



Analytical Methods

Multi-element determination of Cu, Fe, Ni and Zn content in vegetable oils samples by high-resolution continuum source atomic absorption spectrometry and microemulsion sample preparation

Luana S. Nunes^a, José T.P. Barbosa^a, Andréa P. Fernandes^a, Valfredo A. Lemos^{b,c}, Walter N.L. dos Santos^{c,d}, Maria Graças A. Korn^{a,c}, Leonardo S.G. Teixeira^{a,c,*}

^a Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Salvador, Bahia 40170-290, Brazil

^b Laboratório de Química Analítica, Universidade Estadual do Sudoeste da Bahia, Campus de Jequiê, Jequiê, Bahia 45206-190, Brazil

^c INCT de Energia e Ambiente, Universidade Federal da Bahia, Salvador, Bahia 40170-280, Brazil

^d Departamento de Ciências Exatas e da Terra, Universidade do Estado da Bahia, Salvador, Bahia 41195-001, Brazil

ARTICLE INFO

Article history:

Received 14 July 2010

Received in revised form 13 October 2010

Accepted 30 December 2010

Available online 9 January 2011

Keywords:

Metals analysis

Vegetable oil

HR-CS FAAS

ABSTRACT

The aim of this work was to evaluate the microemulsification as sample preparation procedure for determination of Cu, Fe, Ni and Zn in vegetable oils samples by High-Resolution Continuum Source Flame Atomic Absorption Spectrometry (HR-CS FAAS). Microemulsions were prepared by mixing samples with propan-1-ol and aqueous acid solution, which allowed the use of inorganic aqueous standards for the calibration. To a sample mass of 0.5 g, 100 μL of hydrochloric acid and propan-1-ol were added and the resulting mixture diluted to a final volume of 10 mL. The sample was manually shaken resulting in a visually homogeneous system. The main lines were selected for all studied metals and the detection limits (3σ , $n = 10$) were 0.12, 0.62, 0.58 and 0.12 mg kg^{-1} for Cu, Fe, Ni and Zn, respectively. The relative standard deviation (RSD) ranged from 5% to 11% in samples spiked with 0.25 and 1.5 $\mu\text{g mL}^{-1}$ of each metal, respectively. Recoveries varied from 89% to 102%. The proposed method was applied to the determination of Cu, Fe, Ni and Zn in soybean, olive and sunflower oils.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The metal contents in vegetable oils are important because of toxicological as well as their nutritional viewpoints. Trace metals present in oils may be of natural origin or present due to processing procedures. It is possible to find the presence of metals due to a variety of factors such as treatment processes (by processing steps as bleaching, hardening, refining and deodorization, as well as corrosion of the processing equipments), packaging procedures, from water plumbing, presence of fungicide residues used in agriculture or the presence of highways, industries near the site of cultivation (Ansari et al., 2009; Cypriano, Matos, & Matos, 2008; Dugo, La Pera, Loredana La Torre, & Giuffrida, 2004; Sahan, Basoglu, & Gucer, 2007).

The determination of trace metal content in vegetable oils is an important criterion for the assessment of oil quality with regard to freshness, keeping properties, storage and their influence on human nutrition and health. Many reports have described the deleterious effects that trace metal has on the flavour and oxidative

stability of oils, since some metals could catalyse oxidation of fatty acid chains, exerting a deleterious influence on shelf life and nutritional value (Galeano Díaz, Guiberteau, López Soto, & Ortiz, 2006). Furthermore, some of these metals are subject to food legislation (Cypriano et al., 2008; Reyes & Campos, 2006), and have been used for detection of adulterations in oil samples (González, Armenta, & de la Guardia, 2010). It is important to emphasize either that in tropical countries with large territorial areas as Brazil, the cultivation of vegetable oil sources to produce biodiesel could also achieve an economic up-scale and the presence of metals in the raw material can affect the biodiesel quality (Chaves et al., 2008; de Jesus, Silva, & Vale, 2008; de Souza, Leocádio, & da Silveira, 2008; Vieira, de Oliveira, Gonçalves, de Souza, & Campos, 2009). However, the accurate determination of trace metals in this kind of samples is still an analytical challenge, owing to their low concentration level and the difficulties that arise due to the characteristics of the matrix.

