Talanta 84 (2011) 995–999

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Short communication

Determination of sulfur in biodiesel microemulsions using the summation of the intensities of multiple emission lines

Carl G. Young[a,*], Renata S. Amais[b], Daniela Schiavo[c], Edivaldo E. Garcia[d], Joaquim A. Nóbrega[b], Bradley T. Jones[a]

[a] Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109, USA
[b] Grupo de Análise Instrumental Aplicada, Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brazil
[c] Agilent Technologies, São Paulo, SP, Brazil
[d] Departamento de Química, Universidade Estadual de Maringá, Maringá, PR, Brazil

ARTICLE INFO

Article history:
Received 5 October 2010
Received in revised form
22 December 2010
Accepted 7 January 2011
Available online 15 January 2011

Keywords:
Biodiesel
Microemulsion
Inductively coupled plasma optical emission spectrometry (ICP OES)
Multiple lines
Summation of signal intensities

ABSTRACT

A method for the determination of sulfur in biodiesel samples by inductively coupled plasma optical emission spectrometry which uses microemulsion for sample preparation and the summation of the intensities of multiple emission lines has been developed. Microemulsions were prepared using 0.5 mL of 20% v/v HNO_3, 0.5 mL of Triton X-100, 2–3 mL of biodiesel sample, and diluted with n-propanol to a final volume of 10 mL. Summation of the emission intensities of multiple sulfur lines allowed for increased accuracy and sensitivity. The amounts of sulfur determined experimentally were between 2 and 7 mg L^{-1}, well below legislative standards for many countries. Recoveries obtained ranged from 72 to 119%, and recoveries obtained for the 182.562 nm line were slightly lower. This is most likely due to its lower sensitivity. Using microemulsion for sample preparation and the summation of the intensities of multiple emission lines for the successful determination of sulfur in biodiesel has been demonstrated.

1. Introduction

Due to the instability in the petroleum market in recent years, development of an alternative fuel is gaining increased importance. Moreover, the use of petrol products has inundated the environment with pollutants such as NO_x, SO_x, CO and metals such as Cd, Co, Cu, Pb, V, and Ni [1]. One alternative fuel attracting a lot of attention in publications and government agencies is biodiesel. Biodiesel is created by the alcoholic transesterification of vegetable oil, vegetable fat, or animal fat in the presence of catalyst [2]. Biodiesel is advantageous to the environment because it is mainly produced from renewable resources.

Limits to the sulfur content in biodiesel have been restricted by certain governments and agencies across the world. According to EN 14214 in Europe, the maximum allowable amount of sulfur in biodiesel is 10 mg kg^{-1}, compared with that of 500 mg kg^{-1} according to ASTM D6751 in the United States [3]. Although, the sulfur content in biodiesel is generally believed to be between 0.2 and 25 mg kg^{-1}, depending on the feedstock and the supplier [4]. In order to measure such low levels, analytical methods with high sensitivity are needed. However, relatively little work is described in the literature regarding the analysis of sulfur in biodiesel. The published work for sulfur analysis ranges from chromatographic to spectroanalytical methods. A combustion ion chromatographic system has been described for the simultaneous, speciated analysis of halides (F, Cl, Br, and I) and sulfur compounds in any non-aqueous sample matrix [5]. Detection limits in the sub-ppm range were reported. X-ray fluorescence may be successfully applied for determining S in petroleum diesel because it is rapid, precise, inexpensive, and accurate if properly calibrated [4]. X-ray fluorescence with gravimetric standard additions method was performed for the determination of S in biodiesel to help overcome the *ca.* 16% low bias caused by an oxygen matrix effect [4]. The use of the standard additions method overcame the low biased measurements obtained with using petroleum diesel for calibration at the 3, 7, and 12 mg kg^{-1} levels. However, if hundreds of biodiesel samples are to be analyzed, using the standard additions method may be impractical.

Ultrasound-assisted oxidative desulfurization is used for the removal of sulfur from petroleum product feedstock [6]. Under optimized conditions, the sulfur removal was about 95% after 9 min of ultrasonic irradiation using hydrogen peroxide and acetic acid, followed by extraction with methanol. However, the procedure developed by Mello et al. is strictly for sulfur removal and not quan-

---

* Corresponding author.
E-mail address: youncg7@wfu.edu (C.G. Young).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.01.008

tification. The total amount of sulfur had to be determined by other spectroscopic techniques such as ultraviolet fluorescence and ICP OES.

