J. Braz. Chem. Soc., Vol. 21, No. 12, 2278-2284, 2010.
Printed in Brazil - ©2010 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Evaluation of Digestion Procedures for Simultaneous Determination of Ca, P, Mg, K and Na in Biodiesel by Inductively Coupled Plasma Optical Emission Spectrometry

Maria Graças A. Korn,*[,a] Daniele Cristina M. B. Santos,[a] Mauro Agildo B. Guida,[a] Isa S. Barbosa,[a] Marieta L. C. Passos,[b] Maria Lúcia M. F. S. Saraiva[b] and José Luis F. C. Lima[b]

[a] *Grupo de Pesquisa em Química Analítica, Instituto de Química, Universidade Federal da Bahia, Campus de Ondina, 40170-115 Salvador-BA, Brasil*

[b] *REQUIMTE, Departamento de Química, Faculdade de Farmácia, Universidade do Porto, Rua Aníbal Cunha, 164, 4099-030 Porto, Portugal*

Neste trabalho foi avaliada a eficiência de dois procedimentos para digestão ácida de amostras de biodiesel visando à determinação de Ca, P, Mg, K e Na por espectrometria de emissão óptica com plasma acoplado indutivamente com configuração axial (ICP OES). Nas digestões em sistema aberto, foi utilizada a mistura contendo ácidos nítrico, sulfúrico e peróxido de hidrogênio e aquecimento condutivo; enquanto que no procedimento empregando forno de microondas com cavidade foi utilizada a mistura contendo ácido nítrico e peróxido de hidrogênio. Os procedimentos foram avaliados considerando-se limites de quantificação, precisão, acidez final dos digeridos e teor de carbono residual. Os teores de carbono residual nos digeridos foram 0,358 ± 0,012% para o sistema aberto com aquecimento convencional e 0,614 ± 0,023% para o sistema fechado com aquecimento assistido por radiação microondas, o que demonstra a alta eficiência dos procedimentos propostos. O sistema de digestão em forno de microondas com cavidade resultou em maior rapidez, segurança e resultados analíticos com percentuais de recuperação de 89,0-103,0% e desvios menores que 5%. Os limites de detecção obtidos, ≤ 0.40 µg g^{-1}, são adequados para a determinação dos analitos, conforme os limites estabelecidos na legislação brasileira. Três amostras de biodiesel produzidas de diferentes fontes foram analisadas. Em comparação com outros procedimentos propostos na literatura, o procedimento desenvolvido usando forno de microondas com cavidade apresenta vantagens, tais como não necessitar de soluções orgânicas para calibração e não usar solventes orgânicos tóxicos.

In the present work, the efficiency of two procedures for the digestion of biodiesel was investigated for the simultaneous determination of Ca, P, Mg, K and Na by axial view ICP OES. In the open system with conventional heating, concentrated nitric and sulfuric acids were added to the samples, and the addition of hydrogen peroxide completed the digestion. In the microwave-assisted closed system, complete digestion was performed using concentrated nitric acid and hydrogen peroxide. The analytical performances were evaluated through limits of quantification, precision of the overall procedures, final acidity of the digests, and residual carbon contents. The contents of residual carbon for the biodiesel samples digested were 0.358 ± 0.012% using the open system with conventional heating and 0.614 ± 0.023% using the microwave-assisted closed vessel system, demonstrating the high efficiency of both proposed procedures. The optimized microwave-assisted decomposition procedure produced the fastest, safest and most accurate analytical results with recoveries of 89.0-103.0% and deviations lower than 5% in most cases. Low limits of detection were obtained (≤ 0.40 µg g^{-1}), adequate for the established limits set out in Brazilian legislation for these analytes. Three biodiesel samples produced from different oil sources were analyzed. In comparison with other procedures proposed in the literature, the developed procedure using the microwave-assisted closed system is advantageous because it neither require organic standard solutions for calibrations nor use toxic organic solvents.