The most common technique used for metals determination in vegetable oil is atomic absorption spectrometry (de Leonardis, Macciola, & de Felice, 2000). However, in general, atomic spectrometric methods for metals determination in organic matrix present some disadvantages, such as the reduced stability of the analytes in the solution, the need of organometallic standards for

* Corresponding author at: Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Salvador, Bahia 40170-290, Brazil. Tel.: + 55 71 3283 6829; fax: +55 71 3235 5166.

E-mail address: lsigt@ufba.br (L.S.G. Teixeira).

calibration, and the use of dangerous organic solvents or sample digestion with an acid or acid mixture (de Souza et al., 2008). Sample preparation is a critical step in oil analysis and due to the high organic content, sample pre-treatment is frequently necessary. Normally, the analytical methods request a sample pre-treatment step, involving the complete destruction of the organic matrix or other time consuming procedures such as acid extraction (de Leonardis et al., 2000), solid phase extraction (Bati & Cesur, 2002) as well as dry (Raptis, Kaiser, & Tölg, 1982) or wet ashing (Juranovic, Breinhoelder, & Steffan, 2003), at times with microwave assisted heating (Sahan et al., 2007).

Alternatively, some methodologies use the modification of these organic liquid samples by the formation of emulsions or microemulsions, avoiding previous mineralization of the sample and making possible the use of simple aqueous standards for calibration instead of expensive and instable organometallic standards (Aucélio, Doyle, Pizzorno, Tristão, & Campos, 2004; dos Santos, Teixeira, Korn, & Teixeira, 2006). The systems are thermodynamically stable and composed of water, oil and surfactant, and, in some cases, an alcohol can be added as co-surfactant. Additionally, they are apparently homogeneous under visual observation, but in fact the systems are formed of particles with diameters in the order of 5–100 nm suspended in a continuous phase (de Jesus et al., 2008). Detergentless microemulsions can also be used. In this case, a co-solvent allows the formation of a homogeneous system containing both the aqueous phase and the liquid organic phase resulting in a homogeneous and long-term stable three-component solution (Aucélio et al., 2004). The use of emulsification as sample preparation for the determination of trace metals in vegetable oils by ICP OES (de Souza, Mathias, da Silveira, & Aucélio, 2005), ICP-MS (Castillo, Jiménez, & Ebdon, 1999) and FAAS (Jiménez, Velarte, Gomez, & Castillo, 2004) has been proposed. However, the use of microemulsion as sample preparation for vegetable oil analysis by High-Resolution Continuum Source Flame Atomic Absorption Spectrometry (HR-CS FAAS), to the best of our knowledge, has not been described yet.

The main advantages of HR-CS FAAS are the possibility of performing fast sequential multi-element measurements, measuring major and secondary atomic lines, adding absorbance of different lines for a given element, and integrating the absorbance signal over the centre pixel (CP) by including part of the line wings to extend the linear work range. These two last strategies can be used to improve sensitivity (Amorim Filho & Gomes Neto, 2008). Additionally, in comparison with conventional atomic absorption spectrometry, the technique has other inherent advantages such as random access to all wavelengths in the range from 189 nm to 900 nm, and effective and flexible background correction by means of mathematical algorithms (Huang, Becker-Ross, Florek, Heitmann, & Okruss, 2006).

In this paper, a multi-element HR-CS FAAS method for the determination Cu, Fe, Ni and Zn content in vegetable oils samples was developed. A simple and fast sample preparation procedure based on the emulsification of the sample in propan-1-ol and water was employed. Using the proposed procedure, the system kept its homogeneity and stability for a few hours and allowed the metals quantification using simple calibration procedure against inorganic standard solutions when these dispersions were acidified with hydrochloric acid.

2. Experimental

2.1. Instrumentation

An Analytik Jena contraA 300 high-resolution atomic absorption spectrometer equipped with a 300 W xenon short-arc lamp

(XBO 301, GLE, Berlin, Germany) as a continuum radiation source was used throughout the work. The equipment presents a compact high-resolution double echelle monochromator and a charge-coupled device (CCD) array detector with a resolution of about 2 pm per pixel in the far ultraviolet range. Measurements were carried out in the following wavelengths (in nm): Cu (324.754), Fe (248.327), Ni (232.003) and Zn (213.867). The number of pixels of the array detector used for detection was 3 (central pixel 1). Oxidizing air/acetylene flame was used and all measurements were carried out in triplicate.