Sample preparation is a critical step in any analytical procedure. Microwave-assisted digestion in a closed system was compared to an open system with conventional heating for the simultaneous determination of Ca, P, Mg, K, and Na in biodiesel by ICP OES with axial viewing [7]. The optimized microwave assisted digestion procedure provided recoveries of 89.0–103.0% and deviations lower than 5%, in most cases. Microwave-assisted digestion procedures are desirable because they do not require the preparation of calibration standards, or the use of toxic solvents [7]. Organic samples may also be analyzed by emulsions. An emulsion is a heterogeneous system made up of two liquid phases, one of them dispersed in the other by means of a mechanical process [1]. Murillo and Chirinos emulsified NIST crude oil samples in water for the determination of S, Ni, and V in crude oil [8]. Aqueous calibration standards were made with the same amount of emulsifier and solvent. No statistically significant differences were reported for the results of their method and the certified values. Emulsions are not very stable systems and have a problem with the miscibility of the liquids, although adding surfactant can improve emulsion stability [1].

Alternatively, a microemulsion is a transparent, three component system composed of water, oil, and an amphiphilic compound, such as an alcohol [2]. The benefits to using a microemulsion are the following: instant formation, thermodynamically stable, and possesses low viscosity [2]. The main difference between an emulsion and a microemulsion is the droplet size. Since a microemulsion shows characteristic structural dimensions between 5 and 100 nm, the medium present is a poor scatter of visible light, thus transparency is a consequence [9]. Perhaps the biggest advantage that microemulsions provide is the ability to use an inorganic standard to perform a matrix matched calibration [11]. Preparation of calibration solutions with a matrix that matches that of the sample will provide accurate results. Direct introduction of biodiesel samples into an ICP-MS by using microemulsions for the determination of Cd, Co, Cu, Mn, Ni, Pb, Ti, and Zn has been described [12]. An argon–oxygen gas mixture was introduced to the plasma as an auxiliary gas to help correct any matrix effects caused by the high carbon load from the microemulsion preparation.

In this work, an analytical procedure using microemulsion for sample preparation and the summation of the intensities of multiple emission lines was evaluated for the determination of sulfur in biodiesel samples made from different vegetable and animal sources. The summation of signal intensities was recently demonstrated for ICP-OES measurements [10]. In order to avoid out-of-control error propagation some criteria should be met for successfully applying the summation of signal intensities procedure:

1. No line added should be critically affected by spectral interferences.
2. No line added may present poor repeatability for successive measurements of signal intensities.
3. Lines with very low relative intensities should not be used because their contribution to sensitivity will be minor, but they may exert a major effect on repeatability.
4. Samples with a deviation higher than ±20% should be omitted from calculating the mean sample concentration value in order to avoid bias to the global data.

These criteria must be applied when the analyte presents a large number of suitable emission lines, but they may be too restrictive for elements with a lower number of emission lines which are also less intense.

Table 1
ICP OES instrument parameters.

Parameter	Value
Generator frequency (MHz)	40
Torch Inner diameter	2.3 mm
Sample introduction system	
Spray chamber	Cyclonic
Nebulizer	Concentric
RF applied power (kW)	1.4
Signal integration time (s)	1.0
Plasma gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	1.5
Oxygen flow rate (mL min^{-1})	165.0
Nebulizer gas flow rate (L min^{-1})	0.7
Sample flow rate (mL min^{-1})	1.0

2. Materials and methods

2.1. Instrumentation and operating conditions

An inductively coupled plasma optical emission spectrometer (Varian Vista AX, Mulgrave, Australia) with an axially viewed configuration and CCD solid state detector cooled at −35 °C by a Peltier system was employed. The echelle polychromator was thermostated and allows for spectral measurements in the 174–766 nm range. An additional gas flow controller (AGM-1, Varian) for adding oxygen (99.99%, White Martins, Sertãozinho, SP, Brazil) as auxiliary gas in the ICP was used. Instrumental parameters are summarized in Table 1.

2.2. Chemicals and reagents

All reagents used were of analytical grade unless otherwise specified. Solutions were prepared with distilled and deionized water obtained by using a Milli-Q® system (Millipore, Billerica, MA, USA) to a resistivity of 18.2 MΩ cm. In order to avoid contamination, all glassware and polypropylene flasks were washed and soaked in a 10% v/v HNO_3 solution and rinsed thoroughly with deionized water prior to use.

