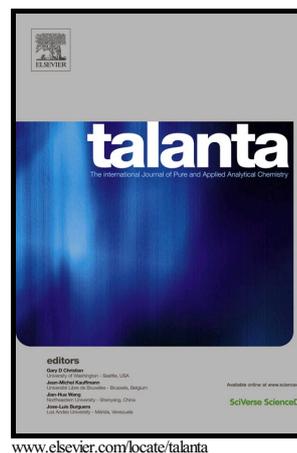


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**Determination of lead in biomass and products of the pyrolysis process
by direct solid or liquid sample analysis using HR-CS GF AAS**

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Abstract

A method has been developed for the determination of lead in biomass, bio-oil, pyrolysis aqueous phase, and biomass ashes by high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) and direct solid or liquid sample analysis. All measurements were performed without chemical modifier and calibration could be carried out using aqueous standard solutions. A pyrolysis temperature of 800 °C and an atomization temperature of 2200 °C were applied. The limits of detection and quantification were, respectively, 0.5 $\mu\text{g kg}^{-1}$ and 2 $\mu\text{g kg}^{-1}$ using the analytical line at 217.001 nm and 6 $\mu\text{g kg}^{-1}$ and 19 $\mu\text{g kg}^{-1}$ at 283.306 nm. The precision, expressed as relative standard deviation, was between 3% and 10%, which is suitable for direct analysis. The lead concentrations found for the solid samples varied between 0.28 and 1.4 mg kg^{-1} for biomass and between 0.25 and 2.3 mg kg^{-1} for ashes, these values were much higher than those found for bio-oil (2.2 - 16.8 $\mu\text{g kg}^{-1}$) and pyrolysis aqueous phase (3.2 - 18.5 $\mu\text{g kg}^{-1}$). After the determination of lead in the samples, it was possible to estimate the relative distribution of this element in the fractions of the pyrolysis products, and it was observed that most of the lead present in the biomass was eliminated to the environment during the pyrolysis process, with a significant portion retained in the ashes.

Keywords: Lead determination; Biomass; Pyrolysis products; HR-CS GF AAS; Direct analysis.

1. Introduction

Fossil fuels, such as oil, coal and natural gas represent the prime energy sources in the world. However, the environmental problems associated with the extended use of fossil fuels are well known and established, such as global warming, acid rain and urban smog [1]. Because of this, the government agencies are interested in the investigation of alternative sources for energy generation. One of the resources that has aroused great interest in the scientific community is the biomass, a renewable energy source, in that it is carbon-based and provides fuels comparable to fossil fuels [2-5].

Biomass is a complex material, mainly composed of cellulose, hemicelluloses and lignin, and to a lesser extent of tannins, fatty acids, resins and inorganic salts. This renewable raw material is of great potential, as it can be used for energy generation and for the production of high-value chemicals [4, 6]. Forest residues, energy crops, organic wastes, agricultural residues, etc. are materials that can be used for energy production [4, 7]. The use of agricultural and industrial residues as biomass sources is an environmentally friendly choice because, in many cases, the final disposal of these materials might be an environmental and/or toxicological risk [8].

The biomass can be converted into energy through various thermochemical processes. The choice of process will depend on the type and quantity of biomass available, the desired type of energy, environmental regulations, and economic conditions, among other factors. These processes can be classified into two categories: i) direct combustion process, which involves the direct use of biomass as fuel and ii) processes that convert biomass into other useful energetic products before their use as an energy source. This category includes the gasification and pyrolysis processes [7, 9].

The pyrolysis process is a thermal decomposition operated in the absence of oxygen, in which biomass is rapidly heated and converted mostly into condensable vapors and aerosols which, after cooling and condensation, give rise to a liquid product [1]. This liquid product is a complex mixture of hundreds of organic compounds, consisting mainly of alcohols, ketones, aldehydes, phenols, and oligomers derived from lignin [10]. Generally, this liquid product comprises two phases, a non-aqueous phase, called bio-oil, consisting of high molecular weight molecules, and an aqueous phase, called pyrolysis aqueous phase, which consists of low molecular weight compounds [5].

This aqueous phase is derived from the moisture present in the biomass and from products of reactions that occur during the pyrolysis process [11].

However, the process of direct combustion or pyrolysis of biomass produces also a solid byproduct, the ashes, which must be considered. The ashes may contain heavy metals as part of the organic structure of the fuel and/or inorganic material that was added to the biomass during harvesting and processing of the raw material [1].

There is little information about the concentration of metals in biomass and the products (bio-oil and pyrolysis aqueous phase) and byproducts (ashes) obtained by the pyrolysis process. In order to assess possible emissions of metals, such as lead, to the environment during their use or disposal, it is important to characterize these materials. Lead is toxic already at low concentration; it might increase the blood pressure and cause anemia and tumors. High levels of exposure severely damage the brain and kidneys in adults and children and might ultimately cause death [12].

Most of the studies present in the literature report that the determination of metals in biomass and their ashes is usually carried out by methods involving some type of sample digestion with a mixture of strong acids, due to the complexity of the matrix and the refractory nature of the waste. Different analytical techniques are then used for the determination of trace elements, such as inductively coupled plasma optical emission spectrometry (ICP OES) [13, 14], inductively coupled plasma mass spectrometry (ICP-MS) [15, 16] and atomic absorption spectrometry (AAS) [17, 18].

