

A slurry sampling high resolution continuum source graphite furnace atomic absorption spectrometry approach to determine metals in biomass bottom ash

Ana San-Felipe, Beatriz Gómez-Nieto^{*}, María Jesús Gismera, María Teresa Sevilla, Jesús R. Procopio

Departamento de Química Analítica y Análisis Instrumental. Facultad de Ciencias. Avda. Francisco Tomás y Valiente, 7. Universidad Autónoma de Madrid, Madrid 28049, Spain

ARTICLE INFO

Keywords:

Biomass bottom ash
Multivariate optimization
Slurry sampling
HR-CS GFAAS
Muelelement determination

ABSTRACT

Industrial by-products such as biomass bottom ash (BBA) should be reused in the context of the Circular Economy, but their use depends on the content of major, minor, and toxic elements. In this work, a slurry sampling method based on High Resolution Continuum Source Graphite Furnace Atomic Absorption Spectroscopy (HR-CS GFAAS) was developed for the determination of Pb, Cu, and Fe in these by-products. Using a two-step multivariate experimental design, the optimal conditions for the preparation of the sample suspensions (dispersion of 10.0 mg of 32 μm sieved BBA sample in 10.0 mL of 1.4% (v/v) HNO_3 and 0.7% (v/v) Triton X-100 solution using an ultrasonic bath for 1.0 min (50% power; 80 kHz)) were established. The GFAAS temperature program was optimized using both aqueous standards and BBA slurries, allowing the determination of the three metals in a single analytical run and with the same sample aliquot. Under the optimal conditions the limits of detection (LODs) were 0.55 $\mu\text{g g}^{-1}$, 0.21 $\mu\text{g g}^{-1}$, and 0.72 mg g^{-1} for Pb, Cu, and Fe, respectively. Different BBA samples were analyzed using the proposed method. The suitability of the method was probed by determining the concentrations of the metals in the solutions obtained after microwave acid digestion of the BBA samples, obtaining statistically comparable results (Student-t test for two independent samples at a 95% confidence level).

Introduction

One of the main challenges of actual societies is the production of energy from environmentally friendly sources. In this context, biomass combustion for power generation is a widely used alternative since it is considered a carbon neutral energy source [1]. However, the combustion of these materials generates very large amounts of ash that are classified as solid waste in the European List of Wastes [2]. These wastes are commonly divided into two categories: biomass fly ash (BFA) and biomass bottom ash (BBA) that are different in composition and properties [3]. BFA, with average particle size between 10 and 100 μm , is the lower density fraction from the combustion process and mostly recovered from the air pollution control devices. BBA is the unburned residue that remains in the furnace after the combustion process, with average particle size > 100 μm .

To minimize storage of biomass ash in landfills, in agreement with the EU Waste Legislation and in the context of the Circular Economy [4],

these wastes should be re-used or recycled. Different uses of biomass ash have been investigated [5–9] and successful results have been obtained by using them as alternative soil amendment, fertilizer material, or as supplementary cementitious material to prepare sustainable concretes. However, the new uses of these by-products of power generation processes are conditioned by their mineral composition and properties, which highly depend on the type of biomass, its production conditions, and the combustion furnace and conditions used for its incineration. BBA usually have high concentrations of K, P, Fe, Mg, and Ca, which are essential to promote plant growth, and tend to present high pH values, so they are used as acid-neutralizing material in soils, improving soil qualities for agricultural uses. BBA could be rich in other metals such as Cu, Mo, or Zn that are also necessary in small dose for plant growth, and Pb, Cd, or As, that are considered toxic elements and can be absorbed by plants or released into the environment [7–9]. Therefore, it is crucial to evaluate the metal content of these wastes to predict their potential applicability in soils ensuring that their reuse does not suppose a risk to

^{*} Corresponding author.

E-mail address: beatriz.gomez@uam.es (B. Gómez-Nieto).

<https://doi.org/10.1016/j.greeac.2023.100068>

Received 7 June 2023; Received in revised form 14 July 2023; Accepted 17 July 2023

Available online 17 July 2023

2772-5774/© 2023 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

the environment and human health.

Metal determination in biomass ash samples is commonly carried out by methods based on techniques as X-Ray Fluorescence (XRF), Atomic Absorption Spectroscopy (AAS) with flame (F) or graphite furnace (GF) atomizer, and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) or Mass Spectrometry (ICP-MS) [10–12]. Direct methods present several analytical advantages as they minimize the risks of contamination and/or analyte loss. Furthermore, these methods are in accordance with the principles of Green Analytical Chemistry (GAC), as it is reduced the use of corrosive and toxic chemicals such as concentrated HF, HNO₃, and/or HCl to carry out the sample pretreatment, reducing the generation of waste, and the total time required for the determination and thereby, the energy consumption [13–15]. XRF is a widely used technique for direct solid analysis, but its sensitivity is not enough to determine elements that are present at trace or ultra-trace level in the samples. In addition, XRF determinations can be affected by the components of sample matrix that can intensify or attenuate the analyte signals [11]. GFAAS, ICP-OES, and ICP-MS techniques, although usually require a previous sample treatment for metal extraction and/or destruction of sample matrix, present a high sensitivity allowing the determination of elements present at low concentrations in the samples. GFAAS can be applied for the direct analysis of solid samples or slurries [12,13,16,17].

The introduction of high-resolution continuum source GFAAS (HR-CS GFAAS) instruments greatly increased the use of GFAAS to perform direct analysis of solid samples due to the higher possibilities to correct the matrix effect using these spectrometers [13,18–21]. In addition, the main or secondary absorption lines can be selected and used for quantification purposes with optimal results. This fact allows the sequential and/or simultaneous determination of several elements in the same run and aliquot of sample reducing the amount of sample and time required for the analysis [20–25]. Direct solid sampling GFAAS methods are very attractive analytical options but also present certain limitations. One of them is the increase of the imprecision of the results due to the small amount of solid sample introduced into the graphite tube for the analysis (between 0.1 and 1 mg) and the low intrinsic homogeneity of solid samples [13]. The potential applicability of HR-CS GFAAS for the sequential and/or simultaneous determination in direct solid sampling may be also limited due to the difficulty of adjusting the sensitivity of the available absorption lines to the content of all the analytes to be determined in the same sample and/or the difficulty to dilute the samples. These limitations can be reduced introducing the solid sample as a suspension in an adequate liquid medium. For instance, when the sample is prepared as a slurry, the ratio of solid sample mass to dispersant volume can be adjusted according to the expected concentrations and the sensitivity of the GFAAS method to get an adequate and precise quantification of the analytes.

To develop slurry sampling methods, it is essential to select the adequate conditions to prepare homogeneous suspensions that must be stable, at least, over the needed time to carry out the GFAAS measurements. Homogeneity and stability of suspensions depend on parameters as the particle size of the solid sample, the characteristics of the dispersant, the mass of solid sample in the dispersant solution, and the instrumentation and conditions to mix the solid sample in the dispersant [16]. Therefore, these experimental variables must be evaluated and optimized to achieve an adequate performance of the analytical method in terms of precision and accuracy. Multivariate methods are powerful tools for the optimization of analytical procedures as they consider interactions between the different factors or variables using mathematical models, and find the optimal conditions with fewer experiments than one-variable-at-a-time methods, reducing the cost, time, and amount of energy and reagents require to develop the methods [26–30].

In this work a direct, green, and fast slurry sampling HR-CS GFAAS multielement method has been developed to determine Pb, Cu, and Fe in BBA samples. To achieve this purpose, firstly the experimental conditions for the slurry preparation have been optimized using a multivariate

method. Then, the absorption lines have been selected and the GF temperature program has been optimized to carry out the determination of Pb, Cu, and Fe in the same sample aliquot and measurement run. Finally, the developed method has been validated and applied for the multielemental analysis of different BBA samples.

