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ARTICLE

Ultrasound-assisted Extraction Method for Element Determination in Lignocellulosic Biomass

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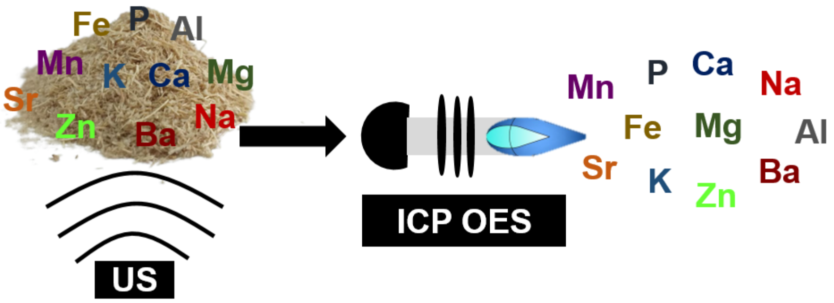

In this work, a sample preparation method based on ultrasound-assisted extraction (UAE) for the determination of Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, Sr, and Zn in lignocellulosic biomasses (sugarcane bagasse, eucalyptus wood residues, and pine wood residues) was evaluated. Reference values were achieved following the EN ISO 16967, which was based on a microwave-assisted wet digestion sample preparation method for further element determination by inductively coupled plasma optical emission spectrometry (ICP OES). The optimizations for the proposed UAE method were performed using 250 mg of sugarcane bagasse sample, where the ultrasonic bath frequency (25, 35, 37, 45, 80, and 130 kHz), and acoustic amplitude (50, 70 and 100%) were evaluated. After selecting the most efficient extractant solvent (20 mL of 1 mol L^{-1} of H_2O_2, HNO_3, H_2SO_4, H_2O, or CH_2O_2), the extraction temperature (20, 50, or 70 ºC) and time (15, 30, or 40 min) were evaluated. The most efficient extraction condition using the UAE method employed 45 kHz (70% amplitude), 20 mL of 1 mol L^{-1} of H_2SO_4, and 50 °C for 30 min. The optimized UAE was used for extraction and subsequent element determination in residues of pine wood and eucalyptus wood. Although poor recoveries were observed for Al, Ba, and Fe (lower than 75%), the results for Ca, K, Mg, Mn, Na, P, Sr, and Zn were in agreement (Student *t*-test, 95% confidence level) with those obtained by EN ISO 16967. Therefore, the proposed UAE method proved to be efficient for the determination of most of the evaluated elements in lignocellulosic biomasses with different matrix complexity, employing milder extraction conditions and diluted reagents.

Keywords: lignocellulosic residues, ultrasound-assisted extraction, ultrasound energy, ICP OES, energy

INTRODUCTION

Biomass waste originates from various activities, which can be of animal, vegetable, or microbial origin. Lignocellulosic biomass, such as sugarcane, straw, bagasse, forest residues, etc., can be generated from several industrial activities as those designed for biofuel generation, thermal conversion, and paper

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production. These activities originate several industrial and agricultural residues that present the potential to be further used as starting material for another chemical process.[1]

Lignocellulosic biomass can be industrially used to produce biofuels (second-generation ethanol, bio-oil, biochar, biogas, among others), and to generate energy by thermal conversion.[2] Beyond the advantage of its high availability, lignocellulosic biomass does not compete with the food sector. It present lower cost when compared with other sources of energy generation (such as hydroelectric power plants), and reduces the use of petroleum derivatives, minimizing the release and further effects associated with greenhouse gases.[3] The biomass samples consist of cellulose, hemicellulose, lignin, extractives (sucrose, nitrate, protein, and chlorophyll), and inorganic constituents (e.g., K, Na, Mg, Mn, among others) being a feedstock of great potential to be industrially used.[1,4]

However, the concentration of inorganic constituents in these lignocellulosic residues can cause problems in the industry while biomass is converted, as well as environmental issues would be related when the wastes are disposed. Inorganic constituents are undesirable for many industrial processes, as their presence is associated with the clogging of pipes and corrosion of reactors during biomass conversion.[2,5,6] The inorganic constituents (named as minerals or simply elements) can be extracted by conventional methods (mechanical shaking, leaching, Soxhlet, or extraction) aiming their further determination to assure the quality control and appropriate residues management. However, these methods tend to require long processing times, excessive volumes of reagents, high temperatures, among others.[2,7,8] As an alternative to speed up the extraction process the ultrasound (US) energy can be used.

