEP: 40170-270 Salvador, Bahia, Brazil
Instituto Nacional de Ciência e Tecnologia, INCT, de Energia e Ambiente, Universidade Federal da Bahia, 40170-290 Salvador, BA, Brazil

ARTICLE INFO

Article history:

Received 4 February 2013
Received in revised form 12 March 2013
Accepted 12 March 2013
Available online 23 March 2013

Keywords:

Gallium determination
Bauxite samples
ICP OES
Reference elements

ABSTRACT

The determination of gallium in bauxite samples using inductively coupled plasma optical emission spectrometry (ICP OES) is complicated because aluminum in high concentrations interferes strongly in this analysis. This paper proposes a direct method for the determination of gallium in bauxite samples by ICP OES employing the reference element technique for correction of aluminum interference.

The experimental parameters: hydrochloric acid concentration used for preparation of gallium standard solutions and bauxite samples, nebulizer flow rate and RF power were optimized by multivariate technique. Firstly, a factorial design was performed for preliminary evaluation. Afterward, a Box–Behnken design was also performed for determination of the critical conditions for these factors. Box–Behnken design is a chemometric technique that in the last years has been often used for optimization of analytical methods.

The procedure proposed using the established conditions (in presence of yttrium and/or scandium as reference element) allows the determination of gallium with limits of detection and quantification of 0.0006 and 0.0019 mg L⁻¹ and precision expressed as relative standard deviation of 4.37 and 1.78% for bauxite samples with gallium content of 21.00 and 36.00 mg Kg⁻¹. For sample mass of 0.20 g the limits of detection and quantification are 0.042 and 0.140 mg Kg⁻¹, respectively. The accuracy of the method was evaluated and confirmed using standard reference materials of alumina and marine sediment.

The method proposed was applied for the determination of gallium in five bauxites, having yttrium and scandium as reference element, being that the sample preparation was done employing microwave-assisted digestion. The gallium content in the five samples varied from 19.70 to 100.59 mg Kg⁻¹. These concentrations are in agreement with the data reported by literature.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Gallium is a chemical element that is relatively rare and it has been used largely in electronics industry. In nature it occurs as gallium(III) compounds in trace amounts principally in bauxite (aluminum matrix) and zinc ores [1,2].

Aluminum in high concentrations (>1000 µg mL⁻¹) interferes strongly in the determination of trace amounts of several chemical elements when inductively coupled plasma optical emission spectrometry (ICP OES) is used as analytical technique. This interference is well known [3] and it has been subject for the development of several works [3–10]. Ishizuka et al. determined trace amounts of calcium, copper, iron, magnesium, manganese, sodium and silicon in

99.99% aluminum oxide by ICP OES. Matrix effects on the calibration graphs for each element were studied [4]. Saleem et al. evaluated the aluminum matrix effect on the determination of boron, calcium, cadmium, cobalt, chromium, copper, iron, magnesium, manganese, nickel, silicon and zinc by ICP OES [5]. Our research group proposed a separation procedure using polyurethane foam to overcome the interference of aluminum on zinc determination by ICP OES [6]. Zarcinas studied the effect of the aluminum matrix on the emission lines (168-nm and 220-nm) employed for determination of lead by ICP OES [7]. Zhong et al. used matrix match and interference coefficient during the determination of iron, silicon, copper, magnesium, manganese, nickel, zinc, titanium, chromium and strontium in aluminum alloy by ICP OES [8]. Recently, Oliveira et al. proposed a separation procedure involving precipitation of aluminum as hydroxide during the determination of calcium, iron, gallium, sodium, silicon and zinc in alumina employing ICP OES. Also some elements were investigated as reference elements [9]. Pojedniok et al. determined gallium in natural soils and soils polluted by industry. The procedure used involved a separation and preconcentration step where gallium

[☆] Paper presented at 5th Ibero-American Congress of Analytical Chemistry 2012.

^{*} Corresponding author at: Universidade Federal da Bahia, Grupo de Pesquisa em Química e Quimiometria, CEP: 40170-270 Salvador, Bahia, Brazil. Tel./fax: + 55 71 32355166.