Keywords: biodiesel, sample preparation, metals, phosphorus, ICP OES

---

*e-mail: korn@ufba.br

Introduction

Biodiesel represents a promising substitute for fossil fuels since it is derived from renewable energy resources. Biodiesel can be obtained through trans-esterification of the triglycerides of oils and fats of vegetable or animal origin with a short chain mono-alcohol (typically methanol or ethanol) in the presence of catalysts, producing a mixture of ethyl or methyl ester (biodiesel) together with a byproduct, glycerin. Various sources of vegetable oil exist for the production of biodiesel such as: palm, soybean, rape, castor bean, avocado, cotton, peanut and sunflower. In addition to the existing sources of vegetable oils there are also oils derived from residual frying and animal fats. The source for the production of biodiesel is chosen according to viability in each region or country, percentage oil in each plant and oil production per hectare.[1,2]

In the evaluation of quality control in biodiesel, apart from structural analysis, the determination of inorganic constituents is also important since high concentrations can cause environmental problems and engine damage. The determination of K and Na is particularly important since some biodiesel production processes utilize KOH or NaOH as catalysts. Phosphorus has a strongly negative impact on the long term activity of exhaust emission catalytic systems. It poisons the catalytic converters in the exhaust system of diesel engines, increasing the emission of CO, CO_2, SO_2, hydrocarbon and particulate materials and may affect fuel behavior. In addition to these elements, the monitoring of Ca and Mg is also important since these elements form undesirable compounds in the engine.[1-3] In Brazil, the specifications for quality control of biodiesel have been developed and controlled by the National Petroleum, Natural Gas and Biofuel Agency (ANP). For pure biodiesel (B100), ANP published Resolution 07/2008[3] which regulates the specifications and standard tests to monitor biodiesel quality. Standards ASTM 6751[4] and EN 14214[5] also specify the limits and methods to be used in biodiesel quality control.[2]

Inductively coupled plasma optical emission spectrometry (ICP OES) has been employed for the determination of metals due principally to its multi-element capacity, wide linear dynamic range and applicability to many sample types. The determination of Ca, P, Mg, K and Na in biodiesel by ICP OES has been proposed after dissolution with kerosene or ethanol and using an argon–oxygen mixture as the nebulizer gas in an effort to deal with the organic load in the plasma.[6-9] However the commented methods do have some disadvantages such as the low stability of the analyte in the organic diluted standard solutions, the fact that an oxygen flow can be added to the auxiliary argon flow to decrease the background, the need for organometallic standards for calibration, and the use of dangerous organic solvents that require special handling conditions (mask and gloves).[9] Alternatively, biodiesel samples may be prepared as a micro-emulsion due to the homogeneous dispersion and stabilization of the oil micro-droplets in the aqueous phase, which brings the viscosity close to that of an aqueous solution and reduces the organic load in the system.[10-14] However, this promotes a high sample dilution and has also required specific accessories for sample introduction. In a recent paper, an alternative procedure for sodium determination in biodiesel by flame atomic emission spectrometry (FAES) using dry decomposition for the sample preparation was proposed.[15]

Considering the above-mentioned difficulties and the lack of information on digestion procedures for this type of matrix, the objective of this work was to study and compare two wet digestion procedures for the simultaneous determination of Ca, P, Mg, K and Na by axial view ICP OES. Analytical performances, such as limits of detection and quantification, precision of the overall procedures and accuracy were assessed statistically to optimize the ICP OES parameters and to evaluate the investigated procedures. Optimized procedures were applied to various biodiesel samples.

Experimental

Reagents, solutions and samples

All chemicals used were of analytical reagent grade with no further purification and water from a MilliQ plus system (Millipore, Billerica, MA, USA) of specific conductivity lower than 0.1 µS cm^{-1} was used throughout.

Mineral acids and oxidizing agents 65% v/v HNO_3 (d = 1.40 kg L^{-1}), 30% (m/m) H_2O_2 (d = 1.11 kg L^{-1}), 97% v/v H_2SO_4 (d = 1.84 kg L^{-1}) were used. Multi-element working standard solutions containing 50 mg L^{-1} of Ca, K, Mg, Na and P were prepared from 1000 mg L^{-1} stock solutions (Merck).

For the determination of residual carbon, working solutions were prepared from a stock urea solution (5000 mg L^{-1} C stock solution).

