Feasibility of a Fast and Green Chemistry Sample Preparation Procedure for the Determination of K and Na in Renewable Oilseed Sources by Flame Atomic Emission Spectrometry

Kamyla Cabolon Pengo[a], Vanessa Cruz Dias Peronico[a], Luiz Carlos Ferreira de Souza[b], and Jorge Luiz Raposo, Jr.[a]*

[a] Federal University of Grande Dourados, School of Exact and Technology Science, PO Box 364, 79804-970 Dourados, MS, Brazil

[b] Federal University of Grande Dourados, School of Agronomic Science, PO Box 364, 79804-970 Dourados, MS, Brazil

ABSTRACT

This work describes a fast and green chemistry procedure to determine potassium (K) and sodium (Na) in alternative oilseed crops by flame atomic emission spectrometry (FAES) using an ultrasound (US) system for sample preparation. The use of 10 mL of a 0.12 mol L^{-1} HCl solution, 10 minutes of extraction, and 25 ºC allowed the use of ≈0.1000 g of samples to extract the mineral content of the samples. The main and secondary atomic lines were evaluated, but only the secondary (404.4 nm for K and 330.3 nm for Na) provides a satisfactory (1.00–150.00 mg L^{-1} K and 1.00–120.00 mg L^{-1} Na) analytical calibration range for the determination of K and Na in a single run without need of further dilution of the samples. Recoveries of K and Na added to samples varied from 93.7–99.1% with the precision better than 3.5%. Five samples of renewable oilseeds were analyzed by FAES with the proposed sample preparation procedure using a closed-vessel microwave-assisted acid digestion for comparative purposes. The results obtained using an ultrasound sample preparation procedure were in agreement at the 95% confidence level (paired *t*-test), with those obtained by microwave-assisted digestion. The found concentrations were 6.02±0.11 – 7.75±0.47 mg g^{-1} K and 1.41±0.05 – 2.01±0.10 mg g^{-1} Na, with a precision better than 5.3%. The limit of detection was 52.45 and 73.83 µg g^{-1} for K and Na, respectively.

INTRODUCTION

Agriculture is a modern, prosperous, and highly competitive sector in Brazil, and it is considered as the propelling agent of the national economy. Among various sectors of agriculture, soybeans and sugarcane are the most important, and together with coffee and livestock they are currently the pillars of Brazil's economy (1). Although soybeans are one of the main products used in the Brazilian culture and are raw materials used for the production of vegetable oil and/or biodiesel, alternative and renewable oilseed sources are often evaluated as another effective option for these purposes. Oilseed crops require no new investment of agricultural implements, contributes to improving the crop rotation system, and can increase the farmer's income by offering competitive profits. Since there is a lack of research done about the alternative uses of oilseed crops, an investigation related to the mineral content of these oilseed crops should be performed.

Potassium and sodium are the most important elements for vegetative growth, and constitute around 10% of its dry matter (2-4). These elements are required for many metabolic processes such as osmoregulation, protein synthesis, photosynthesis, opening and closing of the stomata, soil and water absorption, enzymatic activity, and therefore monitoring of the quality of agricultural crops is essential (5-7).

The elemental determination of K and/or Na is frequently performed by spectrometric techniques (8-15). Most of these methods involve a sample pretreatment step, which can be done by converting the sample into an aqueous solution using mineral acids and thermal or radiant energy for organic matter decomposition (16-19). This is a critical step in routine analysis, but is very time-consuming, results in incomplete solubilization of the matrices, analyte losses by volatilization, contamination in the handling processes due to the interaction between analyte and bottles, and contamination of the solutions by the reagents used (16-18, 20, 21).

From this perspective, non-destructive sample pretreatment procedures, such as those employing ultrasonic waves, are an alternative to circumvent acid digestions, and can be used for extraction, solubilization, and digestion processes using an ultrasonic bath or a probe (22, 23) with diluted acids and is

Corresponding author.
E-mail: jorgejunior@ufgd.edu.br
Tel.: +55 67 34102092

performed at room temperature (23-25). The most important advantages associated with the ultrasonic waves includes: (a) reduced time required for sample preparation, (b) reduced consumption of concentrated reagents, and (c) sample preparation is simple and relatively low cost (23, 25, 26).