E-mail address: slcf@ufba.br (S.L.C. Ferreira).

was extracted as chloro complexes in presence of ascorbic acid for reduction of iron. Gallium was determined by ICP OES [10]. Mahamuni et al. [11] proposed a separation and preconcentration procedure for the determination of gallium in bauxite ores by liquid–liquid extraction using 2-octylaminopyridine in chloroform media.

Chemometric techniques allow optimization of analytical methods with higher efficiency than the univariate techniques. In these, the interactions between the experimental factors are considered during the optimization step. This way, these techniques have been often used in analytical chemistry [12–14].

Two-level full factorial design is a chemometric technique used for preliminary evaluation of the experimental factors on the processes. Box–Behnken designs (BBD) are a class of rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs. The number of experiments (N) required for the development of BBD is defined as $N = 2k(k - 1) + CO$ (where k is the number of factors and CO is the number of central points). A great advantage of the BBD is that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels [15]. This multivariate design has been often employed for optimization of analytical methods from last year's [16–18].

Reference element (internal standardization) is a technique widely used for compensating nonspectral interference in inductively coupled plasma (ICP) spectrometry. In this technique, the ratio of analyte signal and reference element signal is used instead of the direct analyte emission intensity. Thus, internal standardization is, in principle, an ideal technique to reduce correlated noise and to correct multiplicative errors [19,20].

The paper proposes a procedure for the direct determination of gallium in aluminum matrices by ICP OES employing the reference element technique for elimination of the aluminum interference. The experimental conditions for the analytical measure were established using full two-level factorial design and Box–Behnken design.

2. Material and methods

2.1. Instrumentation

An inductively coupled plasma optical emission spectrometer (ICP OES) with an axially viewed configuration (VISTA PRO, Varian, Mulgrave, Australia) that was equipped with a charge coupled device (CCD) detector was used for the determination of gallium. The seaspray nebulizer coupled with a cyclonic chamber was used as sample introduction system. The operating conditions of the ICP OES instrument are described in Table 1. The ionic emission line used was recommended by the equipment software: Ga(II) 294.363 nm. A closed-vessel microwave digestion system (ETHOS EZ, Milestone, Sorisole, Italy) was used for sample decomposition.

2.2. Reagents, solutions and samples

All labware used was stored in a 10% (v/v) HNO₃ solution bath for 24 h for cleaning and was rinsed with high-purity water. After that, all

materials were dried under clean-air conditions at ambient temperature. The reagents employed were of the highest commercially available purity grade: 65% (m/m) HNO₃ and 37% (m/m) HCl (Merck, Germany). Ultrapure water (resistivity 18 MΩ cm⁻¹) that was obtained from a Milli-Q Pluswater purification system (Millipore Molsheim, France) was used to prepare all standard and sample solutions. A monoelemental, high-purity grade 1 g L⁻¹ stock solution of gallium, scandium and yttrium (Titrisol, Merck) was employed to prepare the test and reference solutions.

2.3. Digestion procedure

Approximately 200 mg of sample or certified reference material was placed directly into a microwave-closed vessel. Nine milliliter of 65% (m/m) HNO₃ and 3.0 mL of 37% (m/m) HCl were added to each vessel. The microwave oven was operated according to the parameters presented in Table 2, for the simultaneous digestion of nine vessels. All experiments were performed in triplicate. The digests were put into a 50 mL erlenmeyer and heated on a hot plate at 110 °C to near dryness. After drying, the digested sample was diluted to 15 mL with 0.53 mol L⁻¹ hydrochloric acid. In standard solutions and bauxite samples were added 10 mg L⁻¹ of internal standard. Gallium was determined by ICP OES.

2.4. Optimization procedure

The optimization was performed using full two-level factorial and Box–Behnken design, considering the factors: RF power, acid concentration and nebulizer gas flow rate. All these experiments were performed using a gallium solution of 1.00 mg L⁻¹ in a random order and triplicates of the center point were determined to evaluate the experimental error. The curvature test was also performed. The analytical response was recorded as emission intensity, and the 6.0 STATISTICA software was used to process the experimental data.