2. Experimental

2.1. Instrumentation

The determination of Pb, Cu, and Fe was carried out using a HR-CS AA spectrometer ContraAA 700 (Analytik Jena, Germany). This equipment comprises a xenon short-arc lamp as unique continuum radiation source (wavelength range between 190 and 900 nm), a high-resolution double monochromator, and a linear array detector constituted by 588-pixel charge-coupled device for monitoring the absorbance signal and simultaneous background correction. This instrument is equipped with a transversely heated GF atomization unit and a MPE 60 model auto-sampler (Analytik Jena, Germany) for the introduction of liquid or suspensions into the GF. Pyrolytically coated graphite tubes with integrated platforms (Part No. 407-A81.025, Analytik Jena, Germany) were used in all experiments. HR-CS AAS equipment and additional instrumental devices are fully controlled by the Aspect CS 2.1.2.0 software (Analytik Jena AG, Germany).

An analytical balance (AX205DR model, Mettler Toledo, Switzerland) with a sensitivity of ± 0.01 mg was used to weigh the solid samples and an ultrasonic bath (P30HS model, ELMA, Germany) was used to prepare the solid sample suspensions. To evaluate the stability of the suspensions a UV-vis spectrophotometer (Specord205 UV model, Analytik Jena, Germany) and 10 mm PMMA UV grade cuvettes were used. A microwave sample preparation system (Perkin Elmer-Anton PAAR Multiwave, Austria) and MF 100 model perfluoroalkoxy (PFA) digestion vessels were used for acid digestion of the solid samples. The particle size distribution (PSD) in BBA samples was studied by laser diffraction in aqueous suspension using a Mastersizer 2000 (Malvern Instruments, United Kingdom). Total organic carbon (TOC) content in the solid samples was measured with a TOC 5000-A Analyzer provided with the solid sample module SSM-5000 (Shimadzu, Japan).

2.2. Reagents and standard solutions

Ultrapure water with a resistivity not less than 18.2 M Ω cm from a Milli-Q Direct water purification system (Merck Millipore, Germany) was used throughout. Trace analysis grade 37% hydrochloric acid (HCl) (Scharlau, Spain), 65% nitric acid (HNO₃) (Scharlau, Spain), and 47–51% hydrofluoric acid (HF) (Fluka, Switzerland) were used to carry out the microwave-assisted acid treatment of the solid samples. This HNO₃ was also used to obtain the corresponding diluted solutions to prepare sample suspensions and standard solutions. Triton X-100 (Fluka, Switzerland) was used as dispersant to prepare the slurries of the samples. Standard solutions containing Pb, Cu, and Fe were daily prepared by adequate dilution of the 1000 mg L⁻¹ commercial standard solutions for AAS of each element (Scharlau, Spain) in 1.4 % (v/v) HNO₃ and 0.7% (v/v) Triton-X 100 solution. All reagents used throughout this work were of analytical or trace analytical grade and were used as received without further purification. Plastic and/or glass containers used to prepare or store solutions and sample suspensions were cleaned by immersion in 10 % (v/v) HNO₃ solution for 24 h, and after that rinsed with ultrapure water before use.

2.3. Samples and sample preparation procedures

Three BBA samples from power plants (Spain) were analyzed in this work. The samples denoted as: BBA 1, BBA 2, and BBA 3 were provided by the *Recycling Materials Group of the Department of Cement and Recycling Material of Eduardo Torroja Institute for the Construction Sciences of*

CSIC (Madrid, Spain). Different residues are burned in these power plants. BBA1 and BBA3 were produced from incineration of various agricultural residues, and crushed pruning of fruit trees, branches and vines, eucalyptus, or holm oaks in different percentages, whereas BBA2 was produced from olive tree (25%) and olive coke (75%). Photographs of these biomass ash are shown in the Electronical Supplementary Material (ESM) (section S1, Fig. S1). The chemical composition determined by X-Ray fluorescence, the TOC content, and the pH of the three BBA samples are shown in Table S1. The three BBA samples present high pH values, a similar content of P_2O_5 and different contents of MgO , CaO , Na_2O , Al_2O_3 , and TOC. The main differences in their composition are found in the SiO_2 content with 53.1% in BBA 1, 40.5% in BBA 3, and only 1.90 % in BBA 2, and in the K_2O content with a 50.4 % in BBA 2 and a lower content in BBA 1 (10.1%) and BBA 3 (3.34%). The PSD analysis shown that particle size in BBA samples is lower than 100 μm . The optimization of the slurry sampling HR-CS GFAAS method was carried out using the BBA 1 sample.

2.3.1. Slurry optimization and preparation procedures

A two-steps multivariate method was used to select and optimize the experimental conditions to prepare the BBA suspensions [27]. In the first step, a two-level Plackett-Burman design was used to identify the variables with a significant influence on the slurry preparation. The evaluated conditions in this step were: concentrations of HNO_3 and Triton X-100 (0% or 1%), particle size of solid sample (32 or 100 μm), percentage of solid sample in the dispersant (0.05% or 0.1%), conditions of the ultrasonic bath, frequency (37 or 80 kHz) and power (50% or 100%), and agitation time (10 or 60 s). HNO_3 and Triton X-100 were selected as dispersing compounds due to their good properties for the preparation of stables slurries reported in previous studies and the high purity and absence of remarkable interferences of HNO_3 for GFAAS measurements [16,17,31]. The levels for each variable were selected considering the range of the dispersing compounds usually used in GFAAS determinations, the expected concentrations of the analytes in the samples and the sensitivity of GFAAS measurement, as well as the values that can be set in the ultrasonic bath used in this work. A more detailed description of this experimental design and evaluation is included in section S2.1 of the ESM. In the second step of the multivariate optimization, the experimental conditions with a significant contribution on the preparation of the suspensions were optimized using a Central Composite Design (CCD) at five-levels and a Response Surface Model (RSM).

The optimal conditions and procedure to prepare the BBA suspensions are as follow: 10.0 mL of a solution containing 1.4% (v/v) HNO_3 and 0.7% (v/v) Triton X-100 are added to approximately 10.00 mg of solid sample previously sieved through a nylon sieve of 32 μm mesh size. Then, the mixtures are sonicated for 1.0 min using the ultrasonic bath (80 kHz; 50% power). To analyze the samples, this procedure was carried out in quadruplicate. The stability of the obtained suspensions was checked by measuring in continuous (0.5 s data acquisition time) the transmittance percentage values (T%) along 10 min at a wavelength of 310 nm [31].

2.3.2. Procedure for the digestion of the BBA solid samples

To corroborate the suitability of the slurry sampling method, the BBA samples were treated in the microwave sample preparation system, and then the content of Pb, Cu, and Fe was measured in the obtained solutions. For this purpose, four replicates of about 50.0 mg of each sample were weighed into cleaned digestion vessels, and 2.00 mL of HNO_3 (65%), 6.00 mL of HCl (37%), and 0.20 mL of HF (47–51%) were added [32]. A power program with two steps (500 W for 5 min and 1000 W for 20 min) was used with maximum temperature (265°C) and pressure (30 bars) control. After cooling, the acid solutions were transferred to 25.0 mL volumetric flasks and diluted up to the mark with ultrapure water.

2.4. HR-CS GFAAS metal measurement procedure

Considering the concentrations of Pb, Cu, and Fe that can be expected in BBA samples the analytical lines of Pb at 283.306 nm (relative sensitivity of 42%), Cu at 324.754 nm (relative sensitivity of 100%) and the nearby secondary line of Fe at 324.600 nm (relative sensitivity of 0.014%) were selected to develop the method. The GF temperature program optimized for the determination of Pb, Cu, and Fe using the same aliquot of sample is shown in Table 1. First, the temperature program (drying, pyrolysis, and atomization steps) to determine Pb is applied. Then the wavelength is automatically changed, and higher temperatures are applied for the atomization and simultaneous determination of Cu and Fe. These elements can be determined simultaneously, since their analytical lines (324.754 nm for Cu and 324.600 nm for Fe) are within the wavelength interval that is covered by the detector (approximately 0.2–0.3 nm at 200 nm). Argon (Ar) with a purity of 99.9992% from Nippon Gas (Spain) was used as purge and protective gas in all heating GFAAS steps at a flow rate of 2.0 L min^{-1} except during the atomization steps in which the flow of Ar was stopped.