Some metals present in the biomass, such as potassium, sodium, calcium and magnesium, might have a negative influence on the production of bio-oil generated in the pyrolysis processes. Most problems reported in the literature are: a reduction in the yield of bio-oil and favoring the production of ashes, the destabilization of bio-oil and the corrosion of pyrolysis reactors [19-24]. We found only one paper that reports the distribution of metals in the bio-oil and ashes produced during the pyrolysis process [25]. The authors reported the distribution of potassium, calcium, sodium and magnesium in the bio-oil and ashes produced after the pyrolysis processes for wheat straw and beech wood as biomass samples. Fractions of biomass samples, bio-oil and ashes were submitted to calcination followed by mineralization processes with HCl and HF and analysis by ICP OES. According to the authors, the data indicate that the majority (over 99%) of the studied elements contained in the analyzed biomass samples remained trapped in the ashes after the pyrolysis process.

High-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) appears to be a good alternative for the determination of trace elements in biomass, their ashes, bio-oil and pyrolysis water. This technique brings significant advantages due to the use of a high-intensity xenon short-arc lamp as a primary radiation source, a high-resolution double monochromator and a linear charge-coupled device (CCD) detector [26, 27]. This combination makes it possible to achieve better limits of detection (LOD) and an extended linear working range; it offers unparalleled background correction, and it allows three-dimensional imaging of the environment of the analytical line, which greatly facilitates method development and detection of potential spectral interferences [28, 29].

HR-CS GF AAS greatly facilitates alternative sample introduction techniques, such as direct solid sample analysis (SS). This technique is characterized by several interesting advantages, such as improved LOD, as samples are not diluted, a reduced risk of contamination and/or analyte losses, high sample throughput, relatively moderate cost and the fact that no toxic and corrosive acids are used [30].

The goal of this study is to report the development of a simple and fast method for the determination of lead in biomass, bio-oil, pyrolysis aqueous phase and biomass ashes (obtained by pyrolysis process) using HR-CS GF AAS.

2. Experimental

2.1. Instrumentation

All measurements were carried out using a high-resolution continuum source atomic absorption spectrometer, model contrAA 700 (Analytik Jena AG, Germany). It is equipped with two types of atomizers, a flame atomizer and a transversely heated graphite tube atomizer. In this work, only the graphite tube atomizer was used. This spectrometer consists of a high-intensity xenon short-arc lamp operating in a hot-spot mode as a continuum radiation source that covers a range between 185 and 900 nm, a high resolution double monochromator and a CCD array detector with 588 pixels, 200 of which are used for analytical purposes. The double monochromator consists of a pre-dispersing prism monochromator and a high-resolution echelle grating monochromator, both in Littrow mounting.

The analytical lines at 217.001 nm (100% relative sensitivity) and at 283.306 nm (42% relative sensitivity) were used for lead determination. The peak volume selected absorbance (PVSA) has been used for signal evaluation, i.e., the integrated absorbance summated over three pixels around the line core (center pixel plus the adjacent ones, $CP \pm 1$). In this case, it corresponds to a spectral interval of 3.6 pm for the analytical line at 217.001 nm and 4.8 pm for the analytical line at 283.306 nm.

All experiments were carried out using solid sampling (SS) graphite tubes (Analytik Jena, part number: 407-A81.303) and SS graphite platforms (Analytik Jena, part number: 407-152.023), both pyrolytically coated. An M2P microbalance (Sartorius, Göttingen, Germany) was used for weighing the samples directly onto the SS platforms. The sample mass was automatically transmitted to the computer of the instrument, after each measurement, to calculate the normalized integrated absorbance, i.e., the integrated absorbance was calculated for an adequate fixed mass, which varied for each sample. This is necessary as it is impossible to always introduce exactly the same sample mass onto SS platforms in direct SS analysis. A pre-adjusted pair of tweezers, which is part of the SSA 6 manual solid sampling accessory (Analytik Jena), was used to transfer the SS platforms to the atomizer.

The graphite furnace heating program for the determination of lead is shown in Table 1. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) was used as the purge gas with a flow rate of 2.0 L min^{-1} during all stages, except during atomization stage, when the argon flow rate was interrupted.

2.2. Reagents and solutions

Analytical grade reagents were used throughout. Distilled, deionized water with a specific resistivity of $18.2 \text{ M}\Omega \text{ cm}$, from a Milli-Q water purification system (Millipore, Bedford, MA, USA), was used for the preparation of the standard solutions. The nitric acid (Merck, Darmstadt, Germany), used to prepare the aqueous calibration solutions, was previously purified by sub-boiling distillation in a quartz sub-boiling still (Kürner Analysentechnik, Rosenheim, Germany). All containers and glassware were soaked in 1.4 mol L^{-1} nitric acid for at least 24 h and rinsed three times with deionized water before use. The working standard solutions of lead were prepared by serial dilutions of lead stock standard solution (1000 mg L^{-1} in 0.014 mol L^{-1} nitric acid) from Specsol (Brazil). The lead organometallic standard (1000 mg kg^{-1}) from Conostan

(Ponca City, OK, USA) was appropriately diluted in mineral oil from High Purity Standards (Charleston, SC, USA) and was used in the recovery tests.