3. Results and discussions

3.1. Optimization of experimental factors for determination of gallium by ICP OES

Preliminary studies were performed involving the nebulizers (VGroove and seaspray) and also the hydrochloric and nitric acids. Under the conditions established the results obtained demonstrated that the combination of hydrochloric acid and the nebulizer seaspray allows the determination of gallium with higher sensitivity. So, some experimental parameters were optimized using multivariate techniques for determination of gallium employing this nebulizer in the presence of hydrochloric acid. Firstly, a full two-level factorial design was performed involving the factors: RF power, hydrochloric acid concentration and nebulizer gas flow rate. Triplicate of the central point were performed in order to determine the experimental error and evaluation of the curvature. The experimental dominions (as coded and real values) for each factor and the chemometric response (emission intensity at 294.363 nm) are shown in Table 3.

Table 1
Instrumental optimized conditions for the ICP OES with axially-viewed configuration.

Parameter	Value
RF generator (MHz)	40
RF incident power (kW)	1.1
Spray chamber	Cyclonic
Nebulizer	Seaspray
Plasma gas flow rate (L min ⁻¹)	15
Auxiliary gas flow rate (L min ⁻¹)	1.5
Nebulizer argon gas flow rate (L min ⁻¹)	0.4
Replicate read time (s)	1.0
Instrument stabilization delay (s)	15
Pump rate (rpm)	15

Table 2
Heating program for microwave assisted digestion.

Steps	Power (W)	Time (min)	Temperature (°C)
1	800	3	100
2	800	2	100
3	1000	15	180
4	1000	2	180
5	1000	5	200
6	1000	15	200
Ventilation	–	10	–

Table 3
Matrix of the factorial design 2³.

Experiment	[HCL]	Flow rate	Power RF	Emission intensities
1	-1 (0.50)	-1 (0.35)	-1 (1.00)	5306
2	1 (3.00)	-1 (0.35)	-1 (1.00)	4446
3	-1 (0.50)	1 (0.45)	-1 (1.00)	4397
4	1 (3.00)	1 (0.45)	-1 (1.00)	3756
5	-1 (0.50)	-1 (0.35)	1 (1.30)	5624
6	1 (3.00)	-1 (0.35)	1 (1.30)	4847
7	-1 (0.50)	1 (0.45)	1 (1.30)	6095
8	1 (3.00)	1 (0.45)	1 (1.30)	5279
9 (C)	0 (1.75)	0 (0.40)	0 (1.15)	5377
10 (C)	0 (1.75)	0 (0.40)	0 (1.15)	5501
11 (C)	0 (1.75)	0 (0.40)	0 (1.15)	5454

The evaluation of the factorial design demonstrated that the factors: RF power (Effect = +985), hydrochloric acid concentration (Effect = -774) and the interaction (nebulizer gas flow rate) × (RF power) are significant.

The curvature with value of (-475) demonstrates that there is a maximum condition of emission intensity in the point central region.

Considering the result of the curvature test, a Box-Behnken design was performed being that the experimental conditions for these three factors and the response are shown in Table 4.

The evaluation of the data obtained in this design results in a quadratic model, which presents a maximum condition of emission intensity for the critical values of the factors studied. These coded and real values are shown in Table 5.

Considering these results, the experimental conditions established for the procedure are: hydrochloric acid concentration = 0.53 M, nebulizer gas flow rate = 0.40 mL min⁻¹ and RF power = 1.1 kW.

3.2. Validation studies

Firstly, the aluminum interference on the determination of gallium in the established conditions was evaluated. Seven gallium solutions (with concentration 1.0 mg L⁻¹) containing aluminum with concentration of 0.0, 100.0, 500.0, 1000.0, 2000.0, 3000.0, 4000.0 and 5000.0 mg mL⁻¹ were prepared, and gallium was quantified by ICP OES. The results in Fig. 1 demonstrated that aluminum with concentration higher than 500.0 mg mL⁻¹ decreases the emission intensity of gallium.

Considering these results, yttrium and scandium were tested as reference elements for elimination of the aluminum interference during the determination of gallium. It was possible; because some experiments evidenced that the emission intensities for these elements also decrease in similar form as aluminum. The addition analyte technique was established using a bauxite sample (with aluminum concentration of 3443.50 mg L⁻¹) and the gallium concentration was varied from 0.00 to 2.50 mg L⁻¹, six standard solutions were prepared. Yttrium

Table 4
Box-Behnken design.