To carry out the determination of Pb, Cu, and Fe approximately 1 mL of the suspension or sample digestion solution was transferred into a clean autosampler cup immediately before carrying out the GFAAS measurement. Then, 20 μL of the sample suspension or digestion solution were automatically injected onto the graphite tube PIN-platform using the MPE 60 liquid furnace autosampler and the optimized temperature program was run. All determinations were performed in triplicate. External calibration was carried out using aqueous multi-elemental standard solutions (20 μL of injection volume) prepared in the dispersing solution (1.4% (v/v) HNO_3 - 0.7% (v/v) Triton X-100). The peak volume selected absorbance (PVSA), obtained by summing up the individual integrated absorbance values of three pixels (the central pixel plus the adjacent ones, $CP \pm 1$), was chosen as analytical signal for quantification purposes.

3. Results

3.1. Multivariate optimization of experimental conditions to prepare BBA suspensions

A multivariate method was used to select and optimize the experimental conditions to prepare the BBA suspensions to determine Pb, Cu, and Fe by GFAAS. As it was indicated in Section 2.3.1 the method has two steps: (1) Screening step: designed to identify variables with significant contribution in the obtained results, and (2) Optimization step: designed to choose the optimal conditions for those significant variables identified in the screening step.

Table 1

Optimized temperature program for the determination of Pb, Cu, and Fe by HR-CS GFAAS.

	Temperature (°C)	Ramp (°C s^{-1})	Hold time (s)	Ar flow rate (L min^{-1})
Stage 1: Pb measurement (λ_{Pb} = 283.306 nm)				
Drying 1	80	6	20	2.0
Drying 2	90	3	20	2.0
Drying 3	110	5	10	2.0
Pyrolysis	800	300	10	2.0
Atomization of Pb	1300	1500	9	0.0
Stage 2: Simultaneous Cu and Fe measurement (λ_{Cu} = 324.754 nm; λ_{Fe} = 324.600 nm)				
Pyrolysis ^a	1300	300	1	2.0
Atomization of Cu-Fe	2100	1500	10	0.0
Cleaning	2450	500	4	2.0

^a Pyrolysis step mandatory due to the configuration of Aspect CS 2.1.2.0 software

3.1.1. Screening step

A two-level Plackett-Burman design was used to obtain information about the effect (magnitude and direction) of the experimental conditions to prepare BBA suspensions on the analytical response. In Fig. 1 are shown the effect values (E_x) calculated for each variable and the critical effect (E_{crit}) (dotted black line). For variables with a positive effect, it was observed an increase in the overall response when the factor changes from low to a high level, whereas a negative effect indicates an increase on the overall response when the variable change from high to a low level. The particle size of the solid sample and the power of the ultrasonic bath show a negative effect, whereas the other variables evaluated have a positive effect. As it can be seen in Fig. 1 only the concentration of HNO_3 , the concentration of Triton X-100, and the particle size of solid sample have a significant effect ($|E_x| \geq E_{crit}$) and therefore, they should be optimized. However, the particle size will not be considered in the next optimization step because the possibility to evaluate other higher and lower values is limited by the initial particle size of the sample and the pore size of the available sieves being the sieve with the lowest pore size $< 32 \mu\text{m}$. For the non-significant factors, the value of each variable was selected considering the sign of its effect. Thus, the following studies were performed using 0.1% (w/v) suspensions of solid BBA samples with a particle size $< 32 \mu\text{m}$, prepared by sonication in the ultrasonic bath (50% power and 80 kHz) for 60 s.

3.1.2. Optimization step

The HNO_3 and Triton X-100 percentages in the dispersing solution were optimized using a five-level central composite design (CCD) and the response surface model (RSM). A detailed description of the experimental design of the CCD and the evaluation of the response function obtained was included in the ESM (Section S2.2, Tables S3 and S4). From the obtained mathematical model, the three-dimensional response surface plot was constructed (Fig. 2). As it can be seen in this figure, the maximum response is obtained for BBA suspensions prepared using a HNO_3 concentration of 1.40% (v/v) ($X_2 = 0.6$) and a Triton X-100 concentration of 0.70% (v/v) ($X_3 = -0.6$). The final conditions used for the preparation of the suspensions of BBA are summarized in the procedure detailed in Section 2.3.1.

3.2. Evaluation of the stability of BBA suspensions

The stability of BBA 1, BBA 2, and BBA 3 suspensions along time was evaluated using the optimized preparation conditions summarized in Section 2.3.1. For this purpose, the transmittance percentage (%T) of these suspensions was measured in continuous for 10 min, which is considered an enough time to perform replicate GFAAS measurements using the same suspension. Fig. 3 shows the transmittance signals over the measurement time. The initial %T values obtained for each sample

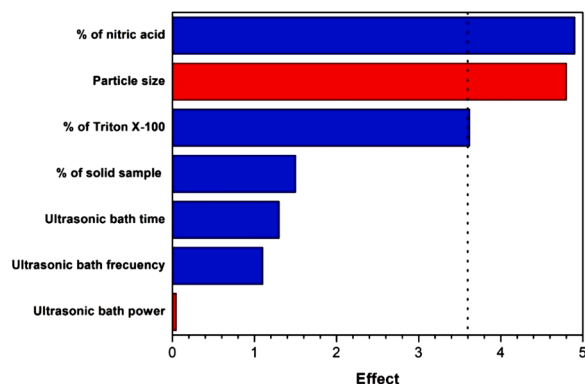


Fig. 1. Effects of the variables obtained in the Plackett-Burman screening step. In blue the values of positive effects and in red the values of negative effects. Dotted black line represents the critical effect value.

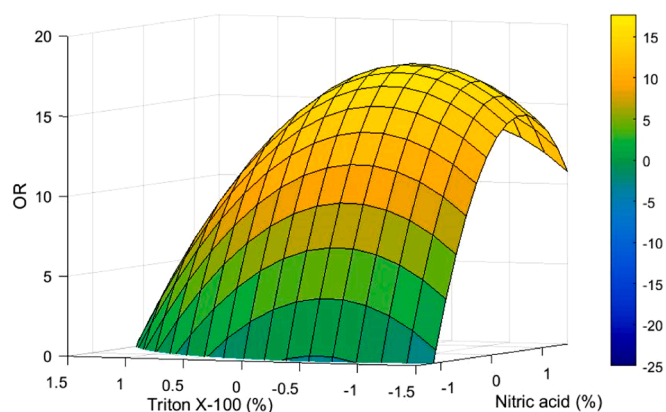


Fig. 2. Response surface obtained in the optimization of HNO_3 and Triton X-100 concentrations to prepare BBA suspensions.

suspension are related to their matrix composition and their grade of solubility in the dispersing media, whereas the rate of increase of the %T values over time is an indicator of the suspension stability. As it can be seen in Fig. 3, the suspension of BBA 1, presents the lower initial T% value (about 10%, Fig. 3A), while the suspension of BBA 2, presents the highest initial T% value (about 80%, Fig. 3B). This highest T% value seems to indicate an important solubilization of the majority components of BBA 2, the alkaline oxides, as they are easily soluble in the presence of HNO_3 under ultrasonic treatment. However, while the differences in the majority components of the different BBA samples appear to influence the initial T% values, no significant variations were observed on the transmittance percentage values along the measurement time (Fig. 3). Thus, suspensions prepared under these conditions can be considered stable and adequate for GFAAS measurements.