In this sense, this work describes the first development of a simple and robust sample preparation procedure using an ultrasonic extraction system for the determination of K and Na in renewable oilseed sources by flame emission absorption spectrometry.

EXPERIMENTAL

Instrumentation

The measurements were carried out using a Varian 240FS flame atomic absorption spectrometer (Agilent Technologies®, Mulgrave, Victoria, Australia) operating in emission mode. The instrumental operating parameters are listed in Table I. High-purity acetylene (99.7% White Martins, Dourados, Brazil) was used as fuel, and an air-acetylene flame was used for atomization of K and Na.

A 515 Orion (Fanem®, São Paulo, SP, Brazil) forced air oven and a TE-361 (Tecnal®, Piracicaba, SP, Brazil) stainless steel mill were used to dry and powder the oilseed samples, respectively. A Unique USC-14004 (Unique®, Indaiatuba, SP, Brazil) ultrasonic bath, operating at 40 kHz, was used to leach the element from the oilseed samples. An Excelsa™ 206 BL (Fanem®, São Paulo, SP, Brazil) centrifuge was used to separate the solid and liquid phases. A Multiwave® 3000 microwave oven (Anton Paar, Graz, Austria) was used as a comparative sample preparation procedure which employed acid digestion of the samples.

Reagents and Analytical Solutions

High purity deionized water obtained from a Milli-Q® Plus reverse osmosis system (resistivity 18.2 MΩ-cm, Millipore Corporation, Bedford, MA, USA) was used to prepare all solutions. Nitric acid [65% (v/v), Sigma-Aldrich®, St. Louis, MO, USA] was used to prepare all analytical solutions, to optimize the extracting acid solutions, and for the microwave-assisted acid digestion. Hydrochloric acid [37% (v/v), Sigma-Aldrich®, St. Louis, MO, USA] was used as the extracting acid solution. A 150.000 mg L^{-1} Cs solution was prepared by dissolving 9.56 g CsCl [99.5% purity, Sigma-Aldrich®, St. Louis, MO, USA) with deionized water, followed by adding 1.5 mL HNO_3, and dilution to 50 mL using deionized water.

Different dilute hydrochloric acid solutions (0.012, 0.120, and 1.200 mol L^{-1}) were prepared for the evaluation of the effect of the acid concentration of the extraction solution on the ultrasonic-assisted extraction.

Analytical solutions containing 1.00 – 150.0 mg L^{-1} K and 1.00 – 120.0 mg L^{-1} Na were prepared daily using appropriate dilution of 1000 mg L^{-1} single-element standard stock solutions (SpecSol®, SRM-682, USA) in 1.0% (v/v) nitric acid and 1000 mg L^{-1} Cs media.

All of the solutions were stored in high-density polypropylene bottles (Nalgene®, Rochester, NY, USA). Plastic bottles and glassware were cleaned by soaking in 10% (v/v) HNO_3 for at least 24 hours, followed by thorough rinsing with deionized water before use.

Sampling and Sample Preparation

A 1000-g amount of four-months old seeds of the genus *Crambe abyssinica Hochst, Guizotia abyssinica, Brassica napus var. oleífera, Carthamus tinctorius L.*, and *Raphanus sativus L. var. oleiferus Metzg* renewable oilseed sources were randomly collected during the 2014 harvest time from five different areas (15 x 30 m) located in the Experimental Farm of the Agricultural Sciences (22º 14'S and 54º 49'W), which is situated 8 km from the Federal University of Grande Dourados (Dourados, MS, Brazil). The samples of each species were stored in individually labeled paper bags, and then transported to the laboratory. The seeds were separately and thoroughly washed with tap water and then with deionized water. A 10.0-g subsample of each oilseed sample was dried at 80 ºC for 120 hours in a forced air oven, ground in a stainless steel mill, and then sieved using a No. 20 sieve (0.84 mm opening size).