The US has mechanical nature, being propagated through the medium by consecutive cycles of compression and rarefaction, which are normally generated by piezoelectric transducers. While US propagates an increase in the mass transfer mechanism is observed. In addition, under specific conditions, the US wave can generate acoustic cavitation, when the rarefaction cycle of the wave overcomes the cohesive forces of the liquid to form cavities (bubbles) filled with gases and solvent vapor. These bubbles can collapse (implosion) in the compression cycle of the US wave, promoting an environment conducive to the occurrence of chemical reactions, which through the gases and vapors present inside the bubbles can generate intense heat (hot spots) in the reaction medium. Additionally, the bubble collapse generates microflows, shockwaves, and the formation of radical species. Thus, acoustic cavitation has been considered effective for promoting extractions and chemical reactions.[9]

In this work, the use of ultrasound assisted extraction (UAE) for the elements extraction from biomasses considered as feedstock or industrial wastes and further determination by inductively coupled plasma optical emission spectrometry (ICP OES) was investigated, providing useful information for process monitoring, quality control and waste management. UAE was evaluated for Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, Sr, and Zn extraction from lignocellulose biomass samples, where acoustic and extraction parameters as US frequency, acoustic amplitude, extraction solution, time, and temperature were evaluated. The results obtained in the proposed UAE method were compared with those obtained using EN ISO 16967.

MATERIALS AND METHODS

Instrumentation

The UAE was performed using ultrasound bath systems working at several frequencies and nominal powers. Three equipment were evaluated: i) US bath working at 25 or 45 kHz with nominal power of 100 W (Transsonic TI-H-5 3.5 L, Elma GmbH & Co., Germany); ii) US bath working at 37 or 80 kHz with nominal power of 330 W (Transsonic P120H 9.0 L or P120H 12.9 L, Elma GmbH & Co.); iii) US bath working at 35 or 130 kHz with nominal power of 200 W (Transsonic TI-H-10 8.6 L, Elma GmbH & Co.). For all the evaluated systems the acoustic amplitude ranged from 10 to 100%. Microwave-assisted wet digestion (MAWD), used as reference method (EN ISO 16967), was performed using a microwave heated autoclave system with a single reaction chamber design (SRC-Ultrawave, Milestone, Italy), equipped with a rack with fifteen positions (15 mL TFM vessels).

After the extraction step, the samples were centrifuged (Quimis, Brazil) before ICP OES analysis. After sample extraction or digestion, the analytes were determined by using an ICP OES instrument (Optima 4300 DV, Perkin Elmer, USA) with axial view mode, equipped with a cyclonic spray chamber and a GemCone nebulizer.

Reagents

The water used in the experiments for preparing all the solutions and reagents was distilled, deionized, and further purified using a Milli-Q system (Millipore Corp., Burlington, VT, USA). The reagents used for sample digestion or extraction were HNO_3 P.A. 65% (1.4 kg L^{-1}, Merck, Germany) distilled at sub-boiling conditions (model duoPUR® 2.01E, Milestone, Italy) previous its use, H_2SO_4 (95-98%, Sigma Aldrich, USA); CH_2O_2 (85%, ISOPAR); H_2O_2 (30%, Merck) and HF (45%, Merck). A multielement stock reference solution of 10 mg L^{-1} (SCP33MS, SCP Science, Canada), a multielement stock reference solution of 1000 mg L^{-1} (Merck), an elemental phosphorus solution of 1000 mg L^{-1} (Inorganic ventures) were used to prepare the calibration curve, and for analytes determination by ICP OES. For the determination of dissolved organic carbon (DOC), the calibration curve was prepared by dilution of a carbon stock solution of 10000 mg L^{-1} prepared by dissolution of anhydrous citric acid (P.A., Synth), and yttrium (1000 mg L^{-1}) as internal standard. Argon (purity of 99.998%, White Martins, Brazil), was used for plasma generation in the ICP OES technique.

Biomass samples

The biomass samples (sugar cane bagasse, residues of pine wood, and residues of eucalyptus wood) used in this work were obtained through a project within the scope of the initiative Horizon 2020 (Biovalue and BECOOL) of the European Union and Brazil, which use biomass sources for research, development and sustainable deployment of advanced biofuels. The Brazilian Biorenewables National Laboratory (LNBR) coordinates the BioValue initiative (Brazilian side). The selected samples have been used as subproducts of industrial processes for biofuel and energy generation. For the optimization of the UAE the sugar cane bagasse sample was selected. The optimized UAE was applied for the other samples (residues of pine wood, and residues of eucalyptus wood).

Methods

Before the UAE method all the samples were ground and sieved to obtain a particle diameter of less than 0.84 mm (> 20 mesh), as recommended by LNBR – CNPEM (Brazilian Biorenewables National Laboratory - Brazilian Center for Research in Energy and Materials), which established a particle size for the initial biomass characterization and further extraction of the minerals.[10] To obtain the reference values of elemental content in all the evaluated biomass, samples were digested using the SRC-Ultrawave system with concentrated HNO_3, following a standard method for biomass (EN ISO 16967).[11] The reference method used 250 mg of sample digested with 4 mL of HNO_3 14.4 mol L^{-1}, 1.5 mL of 30% H_2O_2, 0.5 mL of 40% HF, followed by the addition of 5 mL of 4% H_3BO_3. After the sample digestion an ICP OES analysis was performed for the determination of Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, Sr, and Zn.