3.3. Optimization of HR-CS GFAAS temperature program

To carry out the simultaneous determination of elements with analytical lines in the same spectral window (Cu and Fe), these elements must have similar thermal behavior in the pyrolysis and atomization processes, such that both elements can be determined using the same temperature program. On the other hand, the sequential determination of elements (Pb and Cu/Fe) is only possible if these elements present different thermal behavior and the less volatile element is thermally stable at the atomization temperature of the more volatile one [22].

To evaluate the feasibility of performing the determination of Pb, Cu, and Fe in a single analytical run, pyrolysis and atomization curves were established using standards of Pb ($25.0 \mu\text{g L}^{-1}$), Cu ($50.0 \mu\text{g L}^{-1}$), and Fe (50.0 mg L^{-1}), and a 0.1% (w/v) suspension of the BBA 1 prepared in 1.4% (v/v) HNO_3 and 0.7% (v/v) Triton X-100. The obtained curves are shown in Fig. 4. As it can be seen in Fig. 4A, Pb was thermally stable up to a pyrolysis temperature of 900°C in the standard solution and not significant difference on integrated absorbance values were observed for atomization temperatures between 1300 and 1600°C . On the other hand, Cu and Fe in the standard solution were thermally stable up to pyrolysis temperatures of 1300°C and 1500°C , respectively, and their maximum integrated absorbances were observed for atomization temperatures between 1900 and 2100°C for Cu and between 2100 and 2300°C for Fe (see Fig. 4C and E). In the BBA suspension, Pb was thermally stable up to a pyrolysis temperature of 800°C , and its maximum integrated absorbance was found at atomization temperatures between 1300 and 1700°C (see Fig. 4B). Cu and Fe were thermally stable in the BBA suspension up to 1300 and 1700°C , respectively. The maximum integrated absorbances of both elements were observed for atomization temperatures between 2100 and 2300°C for Cu and between 2100 and 2500°C for Fe (see Fig. 4D and F for Cu and Fe, respectively). According to these results, the highest pyrolysis temperatures that can be applied

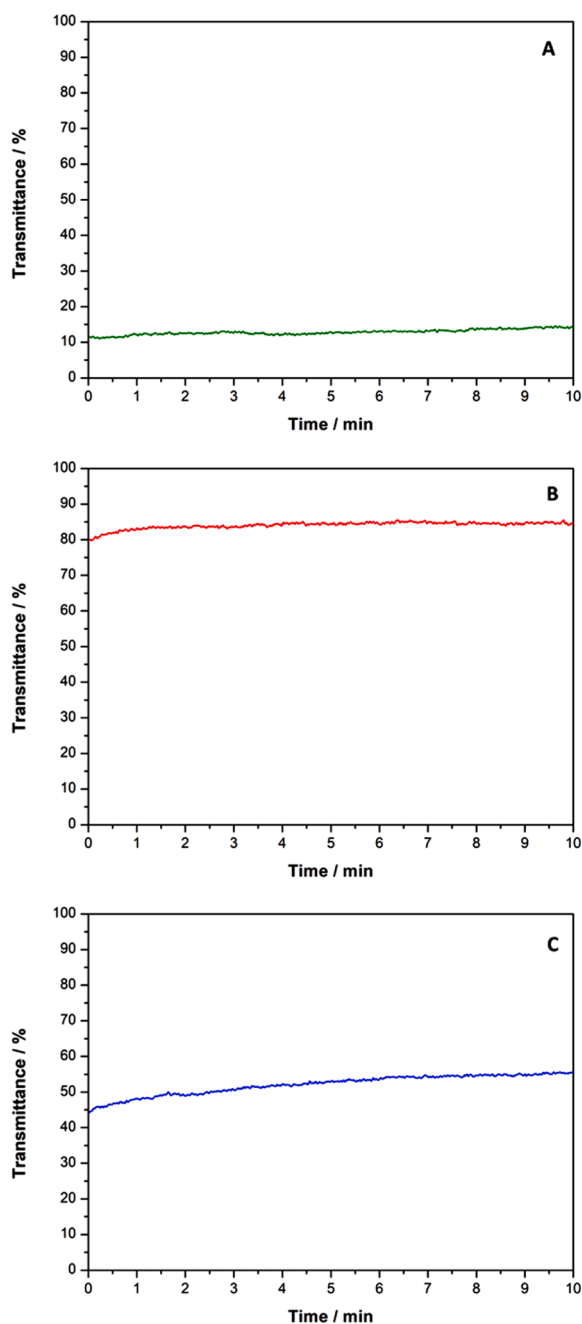


Fig. 3. Transmittance signals over time for BBA 1 (A), BBA 2 (B), and BBA 3 (C) suspensions prepared under the optimal conditions.

without loss of Pb or Cu are 800°C and 1300°C, respectively. Atomization of Pb is produced at temperatures between 1300°C and 1400°C. Therefore, a sequential determination of Pb and Cu is possible choosing 800°C for the pyrolysis step of Pb and 1300°C for atomization of Pb and pyrolysis of Cu. For the simultaneous determination of Cu and Fe, 2100°C was selected as atomization temperature. The final temperature programs for the determination of Pb, Cu, and Fe in the same run are shown in Table 1.

3.4. Calibration and figures of merit

Aqueous calibration curves were established using the dispersing solution (1.4% HNO₃ solution containing 0.7% Triton X-100) as blank and multielement standard solutions ranging from 2.50 to 200 µg L⁻¹ for

Pb and Cu and from 2.50 to 200 mg L⁻¹ for Fe prepared in the dispersant. The obtained calibration curves are shown in Fig. 5. The upper limits of the linear range (ULLR) were graphically calculated as the concentrations at which the deviation from the ideal linearity of the calibration slope was less than 5%. As it can be seen in Fig. 5, the calibration curve of Pb was linear over the entire concentration range tested (between 2.50 and 200 µg L⁻¹). For Cu and Fe, ULLR values of 80 µg L⁻¹ and 100 mg L⁻¹, respectively, were obtained using three pixels (CP±1) for signal quantification. Linear correlation coefficients (*r*) of the calibration plot for the three analytes were better than 0.995. Although preliminary assays showed that the sample matrix does not significantly influence the analytical signal, to determine if the analysis of the slurry samples can be carried out using aqueous calibration curves, the external calibration curves were compared with those obtained by adding increasing concentrations of Pb, Cu, and Fe to a fixed volume of the BBA 1 slurry. The slopes of the standard addition calibration curves (0.0083±0.0002 s L µg⁻¹, 0.0127±0.0009 s L µg⁻¹, and 0.0027±0.0002 s L mg⁻¹ for Pb, Cu, and Fe, respectively) were statistically comparable to those obtained for the aqueous calibration curves (0.00839±0.00006 s L µg⁻¹, 0.0129±0.0003 s L µg⁻¹, and 0.00273±0.00005 s L mg⁻¹ for Pb, Cu, and Fe, respectively). These results indicate that calibration can be performed using aqueous calibration curves. The figures of merit for the determination of Pb, Cu, and Fe using aqueous calibration curves are summarized in Table 2.

The characteristic concentrations (*C*₀), define as the amount of analyte that produces an absorbance signal of 0.0044, were also calculated by dividing this value to the slope of the calibration curve. The limits of detection (LODs) and quantification (LOQs) of each analyte were calculated as 3 times and 10 times, respectively, the standard deviation obtained for 10 consecutive measurements of the blank solution (1.4% of HNO₃ and 0.7% of Triton X-100), divided by the slope of the ideal calibration curve. The LODs and LOQs of all the analytes were also expressed in mass units considering the volume of standard injected in the GF to obtain the calibration curves (20 µL). The instrumental LODs and LOQs values for Pb and Cu were better or similar than those previously reported using single element determination HR-CS GFAAS methods [19,33,34]. To the best of our knowledge, this is the first analytical method in which the secondary Fe line at 324.600 nm was used, so there are not literature data available to compare the figures of merit obtained using this line.