Experiment	[HCL]	Flow rate	Power RF	Emission intensities
1	-1 (0.00)	-1 (0.30)	0 (1.20)	28
2	1 (3.00)	-1 (0.30)	0 (1.20)	27
3	-1 (0.00)	1 (0.40)	0 (1.20)	5506
4	1 (3.00)	1 (0.40)	0 (1.20)	5215
5	-1 (0.00)	0 (0.35)	-1 (1.00)	5391
6	1 (3.00)	0 (0.35)	-1 (1.00)	4369
7	-1 (0.00)	0 (0.35)	1 (1.40)	2228
8	1 (3.00)	0 (0.35)	1 (1.40)	1625
9	0 (1.50)	-1 (0.30)	-1 (1.00)	0
10	0 (1.50)	1 (0.40)	-1 (1.00)	4945
11	0 (1.50)	-1 (0.30)	1 (1.40)	0
12	0 (1.50)	1 (0.40)	1 (1.40)	3044
13	0 (1.50)	0 (0.35)	0 (1.20)	4681
14	0 (1.50)	0 (0.35)	0 (1.20)	4634
15	0 (1.50)	0 (0.35)	0 (1.20)	4717

Table 5
Coded and real values for the maximum condition of emission intensity.

Factor	Coded value	Real value
Hydrochloric acid concentration	-0.6472	0.53 M
Nebulizer flow rate	0.8032	0.39 mL min ⁻¹
RF power	-0.7234	1.06

and scandium with concentration of (10.0 mg L⁻¹) were tested as reference elements, being that the emission lines used for measured of these elements were 371.029 nm and 363.074 nm, respectively. The slopes (expressed as interval confidence) and correlation coefficients obtained in this experiment are shown in Table 6.

In this table, it can be seen that the results demonstrated that there is no significant difference between the slope obtained by external calibration technique using gallium standards in 0.53 M hydrochloric acid and the slopes achieved by reference element technique employing yttrium or scandium. So, it confirms that gallium can be determined directly in aluminum matrices using yttrium and scandium as reference element.

The precision was evaluated for two bauxite samples using the two reference elements. For a bauxite sample with gallium concentration of 21.00 mg Kg⁻¹, the precision expressed as relative standard deviation was 4.37% for scandium and 3.91% for yttrium. For another bauxite sample of concentration 36.00 mg Kg⁻¹, RSD was 1.78% for scandium and 2.02% for yttrium.

The limits of detection and quantification obtained were 0.0006 and 0.0019 mg L⁻¹, being determined as IUPAC recommendation. These limits calculated for sample mass of 0.20 g are 0.042 and 0.140 mg Kg⁻¹, respectively.

The accuracy was evaluated by analysis of the standard reference materials furnished by National Institute of Standards & Technology (NIST) 699 SRM alumina (reduction grade) and NIST 2702 inorganic in marine sediment. The results are shown in Table 7. The accuracy of the method was evaluated using these two certified samples because there is no certified reference material of bauxite with value of gallium certified.

3.3. Application

The procedure proposed was applied for the determination of gallium in five bauxite samples. Table 8 shows the results found using the two reference elements. A statistical test demonstrates that there is no significant difference between the results found using the two reference elements (yttrium and scandium) employed for correction of the aluminum interference.

The gallium concentrations found in these samples are in agreement with those results reported by literature [11,21,22].

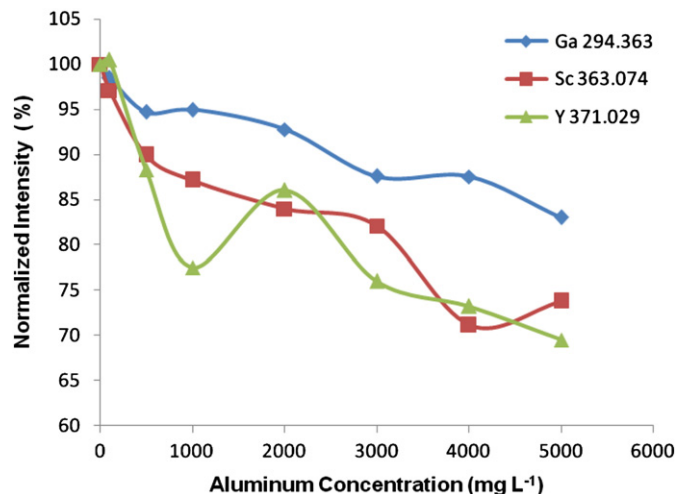


Fig. 1.