A Varian (Mulgrave, Australia) Vista simultaneous inductively coupled plasma optical emission spectrometry instrument with axial viewing and a charge-coupled device (CCD) detector was used as a comparative method. A Sturman–Master chamber and a V-Groove nebulizer were also used. The metal determinations were carried out under manufacturer-recommended conditions for power (1.3 kW), plasma gas flow (15.0 L min⁻¹), auxiliary gas flow (1.5 L min⁻¹) and nebulizer gas flow (0.7 L min⁻¹). The analytical wavelength chosen were 324.754, 248.327, 232.003 and 213.857 nm for Cu, Fe, Ni and Zn, respectively.

2.2. Reagents and samples

All reagents were of analytical grade quality and freshly distilled and deionized water was used for dilutions. The hydrochloric acid (37%), propan-1-ol, and monoelementar 1000 mg kg⁻¹ aqueous standards of Cu, Fe Ni and Zn were supplied by Merck (Darmstadt, Germany). A 900 µg g⁻¹ metallo-organic multi-element standard was from AccuStandard Inc. (New Haven, USA) and propan-1-ol was used for the dilutions of metallo-organic standard solution. Soybean, olive and sunflower oils were obtained from local vendors.

2.3. Microemulsion preparation

Microemulsions were prepared by mixing samples with propan-1-ol and aqueous acid solution. Approximately 0.5 g of vegetable oil samples were placed in 10 mL volumetric flasks, where 100 µL of hydrochloric acid was added. Propan-1-ol was then added under continuous agitation until a final volume of 10 mL. After vigorous shaking, the samples were evenly dispersed in the emulsion resulting in a visually homogeneous system and remained stable for a few hours.

2.4. Calibration procedure

Analytical curves were carried out using standards prepared similar to the samples and the metals were added as metallo-organic standard solutions. Analytical curves using aqueous standard solutions were obtained for the purpose of comparison with analytes concentration ranging from 0.10 to 4.5 mg kg⁻¹. Non-spiked oil dispersions were used as blanks and the analytes concentrations in the blank was determined by the analyte addition technique. The results obtained were evaluated based on the intensity of the corrected blank.

2.5. Sample preparation for ICP OES

Samples of vegetable oils were weighed and subsequently digested using a microwave unit. After digestion with a mixture of nitric acid and hydrogen peroxide clear solutions were obtained and the analytes were determined by ICP OES. In the procedure, each sample of oil (0.5 g) was weighed into the digestion vessels. The digestions were performed by adding 3.5 mL of HNO₃ conc. and 1.0 mL H₂O₂ (30%) to the sample. The microwave oven heating programme was performed in five steps using 35 Bar of pressure,

Table 1
Microwave heating programme for sample digestion.

Step	Time (min)	Power (W)	T (°C)
1	6	750	90
2	4	750	90
3	8	1000	180
4	15	1000	180
Ventilation	20	–	–

as depicted in Table 1. The fifth step was a cooling down procedure of the system through forced ventilation over 20 min. After cooling all the digests were transferred into 10 mL volumetric flasks and diluted to volume with HNO₃ (1% v/v). The digestion procedure was done in triplicate for each sample and reagent blanks were prepared similar to the samples.

3. Results and discussion

3.1. Microemulsion stability

Experiments were conducted to determine the minimum amount of propan-1-ol required to form emulsions whose phases did not separate within 3 h, which is an enough period to consider the stability of the system and to realize the measurements in the equipment. This test consisted of preparing microemulsions, after which their stability was monitored by simple visual inspection of the emulsion samples. In these experiments, the propan-1-ol was tested in the range of 2 to 9 mL, using 0.5 g of vegetable oil sample and 100 µL of hydrochloric acid. Water was added under continuous agitation until a final volume of 10 mL. The results indicated that only volumes of propan-1-ol higher than 8 mL produced emulsions that remained homogeneous. Therefore, after the addition of sample and hydrochloric acid aliquot, the final volume of 10 mL was completed with the alcohol, avoiding phase separation when the absorbance measurements were performed.

Additionally, the stability of Cu, Fe, Ni and Zn concentrations in the microemulsion were checked every 30 min, for 240 min. The signal was stable during the monitoring time, indicating stability of the analytes.