The intraday and interday precisions of the method, expressed as relative standard deviation (RSD%), were evaluated. To estimate the intraday precision, multi-element standards of two different concentrations of each element (10 and 80 µg L⁻¹ of Pb and Cu, and 10 and 80 mg L⁻¹ of Fe) were measured in triplicate on the same day. For the interday precision study, these solutions were measured in triplicate on three different days. The results are summarized in Table 2. For the multi-element standards containing 10 µg L⁻¹ of Pb and Cu and 10 mg L⁻¹ of Fe, RSD values lower than 4.0 % and 7.0% for intraday and interday precisions, respectively were found for all elements, while for the standards containing 80 µg L⁻¹ of Pb and Cu and 80 mg L⁻¹ of Fe, the RSD values were lower than 1.0 % and 2.0% for intraday and interday precisions, respectively.

3.5. Application and validation of the slurry sampling HR-CS GFAAS method for Pb, Cu, and Fe determination in BBA

The method was applied to carry out the determination of Pb, Cu, and Fe in slurries of different BBA samples. Four replicate suspensions of each sample were prepared for the analysis. The results are shown in Table 3. The content of Pb and Cu in all the analyzed BBA is lower than the maximum limits recommended in the European countries to reuse these wastes, so all of them could be used as amendments on forest and agricultural soils [5]. Moreover, the contents of Pb, Cu, and Fe in the analyzed BBA are lower than the upper limits for these metals in the EU regulation and the Spanish normative of fertilizers [9,35,36]. Also, these

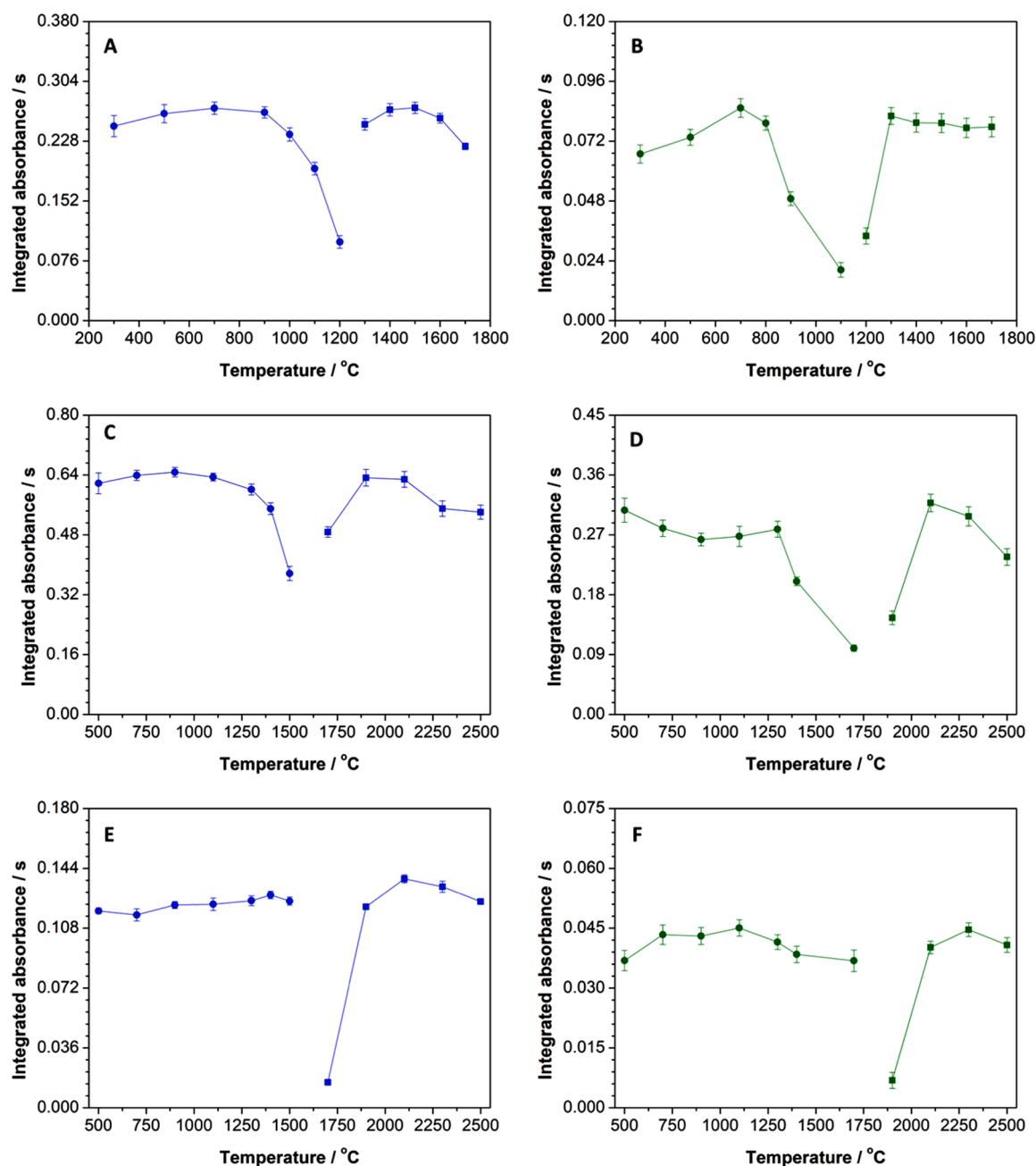


Fig. 4. Pyrolysis (circles) and atomization (squares) curves for Pb (A and B), Cu (C and D), and Fe (E and F) for standard solution (blue) of $25 \mu\text{g L}^{-1}$ of Pb, $50 \mu\text{g L}^{-1}$ of Cu, and 50mg L^{-1} of Fe and for a 0.1% (w/v) BBA 1 suspension (green). Error bars correspond to the standard deviation of $n = 3$ measurements.

materials meet the indications about the upper limits of Pb, Cu, and Fe in biomass ash for application of this by-product (with additives) on and in topsoil that are included in a published document on proposals for technical regulations for ash uses [37].

To corroborate the suitability of the developed slurry sampling HR-CS GFAAS method, all BBA samples were subjected to a microwave-assisted acid digestion. Pb, Cu, and Fe contents were determined in these acid solutions by HR-CS GFAAS. For all analyzed BBA samples, the content of Pb, Cu, and Fe obtained using both methods (Table 3) were statistically comparable (Student t-test for two independent samples at a 95% confidence level). These results demonstrate that the developed HR-CS GFAAS method, using a simple slurry as sample preparation previous introduction in the GFAAS, can be successfully applied to determine Pb, Cu, and Fe in BBA samples, even considering the important difference in matrix components of these samples (see section S1,

Table S1).

3.6. Comparison of some analytical properties and greenness profile with other methods

Some analytical properties and the greenness profile of the developed method were compared with those of other reported methods in the literature dedicated to the analysis of biomass ash samples or samples with a similar inorganic matrix by XRF, GFAAS and/or FAAS using a previous wet digestion of the samples or direct sampling of solids or slurries (Section S3, Tables S5 and S6). In terms of detectability capabilities, the LODs for Pb and Cu in the here proposed method are about ten times lower than those reported in the XRF-based method [11] and the FAAS or GFAAS method with previous acid digestion of the sample [12], whereas the LOD for Fe is higher than those reported in those