The samples of castor bean, palm and soybean biodiesel were obtained from researchers at the Bahia State Universities, through the RECOMBIO-CNPq network.

Instrumentation and apparatus

Digestion by conductive heating was made in a heating block (Model TE-040/25) with temperature controller and capacity for 40 borosilicate tubes (25 × 250 mm).

The cavity-microwave oven (Model Ethos EZ - Milestone, Sorisole, Italy) incorporates a rotor for 10 flasks of 100 mL produced in TFM® (PTFE modified) and operates at high temperatures and pressures. This system permits the coupling of sensors for temperature and pressure which makes it possible to accompany the digestion system and promote a greater operational security.

All measurements were carried out using a simultaneous axial view ICP OES spectrometer, model VISTA PRO (Varian, Mulgrave, Australia). The optical system of the ICP OES was calibrated with a multi-element stock solution while the optical alignment utilized a solution containing 5.0 mg L^{-1} of Mn. Spectral lines were selected according to the absence of spectrum interferences and adequate sensitivity for the determination of elements in low and high concentrations. Table 1 shows the operational conditions adopted.

Table 1. Optimized operational conditions for multi-element ICP OES determinations in digested biodiesel samples

RF incident power (W)	1300	
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})	0.70	
Nebulizer	V-groove	
Spray chamber	Sturman-Master	
Replicate read time (s)	1	
Instrument stabilization delay (s)	15	
Solution flow rate, mL min^{-1}	0.8	
Spectral lines (nm)	C (II) 193.024 K (I) 766.468 Mg (II) 280.267 P (I) 177.434	Ca (II) 396.847 Mg (I) 285.209 Na (I) 589.592 Y$^{(a)}$ (II) 371.029

$^{(a)}$ internal standard (1.0 mg L^{-1}); (I) atomic emission line; (II) ionic emission line.

An Analytik Jena contrAA 300 high-resolution atomic absorption spectrometer equipped with a 300W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany) as a continuum radiation source was used for Na and K determination in castor bean and soybean biodiesel samples. Measurements were carried out in the following wavelengths (in nm): Na (588.9953), and K (766.4908).

Digestion procedures

Two different procedures were applied to digest the three different types of biodiesel samples. In both cases, three digestion blanks were prepared together with each sample batch.

Due to the unavailability of a certified reference material for this study, the accuracy was checked by analyte recovery test. Samples were spiked with 2 and 5 µg g^{-1} of the multi-element solution biodiesel samples. These samples were digested following the same procedures as that of the others.

Open system with conventional heating (WD1)

The following procedure was used: masses of 1.000 g of each sample was weighed in borosilicate tubes, followed by the initial addition of 5.0 mL HNO_3 + 2.0 mL H_2SO_4 + 1.0 mL of H_2O_2. The temperature was adjusted to 90 °C and maintained constant for 2 h. Thereafter, a further 3.0 mL of HNO_3 and 1.0 mL of H_2O_2 were added and the temperature of the hot plate adjusted to 220 °C. After 40 min a further addition of 2.0 mL HNO_3 and 4.0 mL H_2O_2 was made. The total time for the procedure was 3 h and the final dilution was made to 10 mL.

Closed system with microwave-assisted radiation (WD2)

About 250 mg of each sample was accurately weighed into dry, clean microwave closed vessels made of perfluoroalcoxi polymer (PFA) with a volume of 100 mL. Volumes of 7.0 mL HNO_3 were added. After the selected pre-digestion time (30 min), 1.0 mL of H_2O_2 was added and the vessels were gently shaken and sealed. The heating program was performed in five steps: (1) 4 min at 500 W; (2) 2 min at 750 W; (3) 6 min at 1000 W; (4) 10 min at 1000 W; and (5) 5 min at 750 W and finally 15 min for ventilation before removing the microwave digestion rotor from the microwave oven. The digestion time was approximately 42 min in total. Temperature and pressure sensors were used in all digestions. After digestion, samples and blank solutions were transferred to 25 mL volumetric flasks and the volume was made up with distilled-deionized water.