3.2. Analytical performance, validation and application

One of the principal problems related with the determination of trace elements in organic matrix is the lack of knowledge about the form of the analyte in the sample. The standard addition techniques provide the compatibility among the calibration curves and samples in terms of possible matrix interferences, but also may provide errors since the forms of element compounds in the materials to be analysed behave differently to the spiked form (dos Santos et al., 2007). Due to this, the feasibility of using aqueous standards for calibration was evaluated by the comparison with the standard addition using metal-organic standards. The resulting equations and their respective correlation coefficients are shown in Table 2. As can be seen, the slopes of the calibration curves obtained using either inorganic or organic standards are very similar. This means that the Cu, Fe Ni and Zn present in vegetable oils samples can be determined through the calibration technique using either inorganic or organic standards.

Table 3 presents the limits of detection (LOD) and of quantification (LOQ) in samples, as well the precision for the determination of Cu, Fe, Ni and Zn in vegetable oils prepared as microemulsion by HR-CS FAAS. The LOD and LOQ of each analyte were calculated as the analyte concentration corresponding to three and ten times, respectively, the standard deviation for ten independent measure-

Table 2
Calibration equations ($A = aC + b$)^a and correlation coefficients for determination of Cu, Fe, Ni and Zn in vegetable oils samples using organic or inorganic standards.

Calibration	Analyte	Equation	Correlation coefficient
Analytical curve using inorganic standard	Cu	$A = 0.111 (\pm 0.007)$ $C + 0.008 (\pm 0.003)$	0.9985
	Fe	$A = 0.062 (\pm 0.005)$ $C + 0.005 (\pm 0.001)$	0.9986
	Ni	$A = 0.058 (\pm 0.005)$ $C + 0.004 (\pm 0.001)$	0.9993
	Zn	$A = 0.391 (\pm 0.011)$ $C + 0.006 (\pm 0.002)$	0.9983
	Cu	$A = 0.115 (\pm 0.006)$ $C + 0.004 (\pm 0.002)$	0.9991
	Fe	$A = 0.061 (\pm 0.004)$ $C + 0.005 (\pm 0.002)$	0.9986
Analytical curve using organic standard	Ni	$A = 0.059 (\pm 0.006)$ $C + 0.004 (\pm 0.002)$	0.9995
	Zn	$A = 0.371 (\pm 0.015)$ $C + 0.004 (\pm 0.001)$	0.9992

^a A = absorbance; a = slope; C = concentration (µg mL⁻¹); b = intercept.

Table 3
LOD, LOQ and RDS for the determination of Cu, Fe, Ni and Zn in vegetable oils samples by HR-CS FAAS.

Parameter/Elements	Cu	Fe	Ni	Zn
LOD, mg kg ⁻¹	0.12	0.62	0.58	0.12
LOQ, mg kg ⁻¹	0.40	2.1	1.9	0.40
RSD, %	5–8	6–8	5–11	5–9

ments of the microemulsion blank, divided by the slope of the calibration curve. The precision was evaluated as the relative standard deviation (RSD). In Table 3, the RSD range obtained for all samples are shown.

The proposed method has been applied to the determination of Cu, Fe Ni and Zn in vegetable oils samples obtained from local vendors. Initially, the method was verified through spike recovery tests, by adding 2.0 and 4.0 mg kg⁻¹ of each metal (metallo-organic standard) to three different samples. The results were obtained as the average of three replicates of each fuel sample and are shown in Table 4. As can be seen, the method has good accuracy and the recoveries were between 89% and 102%. The proposed method was then applied to Cu, Fe, Ni and Zn determination in three more vegetable oils samples. The results, obtained as the average of three

Table 4
Recoveries (%) and relative standard deviations for spiked vegetable oil samples (n = 3).