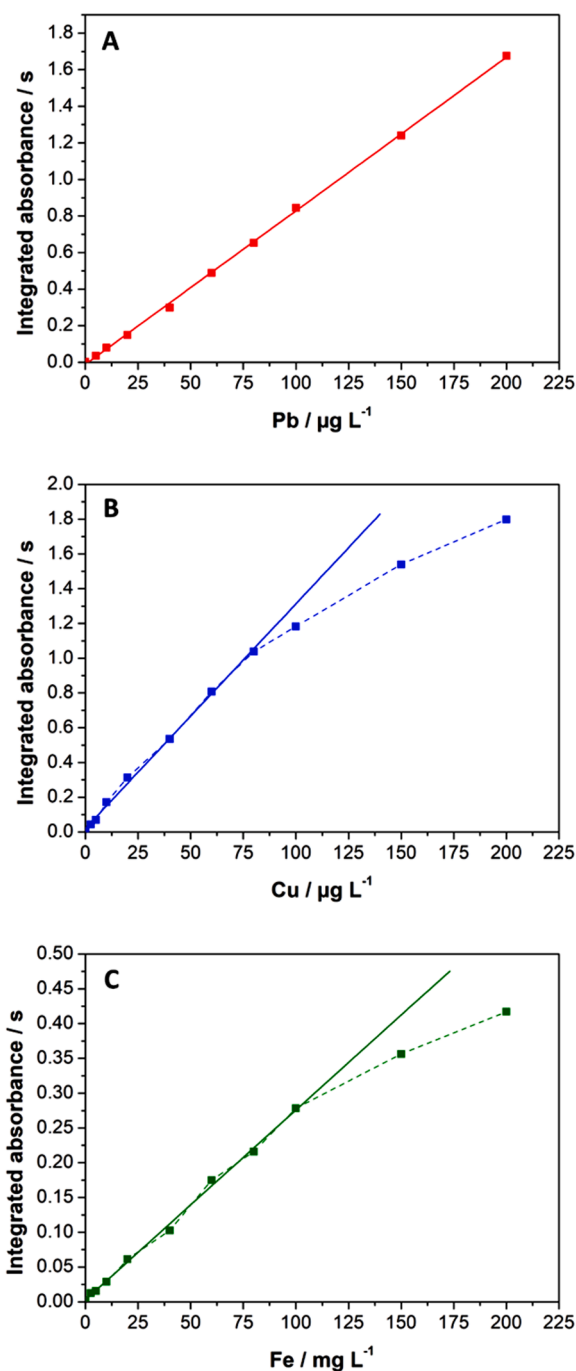


Fig. 5. Calibration curves for aqueous standards prepared in the dispersing solution: Pb (A), Cu (B), and Fe (C).

works [11,12]. This LOD value for Fe is due to the necessity of selecting a secondary line of the analyte and therefore with a low sensitivity to perform the determination of the three elements (Pb, Cu, and Fe) in the same suspension and measurement run. Comparing with the slurry sampling GFAAS method cited in the table [17], the LOD values for Pb and Cu are similar. The LOD of Pb in the present work is higher than that obtained using the direct solid sampling HR-CS GFAAS method [19] but this increase of the LOD value is due to the dilution required for the preparation of the slurry. On the other hand, in that work only one analyte (Pb) can be determined in the same sample aliquot whereas with the here proposed method the determination of the three analytes (Pb, Cu, and Fe) is performed in a sequential-simultaneous mode in a single measurement run and in the same sample aliquot, requiring only about

Table 2

Figures of merit for the determination of Pb at 283.306 nm, Cu at 324.754 nm, and Fe at 324.600 nm in the same run and sample aliquot. (Analytical signal: peak volume selected absorbance (PVSA), obtained by summing up the individual integrated absorbance values of the central pixel plus the adjacent ones, $CP \pm 1$)

Parameters	Pb	Cu	Fe
Sensitivity	0.00839 ± 0.00006 s L μg^{-1}	0.0129 ± 0.0003 s L μg^{-1}	0.00273 ± 0.00005 s L mg^{-1}
r	0.9997	0.9986	0.9981
C_0	$0.52 \mu\text{g L}^{-1}$	$0.34 \mu\text{g L}^{-1}$	1.6 mg L^{-1}
LOD ^a	$0.55 \mu\text{g L}^{-1}$ (11 pg) ^b	$0.21 \mu\text{g L}^{-1}$ (4.2 pg) ^b	0.72 mg L^{-1} (14.4 ng) ^b
LOQ ^a	$1.8 \mu\text{g L}^{-1}$ (36 pg) ^b	$0.69 \mu\text{g L}^{-1}$ (14 pg) ^b	2.4 mg L^{-1} (48 ng) ^b
ULLR	$200 \mu\text{g L}^{-1}$	$80 \mu\text{g L}^{-1}$	100 mg L^{-1}
Intraday precision, RSD% (n=3) ^c	0.4-3.2%	0.5-2.4%	0.9-3.5%
Interday precision RSD% (n=3; N=3) ^c	1.5-6.0%	1.9-5.0%	1.6-6.7%

^a Considering the amount of solid sample in the dispersant (0.1%) same values for relative LODs and LOQs are obtained.

^b Analyte LOD and LOQ calculated considering an injection volume of 20 μL .

^c Calculated at two concentration levels: 10 $\mu\text{g L}^{-1}$ of Pb and Cu, and 10 mg L^{-1} of Fe; 80 $\mu\text{g L}^{-1}$ of Pb and Cu, and 80 mg L^{-1} of Fe.

1.5 min per replicate to perform the measurement of all the analytes. The slurry sampling method proposed in this work does not require the use of concentrated acids and the application of high temperatures for long times compared to methods based on acid digestion [12].

Three different assessment metric tools, the Analytical Eco-Scale (AES), the Chloroform-oriented Toxicity Estimation Scale (ChlorTox Scale), and the Analytical GREENness (AGREE) metric were applied to evaluate the impacts of the developed method [38–40]. In addition, the greenness profile of the proposed method was compared with that obtained for the reported methods in Table S5. The results of these evaluations are shown in Table S6. The AES is a semi-quantitative tool used to evaluate the greenness of an analytical method based on four factors: hazard and amount of the reagents, energy consumption, occupational hazards, and waste generation. Initially, an ideal score of 100 points is assigned to the methods, and then penalty points are subtracted based on these four criteria. Considering the final score obtained, the method is categorized as excellent (>75 points), acceptable (75-50 points), or inadequate (<50 points) in terms of greenness. As it can be seen in Table S6, the score of the proposed slurry sampling HR-CS GFAAS method is 80, demonstrating that the method provides an excellent green protocol for the analysis BBA samples. The scores of methods based on solid sampling are lightly higher than those with slurry sampling approaches, obtaining the lowest scores the methods with acid digestion of the samples.

The ChlorTox Scale, a new tool recently developed in 2023 by Nowak et al. [38], was also used to evaluate the greenness profile of these methods. This approach estimates the environmental risk of an analytical method by considering the hazards of the reagents used in the procedure in relation to the hazards associated to the reference substance chloroform. It considers the exact mass of substances used in the method to carry out a single measurement and the final score is expressed in equivalent mass of chloroform. The ChlorTox values found for the direct sampling and the slurry sampling methods were closed to 0 g, obtaining a chloroform equivalent mass of 0.20 g for the method developed in this work. On the other hand, an equivalent mass of chloroform of 24 g was found for the method with acid digestion of the samples [12] due to the higher amount of concentrated HNO_3 (25 mL) required.

Finally, the AGREE tool was used to provide an overview of the entire analytical procedure based on the 12 principles of GAC. The

Table 3

Concentrations (mean \pm standard deviation ($n = 4$)) of Pb, Cu, and Fe in biomass bottom ash (BBA) samples obtained using the optimized slurry sampling HR-CS GFAAS method, and by HR-CS GFAAS after microwave digestion of the samples.