2.3. Samples and certified reference material

The biomass samples investigated in this work were acquired from agricultural waste, widely available in Brazil: peach pit, rice husk and sugarcane straw. These matrices were chosen as biomass samples because of their potential energy and their economic viability, since they are waste from local industry and easily and cheaply available.

In this work, besides biomass samples, different kind of samples were analyzed: bio-oil, pyrolysis aqueous phase and ashes, which were obtained by a fast pyrolysis process, where the different biomass samples were heated to 700 °C during 10 min in a nitrogen atmosphere. This pyrolysis process was performed in a lab-made vertical oven, containing a quartz reactor, as described by Moraes *et al.* [4, 31]. Table 2 shows the approximate quantities of bio-oil, pyrolysis aqueous phase and ashes that were obtained in the pyrolysis process of 10 g of biomass.

The certified reference materials (CRM) NCS ZC 73014 - Tea (China National Analysis Center for Iron and Steel, Beijing, China) and CRM-SA-A - Sandy Soil A (High-Purity Standards, Charleston, SC, USA) were used to verify the trueness of the developed method for direct solid sample analysis (biomass and ashes).

2.4. Sample preparation

The biomass samples, their ashes, and the CRM NCS ZC 73014 and CRM-SA-A were ground in a micro-mill A-11 Basic (IKA-Werke, Germany). The sample of peach pits needed to be fragmented into pieces of approximately 1 cm prior to this grinding step, whereas the samples of sugarcane straw, rice husk and CRM were inserted directly into the mill. Quantities of samples were used to fill about 50% of the volume of the sample container of the micro-mill. The milling consisted of 3 cycles of 20 s each. The samples were dried at 65 ± 5 °C for 3 h in a stove. After cooling to room temperature, the samples were sieved through a 45 µm polyester sieve and kept in sealed plastic vials inside of a desiccator until further sample processing.

The sample mass of biomass and their ashes, weighed onto the SS platforms and introduced into the graphite furnace for SS-GF AAS, was between about 0.05 and 1.5

mg. The bio-oil and pyrolysis aqueous phase samples did not need any pre-treatment. These samples were directly deposited onto the SS platforms with a micropipette. The sample mass varied between 5 and 10 mg.

2.5. Recovery tests

The recovery tests were carried out to investigate possible matrix effects. These experiments were performed in duplicate, adding known amounts of lead to bio-oil and pyrolysis aqueous phase samples, both obtained from peach pit fast pyrolysis process.

Inorganic lead standards were added to the pyrolysis aqueous phase samples, and organometallic lead standards diluted in mineral oil were used for the bio-oil samples. In both cases were added appropriate amounts of standards to obtain a final added concentration of $10 \mu\text{g kg}^{-1}$ Pb. After the standard addition, the samples were kept in closed vials and submitted to an ultrasonic bath heated to $40 \text{ }^\circ\text{C}$ for 90 min to achieve complete homogeneity of the samples. The samples were allowed to cool to room temperature and the measurements were carried out.

2.6. Estimated lead retention in pyrolysis products

Estimates of the lead retention in biomass ashes, bio-oil and pyrolysis aqueous phase samples were calculated using the equations described below.

$$\text{Retention in Ashes (\%)} = \frac{(C_{\text{ashes}} * \frac{m_{\text{ashes}}}{m_{\text{bm}}})}{C_{\text{bm}}} * 100 \quad \text{Equation 1}$$

$$\text{Retention in Bio-oil (\%)} = \frac{(C_{\text{bo}} * \frac{m_{\text{bo}}}{m_{\text{bm}}})}{C_{\text{bm}}} * 100 \quad \text{Equation 2}$$

$$\text{Retention in Aqueous Phase (\%)} = \frac{(C_{\text{ap}} * \frac{m_{\text{ap}}}{m_{\text{bm}}})}{C_{\text{bm}}} * 100 \quad \text{Equation 3}$$

where:

C_{ashes} is the concentration of analyte in biomass ashes

m_{ashes} is the mass of biomass ashes obtained by the pyrolysis process (Table 2)

m_{bm} is the mass of biomass used in the pyrolysis process

C_{bm} is the concentration of analyte in the biomass.

C_{bo} is the concentration of analyte in bio-oil

m_{bo} is the mass of bio-oil obtained by the pyrolysis process (Table 2)

C_{ap} is the concentration of analyte in pyrolysis aqueous phase

m_{ap} is the mass of pyrolysis aqueous phase obtained by the pyrolysis process (Table 2)

3. Results and discussion

3.1. General considerations

The optimization experiments were carried out using a peach pit biomass sample and its pyrolysis products (bio-oil and pyrolysis aqueous phase). For bio-oil and pyrolysis aqueous phase analysis, it was necessary to use the analytical line at 217.001 nm, because of the low lead concentration in these samples. However, for biomass analysis the analytical line at 283.306 nm was used because at the analytical line at 217.001 nm the rice husk and sugarcane straw samples showed spectral interferences. As can be seen in Figs. 1a and 1c, the absorbance signals obtained when the analytical line at 217.001 nm was used, presented a background together with the Pb peak. At 283.306 nm the absorbance signals did not show any background (Fig. 1b and 1d). The same behavior was reported by Borges *et al.* [32] for other matrices. Therefore, the analytical line at 283.306 nm has been used for further experiments for biomass samples.