Determination of the acidity and residual carbon of the digests

To determine the final acidity, acid-base titrations of the digests were made for the above-mentioned procedures. The titration was carried out with a standard solution of sodium hydroxide (0.0997 mol L^{-1}) and phenolphthalein (1.0% m/v in ethanol). The standards for the analytical calibration curve were prepared with the same acid concentration for each digestion procedure. Residual carbon was also measured in the ICP OES using urea for preparing the standard solutions of carbon for the construction of the analytical calibration curve.[16]

Matrix effect and internal standard evaluation

Matrix effect studies were carried out by spiking some of the original undigested samples with variable amounts of standard solution of the metals. Spiked samples were then mineralized using the same digestion procedures as those applied to the non-spiked samples. All digestions were performed in triplicate.

For all samples and reference solutions in nitric/sulfuric medium, yttrium was used as internal standard at the final concentration of 1.0 mg L^{-1}. The digests were analyzed by ICP OES using conventional calibration and internal standard calibration.

Results and Discussion

Optimization of ICP OES parameters

It is important to optimize ICP OES parameters in the presence of the sample matrix because the intensity and shapes of the element signals clearly depend on the matrix. In this study, the instrumental parameters namely radio-frequency (RF) incident power and nebulizer argon gas flow rate were optimized using the digested biodiesel matrix rather than aqueous standard solution. These parameters exert a significant effect on emission intensities and, depending on the type of emission line, they are subjected to change. In this study, two calibration techniques (aqueous standards and standard additions) were evaluated using a biodiesel digested solution to select the calibration techniques and optimize the ICP OES operating parameters. The RF incident power was optimized as it seriously affects the plasma temperature and improves atom excitation performance. It was studied in the range 1000-1400 W. Results indicate that sensitivity and linearity are better at 1300 W for almost all analytes while the stability of plasma are also improved. The effect of nebulizer argon gas flow rate was studied from 0.60 to 0.90 L min^{-1} with a maximum intensity appearing at 0.70 L min^{-1} for all analytes. Thus, a 0.70 L min^{-1} nebulizer argon gas flow rate was adopted throughout this study, which provides high sensitivity and good precision. Optimum values for all studied parameters are presented in Table 1.

Evaluation of the efficiency of digestion

The efficiency of the digestion process carried out in the open system with conventional heating (WD1) and in the microwave-assisted closed system (WD2) was evaluated through determination of the residual carbon content and residual acidity.

Decomposition of the organic matrices by wet ashing is usually undertaken by heating the sample with a concentrated oxidizing mineral acid or mixtures of oxidizing acids with hydrogen peroxide. Residual carbon content is an important parameter for evaluating the efficiency of an acidic digestion procedure for the digestion of organic material. The digestion of oily matrices requires the use of mineral acids and generally nitric acid can be used, considering that this possesses a strong oxidizing power. However, the limitation in the use of this acid is its low boiling point at atmospheric pressure, around 120 ^{o}C. To facilitate digestion in open flasks that operate at atmospheric pressure, the addition of an aliquot of sulfuric acid is recommended (which has a boiling point of 330 °C), thereby increasing the oxidative efficiency of the medium and making the decomposition of fat globules possible.[14-20]

Ideally, the best digestion should lead to a complete decomposition of organic material using minimal amounts of nitric acid which should be diluted as much as possible to decrease residual carbon and the acid concentration in the resulting digest solution, with the aim of avoiding critical effects on instrument parts, such as the nebulizer, nebulization chamber and torch in ICP OES.[11] Furthermore, solutions of differing viscosity and surface tension lead to changes in the flow rates of aspiration and nebulization, while the density and volatility affect the transport of the aerosol through the nebulization chamber.[6,21,22]

The residual carbon contents for the biodiesel samples digested in the WD1 and WD2 procedures were determined using axial view ICP OES and the mean results for the digests, for n = 3, were: 0.358 ± 0.012% (m/v) and 0.614 ± 0.023% (m/v) respectively, demonstrating the high efficiency of both proposed procedures. The lower content was related to the WD1, implying that the digestion process was more efficient, which may be related to the use of higher temperatures with the addition of H_2SO_4, leading to a greater destruction of the organic material.