TABLE I
FAES Instrumental Operations Conditions for the Determination of Na and K

Instrumental Conditions	K	Na
Working range (mg L^{-1})	1.00 – 150.00	1.00 – 120.00
Wavelength (nm)	404.4	330.3
Burner head (mm)	100	
Air flow rate (L min^{-1})	13.0	
Acetylene flow rate (L min^{-1})	2.0	
Slit width (nm)	0.5	

A 0.1000-g portion of pretreated sample was accurately weighed (± 0.0001 g) and transferred to a 50-mL polypropylene flask, followed by addition of 15 mL acid leaching solution. The mixtures were subjected to an ultrasound energy corresponding to 40 kHz for 30 seconds to leach the elements from the seeds into the acid solution. After sonication, the acid extracts obtained were separated from the remaining solid materials using centrifugation for 5 minutes at 4000 rpm, followed by filtration into 25-mL polypropylene flasks. All of the acid leaching solutions (samples and blanks) were prepared in 1000 mg L^{-1} Cs. Three replicates of each alternative oilseed sample and blank were used to optimize the analytical parameters of the extraction procedure. All of the measurements were performed using five replicates.

For comparative purposes, the alternative oilseed materials were also mineralized in a closed-vessel microwave-assisted digestion procedure. For microwave digestion, an accurately weighed 0.1000-g sample was transferred into a microwave flask, followed by addition of 6.0 mL of HNO_3 and 2.0 mL of deionized water. The optimized heating program is listed in Table II. After digestion and cooling, the resulting solutions obtained were transferred into 25-mL volumetric flasks, and brought to volume with deionized water in 1000 mg L^{-1} Cs media. Three sample replicates were used for microwave-assisted acid decompositions.

Ultrasonic (US) Extraction Conditions and Measurement Procedure

The influence of the extracting solution (acid, concentration, and volume), sample mass, and sonication time on the sensitivity for K and Na was investigated using PIATV 02/2010 Soybean reference material (0.84 mm particle size) obtained from Embrapa Agropecuária Oeste (Dourados, MS, Brazil) by varying the acid solution [HNO_3, HCl or HNO_3:HCl (1:1, v/v)], concentration (0.012, 0.120 and 1.200 mol L^{-1}), the volume of the extracting solution (7.5, 10.0 and 15.0 mL), sample mass (0.1000, 0.2500 and 0.5000 g), and the sonication time (30, 60, 120 and 180 seconds). Due to the absence of Na in PIATV 02/2010, an aliquot of 1000 mg L^{-1} Na standard solution was added to the selected soybean reference material in order to achieve a 10.0-mg g^{-1} Na content.

At a 5.0-mL min^{-1} sample flow rate, the integrated emission intensity for blanks, working standard solutions, reference material extraction solution, and the sample solutions were measured at less sensitive atomic lines for K at 404.4 nm and Na at 330.3 nm under optimal instrumental conditions to obtain the calibration curve within the 1.00 – 150.0 mg L^{-1} K and 1.00 – 120.0 mg L^{-1} Na ranges. All measurements were carried out in five replicates.

The matrix effect was checked using recovery tests for spiked samples performed at two levels by adding aliquots of the 1000 mg L^{-1} single-element standard stock solutions to all alternative oilseed samples before the extraction procedure to obtain extracts with 25.0 and 50.0 mg L^{-1} of K and Na. The limit of detection (LOD) and limit of quantification (LOQ) were calculated according to the IUPAC recommendation (27). Statistical tests used in the data processing (mean, standard deviation, and precision) were done using the Microcal OriginPro® 8.0 program and Microsoft® Office Excel® 2007.