In the preliminary experiment, for bio-oil and pyrolysis aqueous phase samples, it was verified that pyrolysis temperatures equal to or lower than 600 °C were not sufficient to completely eliminate the background signal. In these cases, there was a background in the first second of the atomization stage, which caused a significant interference in the measurements. However, analyzing the time-resolved spectra for these samples obtained with low pyrolysis temperatures (600 °C or lower - Figs. 2a and 2c), it could be seen that the analytical signal for lead was temporally separated from the background. So, in the pyrolysis curves, when the temperatures were equal to or lower than 600 °C, a delay was employed to begin the measurement of the integrated absorbance, avoiding the background, as can be seen in Figs. 2b and 2d.

3.2. Temperature optimization

The pyrolysis and atomization curves were established to compare the thermal behavior of lead in aqueous standard solution, peach pit biomass sample and their pyrolysis products (bio-oil and pyrolysis aqueous phase).

The pyrolysis curves are shown in Fig. 3. Temperatures between 300 °C and 1000 °C were investigated without using a chemical modifier. Lead was thermally stable in all samples up to a pyrolysis temperature of 800 °C. Using pyrolysis temperatures higher than 800 °C a decrease in the integrated absorbance was observed, which indicated losses of lead in the pyrolysis stage when these temperatures were employed. For aqueous standard solutions the highest integrated absorbance values were obtained between 300 °C and 500 °C, but the analytical signals for these temperatures show asymmetrical absorbance profiles. There is a slight decrease in the integrated absorbance values, and a plateau established between 600 °C and 800 °C. Hence, it can be considered that lead is thermally stable up to 800 °C in all samples and in the aqueous standard solution. Thus, a pyrolysis temperature of 800 °C was chosen as optimal pyrolysis temperature.

Although it was possible to use the same pyrolysis temperature for all samples, for liquid samples (bio-oil and pyrolysis aqueous phase) it was necessary to employ a longer residence time (45 s) in the pyrolysis stage than that employed for solid samples (30 s for biomass and ash). It was necessary because the sample mass of bio-oil and pyrolysis aqueous phase weighed onto the platform was higher than the mass of solid samples.

After the best pyrolysis temperature has been established as 800 °C, the atomization temperature had to be optimized. Fig. 4 shows the atomization curves for lead in an aqueous standard solution and a peach pit biomass sample and their pyrolysis products (bio-oil and pyrolysis aqueous phase). There is kind of a plateau established between temperatures of 1800 °C and 2200 °C for all samples and the standard aqueous solution. The slight decrease in sensitivity with increasing temperature is due to the faster diffusion of the analyte atoms at higher temperatures, but this decrease appears to be the same for all samples and the aqueous standard. Hence, a temperature of 2200 °C was chosen as optimal atomization temperature. This temperature provided the best analytical profiles for lead in standard solution (Fig. 5a) and in the investigated samples (Figs. 5b, 5c and 5d).

3.3. Method validation

The figures of merit for the determination of Pb using HR-CS GF AAS are presented in Table 3. The limits of detection (LOD) and quantification (LOQ) have been calculated as three and ten times, respectively, the standard deviation of ten measurements of the blank, divided by the inclination of the calibration curve. In the case of analysis of the solid samples (biomass and ashes), the blank measurements were carried out according to the zero-mass response technique [33], i.e., repeatedly introducing an empty platform in the graphite tube and performing a complete cycle of the temperature program, described in Table 1. For the analysis of liquid products of pyrolysis (bio-oil and pyrolysis aqueous phase) a matrix of mineral oil was used to simulate a blank solution. The characteristic mass (m_0) is defined as the mass of an analyte corresponding to an integrate absorption (A_{int}) of 0.0044 s [34].

Calibration curves for the determination of lead were established using a blank solution and five aqueous standard solutions in the concentration range of 10 - 100 $\mu\text{g L}^{-1}$ Pb (0.1 - 1 ng Pb) for measurements at $\lambda = 283.306$ nm and 5 - 50 $\mu\text{g L}^{-1}$ Pb (0.05 - 0.5 ng Pb) at $\lambda = 217.001$ nm.

The figures of merit obtained using the analytical line at 283.306 nm are in agreement with the values reported in the literature (LOD between 0.4 and 40 $\mu\text{g kg}^{-1}$) for determinations using direct analysis of solid samples by GF AAS with line source (LS) or continuum source [35-39].

Using the technique of HR-CS SS-GF AAS, Rego *et al.* [35] determined lead in herbal samples. In this work the authors used a solution of $\text{Pd}(\text{NO}_3)_2$ as modifier, the analytical line at 283.306 nm and aqueous standard solutions for calibration. The authors obtained a value of 7 pg for LOD and a characteristic mass of 12.7 pg, values which agree with those found in the present study (LOD = 9 pg and $m_0 = 7.0$ pg), when compared with the same wavelength.