The final acidity of the digests was determined using acid-base titration with a solution of NaOH 0.0997 mol L^{-1}. Results obtained for the digest solutions of the two procedures were: 2.19 mol L^{-1} for the WD1 and 4.05 mol L^{-1} for the WD2. For the WD2 procedure, the high residual acidity is due to the residual HNO_3 and the impossibility of making a greater dilution of the final digest.

Therefore, despite the microwave-assisted cavity procedure having advantages such as reduction of the analytical blanks due to the lower acid volumes used and maintaining an isolated acidic mixture during the digestion (consequently reducing atmospheric contamination in the laboratory), it also presents some limitations. Regarding digestion of oily matrices in the microwave-assisted closed system, there are restrictions related to the sample mass used not exceeding 250 mg, given that these systems result in elevated pressures and the oxidation reactions of the sample components by the reagents used are generally violent and liberate excessive gas volumes. The initial minimum volume of 7.0 mL is also defined by the supplier, considering the recommendation for using a temperature sensor.

Limits of detection and quantification

The figures of merit for each procedure were evaluated based on the limits of detection (LOD) and limits of quantification (LOQ) under robust conditions of the ICP OES.[6] Limits of detection and quantification were defined, respectively, as 3s/b and 10s/b, where s is the standard deviation of ten measurements of the blank and b is the slope of the calibration curve. Table 2 shows the values obtained for the two procedures. For comparison, LOD values obtained by diluting the sample with kerosene[8] were: 0.1 µg g^{-1} for Ca and Mg, 0.5 µg g^{-1} for P and K and 0.4 µg g^{-1} for Na. These values were lower than those obtained by the proposed procedures, except for Ca.

Table 2. Limits of detection and quantification (LOD and LOQ: µg g^{-1}) for the two digestion procedures: WD1 - conventional heating and WD2 - microwave-assisted heating

	WD1		WD2	
	LOD	LOQ	LOD	LOQ
Ca	0.78	2.44	0.40	1.20
K	0.11	0.44	0.16	0.56
Mg	0.04	0.14	0.02	0.06
Na	0.56	1.78	0.16	0.60
P	0.22	0.78	0.40	1.22

Matrix effect and internal standard evaluation

The goal of this study was to evaluate if the matrix resulting from the decomposition procedure interferes in the determinations made by ICP OES by comparing the slopes of the analytical calibration curves obtained in each medium, employing statistical tests.

A linear regression statistical test and correlation analysis were performed for calculation of slope (b), intercept (a), and correlation coefficient (r) of the regression lines. Statistical analysis was based on triplicate measurements of all samples. The slopes of the curves obtained in the diluted acid medium were compared to the slopes of the digests by applying the paired t test. According to this test it was possible to conclude that no significant difference exists between the slopes at a 95% confidence interval.

Results obtained related to the use of yttrium as internal standard indicated a decrease in the concentrations of those solutions in which the internal standard was not added. In agreement with previous reported work, use of the internal standard is essential in the digests that contain sulfuric acid because its high viscosity, the efficiency in transporting the solution to the plasma is affected, resulting in a decreased intensity of the analyte emission. [22,23]

Analytical results

Since certified reference materials were unavailable for trace elements in biodiesel, results were evaluated by spike recovery tests and comparison of the results with those obtained by FAAS, for Na and K. For the spike recovery test, samples were enriched in order to yield an equivalent concentration of 2.0 and 5.0 µg g^{-1} of each analyte. All recovery values were acceptable (88 to 110%) with relative standard deviations in the 1-10% range (Table 3).

Additionally, results for Na and K determination in soybean biodiesel sample (after acid digestion using the WD2 procedure) were evaluated with a comparative technique (FAAS), following the procedure described by De Jesus *et al.*[12] and are shown in Table 4. Statistical analysis indicated that the results obtained with the proposed methods showed no significant difference from those obtained by the comparative procedure within a 95% confidence level.