SAMPLE	Pb ($\mu\text{g g}^{-1}$)		Cu ($\mu\text{g g}^{-1}$)		Fe (mg g^{-1})	
	Slurry sampling	Microwave digestion	Slurry sampling	Microwave digestion	Slurry sampling	Microwave digestion
BBA 1	4.3 \pm 0.3	3.9 \pm 0.2	22.7 \pm 1.8	23.2 \pm 1.6	17.1 \pm 1.2	15.7 \pm 0.8
BBA 2	12.5 \pm 0.9	11.8 \pm 0.6	50.2 \pm 3.6	51.5 \pm 2.7	<0.72	<0.72
BBA 3	19.8 \pm 1.0	19.2 \pm 0.8	37.1 \pm 1.7	38.4 \pm 1.3	4.2 \pm 0.3	4.0 \pm 0.2

results are presented in a circular pictogram which is divided in 12 sections (one for each GACs principle). Each section has a specific weight, and the score is represented by a color scale that ranges from green (≈ 1 point), to yellow (≈ 0.5 points), to red (≈ 0 points). The final overall score of the analytical procedure is displayed in the center of the pictogram and the method is considered green if it has an overall score higher than 0.60. The AGREE pictograms and overall score are included in Table 6S. The overall score obtained for the method with acid digestion of the samples [12] and the previously reported slurry sampling method included in Tables S5 and S6 [17] are lower than 0.60. An overall AGREE score of 0.62 was obtained for the here proposed slurry sampling HR-CS GFAAS method so it can be considered as green. The higher score obtained in this method is mainly associated to the higher number of analytes determined in the same measurement and the subsequent decrease in energy consumption and increase in sample throughput achieved.

4. Conclusions

In this work, a fast and simple method for the determination of Pb, Cu, and Fe in BBA samples by slurry sampling HR-CS GFAAS was optimized. The experimental variables related to suspension preparation with significant contribution on the slurry stability and the element determination by GFAAS were identified and the optimal values of these variables were estimated using a five-level CCD and RSM. Following this multivariate approach for design of experiments, the slurry preparation procedure was optimized with a significant reduction of time and number of experiments required in one-variable-at-time methods.

The developed method was successfully applied to determine Pb, Cu, and Fe, elements present at different concentration levels in BBA samples, obtaining analyte contents in agreement (Student t-test for two independent samples at a 95% confidence level) with those obtained after solid sample digestion and HR-CS GFAAS measurement. The three elements were determined in a single measurement run and in the same sample aliquot without deterioration of the analytical parameters, reducing the time and energy required for the determination. The analysis can be performed in few minutes, requiring the preparation of the slurry sample only about 2–3 min and the determination of all analytes about 1.5 min per replicate. In fact, the proposed method can be considered green according to AES and ChlorTox Scales as well as the AGREE metric. Moreover, the slurry sampling HR-CS GFAAS proposed method meets the analytical requirements for classification of fertilizers produced from wastes and other organic components according to the EU regulation and the Spanish normative [35,36]. In our opinion, the method can be considered as an appropriate alternative tool for the routine analyses of these by-products.

Declaration of Competing Interest

All authors declare that they have no conflicts of interest.

Data availability

The data that has been used is confidential.

Acknowledgment

This research received funding from Spanish Ministry of Science and Innovation (project BIA2016-76643-C3-1-R).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.greeac.2023.100068.

References

- [1] M.A. Perea-Moreno, E. Samerón-Manzano, A.J. Perea-Moreno, Biomass as renewable energy: worldwide research trends, *Sustainability* 11 (2019) 863, <https://doi.org/10.3390/su11030863>.
- [2] EC (European Commission), Commission decision (2000/532/EC) of 3 May 2000 replacing decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste, *Off. J. Eur. Commun.* (2000). L 226/3, 6 September.
- [3] M.A. Munawar, A.H. Khoja, S.R. Naqvi, M.T. Mehran, M. Hassan, R. Liaquat, U. F. Dawood, Challenges and opportunities in biomass ash management and its utilization in novel applications, *Renew. Sustain. Energy Rev.* 150 (2021), 111451, <https://doi.org/10.1016/j.rser.2021.111451>.
- [4] EPC (European Parliament and the Council of the European Union), Directive 2008/98/EC of the European parliament and of the Council of 19 November 2008 on waste and repealing certain directives, *Off. J. Eur. Commun.* (2008). L 312/3, 22 November 2008.
- [5] L. Tosti, A. van Zomeren, J.R. Pels, J.J. Dijkstra, R.N.J. Comans, Assessment of biomass ash applications in soil and cement mortars, *Chemosphere* 223 (2019) 425–437, <https://doi.org/10.1016/j.chemosphere.2019.02.045>.
- [6] A.K. James, R.W. Thring, S. Helle, H.S. Ghuman, Ash management review—applications of biomass bottom ash, *Energies* 5 (2012) 3856–3873, <https://doi.org/10.3390/en5103856>.
- [7] K. Przygocka-Cyna, P. BBańóg, T. Spizewski, W. Grzebisz, Bio-fertilizers based on digestate and biomass ash as an alternative to commercial fertilizers—the case of tomato, *Agronomy* 11 (2021) 1716, <https://doi.org/10.3390/agronomy11091716>.
- [8] A.R.L. Albuquerque, R.S. Angélica, A. Merino, S.P.A. Paz, Chemical and mineralogical characterization and potential use of ash from Amazonian biomasses as an agricultural fertilizer and for soil amendment, *J. Clean. Prod.* 295 (2021), 126472, <https://doi.org/10.1016/j.jclepro.2021.126472>.
- [9] F.C. Silva, N.C. Cruz, L.A.C. Tarelho, S.M. Rodrigues, Use of biomass ash-based materials as soil fertilisers: critical review of the existing regulatory framework, *J. Clean. Prod.* 214 (2019) 112–124, <https://doi.org/10.1016/j.jclepro.2018.12.268>.
- [10] M. Azam, S. Setoodeh Jahromy, W. Raza, F. Wesenauer, K. Schwendner, F. Winter, Comparison of the characteristics of fly ash generated from bio and municipal waste: fluidized bed incinerators, *Materials* 12 (2019) 2664, <https://doi.org/10.3390/ma12172664>.
- [11] L.K. Andersen, T.J. Morgan, A.K. Boulamanti, P. Álvarez, S.V. Vassilev, D. BBaxter, Quantitative X-ray fluorescence analysis of biomass: objective evaluation of a typical commercial multi-element method on a WD-XRF spectrometer, *Energy Fuels* 27 (2013) 7439–7454, <https://doi.org/10.1021/ef4015394>.
- [12] M. Pazalja, M. Salihović, J. Sulejmanović, A. Smajović, S. Begić, S. Špiritović-Halilović, F. Sher, Heavy metals content in ashes of wood pellets and the health risk assessment related to their presence in the environment, *Sci. Rep.* 11 (2021) 17952, <https://doi.org/10.1038/s41598-021-97305-4>.
- [13] R.C. Machado, D.F. Andrade, D.V. Babos, J.P. Castro, V.C. Costa, M.A. Sperança, J. A. Garcia, R.R. Gamela, E.R. Pereira-Filho, Solid sampling: advantages and challenges for chemical element determination—a critical review, *J. Anal. At. Spectrom.* 35 (2020) 54–77, <https://doi.org/10.1039/C9JA00306A>.
- [14] D.L. Rocha, A.D. Batista, F.R.P. Rocha, G.L. Donati, J.A. Nóbrega, Greening sample preparation in inorganic analysis, *TrAC, Trends Anal. Chem.* 45 (2013) 79–92, <https://doi.org/10.1016/j.trac.2012.12.015>.
- [15] R. Halko, J. Tuček, K. Chovancová, V. Andruš, Some green approaches in atomic absorption spectrometry. The last 10 years, *Appl. Spectrosc. Rev.* (2022) 1–48, <https://doi.org/10.1080/05704928.2022.2148685>.
- [16] S.L.C. Ferreira, M. Miró, E.G.P. da Silva, G.D. Matos, P.S. dos Reis, G.C. Brandao, W.N.L. dos Santos, A.T. Duarte, M.G.R. Vale, R.G.O. Araujo, Slurry sampling—an