RESULTS AND DISCUSSION

Analytical Features for Determining K and Na

Whereas the content of macronutrients in plants is typically in the order of mg g^{-1} (14, 28), the determination of K or Na by line source flame atomic emission spectrometry (LS-FAES) in one run is not feasible if the most sensitive analytical lines (766.5 nm for K or 589.0 nm for Na) are used due to the limited linear calibration interval (29). For K and/or Na concentrations higher than the upper limit of the linear response of the calibration plots built up using the most sensitive analytical lines, the secondary line for K at 404.4 nm or Na at 330.3 nm might be employed to circumvent this problem. The use of a less sensitive atomic line is a better way to reduce sensitivity for determining major elements and to avoid further dilution of the sample solutions. At 5.0 mL min^{-1} of sample flow rate and 100 mm burner opening (standard air/acetylene burner head), the influence of the ratio of air-acetylene flow rates (0.138, 0.146, 0.154, 0.162, and 0.169) on emission intensity of K and Na was evaluated using 1.0 mg L^{-1} at 766.5 nm (K) and 589.0 nm (Na), and 10.0 mg L^{-1} at 404.4 nm (K) and 330.3 nm (Na). For this, different fuel-oxidant ratios were obtained by changing the flow rate

TABLE II
Microwave-Assisted Digestion Heating Program for Renewable Oilseed Samples

Step	T_{ramp} (min)	T_{hold} (min)	Power (W)	T (°C)
1	10	5	600	120
2	15	10	1000	200
3	0	15	0	Ventilation

of acetylene from 1.8 to 2.2 L min^{-1} and fixing the air flow rate at 13.0 L min^{-1}. The best situations achieved for flame composition for all wavelengths studied was 2.0 L min^{-1} of acetylene. Under the established conditions of the 240FS equipment, the linear working range at 766.5 and 404.4 nm for K and 589.0 and 330.3 nm for Na was evaluated by plotting curves of emission intensity versus K or Na concentration within the 0.10 – 150.00 mg L^{-1} intervals. The calibration plots in the 0.10 – 150.00 mg L^{-1} intervals provide calibration curves only up to 4.00 mg L^{-1} at 766.5 nm for K, and up to 2.00 mg L^{-1} at 589.0 nm for Na. However, the less sensitive analytical atomic lines provide calibration plots up to 150 mg L^{-1} K and 120 mg L^{-1} Na, with typical linear correlation coefficients better than 0.9980 for K and 0.9992 for Na. The main figures of merit for the K and Na atomic lines are shown in Table III.

Analysis of Table III reveals that the highest sensitivity, as seen by the slopes, are 0.2463 K and 0.1718 Na. Lower limits of detection were pbtained with the main atomic line, however, with a narrow (0.50–4.00 mg L^{-1} K and 0.50–2.00 mg L^{-1} Na) linear working range and perhaps insufficient for determining high concentrations of K and Na. In this case, where the content of the analyte in the sample digests and/or extracts is naturally above the linear range of calibration for 766.5 nm (K) and 589.0 nm (Na), the alternate atomic line at 404.4 nm (K) and 330.3 nm (Na) can be used to determine K and Na in the selected samples. The use of secondary and less sensitive (0.0063-K and 0.0061-Na slopes) atomic lines allowed extending the linear calibration range up to 150.0 mg L^{-1} K and 120.0 mg L^{-1} Na with a satisfactory limit of detection (0.2098 mg L^{-1} K and 0.2956 mg L^{-1} Na) and low relative standard deviation (< 2.4%), suggesting that the secondary line gives precise measurements. Then, the 404.4 nm for K and 330.3 nm for Na atomic lines were used to optimize the US procedure, to validate the methodology, and to determine the elements by FAES.

Optimization of Ultrasound-assisted Extraction Procedure

Nitric and/or hydrochloric acid are often reported in studies involving extraction of the inorganic species using non-destructive sample preparation procedures (30, 31); however, acid mixtures have also been reported (32). In this sense, different acid solutions [HCl, HNO_3 and HCl:HNO_3 (1:1)] at 1.00 mol L^{-1} were evaluated to check the effectiveness of these solutions for leaching K and Na from PIATV 02/2010 reference material. The influence of these different acid solutions was determined using univariate analysis by fixing the solution volume (10 mL), sonication time (180 seconds), sample mass (0.2500 g), and bath temperature at 25 ºC. The results obtained are shown in Table IV.