Table 6
Determination of the calibration technique of the method.

Calibration technique	Slopes	Determination correlation (R^2)
External calibration technique ^a	4016 ± 130	0.9995
Analyte addition technique using yttrium as reference element ^b	4200 ± 192	0.9989
Analyte addition technique using scandium as reference element ^b	4059 ± 265	0.9978
Analyte addition technique with correction ^b	3323 ± 139	0.9991

^a Gallium in 0.53 M hydrochloric acid solution.^b Analyte Addition technique on bauxite sample.**Table 7**
Evaluation of the accuracy of the method.

SRM	Certified value	Achieved value
Inorganics in marine sediment (NIST) 2702 SRM	(24.3 ± 1.9) mg Kg ⁻¹	(22.58 ± 0.47) mg Kg ⁻¹
Alumina (NIST) 699 SRM	(0.010 ± 0.002) %	(0.0104 ± 0.0003) ^a % and (0.0101 ± 0.0004) ^b %

^a Yttrium as RE.^b Scandium as RE.**Table 8**
Determination of gallium in bauxite samples ($N = 3$).

Samples	Gallium found using yttrium as RE (mg Kg ⁻¹)	Gallium found using scandium as RE (mg Kg ⁻¹)
1	20.72 ± 0.31	20.60 ± 0.78
2	20.00 ± 0.71	19.70 ± 0.88
3	32.17 ± 1.54	32.31 ± 1.75
4	37.04 ± 0.42	35.62 ± 0.61
5	100.59 ± 3.13	98.70 ± 0.48

4. Conclusions

The aluminum interference on the determination of gallium by ICP OES was studied and the results evidenced that it is a necessary correction.

Yttrium and scandium were tested as reference elements and the experiments proved that these elements are efficient for correction of the aluminum interference.

The method proposed has precision, accuracy and limit of quantification necessary for the determination of gallium in bauxite.

The method is very opportune considering, that the bauxite is the principal ore for obtaining gallium.

Acknowledgments

The authors are grateful to Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for providing grants and fellowships and for financial support.

