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Sequential determination of Cd and Cr in biomass samples and their ashes using high-resolution continuum source graphite furnace atomic absorption spectrometry and direct solid sample analysis

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ABSTRACT

High-resolution continuum source graphite furnace atomic absorption spectrometry, because of the use of only one radiation source for all elements, offers the possibility of sequential determination of two or more elements from the same sample aliquot if their volatilities are significantly different. Cd and Cr were determined sequentially in samples of biomass and biomass ashes employing direct solid sample analysis. The use of a chemical modifier was found to be not necessary, and calibration could be carried out using aqueous standard solutions. A pyrolysis temperature of 400 °C and an atomization temperature of 1500 °C were used for the determination of Cd; no losses of Cr were observed at this temperature. After the atomization of Cd the wavelength was changed and Cr atomized at 2600 °C. The limits of detection (LOD) and quantification (LOQ) were 1.1 μg kg^{-1} and 3.7 μg kg^{-1}, respectively, for Cd and 21 μg kg^{-1} and 70 μg kg^{-1}, respectively, for Cr using the most sensitive line at 357.869 nm, or 90 μg kg^{-1} and 300 μg kg^{-1}, respectively, using the less sensitive line at 428.972 nm. The precision, expressed as relative standard deviation was around 10%, which is typical for direct solid sample analysis. The values found for Cd in biomass samples were between < 1.1 μg kg^{-1} and 789 μg kg^{-1}, whereas those for Cr were between 7.9 mg kg^{-1} and 89 mg kg^{-1}; the values found in the ashes were significantly lower for Cd, between < 1.1 μg kg^{-1} and 6.3 μg kg^{-1}, whereas the trend was not so clear for Cr, where the values were between 3.4 mg kg^{-1} and 28 mg kg^{-1}.

1. Introduction

Biomass is the non-fossilized organic matter originating from microorganisms, plants and animals. In the context of biomass as a source of renewable energy, the term includes wood and wood residues, plants and associated residues, agricultural food and feed crop residues, plant fiber, aquatic plants, animal wastes, specific industrial waste, the paper component of municipal solid waste etc. [1,2]. The use of biomass as an energy source contributes to the reduction of the global emission of CO_2, the main goal of the Kyoto protocol, since the burning of biomass does not release more CO_2 than the plants had previously absorbed from the air [3,4].

The use of biomass produces a solid byproduct, the ash, which 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 [5]. The scientific community has become apprehensive for the environmental effects of biofuel products. It is incorrect to assume that biomass ashes do not contain hazardous elements, as in the case of coal ashes [6,7], as some results about biomass ash reported in the literature are very disturbing. The maximum concentrations reported for some elements in biomass ash, especially in filter ash, were for example: 243 mg kg^{-1} As, 3.7 g kg^{-1} Ba, 657 mg kg^{-1} Cd, 1.7 g kg^{-1} Cr, 7.3 mg kg^{-1} Hg, 114 mg kg^{-1} Mo, 50 g kg^{-1} Pb, 264 mg kg^{-1} Sb and 164 g kg^{-1} Zn [8–11]. These values are much higher than those reported for coal ash. Moreover, trace elements in biomass ashes tend to occur in much more mobile and hazardous compounds than in coal ash [7].

There are regulations in some countries, which state the limiting and guiding values for the maximum content of Ca, Cl, K, N, S and some trace elements, such as Cd, Co, Cr, Cu, Ni, Pb, V and Zn in biomass fuel or ashes with respect to their unlimited use [12]. In Brazil, the Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP) created for example maximum limits for the content of Na, K, Ca, Mg, P and S in biodiesel [13].

It is important to characterize biomass and its ash to be sure they will not provide any risk to the environment and human health during their use, disposal and/or reuse of ashes. Different analytical

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techniques could be employed for the monitoring of trace elements in biomass and biomass ash: inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF AAS) and wavelength-dispersive X-ray fluorescence (WDXRF). GF AAS is frequently used to determine trace elements due to its simplicity, low limits of detection and its extremely high tolerance for complex matrices. This technique also allows the introduction of solid samples directly into the atomizer, eliminating the sample preparation procedure, which is time-consuming, requires the use of hazardous acids and results in a significant dilution of the samples, and hence a decrease in the analyte concentration [14]. Another advantage of the GF AAS technique with direct analysis of solid samples is that it often makes possible the use of aqueous standard solutions for calibration [15].

The introduction of high-resolution continuum source atomic absorption spectrometry (HR-CS AAS) has further extended the applicability and advantages of GF AAS with direct solid sample analysis [16]. In HR-CS AAS, a high-intensity xenon short-arc lamp is used; this lamp emits a continuum between 190 nm and 900 nm. The high-resolution double monochromator and a charge coupled device (CCD) array detector provide a resolution of ~2 pm per pixel in the far UV; moreover, the wavelength is selected quickly by the monochromator system [17–20]. All these characteristics of the instrument are in favor of multi-element determination, although truly simultaneous multi-element analysis has not yet been realized.