It can be seen in Table IV that unsatisfactory recoveries were obtained with 1.00 mol L^{-1} HNO_3 (67% for K and 62% for Na) or HCl:HNO_3 (≈76% for K and ≈69% for Na) solutions. However, in both cases the relative standard deviations (%RSD) were < 4.6%. Only for 1.00 mol L^{-1} HCl solution the recovery (89% for K and 83% for Na) can be acceptable and produced RSD of < 2.5%. It is important to note that for a 1.00-mol L^{-1} HCl solution, the recovery was 89% for K (6.50 ± 0.14 mg g^{-1}) and 83% for Na (8.30 ± 0.21 mg g^{-1}). This value is statistically different at the 95% confidence level (paired *t*-test) with those obtained for 1.00 mol L^{-1} HNO_3 or HCl:HNO_3 solutions. By the way, alternative acid mixtures, such as *aqua regia* [3:1 (v/v)] HCl:HNO_3 and HCl:HNO_3 [1:3 (v/v)] at 1.00 mol L^{-1} were also investigated for the extraction procedure. In both cases the results were no better than those obtained using 1.00 mol L^{-1} HCl:HNO_3 [1:1 (v/v)] solution. According to the results presented in Table IV, the remaining study was performed using HCl solution.

In sample preparation using ultrasound-assisted extraction, diluted acid solutions are widely employed as extracting solvent/solution to leach out as much analyte content as possible without destroying the sample matrix by means of minimum amount of selected acids (26, 33). Using the acid solution chosen previously, different concentrations of hydrochloric acid (0.012, 0.120,

TABLE III
Figures of Merit of Main and Secondary Atomic Lines for K and Na by FAES

Element	Wavelength (nm)	Calibration (mg L^{-1})	Slope	R[c]	LOD[d] (µg L^{-1})	RSD (%)
K	766.5[a]	0.50–4.00	0.2463	0.9989	9.61	3.5
	404.4[b]	1.00–150.00	0.0063	0.9980	209.80	0.9
Na	589.0[a]	0.50–2.00	0.1718	0.9991	15.55	1.9
	330.3[b]	1.00–120.00	0.0061	0.9992	295.30	2.4

[a] Main atomic line.
[b] Secondary atomic line.
[c] Linear correlation coefficient.
[d] Limit of detection.

and 1.200 mol L^{-1}) were prepared to evaluate their performance. The influence of these HCl solutions on the K and Na recoveries were done by fixing the solution volume (10 mL), sonication time (180 seconds), sample mass (0.2500 g), and bath temperature (25 °C). The results obtained for these solutions are listed in Table IV.

A significant improvement was observed in the recoveries from the 0.012 to 0.120 mol L^{-1} HCl. While the 0.012 mol L^{-1} HCl solution can leach only 77% K (5.62 ± 0.15 mg L^{-1} of 7.30 mg g^{-1}) and 70% Na (7.00 ± 0.24 mg L^{-1} of 10.0 mg g^{-1}) from the PIATV 02/2010 reference material, the 0.120 and 1.200 mol L^{-1} HCl solutions obtained 91 and 90% recoveries for K and 84 and 86% recoveries for Na, respectively, with a relative standard deviation of < 2.7%. A paired *t*-test, at the 95% confidence level, was performed and the results showed a difference between 0.120 and 1.200 mol L^{-1} with the 0.012 mol L^{-1} HCl solutions. Based on the satisfactory recoveries obtained using 0.120 and 1.200 mol L^{-1} HCl and due to a green chemistry principle, a 0.120 mol L^{-1} HCl was adopted for further study.

Some studies report that small sample masses (high dilutions) could produce low sensitivity and poor precision/accuracy of the analyte measures due to the inhomogeneity of the sample mass of the solid-liquid extracting solution (34-36). In this sense, the increase of the mass of solid materials (sample) can improve the limits of detection and quantification due to the transference of higher contents of the analyte into the liquid phase (37). Taking this into account, portions of 0.1000, 0.2500, and 0.5000 g oilseed sample were evaluated to determine the satisfactory sample mass that produces the best recovery of K and Na. Potassium and Na recoveries using 0.1000 – 0.5000 g of the PIATV 02/2010 reference material were obtained by using 0.120 mg L^{-1} HCl and fixing the solution volume (10 mL), sonication time (180 seconds), and bath temperature (25 °C). The results described in Table IV reveal no significant influence at 95% confidence level (paired *t*-test), of sample mass up to 0.5000 g, and in all cases, the relative standard deviation was < 2.1%. Since no significant differences can be observed for the determination of K and Na using 0.1000 – 0.5000 g, an amount of 0.1000 g was used for further work.