- analytical strategy for the determination of metals and metalloids by spectroanalytical techniques, *Appl. Spectrosc. Rev.* 45 (2010) 44–62, <https://doi.org/10.1080/05704920903435474>.
- [17] M.M. Silva, M. Goreti, R. Vale, E.B. Caramão, Slurry sampling graphite furnace atomic absorption spectrometry: determination of trace metals in mineral coal, *Talanta* 50 (1999) 1035–1043, [https://doi.org/10.1016/S0039-9140\(99\)00216-7](https://doi.org/10.1016/S0039-9140(99)00216-7).
- [18] D.J. Butcher, Innovations and developments in graphite furnace atomic absorption spectrometry (GFAAS), *Appl. Spectrosc. Rev.* 58 (1) (2023) 65–82, <https://doi.org/10.1080/05704928.2021.1919896>.
- [19] A.T. Duarte, A.R. Borges, A.V. Zmozinski, M.B. Dessuy, B. Welz, J.B. de Andrade, M.G.R. Vale, Determination of lead in biomass and products of the pyrolysis process by direct solid or liquid sample analysis using HR-CS GFAAS, *Talanta* 146 (2016) 166–174, <https://doi.org/10.1016/j.talanta.2015.08.041>.
- [20] D.E. Bustos, J.A. Toro, M. Briceño, R.E. Rivas, Use of slow atomization ramp in high resolution continuum source graphite furnace atomic absorption spectrometry for the simultaneous determination of Cd and Ni in slurry powdered chocolate samples, *Talanta* 247 (2022), 123547, <https://doi.org/10.1016/j.talanta.2022.123547>.
- [21] B. Gómez-Nieto, M.J. Gismera, M.T. Sevilla, J.R. Procopio, Simultaneous and direct determination of iron and nickel in biological solid samples by high-resolution continuum source graphite furnace atomic absorption spectrometry, *Talanta* 116 (2013) 860–865, <https://doi.org/10.1016/j.talanta.2013.07.083>.
- [22] I.N. Pasiás, N.I. Rousis, A.K. Psom, N.S. Thomaidis, Simultaneous or sequential multi-element graphite furnace atomic absorption spectrometry techniques: advances within the last 20 years, *At. Spectrosc.* 42 (6) (2021) 310–327, <https://doi.org/10.46770/AS.2021.707>.
- [23] W. Boschetti, M. Orlando, M. Dullius, M.B. Dessuy, M.G.R. Vale, B. Welz, J.B. de Andrade, Sequential and simultaneous determination of four elements in soil samples using high-resolution continuum source graphite furnace atomic and molecular absorption spectrometry, *J. Anal. At. Spectrom.* 31 (2016) 1269–1277, <https://doi.org/10.1039/C6JA00031B>.
- [24] J.S. Almeida, O.C.C.O. Souza, L.S.G. Teixeira, Determination of Pb, Cu and Fe in ethanol fuel samples by high-resolution continuum source electrothermal atomic absorption spectrometry by exploring a combination of sequential and simultaneous strategies, *Microchem. J.* 137 (2018) 22–26, <https://doi.org/10.1016/j.microc.2017.09.012>.
- [25] B. Gómez-Nieto, V. Motyzhov, M.J. Gismera, J.R. Procopio, M.T. Sevilla, Fast-sequential determination of cadmium and copper in milk powder and infant formula by direct solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry, *Microchem. J.* 159 (2020), 105335, <https://doi.org/10.1016/j.microc.2020.105335>.
- [26] C.F.G. Frois, W. Boschetti, A.S. dos Passos, M.L. Potes, M.G.R. Vale, M.M. Silva, A comparison between chemical and photochemical vapor generation techniques for mercury determination using univariate and multivariate optimization, *Microchem. J.* 157 (2020), 105029, <https://doi.org/10.1016/j.microc.2020.105029>.
- [27] A.L.H. Müller, J.A. de Oliveira, O.D. Prestes, M.B. Adaipe, R. Zanella, 22 - Design of experiments and method development, C.F. Poole. *Solid-Phase Extr., Elsevier*, 2020, pp. 589–608, <https://doi.org/10.1016/B978-0-12-816906-3.00022-4>.
- [28] A.I. Khuri, S. Mukhopadhyay, Response surface methodology, *WIREs Comput. Stat.* 2 (2010) 128–149, <https://doi.org/10.1002/wics.73>.
- [29] V.C. Costa, F.C. Pinheiro, F.A.C. Amorim, E.G. Paranhos da Silva, E.R. Pereira-Filho, Multivariate optimization for the development of a sample preparation procedure and evaluation of calibration strategies for nutrient elements determination in handmade chocolate, *Microchem. J.* 150 (2019), 104166, <https://doi.org/10.1016/j.microc.2019.104166>.
- [30] R.R. Gamela, V.C. Costa, E.R. Pereira-Filho, Multivariate optimization of ultrasound-assisted extraction procedure for the determination of Ca, Fe, K, Mg, Mn, P, and Zn in pepper samples by ICP OES, *Food Anal. Methods* 13 (2020) 69–77, <https://doi.org/10.1007/s12161-019-01524-5>.
- [31] B. Gómez-Nieto, C. Isabel-Cabrera, M.J. Gismera, M.T. Sevilla J.R., Procopio and M.I. Sánchez de Rojas, An environmentally friendly approach for the characterization of construction materials: determination of trace, minor, and major elements by slurry sampling high-resolution continuum source graphite furnace atomic absorption spectrometry, *Anal. Methods* 15 (2023) 1105, <https://doi.org/10.1039/d2ay02036j>.
- [32] V. Sandroni, C.M.M. Smith, A. Donovan, Microwave digestion of sediment, soils and urban particulate matter for trace metal analysis, *Talanta* 60 (2003) 715–723, [https://doi.org/10.1016/S0039-9140\(03\)00131-0](https://doi.org/10.1016/S0039-9140(03)00131-0).
- [33] A.V. Zmozinski, T. Pretto, A.R. Borges, Á.T. Duarte, M.G.R. Vale, Determination of Pb and Cr in sunscreen samples by high-resolution continuum source graphite furnace atomic absorption spectrometry and direct analysis, *Microchem. J.* 128 (2016) 89–94, <https://doi.org/10.1016/j.microc.2016.03.020>.
- [34] W.S. Zhong, T. Ren, L.J. Zhao, Determination of Pb (Lead), Cd (Cadmium), Cr (Chromium), Cu (Copper), and Ni (Nickel) in Chinese tea with high-resolution continuum source graphite furnace atomic absorption spectrometry, *J. Food Drug Anal.* 24 (2016) 46–55, <https://doi.org/10.1016/j.jfda.2015.04.010>.
- [35] REGULATION (EU), 2019/1009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL OF 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003, *Off. J. Eur. Union* (2019). L 170/1, 25 June.
- [36] Real Decreto 506/2013, of June 28, about fertilizing products. Ministry of the Presidency, BOE, 164, 51119-51207, 10 July 2013.
- [37] F.V. Dijen, Bioefficiency Ash utilisation - Draft for technical regulations (D6.3), Ref. Ares (2019)6450785, 18 October 2019.
- [38] P.M. Nowak, R. Wietecha-Postuszny, J. Plotka-Wasyłka, M. Tobiszewski, How to evaluate methods used in chemical laboratories in terms of the total chemical risk? – A ChlorTox Scale, *Green Anal. Chem.* 5 (2023), 100056, <https://doi.org/10.1016/j.greac.2023.100056>.
- [39] A. Gałuszka, P. Konieczka, Z.M. Migaszewski, J. Namiesnik, Analytical eco-scale for assessing the greenness of analytical procedures, *TrAC, Trends Anal. Chem.* 37 (2012) 61–72, <https://doi.org/10.1016/j.trac.2012.03.013>.
- [40] F. Pena-Pereira, W. Wojnowski, M. Tobiszewski, AGREE - analytical GREENness metric approach and software, *Anal. Chem.* 92 (2020) 10076–10082, <https://doi.org/10.1021/acs.analchem.0c01887>.