There were essentially three different situations described in the literature for the quasi-simultaneous or fast sequential determination of more than one analyte using HR-CS GF AAS: (i) the analytes have similar volatilities and they have closely located absorption lines that are falling within the spectral range covered by the CCD array detector. In this case the analytes can be atomized together and the absorbance of two or more analytes is registered simultaneously, and the evaluation is done sequentially afterwards [21–23]. (ii) The analytes have closely located absorption lines that are falling within the spectral range covered by the CCD array detector, but significantly different volatilities. In this case it might be possible to use two significantly different atomization temperatures for the two analytes and a fast sequential registration of the absorbance signals, followed by their evaluation [24–26]. (iii) The analytes do not have closely located absorption lines, but they have significantly different volatilities. In this case the analytes might be determined sequentially employing the optimum atomization temperature for each one and changing the analytical wavelength between the two atomization cycles [17]. Obviously, for this kind of sequential determination by HR-CS GF AAS the conditions have to be chosen in a way that the less volatile analyte is not volatilized during the atomization stage of the more volatile one [17,24].

The goal of this work was to investigate the determination of cadmium and chromium in biomass samples and their ashes using HR-CS GF AAS, direct solid sample analysis (SS) and sequential atomization from the same sample aliquot. Although the use of the SS-GF AAS technique for the determination of cadmium and chromium in various matrices has been reported in the literature [27–35], including some that used HR-CS SS-GF AAS [25,36–38], the sequential determination of these elements from the same sample aliquot using HR-CS SS-GF AAS has not been reported yet.

2. Experimental

2.1. Instrumentation

All measurements were carried out using a Model contrAA 700 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany), equipped with a transversely heated graphite tube atomizer. This spectrometer consists of a high-intensity xenon short-arc lamp operating in a hot-spot mode, a high-resolution double monochromator and a charge coupled device (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 228.802 nm for Cd and 357.869 nm or 428.972 nm for Cr were used; peak volume selected absorbance (PVSA) [39], i.e., the integrated absorbance of the center pixel (CP) only, or summated over three pixels around the line core (center pixel plus the adjacent ones, CP ± 1) has been used for signal evaluation, corresponding to a spectral interval of 4.6 pm (CP ± 1) for Cd and 2.3 pm (CP) for Cr at 428.972 nm, or 6.0 pm (CP ± 1) for Cr at 357.869 nm.

The graphite furnace heating program for the sequential determination of Cd and Cr is shown in Table 1. All experiments were carried out using pyrolytically coated solid sampling (SS) graphite tubes without a dosing hole (Analytik Jena, Part No. 407-A81.303) and SS graphite platforms (Analytik Jena, Part No. 407-152.023). 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 to calculate the integrated absorbance normalized to a sample mass of 0.08 mg after each measurement. This is necessary as it is impossible to always introduce exactly the same sample mass 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. 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, when the flow was stopped for the determination of Cd. For Cr determination, the argon flow rate was kept at 0.1 L min^{-1} during the atomization stage in order to reduce the sensitivity, which was reported in the literature as a good approach to decrease the sensitivity in direct solid sample analysis by GF AAS [34].

2.2. Reagents and solutions

Analytical grade reagents were used throughout. Distilled, deionized water with a specific resistivity of 18 MΩ 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 further 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}

Table 1
Graphite furnace heating program for the sequential determination of cadmium and chromium in biomass samples and their ashes, using HR-CS GF AAS.

Stage	Temperature (°C)	Ramp (°C s^{-1})	Hold time (s)	Gas flow rate (L min^{-1})
Drying 1	90	5	10	2
Drying 2	110	10	10	2
Drying 3	150	10	20	2
Pyrolysis	400	100	30	2
Atomization[a]	1500	3000	6	0
	Cooling and change of wavelength			
Pyrolysis	1500	1000	1	2
Atomization[b]	2600	3000	6	0.1
Cleaning	2600	0	8	2

[a] Atomization of Cd.
[b] Atomization of Cr.

nitric acid for at least 24 h and rinsed three times with deionized water before use.

The cadmium and chromium stock standard solutions (1000 mg L^{-1} in 0.014 mol L^{-1} nitric acid) were both from Specsol (Brazil). The working calibration solutions were prepared by serial dilutions of the stock solutions.

2.3. Samples and sample preparation

The biomass samples investigated in this work have been obtained from agricultural waste, widely available in Brazil: peach pit, rice husk, sugarcane straw and their ashes. 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. The ashes were obtained by a fast pyrolysis process, where the biomass samples are heated to 700 °C for 10 min in nitrogen atmosphere, as described by Moraes et al. [40]. The NCS ZC 73012 Tea certified reference material (CRM) (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 for method validation.