For microemulsion preparation, HNO_3 (Merck, Darmstadt, Germany) previously purified using a sub-boiling system (Milestone, Sorisole, Italy) was used. Polyoxylene (10) octylphenil ether (Triton X-100) (Acros Organics, Morris Plains, NJ, USA), n-propanol, and a certified MR-1824 light mineral oil (Tedia, Rio de Janeiro, RJ, Brazil) were used without subsequent purification. Sulfur calibration solutions were prepared by dilution from a 1000 mg L^{-1} S stock solution (Qhemis High Purity, Hexis, São Paulo, SP, Brazil).

The biodiesel samples were composed of the following mixtures: soy oil and cooking oil, soy oil and cottonseed oil, soy oil and beef tallow.

2.3. Microemulsion preparation

A homogenous, transparent microemulsion was obtained when 0.5 mL of 20% v/v HNO_3, 0.5 mL of Triton X-100, and 2–3 mL of biodiesel sample was added to graduated polypropylene flasks. The solution was diluted with n-propanol to a final volume of 10 mL. The mixture was homogenized using a vortex mixer for 2 min.

A similar procedure was used for the preparation of reference solutions. To obtain a similar matrix to the biodiesel samples, 0.4 mL of mineral oil was added to the microemulsion. It was demonstrated that adding a fivefold lower volume of mineral oil than biodiesel adjusts the solution viscosity so that variations in aspiration rate and aerosol formation are avoided [12]. A small amount of the inorganic standard was added so that the microemulsion would be stable. The maximum concentration of reference solution used was 50 mg L^{-1}. However, it should be pointed out that this solu-

Table 2
Emission lines used for signal summation.

Element	Wavelength (nm)	Relative intensity[a]
S (I)	181.972	323.6
S (I)	180.669	304.0
S (I)	182.562	77.7

[a] Relative intensities obtained from the Varian ICP Expert Database.

Table 3
Analytical figures of merit for the method.

λ (nm)	Precision (%RSD)	Sensitivity	Linear dynamic range
181.972	1.98	132.02	1.9
180.669	2.28	113.76	2.4
182.562	27.66	42.92	1.8
181.972 + 180.669	1.64	245.78	2.1
181.972 + 182.562	2.23	174.94	1.9
180.669 + 182.562	4.50	156.68	2.1
181.972 + 180.669 + 182.562	1.82	288.70	2.0

Table 4
Detection limits, PRESS, and RMSEP for the lines and combinations of emission lines.

	Wavelength (nm)	LOD (mg L^{-1})	PRESS	RMSEP
1	181.972	0.60	1.2768	0.5053
2	180.669	0.21	0.0892	0.1336
3	182.562	0.80	1.8026	0.6004
1 + 2	181.972 + 180.669	0.42	0.5314	0.3260
1 + 3	181.972 + 182.562	0.63	0.2846	0.2386
2 + 3	180.669 + 182.562	0.36	0.0473	0.0973
1 + 2 + 3	181.972 + 180.669 + 182.562	0.46	0.1829	0.1913

Table 5
Addition and recovery experiment for sample C.

λ (nm)	% recovery of sample C
181.972	119
180.669	108
182.562	93.0
181.972 + 180.669	114
181.972 + 182.562	113
180.669 + 182.562	104
181.972 + 180.669 + 182.562	111

tion was opaque after being vortexed, and cannot be considered a microemulsion.

3. Results and discussion

3.1. Behavior of sulfur in the ICP OES

Sulfur determination in aqueous media is nontrivial. Sulfur has elevated ionization energy (10 eV) [13] and its main emission lines from the plasma are in the vacuum ultraviolet (110–200 nm) due to its electronic structure. It is reasonable to presume that sulfur determination in organic media will present difficulties as well. Selection of a single, sensitive emission line not affected by matrix effects may be critical for quantitative determinations in ICP OES when working with less sensitive elements.

It has been suggested that the use of multiple emission lines to carry out quantitative analysis may improve the sensitivity, precision and accuracy, and provide high flexibility in the measurements, such as expansion of the linear range [10]. Factors to consider for selecting the best emission line or combination of are elevated slope, a correlation coefficient (r) close to unity, a near zero intercept, and emission lines with the best accuracy [10]. Two additional parameters were also used to aid in the selection as well: PRESS (predicted error sum of squares) and RMSEP (root mean square error of prediction). The best combinations of lines have low PRESS and RMSEP values. The summation of intensities of multiple emission lines was performed after selecting three lines with the highest intensity. All possible combinations between these lines were tested. Table 2 lists the emission lines used for this work.