For the UAE procedure the samples were placed always in the same position of the US bath. After mapping the US bath using the aluminum foil protocol,[12] two main positions of high intensity of the acoustic field were identified. These positions were used for sonicating two samples simultaneously. This approach was followed for avoiding possible interferences in the elemental extraction due to the differences in the US wave distribution through the bath volume. The UAE was carried out using an ultrasonic bath operating at 25 kHz, 70% of acoustic amplitude, extraction temperature of 70 °C for 30 min, and diluted extractor solution. The extraction solution (1 mol L^{-1} of H_2O_2, HNO_3, H_2SO_4, H_2O, and CH_2O_2) was evaluated. Further, a univariate design was followed to select the US frequency (25, 35, 37, 45, 80, or 130 kHz), extraction temperature (20, 50 or 70 °C), acoustic amplitude (50, 70, or 100%), extraction time (15, 30 or 40 min), and 250 mg of sample mass (sugar cane bagasse). The parameters that resulted in better extraction efficiency were applied to other samples of biomass (residues of pine wood and eucalyptus wood). Before the elemental determination by ICP OES the extractant from UAE was centrifuged and separated from solid residues.

The extraction efficiency (E_{ef}) was calculated based on the obtained results ($[element]_{UAE}$) in comparison with those obtained by acid digestion (reference method), which were considered as the total concentration ($[element]_{ref}$), as presented in Equation 1. For the evaluation related to the acid solution, it was considered the sum of all the elements, expressed as E_{ef} percentage, for plotting the figures.

$$E_{ef} = \frac{[element]_{UAE}}{[element]_{ref}} x\ 100 \qquad \text{Equação 1}$$

All the obtained results and comparisons were performed by means of a statistical evaluation (Student *t*-test), with a 95% confidence level for all comparisons using Statistica software (version 1.0).

RESULTS AND DISCUSSION

Elementary determination of minerals in biomass samples

To better evaluate the UAE efficiency, the samples of biomass were microwave digested and Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, Si, Sr, and Zn were determined by ICP OES, as results presents in Table I.

Table I. Analyte determination by ICP OES in samples of biomass after microwave assisted wet digestion, according EN ISO 16967 (results presented as average ± standard deviation, µg g $^{-1}$, n=3)

Analyte	Biomass sample		
	Sugar cane bagasse	**Eucalyptus wood**	**Pine wood**
Al	200 ± 12	20 ± 2.3	1004 ± 21
Ba	4.65 ± 0.63	13.9 ± 1	13.7 ± 0.2
Ca	288 ± 45	784 ± 22	1554 ± 55
Fe	290 ± 22	21.5 ± 1.2	837 ± 85
K	1248 ± 70	1400 ± 40	1002 ± 75
Mg	314 ± 24	214 ± 15	398 ± 12
Mn	19.2 ± 0.9	93.4 ± 6.7	139 ± 3
Na	11.7 ± 0.2	< 10*	< 10*
P	103 ± 7	121 ± 4	125 ± 10
Si**	3285 ± 487	< 61*	1302 ± 144
Sr	3.6 ± 0.3	11.3 ± 0.7	12.7 ± 0.5
Zn	5.53 ± 1.00	4.41 ± 0.47	11.4 ± 0.4
Sum**	2492	2683	5097

*Limit of detection; **not evaluated in UAE proposed protocol; ***sum of all the evaluated elements.

As observed in Table I, some elements are present in relatively higher concentration in all the evaluated samples, such as Al, Ca, Fe, K and Mg. Some of them are used as fertilizers, such as K and P since they are essential elements playing a role as nutrients for the plant tissue. Mg contributes to plant development, photosynthesis, and breathing, and in the synthesis of macromolecules, while the other elements are associated with silica, playing a structural role in the plant.[13]

Evaluation of the extraction solution for the UAE

To evaluate the efficiency of UAE, experiments with several extraction solutions (20 mL of 1 mol L^{-1} of HNO_3, H_2SO_4, CH_2O_2, H_2O_2, or H_2O) were carried out. The initial operational conditions for UAE followed those previously reported in the literature, as 250 mg of sample sonicated for 30 min at 70 ºC using an US bath operating at 25 kHz with 70% of amplitude.[14] The obtained results, presented as the sum of all the evaluated elements, are present in Figure 1.