Sample/Element	Spiked concentration, mg kg ⁻¹	
	2.0	4.0
<i>Soybean oil 1</i>		
Cu	99 ± 11	101 ± 4
Fe	98 ± 2	95 ± 6
Ni	93 ± 4	101 ± 4
Zn	101 ± 2	98 ± 2
<i>Olive oil 1</i>		
Cu	101 ± 4	92 ± 2
Fe	98 ± 5	95 ± 3
Ni	99 ± 5	89 ± 3
Zn	101 ± 3	102 ± 2
<i>Sunflower oil 1</i>		
Cu	101 ± 4	91 ± 3
Fe	98 ± 2	98 ± 2
Ni	89 ± 3	101 ± 4
Zn	101 ± 4	99 ± 4

Table 5Determination of Cu, Fe, Ni and Zn (mg kg⁻¹) in commercial vegetable oils samples by proposed and comparative methods ($n = 3$, at 95% confidence level).

Sample	Ni		Fe		Cu		Zn	
	Proposed	Comparative	Proposed	Comparative	Proposed	Comparative	Proposed	Comparative
Soybean oil 2	2.74 ± 0.12	2.55 ± 0.10	2.26 ± 0.20	2.21 ± 0.11	1.17 ± 0.08	1.02 ± 0.12	<0.4	0.09 ± 0.04
Olive oil 2	<1.9	1.49 ± 0.04	3.13 ± 0.09	2.99 ± 0.10	1.29 ± 0.04	1.33 ± 0.03	4.30 ± 0.04	4.61 ± 0.08
Sunflower oil 2	<1.9	0.20 ± 0.09	<2.1	0.31 ± 0.05	<0.4	0.14 ± 0.07	<0.4	0.31 ± 0.04

replicates of each sample, are shown in Table 5. When compared to the results obtained by the comparative method using ICP OES and digested samples, the results obtained by the proposed procedure show a good agreement. The paired t -test (95% confidence level) did not show significant differences.

4. Conclusions

The developed procedure provides a sensitive and simple approach for the determination of Cu, Fe, Ni and Zn in vegetable oils samples using organic or inorganic standards by HR-CS FAAS, after application of a procedure involving microemulsification with propan-1-ol. The method is simple, fast and does not require the sample to be subjected to any drastic or time-consuming pre-treatment, such as concentrated acid heating.

Acknowledgements

The authors would like to acknowledge the financial support received from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB).