The propagation of error using the summation of intensities of multiple emission lines needs to be considered. Plots of the logarithm of the signal versus the logarithm of the signal-to-noise ratio (S/N) were constructed for all emission lines used, and the dominant source of noise present at each emission line was determined. The log–log plot for the 182.562 nm emission line is the most illustrative plot, and its result can be seen in Fig. 1.

The major source of noise present at 182.562 nm is a combination of shot noise and detector noise, as evidenced by the slope of the log–log plot having a value of 0.85. The log–log plots for the other emission lines had similar slopes (not shown in Fig. 1), thus the major source of noise present at those emission lines is also a combination of shot noise and detector noise. In addition, a graph of all the measured noise points for the 181.972 nm + 180.669 nm and 181.972 nm + 180.669 nm + 182.562 nm emission line combinations versus the calculated quadratic sum of the individual noises for those same points was constructed, and can be seen in Fig. 2.

Below a threshold of approximately 30 signal units, the measured noise is often less than the calculated noise using the quadratic sum. In this region, detector noise and shot noise are expected to be the major noise sources, and the measured value results in a significant improvement of the S/N. Above the threshold, the measured noise is often larger than the calculated noise.

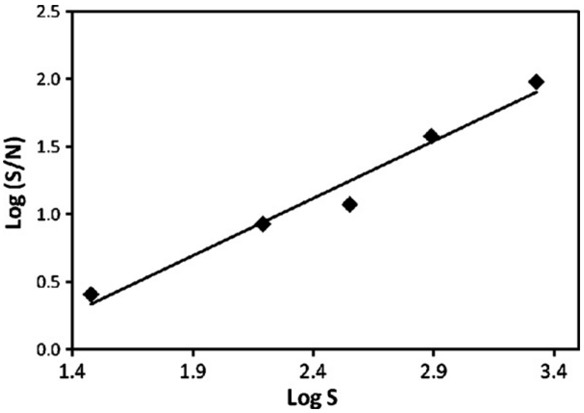

Fig. 1. Noise source determination for 182.562 nm.

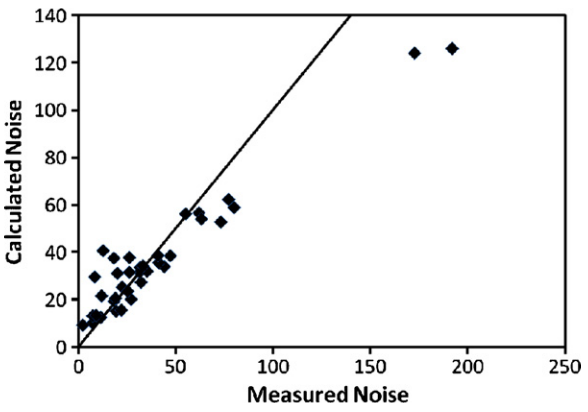

Fig. 2. Comparison of measured noise and calculated noise for emission line combinations 1 + 2 and 1 + 2 + 3.

Table 6
Sample volumes and recoveries.

λ (nm)	Sample D		Sample E		Sample F	
	% recovery of 2.5 mL spike	% recovery of 3 mL spike	% recovery of 2.5 mL spike	% recovery of 3 mL spike	% recovery of 2.5 mL spike	% recovery of 3 mL spike
181.972	109	105	98.0	96.5	96.0	105
180.669	106	90.4	105	91.6	88.3	87.4
181.972 + 180.669	108	98.5	101	94.6	92.9	97.7
181.972 + 182.562	95.0	93.4	91.5	85.6	98.8	97.0
180.669 + 182.562	89.9	81.5	93.4	78.2	93.6	80.3
181.972 + 180.669 + 182.562	98.8	92.4	95.8	87.6	95.0	93.5

In this region, flicker noise and shot noise are expected to be the dominant noise sources, so no improvement in the S/N will be observed.