Table 3. Analyte recovery test (%) for biodiesel samples after heating block digestion (WD1) and microwave-assisted cavity digestion (WD2) (mean ± standard deviation, n = 3)

	Castor bean		Soybean		Palm	
	WD1	WD2	WD1	WD2	WD1	WD2
Ca	98 ± 6	95 ± 3	88 ± 7	91 ± 1	103 ± 1	101 ± 1
K	-	-	101 ± 10	103 ± 2	107 ± 9	103 ± 2
Mg	102 ± 7	97 ± 7	107 ± 7	93 ± 2	108 ± 4	100 ± 2
Na	-	-	103 ± 10	91 ± 1	100 ± 10	94 ± 1
P	96 ± 4	98 ± 3	110 ± 10	92 ± 3	98 ± 9	92 ± 1

Table 4. Contents of K and Na (μg g^{-1}) in castor bean and soybean biodiesel samples after microwave-assisted digestion system (WD2) (mean ± standard deviation, n = 3) by ICP OES and FAAS

	castor bean		soybean	
	ICP OES	FAAS	ICP OES	FAAS
K	7.3 ± 0.1	7.6 ± 0.1	2.1± 0.1	2.1 ± 0.1
Na	6.5 ± 0.2	6.2 ± 0.2	7.6 ± 0.3	7.4 ± 0.2

Finally, the results obtained when these analytical procedures were applied to Ca, K, Mg, Na and P determination in biodiesel samples are summarized in Table 5. On the basis of an analysis of variance (ANOVA) test, the differences between the two sample preparation procedures were found to be insignificant at the 95% confidence level, considering the concentrations obtained for all elements in biodiesel samples. Calcium and K concentrations for all samples and Na concentrations in biodiesel samples from castor bean and palm are higher than those established by the Brazilian and International Fuel Legislations. Sodium and K are residues from NaOH or KOH catalysts and must be washed out of the final product.

The advantage of the WD2 procedure in relation to that of WD1 is the fact that it has a lower digestion time and uses lower volumes and types of reagents. However, this procedure presented a higher instrumentation cost. The WD1 procedure is slow and requires practically continuous operator attention. In comparison with other procedures proposed in the literature, the proposed procedures present advantages because they do not require organic standard solutions for calibrations, they do not use toxic organic solvents, and do not require special accessories for sample introduction.

Conclusions

Both digestion procedures yielded comparable results since recoveries were not statistically different. The closed system with microwave-assisted procedure was preferred instead of the open system with conventional heating procedure for three reasons: it required less time (72 min), it used a lower volume and fewer reagents, and it attained better sample recoveries. However, the open system with conventional heating procedure is less expensive. Limits of quantification for Ca, Mg, Na, K and P in biodiesel samples with ICP OES after acid digestion were suitable to meet legislation on biodiesel quality.

Acknowledgements

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. The authors wish to thank to GRICES (Portugal) and CAPES (Brazil) for the financial support to exchange research work. Marieta Passos thanks the Fundação para a Ciência e Tecnologia and FSE (III Quadro Comunitário) for the PhD grant (SFRH / BD / 22752 / 2005).

References

1. Pinto, A. C.; Guarieiro, L. L. N.; Rezende, M. J. C.; Ribeiro, N. M.; Torres, E. A.; Lopes, W. A.; Pereira, P. A. P.; De Andrade, J. B.; *J. Braz. Chem. Soc.* **2005**, *1313*, 1330.
2. Monteiro, M. R.; Ambrozin, A. R. P.; Lião, L. M.; Ferreira, A. G.; *Talanta* **2008,** *77*, 593.
3. Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, Resolução Nº 07 de 19 de março de 2008, Brasília, 2008. http://www.anp.gov.br, accessed in May, 2010.
4. ASTM D6751 Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, vol.05.04, West Conshohocken, PA, 2009.
5. BSI BS EN 14214 Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods, 2008.
6. Montaser, A. R.; Golightly, D. W.; *Inductively Coupled Plasma in Analytical Atomic Spectrometry,* 2nd ed, VCH: New York, 1996.