Using HR-CS SS-GF AAS and the analytical line at 217.001 nm, Borges *et al.* [36] determined lead in coal samples. These authors obtained, based on the technique of zero-mass response, a LOD of 8 $\mu\text{g kg}^{-1}$ (related to 1 mg of sample) and a characteristic mass of 5 pg, which are also in agreement with the values obtained in the present work.

As there is no work in the literature which reports the determination of lead in bio-oil and pyrolysis aqueous phase samples, the figures of merit obtained for the

method developed in this study were compared with studies that report the determination of this element in oil, vegetable oil or biodiesel samples.

The figures of merit obtained in this work (at 217.001 nm) are better than those reported in the literature for determination of lead in vegetable oil, biodiesel or oil samples by LS GF AAS (at 283.3 nm) using direct analysis of samples (LOD of $4 \mu\text{g kg}^{-1}$) [40] or emulsion or microemulsion (LOD between 6 - $110 \mu\text{g kg}^{-1}$) [41-43] as sample treatment.

Using HR-CS GF AAS, the analytical line at 283.306 nm and zirconium as a permanent modifier, Quadros, *et al.* [44] determined lead in B5 diesel samples (containing 5% of biodiesel). Dilution in n-propanol was used as sample treatment and aqueous standard solutions were used for calibration. Under these conditions, the authors obtained a LOQ and m_0 of $2 \mu\text{g kg}^{-1}$ and 9 pg, respectively. Thus, the figures of merit shown in Table 3 are in agreement with those obtained by these authors [44].

Two CRM were analyzed in order to verify the trueness of the proposed method for analysis of the solid samples. The CRM Tea in order to simulate the biomass samples, and the CRM Sandy Soil A to simulate the ash. The CRM available for ash, such as City Waste Incineration Ash, etc. could not be used for this purpose, as the content of lead in these materials is much higher than that in the samples investigated here, therefore the proposed method could not be applied. As the ashes of the biomass samples were rich in silicates, the sandy soil CRM has been considered appropriate for the purpose.

The results for the determination of lead in both CRM are summarized in Table 4. The found values are not significantly different from the certified values for both CRM, based on Student *t* test at 95% confidence level ($t_{critical} = 2.57$, $t_{calculated} = 1.02$ for CRM ZC 73012 Tea and $t_{calculated} = 1.46$ for CRM Sand soil A).

Due to the lack of CRM for lead in bio-oil and pyrolysis aqueous phase samples (or similar matrices) or a standard method of analysis for this kind of sample, the trueness of the proposed method for the analysis of liquid products of pyrolysis (bio-oil and pyrolysis aqueous phase) was verified by recovery tests, which are shown in Table 5.

The values obtained for the addition and recovery tests were 92% and 98% for pyrolysis aqueous phase samples and 92% and 93% for bio-oil samples. This indicates that there are no significant matrix effects for the proposed method for determination of lead in liquid products of pyrolysis process (bio-oil and pyrolysis aqueous phase) using

HR-CS GF AAS and it has a good accuracy, using direct analysis of these samples and calibration with aqueous standards.

3.4. Lead determination in biomass samples, their ashes and pyrolysis products

The results obtained for lead in three biomass samples (sugar cane straw, rice husk and peach pit), their pyrolysis products (bio-oil and pyrolysis aqueous phase) and in the ashes that remained after the pyrolysis process, are shown in Table 6. The lead concentrations found for the solid samples varied between 0.28 and 1.4 mg kg⁻¹ for biomass and between 0.25 and 2.3 mg kg⁻¹ for ashes, these values were much higher than those found for bio-oil (2.2 - 16.8 µg kg⁻¹) and for pyrolysis aqueous phase (3.2 - 18.5 µg kg⁻¹).

The results presented in Table 6 indicate that the concentration in the ashes did not follow a uniform pattern. While the lead concentration in the rice husk ash was about a factor of 10 times lower than in the biomass, the concentration in the peach pit ash was essentially unchanged and in the sugarcane straw ash the lead concentration was about a factor of 1.6 times higher than in the biomass. Probably, this behavior varies from biomass to biomass and might be associated with the mass loss during pyrolysis process for obtaining the bio-oil.

With the data obtained for determination of lead in the samples (Table 6) and taking into account the mass balance of the pyrolysis process (Table 2), it was possible to apply the equations 1 to 3 (section 2.7) and perform an estimation of the relative distribution of this element in the fractions of the pyrolysis products. In this way, it was possible to establish how much lead present in the biomass samples was retained in the fractions of bio-oil, pyrolysis aqueous phase and biomass ashes after the pyrolysis process and consequently estimate the quantity of lead that was emitted to the environment during the pyrolysis process. This estimative is presented in Table 7.

Analyzing the results shown in Table 7, it can be observed that most of the lead content present in the biomass was eliminated to the environment during the pyrolysis process, with loss rates between 62% and 98%. It is also observed that the amount of the analyte which is retained during the pyrolysis process remains mostly in the ashes of biomass, which presented retention rates between 2% and 38%. The liquid pyrolysis products (bio-oil from pyrolysis and water) showed retention rates between 0.1% and 2%.