References

- Amorim Filho, V. R., & Gomes Neto, J. A. (2008). Different lubricating oil treatments for the determination of Cu, Cr, Fe, Ni, Sb, Pb, and Zn by HR-CS FAAS. *Analytical Letters*, *41*, 1555–1570.
- Ansari, R., Kazi, T. G., Jamali, M. K., Arain, M. B., Wagan, M. D., Jalbani, N., et al. (2009). Variation in accumulation of heavy metals in different varieties of sunflower seed oil with the aid of multivariate technique. *Food Chemistry*, *115*, 318–323.
- Aucélio, R. Q., Doyle, A., Pizzorno, B. S., Tristão, M. L. B., & Campos, R. C. (2004). Electrothermal atomic absorption spectrometric method for the determination of vanadium in diesel and asphaltene prepared as detergentless microemulsions. *Microchemical Journal*, *78*, 21–26.
- Bati, B., & Cesur, H. (2002). Determination of copper in edible oils by atomic absorption spectrometry after lead piperazinedithiocarbamate solid-phase extraction and potassium cyanide back-extraction. *Analytical Sciences*, *18*, 1273–1274.
- Castillo, J. R., Jiménez, M. S., & Ebdon, L. (1999). Semiquantitative simultaneous determination of metals in olive oil using direct emulsion nebulization. *Journal of Analytical Atomic Spectrometry*, *14*, 1515–1518.
- Chaves, E. S., Saint-Pierre, T. D., dos Santos, E. J., Tormen, L., Bascuñan, V. L. A. F., & Curtius, A. J. (2008). Determination of Na and K in biodiesel by flame atomic emission spectrometry and microemulsion sample preparation. *Journal of Brazilian Chemical Society*, *19*, 856–861.
- Cypriano, J. C., Matos, M. C., & Matos, R. C. (2008). Ultrasound-assisted treatment of palm oil samples for the determination of copper and lead by stripping chronopotentiometry. *Microchemical Journal*, *90*, 26–30.
- de Jesus, A., Silva, M. M., & Vale, M. G. R. (2008). The use of microemulsion for determination of sodium and potassium in biodiesel by flame atomic absorption spectrometry. *Talanta*, *74*, 1378–1384.
- de Leonardi, A., Macciola, V., & de Felice, M. (2000). Copper and iron determination in edible vegetable oils by graphite furnace atomic absorption spectrometry after extraction with diluted nitric acid. *International Journal of Food Science & Technology*, *35*, 371–375.
- de Souza, R. M., Leocádio, L. G., & da Silveira, C. L. P. (2008). ICP OES simultaneous determination of Ca, Cu, Fe, Mg, Mn, Na, and P in biodiesel by axial and radial inductively coupled plasma-optical emission spectrometry. *Analytical Letters*, *41*, 1614–1621.
- de Souza, R. M., Mathias, B. M., da Silveira, C. L. P., & Aucélio, R. Q. (2005). Inductively coupled plasma optical emission spectrometry for trace multi-element determination in vegetable oils, margarine and butter after stabilization with propan-1-ol and water. *Spectrochimica Acta Part B*, *60*, 711–715.
- dos Santos, D. S. S., Teixeira, A. P., Barbosa, J. T. P., Ferreira, S. L. C., Korn, M. G. A., & Teixeira, L. S. G. (2007). Use of cetyltrimethylammonium bromide as surfactant for the determination of copper and chromium in gasoline emulsions by electrothermal atomic absorption spectrometry. *Spectrochimica Acta Part B*, *62*, 1072–1077.
- dos Santos, D. S. S., Teixeira, A. P., Korn, M. G. A., & Teixeira, L. S. G. (2006). Determination of Mo and V in multiphase gasoline emulsions by electrothermal atomic absorption spectrometry. *Spectrochimica Acta Part B*, *61*, 592–595.
- Dugo, G., La Pera, L., Loredana La Torre, G., & Giuffrida, D. (2004). Determination of Cd(II), Cu(II), Pb(II), and Zn(II) content in commercial vegetable oils using derivative potentiometric stripping analysis. *Food Chemistry*, *87*, 639–645.
- Galeano Díaz, T., Guiberteau, A., López Soto, M. D., & Ortiz, J. M. (2006). Determination of copper with 5, 5-dimethylcyclohexane-1, 2, 3-trione 1, 2-dioxime 3-thiosemicarbazone in olive oils by adsorptive stripping square wave voltammetry. *Food Chemistry*, *96*, 156–162.
- González, A., Armenta, S., & de la Guardia, M. (2010). Adulteration detection of argan oil by inductively coupled plasma optical emission spectrometry. *Food Chemistry*, *121*, 878–886.
- Huang, M. D., Becker-Ross, H., Florek, S., Heitmann, U., & Okrusch, M. (2006). Determination of phosphorus by molecular absorption of phosphorus monoxide using a high-resolution continuum source absorption spectrometer and an air-acetylene flame. *Journal of Analytical Atomic Spectrometry*, *21*, 338–345.
- Jiménez, M. S., Velarte, R., Gomez, M. T., & Castillo, J. R. (2004). Multielement determination using on-line emulsion formation and ICP-MS/FAAS for the characterisation of virgin olive oils by principal component analysis. *Atomic Spectroscopy*, *25*, 1–12.
- Juranovic, I., Breinhoelder, P., & Steffan, I. (2003). Determination of trace elements in pumpkin seed oils and pumpkin seeds by ICP-AES. *Journal of Analytical Atomic Spectrometry*, *18*, 54–58.
- Raptis, S. E., Kaiser, G., & Tölg, G. (1982). The decomposition of oils and fats in a stream of oxygen for the determination of trace elements. *Analytica Chimica Acta*, *138*, 93–101.
- Reyes, M. N. M., & Campos, R. C. (2006). Determination of copper and nickel in vegetable oils by direct sampling graphite furnace atomic absorption spectrometry. *Talanta*, *70*, 929–932.
- Sahan, Y., Basoglu, F., & Gucer, S. (2007). ICP-MS analysis of a series of metals (Namely: Mg, Cr, Co, Ni, Fe, Cu, Zn, Sn, Cd and Pb) in black and green olive samples from Bursa, Turkey. *Food Chemistry*, *105*, 395–399.
- Vieira, M. A., de Oliveira, L. C. C., Gonçalves, R. A., de Souza, V., & Campos, R. C. (2009). Determination of As in vegetable oil and biodiesel by graphite furnace atomic absorption spectrometry. *Energy Fuels*, *23*, 5942–5946.