One aspect to keep in mind when considering the choice of emission lines is the spectral environment. The background emission at one line could be considerably different from the background emission at another line. A reasonable presumption is that most emission lines are free from spectral interferences, but this is critically dependent on the complexity of the sample medium. Back calculating the analyte concentration from emission intensities should lead to the same analyte concentration. However, emission lines affected by interference would produce results that deviated from an assumed threshold value. If this is the case, the concentration value obtained from this emission line should be omitted from the calculation of the mean concentration value. It has been suggested that samples with a deviation higher than 20% should not be used in the calculation of the mean concentration value [10]. Using the summation procedure may overcome any interference caused by the spectral environment and provide more accurate results for sulfur determination.

The oxygen gas flow rate in the composition of the auxiliary gas was optimized, taking into account signal intensity and signal to background ratio (SBR). The oxygen gas flow rate was varied from 12.5 to 212.5 mL min^{-1}, and the variation of signal intensity and SBR was not significantly different. Thus, an oxygen gas flow rate of 165 mL min^{-1} was chosen because observed Swan bands were very low.

The nebulization gas flow rate also had to be considered, and it was evaluated from 0.7 to 1.0 L min^{-1}. When the nebulization gas flow rate was increased, a decrease of signal intensity was observed, while the SBR value became slightly lower. Therefore, 0.7 L min^{-1} was used for subsequent experiments. It is important to mention that under the optimized conditions, carbon deposits on the torch were not observed.

Analytical figures of merit are an indication of how well an instrumental technique performs for the method of analysis. The figures of merit calculated for this method include accuracy, precision, sensitivity, detection limit, linearity, and linear dynamic range. Analytical figures of merit can be seen in Table 3.

The accuracy of the method will be discussed further below. The detection limits were calculated using the concept of background equivalence concentration (BEC). The BEC is defined as the concentration of analyte that produces a signal equal to the background emission intensity at the spectral line of interest. Limits of detection were calculated for all of the combinations used and can be seen in Table 4.

3.2. Determination of sulfur in biodiesel

Accuracy is how close an obtained experimental value is to a certified or theoretical value. Addition and recovery experiments were performed in order to determine the accuracy of the method. In one approach, a known amount of sulfur standard was spiked into the microemulsion prepared for sample C. Results can be seen in Table 5.

All recoveries were acceptable, and between 93% and 119%. This indicates that a minimal amount of amount of sulfur is lost to the microemulsion preparation, followed by ICP OES determination. The lowest recovery obtained was 93% for the 182.562 nm line. The slightly lower recovery obtained for this line is most likely due to the lower relative intensity of the 182.562 nm line. Further accuracy experiments were performed to double check the validity of the traditional accuracy determination.

In the second approach, 2.5 mL and 3 mL of biodiesel sample were added to the microemulsion for samples D–F, and the results were compared to the result obtained when 2 mL of biodiesel was added. Results can be seen in Table 6.

The recoveries were mostly between 78% and 109%. It must be pointed out that the recoveries obtained for the 182.562 nm line were in general lower than those obtained for the other lines and combinations, i.e. from 51.6 to 71.1% for 5 of the 6 samples (not shown in Table 6). This is most likely due to 182.562 nm having the least sensitivity when compared to the other lines. The recoveries produced for the internal recovery are normalized to the theoretical amount of intensity increase expected. For this reason, it appears that the recoveries are slightly lower than the traditional recovery experiment mentioned above.

It was presumed that using the best combination of emission lines would provide better accuracy than using the most intense emission line alone. In a third approach, the amount of sulfur was determined using different emission lines and their combinations. The amounts of sulfur determined in the biodiesel samples can be seen in Table 7.

Table 7
Sulfur determination in biodiesel samples.

λ (nm)	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
181.972	2.70	1.62	5.72	5.80	6.73	7.23
180.669	3.58	1.71	5.57	5.16	5.13	5.59
182.562	5.14	4.42	6.25	7.07	6.93	3.96
181.972 + 180.669	3.10	1.65	5.64	5.50	5.98	6.46
181.972 + 182.562	3.23	2.24	5.79	6.05	6.72	6.37
180.669 + 182.562	3.98	2.42	5.73	5.65	5.59	5.12
181.972 + 180.669 + 182.562	3.37	2.03	5.70	5.70	6.09	6.07
Average concentration ± std dev (mg L^{-1})	3.59 ± 0.79	2.30 ± 0.98	5.77 ± 0.22	5.85 ± 0.60	6.17 ± 0.67	5.83 ± 1.06

The amount of sulfur found in each sample is between 2 and 7 mg L^{-1}, below the 10 mg kg^{-1} requirement by EN 14214 and 500 mg kg^{-1} by ATSM D6751 in the US [3]. Very similar sulfur concentrations have been obtained when the sulfur concentration was determined using different emission lines. The amounts of sulfur determined from emission lines with the highest relative intensity were the most similar. Emission lines with lower relative intensity produced sulfur concentrations that deviated slightly from the other values. When the combination of lines was used, the line with the higher relative intensity has greater influence on the concentration of sample determined. As a result, the magnitude of the deviation in the sample concentration is lessened.