This distribution behavior of lead in the pyrolysis products was surprising because a smaller loss of this analyte to the environment was expected, with a higher retention of lead in the biomass ashes, followed by lead retention in the aliquots of bio-oil and pyrolysis aqueous phase. This expectation is due to the thermal stability presented by the lead in pyrolysis curves (Fig. 3), in which the lead was stable up to a temperature of 800 °C, which is higher than the temperature used in the pyrolysis process. A possible explanation for such high losses of lead to the environment is the elimination in the form of particulate matter formed during the pyrolysis process, or due to long-time pyrolysis process, which might promote the formation of organic species which could react with the lead, resulting in volatile compounds.

4. Conclusions

The method developed using the technique of direct analysis by HR-CS GF AAS proved to be simple, sensitive, accurate and precise, using calibration with aqueous standards. Only milling was used as treatment for solid samples (biomass and their ashes), while for samples of liquid pyrolysis products (bio-oil and pyrolysis aqueous phase) no sample treatment was required.

Considering the environmental character, the fate of potentially hazardous elements in the pyrolysis process is of great importance. With the results presented in this work, it was possible to estimate that most of the lead present in the biomass samples was eliminated to the environment during the pyrolysis process, with rates between 62% and 98%.

Further research with a greater variety of biomass samples will be necessary to establish a mass balance of potentially hazardous elements and their fate during the pyrolysis process.

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Figure Captions

Fig. 1. Absorbance signals for lead in two biomass samples at different analytical lines: (a) 0.146 mg of sugarcane straw, $\lambda = 217.001$ nm, $A_{\text{int}} = 0.200$ s; (b) 0.248 mg of sugarcane straw, $\lambda = 283.306$ nm, $A_{\text{int}} = 0.319$ s; (c) 0.223 mg of rice husk, $\lambda = 217.001$ nm, $A_{\text{int}} = 0.286$ s and (d) 0.350 mg of rice husk, $\lambda = 283.306$ nm, $A_{\text{int}} = 0.272$ s. (- - -) CP-1, (--) CP e (···) CP+1. $T_{\text{pyr}} = 800$ °C and $T_{\text{at}} = 2200$ °C.

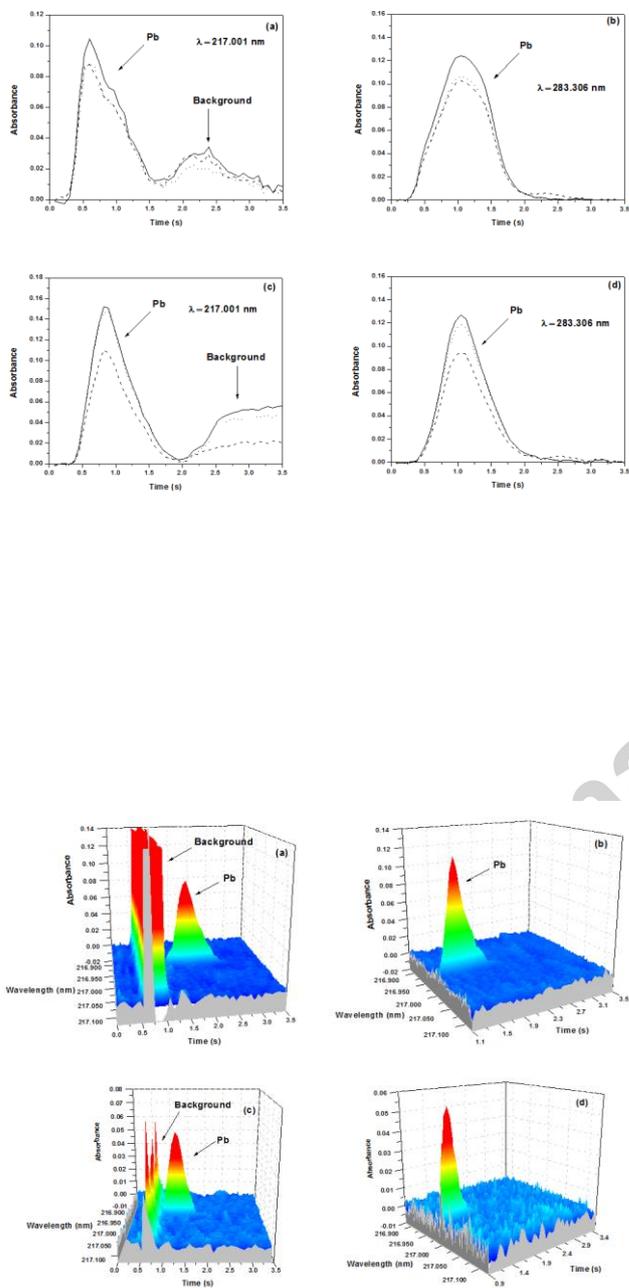
Fig. 2. Time-resolved absorbance spectra for lead in (a and b) pyrolysis aqueous phase samples and (c and d) bio-oil samples: (a) 9.458 mg, $A_{\text{int}} = 0.329$ s, without delay and (b) 10.439 mg, $A_{\text{int}} = 0.174$ s, with delay = 1.1 s, ($T_{\text{pyr}} = 300$ °C); (c) 10.483 mg, $A_{\text{int}} = 0.092$ s, without delay and (d) 13.306 mg, $A_{\text{int}} = 0.0683$ s, with delay = 0.9 s, ($T_{\text{pyr}} = 600$ °C). $T_{\text{at}} = 2100$ °C and $\lambda = 217.001$ nm.