References

- [1] R.R. Moskalyk, Gallium: the backbone of the electronics industry, *Miner. Eng.* 16 (2003) 921–929.
- [2] A.P. Chaves, A. Abrao, W. Avritscher, Gallium recovery as a by-product of bauxites, *Light Met.* 2000 (2000) 891–896.
- [3] M.T. Larrea, B. Zaldivar, J.C. Farinas, L.G. Firgaira, M. Pomares, Matrix effect of aluminium, calcium and magnesium in axially viewing inductively coupled plasma atomic emission spectrometry, *J. Anal. At. Spectrom.* 23 (2008) 145–151.
- [4] T. Ishizuka, Y. Uwamino, A. Tsuge, Determination of trace impurities high-purity aluminum oxide by inductively-coupled plasma atomic emission-spectrometry, *Anal. Chim. Acta* 161 (1984) 285–291.
- [5] M. Saleem, K. Anwar, D. Mohammad, Study of matrix effects on determination of trace elements in aluminum, using inductively coupled plasma atomic emission spectrometry, 1. Selection of spectral lines, *Anal. Lett.* 29 (1997) 1871–1881.
- [6] D.S. de Jesus, M.G.A. Korn, S.L.C. Ferreira, M.S. Carvalho, A separation method to overcome the interference of aluminium on zinc determination by inductively coupled plasma atomic emission spectroscopy, *Spectrochim. Acta B* 55 (2000) 389–394.
- [7] B.A. Zarcinas, Comparison of the lead 168-nm and 220-nm analytical lines in high iron and aluminium matrices by inductively coupled plasma-optical emission spectrometry, *Sci. Total Environ.* (2002) 241–244.
- [8] Z.G. Zhong, Q.Z. Bian, J.G. Zheng, P.L. Chen, C.H. Liu, X.Y. Wei, Study on the method for the determination of Fe, Si, Cu, Mg, Mn, Ni, Zn, Ti, Cr, Sr in aluminium alloy by ICP-AES, *Spectrosc. Spectr. Anal.* 22 (2002) 83–85.
- [9] A.L. Souza, S.G. Lemos, P.V. Oliveira, A method for Ca, Fe, Ga, Na, Si and Zn determination in alumina by inductively coupled plasma optical emission spectrometry after aluminum precipitation, *Spectrochim. Acta B* 66 (2011) 383–388.
- [10] J. Poledniok, A. Kita, P. Zerzucha, Spectrophotometric and inductively coupled plasma-optical emission spectroscopy determination of gallium in natural soils and soils polluted by industry: relationships between elements, communications in soil science and plant analysis, *Commun. Soil Sci. Plant* 43 (2012) 1121–1135.
- [11] S.V. Mahamuni, P.P. Wadgaonkar, M.A. Anuse, Liquid-liquid extraction and recovery of gallium(III) from acid media with 2-octylaminopyridine in chloroform: analysis of bauxite ore, *J. Serb. Chem. Soc.* 75 (2010) 1099–1113.
- [12] C.R.T. Tarley, G. Silveira, W.N.L. dos Santos, G.D. Matos, E.G.P. da Silva, M.A. Bezerra, M. Miró, S.L.C. Ferreira, Chemometric tools in electroanalytical chemistry: methods for optimization based on factorial design and response surface methodology — review article, *Microchem. J.* 92 (2009) 58–67.
- [13] J.S. Santos, L.S.G. Teixeira, R.G.O. Araújo, A.P. Fernandes, M.G.A. Korn, S.L.C. Ferreira, Optimization of the operating conditions using factorial designs for determination of uranium by inductively coupled plasma optical emission spectrometry, *Microchem. J.* 97 (2011) 113–117.
- [14] X. Vecino, R. Devesa-Rey, A.B. Moldes, J.M. Cruz, Optimization of batch operating conditions for the decolorization of vinasses using surface response methodology, *Microchem. J.* 102 (2012) 83–90.
- [15] S.L.C. Ferreira, R.E. Bruns, H.S. Ferreira, G.D. Matos, J.M. David, G.C. Brandão, E.G.P. da Silva, L.A. Portugal, P.S. dos Reis, A.S. Souza, W.N.L. dos Santos, Box-Behnken design: an alternative for the optimization of analytical methods, *Anal. Chim. Acta* 597 (2007) 179–186.
- [16] F. Kamarei, H. Ebrahimzadeh, Y. Yamini, Optimization of ultrasound-assisted emulsification microextraction with solidification of floating organic droplet followed by high performance liquid chromatography for the analysis of phthalate esters in cosmetic and environmental water samples, *Microchem. J.* 99 (2011) 23–26.
- [17] A. Salemi, E. Shafiei, M. Vosough, Optimization of matrix solid phase dispersion coupled with gas chromatography electron capture detection for determination of chlorinated pesticides in soil, *Talanta* 101 (2012) 504–509.
- [18] A.R. Fakhari, H. Tabani, H. Behdad, S. Nojavan, M. Taghizadeh, Electrically-enhanced microextraction combined with maltodextrin-modified capillary electrophoresis for quantification of tolterodine enantiomers in biological samples, *Microchem. J.* 106 (2013) 186–193.
- [19] H. Kola, P. Peramaki, The study of the selection of emission lines and plasma operating conditions for efficient internal standardization in inductively coupled plasma optical emission spectrometry, *Spectrochim. Acta* 59 (2004) 231–242.
- [20] G.A. Zachariadis, D.C. Vogiatzis, An overview of the use of yttrium for internal standardization in inductively coupled plasma-atomic emission spectrometry, *Appl. Spectrosc. Rev.* 45 (2010) 220–239.
- [21] M.S. Carvalho, J.A. Medeiros, A.W. Nobrega, J.L. Mantovano, V.P.A. Rocha, Direct determination of gallium on polyurethane foam by x-ray-fluorescence, *Talanta* 42 (1995) 45–47.
- [22] C.K. Bhat, Estimation of gallium in a bauxite-ore deposit using an energy-dispersive X-ray fluorescence technique, *Radiat. Phys. Chem.* 65 (2002) 193–197.