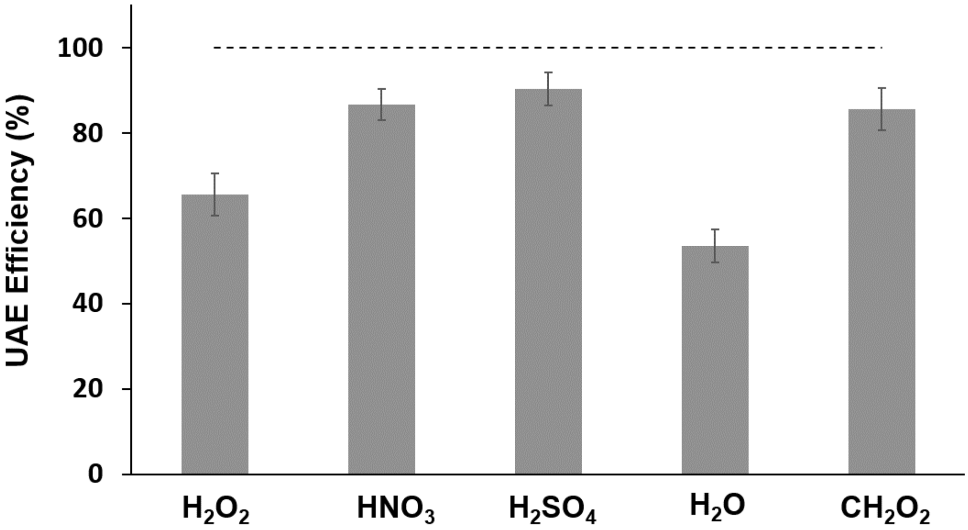

Figure 1. UAE efficiency related to the extraction solution (20 mL of 1 mol L^{-1}) using an ultrasound bath operating at 25 kHz (70% US amplitude). Dashed line is the total concentration of the sum of the elements (value from standard digestion method). Experimental conditions: 250 mg of sugarcane bagasse sample, 30 min at 70 °C (error bars are the standard deviation, n= 3).

Considering the first set of experiments, and the need for further optimizations, Figure 1 presents only results related to the sum of all elements, which makes the image clear as well as turn the interpretation easier. As observed, when the acid solution was used for UAE the extraction efficiency was higher than 85%. The same behavior was not observed when H_2O_2 or H_2O were used, which presented extraction efficiency lower than 65%. Additionally, as previously reported, when extraction procedures are employed the amount of dissolved organic carbon (DOC) in the solution tends to be high, especially when high temperature and pressure are used.[15] High values of DOC represent a condition prone to spectral interferences when ICP-based techniques are used, being recommended to avoid such conditions.[16] Although the experimental conditions of the UAE were considered mild, the higher DOC observed for inorganic acids (HNO_3 and H_2SO_4) came from HNO_3 as an extraction solution, which was almost three times higher than DOC obtained with H_2SO_4 (Figure 2). The organic acid, CH_2O_2, is not present in Figure 2 because the DOC was considered too high (near 900 mg L^{-1}) for ICP-based determination using aqueous-based standard calibration. Thus, considering an extraction efficiency near 90% and lower DOC, H_2SO_4 was selected for further evaluations.

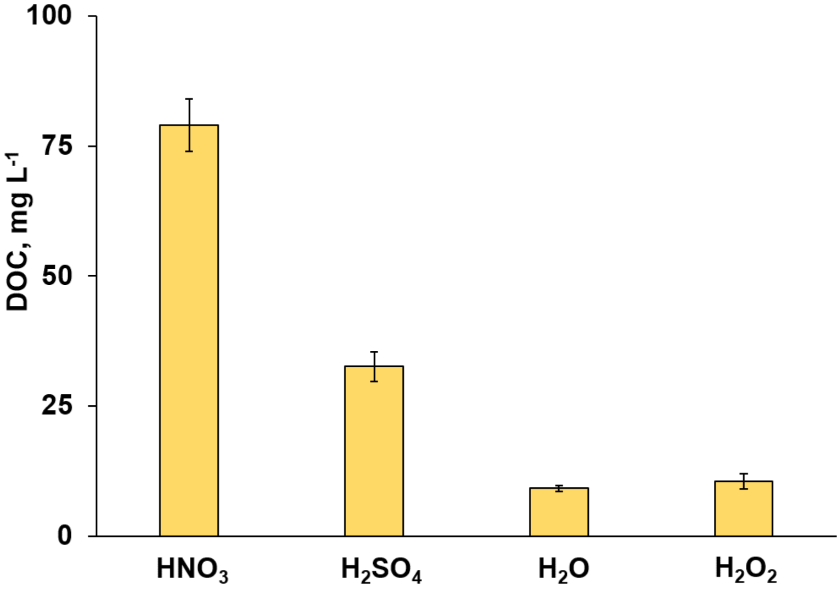

Figure 2. DOC related to the extraction solution (20 mL of 1 mol L^{-1}) using an ultrasound bath operating at 25 kHz (70% US amplitude). Experimental conditions: 250 mg of sugarcane bagasse sample, 30 min at 70 °C (error bars are the standard deviation, n= 3).