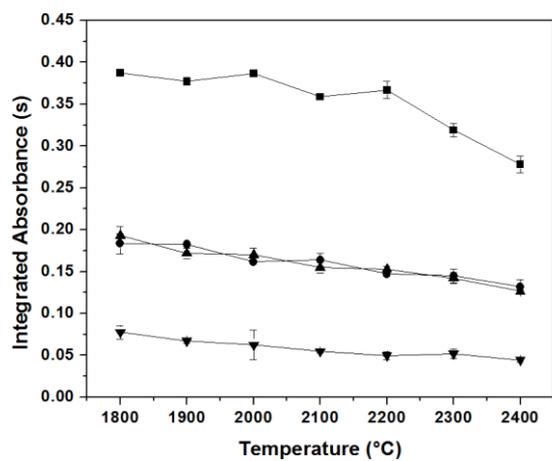
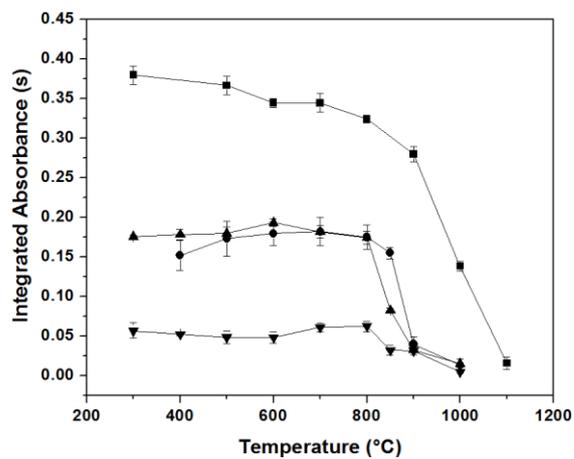
Fig. 3. Pyrolysis curves for lead in standard solutions and peach pit biomass and their pyrolysis products. $T_{\text{at}} = 2100$ °C. (■) 0.5 ng Pb in aqueous standard solution and (●) integrated absorbance normalized to 1.0 mg peach pit biomass sample, both obtained at the 283.306 nm line; (▲) pyrolysis aqueous phase sample and (▼) bio-oil sample, both integrated absorbance normalized to 10 mg and obtained at the 217.001 nm line.

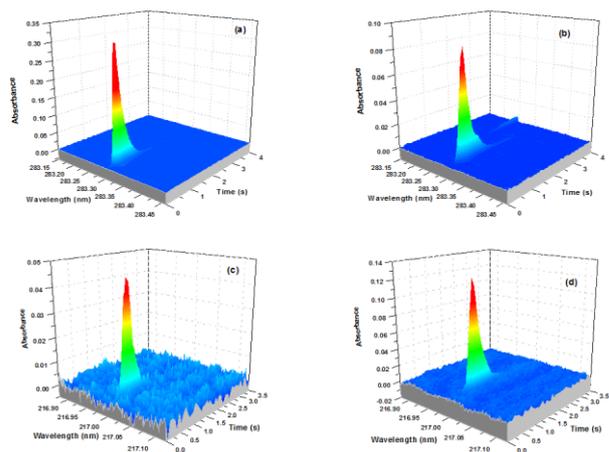
Fig. 4. Atomization curves for lead in aqueous standard solutions and peach pit biomass and their pyrolysis products. $T_{\text{pyr}} = 800$ °C. (■) 0.5 ng of Pb of aqueous standard solution and (●) integrated absorbance normalized to 1.0 mg peach pit biomass sample, both obtained at $\lambda = 283.306$ nm; (▲) pyrolysis aqueous phase sample and (▼) bio-oil sample, both integrated absorbance normalized to 10 mg and obtained at $\lambda = 217.001$ nm.

Fig. 5. Time-resolved absorbance spectra, for lead, obtained using $T_{\text{pyr}} = 800$ °C and $T_{\text{at}} = 2200$ °C. (a) 0.5 ng Pb of aqueous standard solution, $A_{\text{int}} = 0.3550$ s and (b) 0.792 mg of peach pit biomass sample, $A_{\text{int}} = 0.1190$ s, both obtained at the 283.306 nm line;

(c) 9.938 mg of pyrolysis aqueous phase sample from peach pit pyrolysis, $A_{\text{int}}=0.1664$ s, and (d) 9.394 mg of bio-oil sample from peach pit pyrolysis, $A_{\text{int}}=0.0515$ s, both obtained at the 217.001 nm line.







Highlights

- Lead was determined in biomass and pyrolysis products using HR-CS GF AAS
- No sample preparation was necessary and aqueous standards were used for calibration

- The lines at 283.306 nm and 217.001 nm were used to cover the analytical range
- Sugarcane straw, rice husk and peach pit and their pyrolysis products were analyzed
- Between about 60% and 98% Pb were lost to the environment in the pyrolysis stage

Table 1. Graphite furnace heating program for determination of lead by HR-CS DS-GF AAS.