It is important to mention that particle size also plays an important role in the extraction process (38-41), and this was one of the parameters that was evaluated to achieve the best conditions of the extraction procedure. Since PIATV 02/2010 reference material was ground to 0.84 mm (20 mesh) particle size, and the results obtained were 91% (K) and 84% (Na) recovery, it is possible to conclude that particle size does not have a significant influence on the extraction efficiency for these kinds of samples.

TABLE IV
Recovery (Mean ± Standard Deviation, n= 3) of K and Na from PIATV 02/2010 Reference Material on the Optimization of the Ultrasound-Assisted Extraction Conditions

US Extraction Conditions		K Recovery (%)	K RSD (%)	Na Recovery (%)	Na RSD (%)
Extracting Solution	HCl	89	2.2	83	2.5
	HNO_3	67	3.7	62	4.6
	HCl:HNO_3 [1:1(v/v)]	76	3.0	69	4.0
HCl Solution (mol L^{-1})	0.012	77	2.7	70	3.4
	0.120	91	1.9	84	2.7
	1.200	90	1.6	86	2.3
Sample Mass (g)	0.1000	91	1.6	84	1.9
	0.2500	93	1.7	85	2.1
	0.5000	92	1.2	87	2.0
Volume (mL)	7.50	80	4.1	78	3.5
	10.00	92	2.0	86	1.7
	15.00	98	2.7	95	2.2
Sonication Time (s)	30	98	1.9	95	2.1
	60	97	1.4	94	2.0
	120	99	0.9	94	1.9
	180	99	1.1	95	1.5

K: 7.30 ± 0.67 mg g^{-1}, Na: 10.0 mg g^{-1}

For solid-liquid extraction of metals from solid matrices using ultrasound-assisted extraction, different volumes of extracting solutions have been employed (39, 42, 43). In this work, 7.5, 10.0, and 15.0 mL of 1.0 mol L^{-1} HCl were applied to evaluate the recoveries. The analytical results are shown in Table IV. The influence of the extraction volume on extraction efficiency was significant from 7.5 to 15.0 mL, and the recovery obtained for 7.5 mL (80.0% for K and 78.0% for Na) was statistically different, at a 95% confidence level (paired *t*-test), with those obtained for 15.0 mL (98% for K and 95.0% for Na). Thus, 15.0 mL of 0.120 mol L^{-1} HCl was chosen for the optimization parameters of the ultrasound-assisted extraction procedure.

Based on the results obtained in this study (≈95% recovery), the proposed extraction procedure could be applied to determine K and Na using FAES. However, the extraction time efficiency depends on analyte-matrix interaction, extracting solution composition, and the ultrasonic system applied (26, 44). In this study, the extraction time was evaluated to reduce the time consumption of the proposed method. For this, 0.1000 g of PIATV 02/2010 reference material was subjected to 30, 60, 120, and 180 seconds sonication time under the previously optimized conditions. The results obtained are listed in Table IV.

Quantitative extractions of K (97 – 99%) and Na (94 – 95%) were obtained using 30 – 180 seconds sonication intervals with an ultrasound energy corresponding to 40 kHz. The results showed no significant difference at the 95% confidence level (paired *t*-test), and presented relative standard deviations (%RSD) from 0.9 to 1.9% (K) and 1.5 to 2.1% (Na). It is important to point out that 30 seconds of sonication is a very short and satisfactory time to extract K and Na from oilseed samples.

By using 15 mL of 0.12 mol L^{-1} HCl solution, 0.84 mm particle size, 0.1000 g sample mass, and 30 seconds sonication at 25 °C, better conditions for extracting K and Na from the selected samples were achieved. These values were adopted to validate the proposed method and for analysis of the samples.