The three pronged approach for accuracy determination has produced interesting results. Recoveries for the traditional spiking of a known amount of standard into sample C and the internal recovery approach were acceptable. Since the recoveries obtained from both approaches were near 80% and above, either approach will produce accurate results. However, the internal recovery approach may be the best to use if any matrix effects are likely. Adding increased amounts of the same sample will presumably have identical qualitative matrices, but with larger amounts of concomitants. The amount of sulfur determined at each emission line and their combinations was very similar. Based upon the experimental evidence, the accuracy of the method for the determination of sulfur in biodiesel has been established using simple and easily implemented approaches.

4. Conclusions

In the proposed procedure, an alternative approach for sample preparation was demonstrated by simple and fast microemulsion formation. The main advantages compared to the dilution method are the use of inorganic standards in the microemulsions for calibration and the non-use of carcinogenic organic solvents. The summation of the intensities of multiple emission lines in ICP OES was successful for the determination of sulfur in biodiesel samples and it allows for better sensitivity, and good accuracy.

Acknowledgements

The authors would like to thank the Richter Scholarship for research funding. The authors would like to extend their extreme gratitude to the Center for Characterization and Development of Materials (CCDM), UFSCar-UNESP, São Carlos, SP, Brazil for the ICP OES used for this work. Grant funds provided by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Grant 2006/59083-9) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, INCTAA) are appreciated. The authors are also thankful to Prof. Dr. Edenir Rodrigues Pereira Filho for helpful discussions about data treatment.

References

[1] E.S. Chaves, T.D. Saint'Pierre, E.J. dos Santos, L. Tormen, V.L.A.F. Bascuñan, A.J. Curtius, J. Braz. Chem. Soc. 19 (2008) 856–861.
[2] J.S.A. Silva, E.S. Chaves, E.J. dos Santos, T.D. Saint'Pierre, V.L.A. Frescura, A.J. Curtius, J. Braz. Chem. Soc. 21 (2010) 620–626.
[3] I.P. Lôbo, S.L.C. Ferreira, R.S. da Cruz, Quim. Nova 32 (2009) 1596–1608.
[4] L.R. Barker, W.R. Kelly, W.F. Guthrie, Energy Fuels 22 (2008) 2488–2490.
[5] C. Emmenegger, A. Wille, A. Steinbach, LC–GC North America (June (Suppl. S)) (2010) 40–43.
[6] P.A. Mello, F.A. Duarte, M.A.G. Nunes, M.S. Alencar, E.M. Moreira, M. Korn, V.L. Dressler, E.M.M. Flores, Ultrason. Chem. 16 (2009) 732–736.
[7] M.G.A. Korn, D.C.M.B. dos Santos, M.A.B. Guida, I.S. Barbosa, M.L.C. Passos, M.L.M.F.S. Saraiva, J.L.F.C. Lima, J. Braz. Chem. Soc. 21 (2010) 2278–2284.
[8] M. Murillo, J. Chirinos, J. Anal. At. Spectrom. 9 (1994) 237–240.
[9] J.L. Burguera, M. Burguera, Talanta 64 (2004) 1099–1108.
[10] D. Schiavo, L.C. Trevizan, E.R. Pereira-Filho, J.A. Nóbrega, Spectrochim. Acta Part B 64 (2009) 544–548.
[11] R.Q. Aucélio, A. Doylea, B.S. Pizzornoa, M.L.B. Tristão, R.C. Campos, Microchem. J. 78 (2004) 21–26.
[12] R.S. Amais, E.E. Garcia, M.R. Monteiro, A.R.A. Nogueira, J.A. Nóbrega, Microchem. J. 96 (2010) 146–150.
[13] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 89th ed., CRC Press, Boca Raton, 2008.