Stage	Temperature / °C	Ramp (°C s ⁻¹)	Hold (s)
Drying 1	90	5	10
Drying 2	110	10	10
Drying 3	150	10	20
Drying 4 ^a	250	10	30
Pyrolysis	800	150	30 ^b /45 ^a
Atomization	2200	3000	3
Cleaning	2400	1000	4

Stages employed just in experiments for: ^a Bio-oil and pyrolysis aqueous phase obtained by pyrolysis process;

^b Biomass and their ashes.

Table 2. Approximate quantities of bio-oil, pyrolysis aqueous phase and ash obtained in the pyrolysis process of 10 g of biomass

Biomass	Bio-oil (g)	Pyrolysis		Mass Loss (%)
		Aqueous Phase (g)	Ash (g)	
Peach pit	1.2	3.9	2.0	29
Sugarcane Straw	1.4	0.8	2.5	53
Rice Husk	0.6	2.4	2.0	50

Table 3. Figures of merit for the determination of Pb in biomass, their ashes, bio-oil and pyrolysis aqueous phase samples, using HR-CS GF AAS, direct analysis and aqueous standard solutions for calibration. $T_{\text{pyr}}= 800\text{ }^{\circ}\text{C}$, $T_{\text{at}}= 2200\text{ }^{\circ}\text{C}$.

<i>Parameters</i>	$\lambda = 217.001\text{ nm}^{(a)}$	$\lambda = 283.306\text{ nm}^{(b)}$
LOD* ($\text{pg} / \mu\text{g kg}^{-1}$)	5 / 0.5	9 / 6
LOQ* ($\text{pg} / \mu\text{g kg}^{-1}$)	18 / 2	29 / 19
m_0 (pg)	4	7
Linear regression equation	$A_{\text{int}}= 0.0037 + 1.0522m$ (ng)	$A_{\text{int}}= 0.0056 + 0.5699m$ (ng)
Correlation coefficient	0.9919	0.9978

^(a) LOD and LOQ calculated for 10 mg of bio-oil and pyrolysis aqueous phase samples and

^(b) LOD and LOQ calculated for 1.5 mg of biomass and ash samples.

Table 4. Results obtained for the determination of lead in the CRM by HR-CS GF AAS, using direct analysis and aqueous standard solutions for calibration. $T_{\text{pyr}}= 800\text{ }^{\circ}\text{C}$ and $T_{\text{at}}= 2200\text{ }^{\circ}\text{C}$.

CRM	Certified Value (mg kg^{-1})	Found Value* (mg kg^{-1})	RSD (%)
ZC 73012 Tea	1.5 ± 0.2	1.6 ± 0.1	6
Sandy soil A	15.2 ± 2.0	14.3 ± 1.3	9

*All values are the average of $n = 5$ determinations \pm standard deviation

Table 5. Results found for addition and recovery tests for lead in bio-oil and pyrolysis aqueous phase samples.

Sample	Pb added ($\mu\text{g kg}^{-1}$)	Pb found* ($\mu\text{g kg}^{-1}$)	Recovery (%)
Pyrolysis aqueous phase	0	16.3 ± 0.8	—
Pyrolysis aqueous phase 1	10	25.5 ± 0.6	92
Pyrolysis aqueous phase 2	10	26.1 ± 0.5	98
Bio-oil	0	7.9 ± 0.7	—
Bio-oil 1	10	17.1 ± 1.1	92

*All values are the average of n = 5 determinations ± standard deviation

Table 6. Results obtained for the determination of lead in biomass samples, their ashes and products of pyrolysis (bio-oil and pyrolysis aqueous phase) by HR-CS GF AAS, using direct analysis and calibration with aqueous standard solutions. $T_{\text{pyr}} = 800$ °C and $T_{\text{at}} = 2200$ °C.

Samples	Biomass (mg kg ⁻¹)		Ashes (mg kg ⁻¹)		Bio-oil (µg kg ⁻¹)		Pyrolysis Aqueous Phase (µg kg ⁻¹)	
	Found	RSD	Found	RSD	Found	RSD	Found	RSD
	Value*	(%)	Value*	(%)	Value*	(%)	Value*	(%)
Sugarcane straw	1.4 ± 0.1	8	2.3 ± 0.1	4	2.2 ± 0.3	12	18.5 ± 1.0	5
	1.2 ± 0.1	10	0.11 ± 0.01	8	16.8 ± 0.5	3	3.2 ± 0.3	10
Peach pit	0.28 ± 0.02	9	0.25 ± 0.02	7	7.9 ± 0.7	9	16.3 ± 0.8	5

*All values are the average of n = 5 determinations ± standard deviation

Table 7. Estimative of lead distribution in the pyrolysis products (bio-oil and pyrolysis aqueous phase) and biomass ashes after a pyrolysis process employing a temperature of 700 °C.

Sample	Pb in biomass	Pb in	Pb in pyrolysis	Pb loses to
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	ashes (%)	bio-oil (%)	aqueous phase (%)	enviromment (%)
Sugarcane straw	38	0.02	0.1	~ 62
Rice husk	2	0.1	0.1	~ 98
Peach pit	17	0.3	2	~ 80

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