Table 5. Contents of Ca, K, Mg, Na and P (μg g^{-1}) in biodiesel samples after conventional digestion system (WD1) and microwave-assisted digestion system (WD2) (mean ± standard deviation, n = 3)

	Castor bean		Soybean		Palm	
	WD1	WD2	WD1	WD2	WD1	WD2
Ca	14.3 ± 0.5	11.0 ± 2.3	13.8 ± 0.9	14.6 ± 0.2	29.7 ± 3.0	31.6 ± 2.3
K	1121 ± 60	1424 ± 62	14.8 ± 0.3	14.3 ± 0.4	13.4 ± 2.9	14.2 ± 2.6
Mg	0.32 ± 0.06	< LOQ	0.31 ± 0.04	< LOQ	2.0 ± 0.1	2.5 ± 0.1
Na	100 ± 8	103 ± 1	1.8 ± 0.4	2.1 ± 0.1	31.6 ± 1.4	34.3 ± 0.8
P	10.8 ± 0.3	11.1 ± 1.2	9.7 ± 1.5	10.2 ± 1.4	12.4 ± 1.7	16.7 ± 0.3

7. Korn, M. G. A.; Dos Santos, D. S. S.; Welz, B.; Vale, M. G. R.; Teixeira, A. P.; Lima, D. C., Ferreira, S. L. C.; *Talanta* **2007,** *73*, 1.
8. Edlund, M.; Visser, H.; Heitland, P.; *J. Anal. At. Spectrom.* **2002,** *17*, 232.
9. Dos Santos, E. J,; Hermann, A. B.; Chaves, E. S.; Vechiatto, W. W. D.; Schoemberger, A. C.; Frescura, V. L. A.; Curtius, A. J.; *J. Anal. At. Spectrom*. **2007,** *22*, 1300.
10. Chaves, E. S.; Saint'Pierre, T. D.; Dos Santos, E. J.; Tormen, L.; Bascuñan, V. L. A. F.; Curtius, A. J.; *J. Braz. Chem. Soc.* **2008**, *19*, 856.
11. De Souza, R. M.; Leocádio, L. G.; Da Silveira, C. L. P.; *Anal. Lett.* **2008,** 41, 1614.
12. De Jesus, A.; Silva, M. M.; Vale, M. G. R.; *Talanta* **2008,** *74*, 1378.
13. Chaves, E. S.; Lepri, F. G.; Silva, J. S. A.; Quadros, D. P. C.; Saint'Pierre, T. D.; Curtius, A. J.; *J. Environ. Monit.* **2008,** *10*, 1211.
14. Resta, V.; Filho, A.; Gomes, J. A.; *Anal. Lett.* **2008,** *41*, 1555.
15. de Oliveira, A. P.; Villa, R. D.; Antunes, K.C.P.; Magalhães, A.; Silva, E. C.; *Fuel* **2009**, 88, 764.
16. Gouveia, S. T.; Silva, F. V.; Costa, L. M.; Nogueira, A. R. A.; Nóbrega, J. A.; *Anal. Chim. Acta*. **2001,** *445*, 269.
17. Sant'Ana, F. W.; Santelli, R. E.; Cassella, A. R.; Cassella, R. J.; *J. Hazard. Mater.* **2007,** *149*, 67**.**
18. Arruda, M. A. Z.; ed.; *Trends in Sample Preparation.* Nova Science: New York, 2007**.**
19. Costa, L. M.; Ferreira, S. L. C.; Nogueira, A. R. A.; Nóbrega, J. A.; *J. Braz. Chem. Soc.* **2005,** *16*, 1269.
20. Bressani, F. A.; Silva, H. O.; Nóbrega, J. A.; Costa, L. M.; Nogueira, A. R. A.; *Quim. Nova* **2006,** *29*, 1210.
21. Aucelio, R. Q.; Souza, Q.; De Campos, R. C.; Miekeley, N.; Silveira, N. C. L. P.; *Spectrochim. Acta, Part B* **2007**, *62*, 952.
22. Korn, M. G. A.; Oliveira, E.; *Spectrosc. Lett*. **1998**, *31*, 699.
23. Costa, L. M.; Korn, M. G. A.; Castro, J. T.; Santos, W. P. C.; Carvalho, E. V.; Nogueira, A. R. A.; *Quim. Nova* **2006,** *29*, 149.

Submitted: May 12, 2010