Evaluation of the acoustic frequency and extraction temperature for UAE

After selecting the extraction solution (20 mL of 1 mol L^{-1} H_2SO_4), which presented the higher extraction efficiency for the sum of all the evaluated analytes, and the lower DOC among acid solutions evaluated, the operational frequency of the US bath, and the extraction temperature were evaluated, as presented in Figure 3. The evaluated frequencies ranged from 25 to 130 kHz, while temperature ranged from 20 to 70 ºC. All the US baths operated at 70% amplitude and the extraction time was set to 30 min.

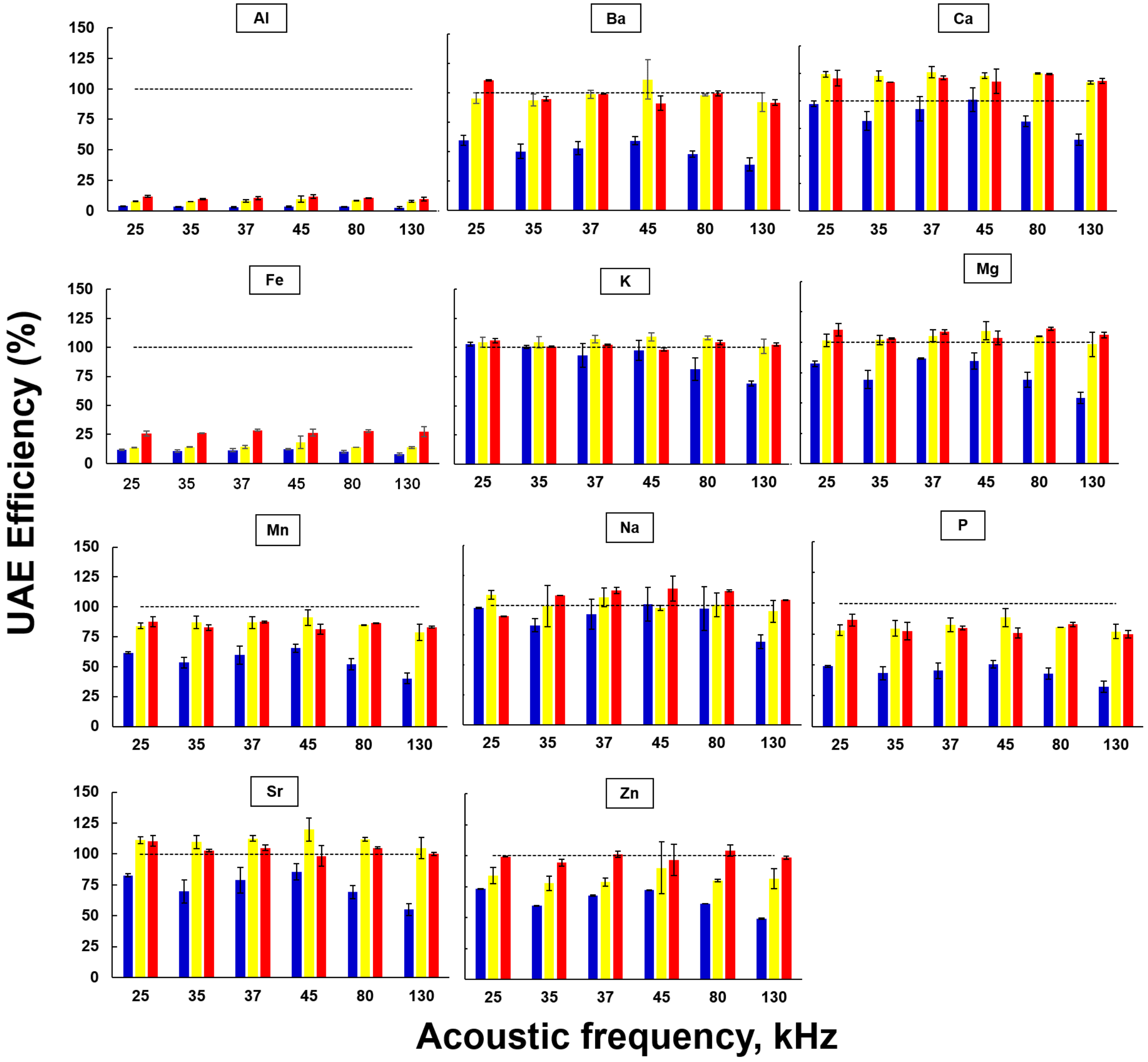

Figure 3. The influence of acoustic frequency (kHz), and extraction temperature (🟦20, 🟨50 and 🟥70 ºC) for the UAE extraction efficiency. Dashed line is the total concentration of each element (from EN ISO 16967). Experimental conditions: 250 mg of sugarcane bagasse sample, 70% amplitude, 30 min extraction (error bars are the standard deviation, n= 3).