Analysis of Oilseed Samples

Five different oilseed samples of the genus *Crambe abyssinica Hochst, Guizotia abyssinica, Brassica napus var. oleífera, Carthamus tinctorius L., and Raphanus sativus L. var. oleiferus Metzg* were submitted to the proposed extraction procedure and the final extracts were analyzed by FAES. The K and Na content, determined in the final extraction solutions, showed concentration intervals within 22.12±0.32 – 30.20±1.12 mg L^{-1} and 5.64±0.20 – 8.04±0.20 mg L^{-1}, respectively. As can be seen, only the secondary atomic line could be used for the determination of K and Na in the concentration range described above in a single run without need of further dilution of the samples. The analytical results, expressed as average values ± standard deviation (n= 3) on a dry matter basis, for the determination of K and Na in five renewable oilseed samples are listed in Table V. The analysis of the samples revealed that the concentration ranges obtained using the established ultrasound-assisted extraction procedure were in the 5.53 ± 0.08 – 7.55 ± 0.28 mg g^{-1} K and in the 1.41 ± 0.05 – 2.01 ± 0.10 mg g^{-1} Na intervals. To ensure the accuracy of the developed methodology by US, the strategies based on the addition/recovery test (using all oilseed samples) and the analysis of PIATV 02/2010 were performed. Recoveries of 97.4 ± 2.1 – 98.8 ± 3.5% K and 93.7 ± 3.3 – 99.1 ± 2.5% Na were obtained by adding an amount of K and Na as the inorganic standard at the beginning of the sample pretreatment procedure in order to achieve 25.0 and 50.0 mg L^{-1} K and Na in the final extracts.

TABLE V
Comparative Results (Mean ± Standard Deviation) of K and Na (mg g^{-1}) of the Five Renewable Oilseed Samples by FAES Using the Proposed Ultrasound-Assisted Extraction Procedure and Microwave-Assisted Acid Digestion

Oilseed Crops	Sample Preparation			
	Ultrasound-assisted Extraction		Microwave-assisted Digestion	
	K	Na	K	Na
Crambe abyssinica Hochst	7.55 ± 0.28	1.41 ± 0.05	7.73 ± 0.18	1.49 ± 0.07
Guizotia abyssinica	5.53 ± 0.14	1.84 ± 0.08	5.64 ± 0.08	1.93 ± 0.06
Raphanus sativus L. var. oleiferus Metzg	5.90 ± 0.21	1.58 ± 0.04	6.10 ± 0.15	1.55 ± 0.05
Brassica napus var. oleífera	6.07 ± 0.32	1.52 ± 0.03	6.47 ± 0.27	1.47 ± 0.04
Carthamus tinctorius L.	6.62 ± 0.16	2.01 ± 0.10	6.94 ± 0.21	2.10 ± 0.09

Finally, the results obtained for the samples using the US method were compared with those obtained using total decomposition in a closed-vessel microwave oven. The results obtained (Table V) show no significant difference at the 95% confidence level (paired *t*-test) between the values obtained for the proposed methodology and acid digestion. These results indicated that the ultrasound extraction procedure proposed in this study is free of matrix interferences. The relative standard deviation (n=12) for all measurements varied within the range of 1.8–5.3% for ultrasound-assisted extraction and 1.1–4.7% for microwave-assisted digestion.

CONCLUSION

Use of a less sensitive atomic line in FAES for K and Na was feasible for the elemental determination in a wide range of concentrations without need of further dilutions of the sample extracts, and allowed to reduce the errors associated with excessive sample handling. The methodology described offers a fast, accurate, and efficient sample preparation for the determination of K and Na in different oilseed crop samples by flame atomic emission spectrometry. In general, the proposed sample preparation makes the ultrasonic bath system advantageous as compared to acid digestion due to low time and reagent consumption, minimal generation of wastes, and therefore contributes to a green chemistry procedure.

ACKNOWLEDGMENT

The authors would like to thank the Fundação de Apoio ao Desenvolvimento do Ensino, Ciência e Tecnologia do Estado de Mato Grosso do Sul (Fundect, Process 23/200.665/2012), and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Process n. 479186/2013-8) for their financial support of this work.

Received October 24, 2016.

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