It was possible to observe that acoustic frequency presented a non-significant effect on extraction efficiency when 50 and 70 ºC were applied for UAE. For temperatures higher than 50 ºC quantitative recoveries were observed for Ba, Ca, K, Mg, Mn, Na, Sr, and Zn, mainly when 45 kHz were employed. It is worth mentioning that Ba is recognized to form insoluble sulphates. However, the use of diluted H_2SO_4 might contribute for quantitative recoveries of Ba in this evaluation.

For 20 ºC, although the extraction efficiency was poor for a major part of the analytes, it was observed a trend for Ba, Ca, K, Mg, Mn, Na, P, Sr, and Zn where the extraction efficiency smoothly increases (or keep constant) from 25 to 45 kHz, and further decreases from 45 to 130 kHz. This trend is somehow predictable, especially when the US operated at lower temperatures. The higher the extraction temperature, the more efficient will be the extraction, which is related to the partition coefficient.[17] US frequency, for instance, contributes with the acoustic cavitation phenomena which is more efficient at lower temperature. So, in a condition of lower extraction temperature, it is possible to observe a more pronounced effect of US over extraction efficiency. In addition to that, the lower the frequency the bigger the bubble size and higher the energy released when the bubble collapse (implosion). Furthermore, the number of bubbles increase while the frequency increase, but the bubble size starts to decrease and the physical effects from cavitation (microflows, shockwaves, and mass transfer) are less intense.[17] Thus, it is possible to assume that a compromise condition between bubble size and number of bubbles allowed to achieve an optimum condition of energy for the analyte extraction, which corroborates the results observed in UAE performed at 20 ºC.

Although the observed trend related to US frequency clearly indicates that these parameters affect the extraction efficiency, it was observed that the best compromise condition between extraction temperature and US frequency was achieved using an ultrasonic bath operating at 45 kHz and extraction performed at 50 ºC. Under these conditions quantitative recoveries were achieved for Ba, Ca, K, Mg, Mn, Na, Sr, and Zn (Student *t*-test, 95% confidence level). For Al, Fe, and P recoveries were not quantitative, ranging from 10 to 88% (Al, and P, respectively). Therefore, to improve the extraction efficiency of Al, Fe, and P, the acoustic amplitude and extraction time were further evaluated using an ultrasonic bath operating at 45 kHz with extraction performed at 50 ºC.

The influence of the acoustic amplitude for UAE

Acoustic amplitude brings the information about how much energy is transported by the acoustic wave while it propagates through a medium. When the delivered energy (W), determined by calorimetric approach, is related to the rector/vessel volume (L), it is possible to calculate the power density ($W L^{-1}$) that the reaction mixture is exposed.[17,18] The increase in the acoustic amplitude results in an increase in the delivered energy ($W L^{-1}$). With the increase in the amplitude, the pressure variation in the reaction medium is larger, which leads to the formation of cavitation bubbles with more energetic collapse (the bubbles are easily formed, and fast approaches to the collapse). One can believe that this phenomenon would contribute for making more effective solid-liquid mass transfer thus favoring the extraction of the elements.[12] In Figure 4 it is possible to observe the effect of 50, 70 and 100% amplitude over UAE efficiency for Al, Fe, and P.

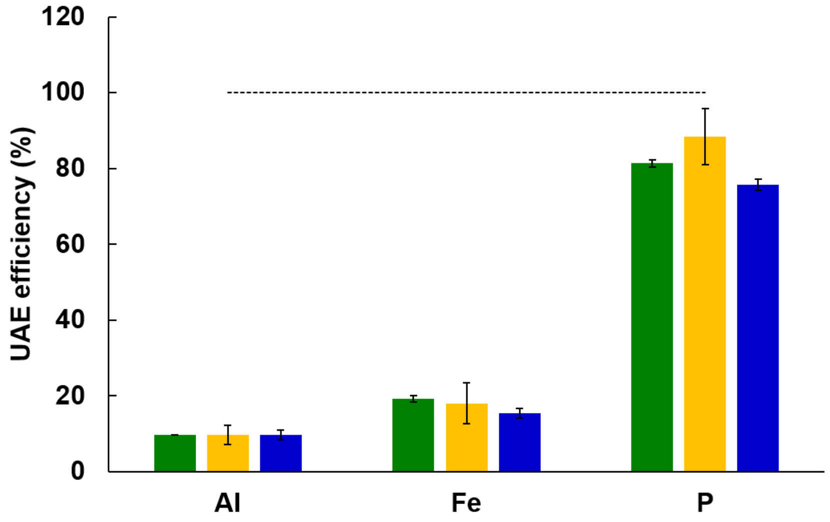

Figure 4. Acoustic amplitude (🟩50, 🟨70, and 🟦100%) effect on UAE efficiency. Dashed line is the total concentration of each element (from EN ISO 16967). Experimental conditions: 250 mg of sugarcane bagasse sample, 20 mL of 1 mol L^{-1} H_2SO_4, 30 min extraction at 50 °C, and 45 kHz acoustic frequency (error bars are the standard deviation, n= 3).

For Al and Fe no differences were observed while acoustic amplitude ranged from 50 to 100%. This result means that for these elements any further contribution to improve the UAE efficiency might come from the extracting solvent condition (concentration, extraction time, temperature, etc.). Phosphorus, for instance, was sensitive to the changes in the acoustic amplitude. A maximum was observed at 70% amplitude, followed by a decrease when 100% amplitude was employed. Such behavior is coherent with the acoustic cavitation theory,[19] since the increase in the amplitude leads to the increase in the bubble size, the number of bubbles, as well as the energy released during bubble collapse. In an environment plenty of bubbles (e.g., 100% amplitude) the sound propagation may become difficult due to the differences in the acoustic impedance of the liquid and the gas phase,[20] as well as the fact that the energy from the collapse of a bubble can be cushioned by the presence of a neighbor bubble. Both phenomena impair the acoustic cavitation effects, reducing the efficiency of UAE for those elements with sensitive behavior to the acoustic amplitude. This means that for P a compromise condition between all the evaluated parameters with acoustic amplitude was achieved when the 70% amplitude was employed.

The influence of the extraction time for UAE

The extraction time was evaluated from 15 to 40 min. The influence of extraction time on the efficiency of the UAE for Al, Fe, and P is present in Figure 5.

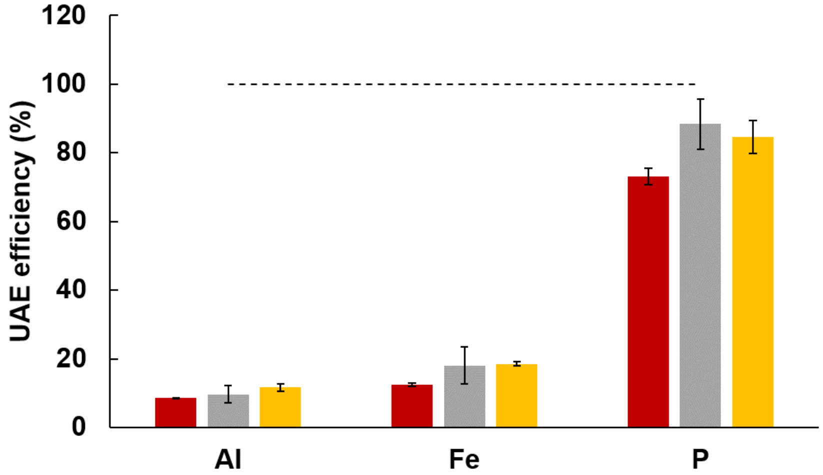

Figure 5. Extraction time (🟥15, ◼30, and 🟨40 min) effect on UAE efficiency. Dashed line is the total concentration of each element (from EN ISO 16967). Experimental conditions: 250 mg of sugarcane bagasse sample, 20 mL of 1 mol L^{-1} H_2SO_4, 50 °C, and 45 kHz at 70% amplitude (error bars are the standard deviation, n= 3).

As shown in Figure 5, there is a growing trend in the extraction efficiency when extraction time increases from 15 to 30 min. However, the same trend is not observed when extraction time further increases up to 40 min, which means that no improvement in the UAE efficiency would be expected for extraction time longer than 30 min. In this condition, P presented a quantitative recovery, agreeing with the result obtained by EN ISO 16967 (Student *t*-test, 95% confidence level), while Al and Fe remained with low extraction efficiency (lower than 20%). This result was already expected since Al and Fe are commonly found as silicate-bound elements, which makes the UAE inefficient at milder extraction conditions as those employed in this study.[13,21]

UAE applied to other lignocellulosic biomasses for elements determination by ICP OES

The optimized conditions of UAE (250 mg extracted in an US bath operating at 45 kHz, and 70% amplitude, using 20 mL of 1 mol L^{-1} H_2SO_4, 50 ºC, and 30 min sonication) allowed quantitative recovery of Ba, Ca, K, Mg, Mn, Na, P, Sr, and Zn in sugarcane bagasse, which was not achieved for Al and Fe (recoveries lower than 20%). Thus, the UAE was applied for ICP OES determination of Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, Sr, and Zn in residues of eucalyptus wood and pine wood, as results presented in Table II. The obtained residues were compared with those obtained by following the reference method (EN ISO 16967),[11] where samples were microwave digested using concentrated reagents. The obtained results (UAE) were statistically compared with those from the reference method.

Similar behavior to those observed with sugarcane bagasse were obtained for residues of eucalyptus wood and pine wood. Al and Fe, as expected, presented recoveries ranging from nearly 40 to 60%. As already discussed, these elements are associated with silica, being difficult to be extracted under milder extraction conditions. Despite quantitative recovery observed for sugarcane bagasse, Ba presented poor recoveries in residues of eucalyptus wood and pine wood (approx. 50 and 75%, respectively). In this sense, the proposed UAE method presented quantitative recoveries for Ca, K, Mg, Mn, Na, P, Sr, and Zn in samples of lignocellulosic biomass as sugarcane bagasse, residues of eucalyptus wood and pine wood, which agreed with results obtained from reference method (Student *t*-test, 95% confidence level). Ba was quantitatively determined only in sugarcane bagasse, but poor recoveries were observed for residues of eucalyptus wood and pine wood. Al and Fe presented poor recoveries for all the evaluated samples and must be disregarded for UAE whether the conditions optimized in this work would be applied.

Table II. ICP OES determination of Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, Sr, and Zn in sugarcane bagasse, eucalyptus wood residues, and pine wood residues after UAE sample preparation method. Experimental conditions of UAE: 250 mg of sample, 20 mL of 1 mol L^{-1} H_2SO_4, 30 min sonication at 50 °C, and 45 kHz at 70% amplitude (results presented as average ± standard deviation, µg g $^{-1}$, n=3).

Analyte	**Biomass sample**								
	Sugarcane bagasse			**Eucalyptus wood**			**Pine wood**		
	UAE (µg g^{-1})	**EN ISO 16967 (µg g^{-1})**	**UAE E_{ef} (%)**	**UAE (µg g^{-1})**	**EN ISO 16967 (µg g^{-1})**	**UAE E_{ef} (%)**	**UAE (µg g^{-1})**	**EN ISO 16967 (µg g^{-1})**	**UAE E_{ef} (%)**
Al	19.4 ± 5.2	200 ± 12	10 ± 2	12.5 ± 1.3	20 ± 2.3	62 ± 6	526 ± 50	1004 ± 21	52 ± 5
Ba	5.18 ± 0.78	4.65 ± 0.63	111 ± 17	6.8 ± 0.7	13.9 ± 1	49 ± 5	10.3 ± 0.2	13.7 ± 0.2	75 ± 1
Ca	353 ± 7	288 ± 45	123 ± 3	782 ± 91	784 ± 22	100 ± 11	1633 ± 6	1554 ± 55	105 ± 1
Fe	52.4 ± 15.7	290 ± 22	18 ± 5	9.22 ± 0.10	21.5 ± 1.2	43 ± 1	323 ± 28	837 ± 85	39 ± 3
K	1362 ± 44	1248 ± 70	109 ± 4	1295 ± 54	1400 ± 40	93 ± 4	894 ± 53	1002 ± 75	89 ± 5
Mg	343 ± 23	314 ± 24	109 ± 8	198 ± 17	214 ± 15	93 ± 8	372 ± 11	398 ± 12	93 ± 3
Mn	17.5 ± 1.3	19.2 ± 0.9	91 ± 7	89.6 ± 3.5	93.4 ± 6.7	96 ± 4	142 ± 7	139 ± 3	102 ± 5
Na	11.4 ± 0.2	11.7 ± 0.2	97 ± 2	< 10*	< 10*	-	< 10*	< 10*	-
P	91.0 ± 7.5	103 ± 7	88 ± 7	109 ± 7	121 ± 4	90 ± 5	101 ± 4	125 ± 10	81 ± 4
Sr	4.31 ± 0.34	3.6 ± 0.3	118 ± 9	10.4 ± 0.9	11.3 ± 0.7	92 ± 8	12.9 ± 0.7	12.7 ± 0.5	102 ± 6
Zn	4.99 ± 1.15	5.53 ± 1.00	90 ± 21	4.74 ± 0.19	4.41 ± 0.47	107 ± 4	10.7 ± 0.2	11.4 ± 0.4	94 ± 2

*Limit of detection.

CONCLUSIONS

From the evaluations performed in the present study, it was observed that the proposed UAE method was efficient for lignocellulosic biomass sample preparation for further metals and nonmetals determination by ICP OES. Even considering the complexity of the evaluated biomasses, an US bath operating at 45 kHz (70% amplitude) was able to quantitatively extract Ca, K, Mg, Mn, Na, P, Sr, and Zn from sugarcane bagasse, eucalyptus wood residue, and pine wood residue. It is noteworthy that the proposed UAE method used diluted reagents (1 mol L^{-1} H_2SO_4), short extraction times (30 min), and milder extraction temperature (50 ºC). Although poor results were observed for Al, Ba, and Fe the extractions were reproducible and presented agreement with results obtained when reference protocol (EN ISO 16967, based on wet digestion) was employed for the same samples. Considering these advantages, UAE can be considered a feasible process for Ca, K, Mg, Mn, Na, P, Sr, and Zn determination by ICP OES in lignocellulosic biomasses with different complexities.

Conflicts of interest

The authors have no conflict of interest.

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