Biomass samples, their ashes and the CRM 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. It took three grinding cycles of 20 s each; after each of the three grinding cycles it was necessary to introduce a hold time of 10 min for cooling the engine of the mill. Then, 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 until further processing.

The sample mass, weighed onto the SS platforms and introduced into the graphite furnace for SS-GF AAS, was between about 0.08 mg and 0.15 mg. Since the sample mass was different for each measurement the integrated absorbance was normalized for an appropriate sample mass for comparison.

3. Results and discussion

3.1. Temperature program and chemical modifiers

Because of the high volatility of Cd, the use of a chemical modifier has been considered initially, and a mixture of 0.5 g L^{-1} Pd+0.3 g L^{-1} Mg+0.05% Triton X-100 has been chosen, which was used successfully in earlier work with direct solid sample analysis [29,31]. The effect of this modifier on the integrated absorbance signal of Cr is shown in Fig. 1. An increasing mass of modifier had a significant influence on the integrated absorbance signal of Cr in the aqueous calibration solution, which was accompanied by significant signal broadening and tailing. Although the influence in the case of the biomass sample was significantly less pronounced, probably due to the stabilizing effect of the matrix, the idea of using a chemical modifier for this determination has been abandoned.

Fig. 2 shows the pyrolysis curves for Cd and Cr in aqueous calibration solutions and a typical biomass sample without the use of a chemical modifier. Cadmium was thermally stable in the aqueous solution and in the solid sample up to a pyrolysis temperature of 400 °C, which is according to expectation, whereas Cr did not show any vaporization loss at least up to 1500 °C. The corresponding atomization curves for the two analytes in aqueous solution and in a biomass sample are shown in Fig. 3. It is obvious

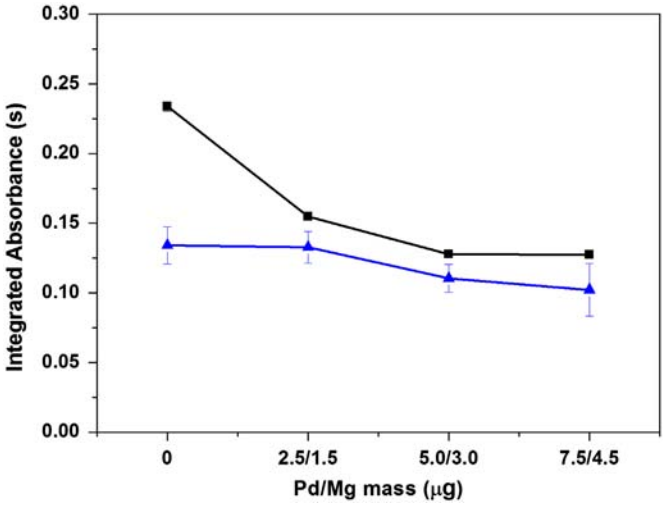

Fig. 1. Influence of the Pd/Mg modifier mass on the integrated absorbance signal for Cr; -■-6 ng Cr in aqueous solution; -▲-integrated absorbance signal normalized for 0.08 mg sugarcane straw; T_{pyr}=400 °C and 1500 °C, T_{atom}=2600 °C.

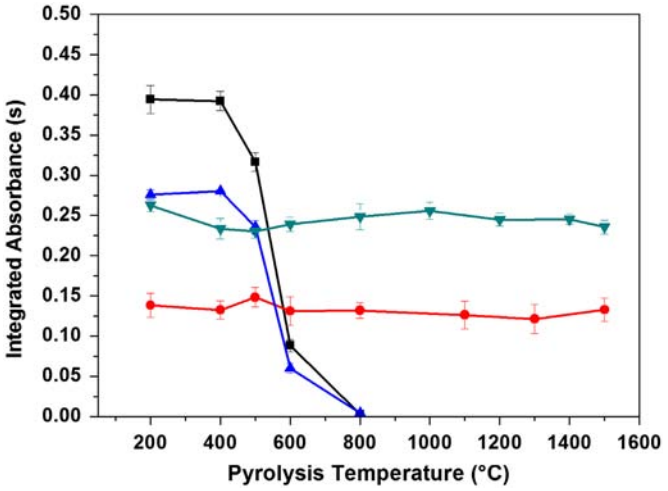

Fig. 2. Pyrolysis curves for Cd (T_{atom}=1500 °C) and Cr (T_{atom}=2600 °C); -▲-25 pg Cd and -▼-6 ng Cr, both in aqueous solution; integrated absorbance signal for -■-Cd and -●-Cr, both normalized for 0.08 mg sugarcane straw.

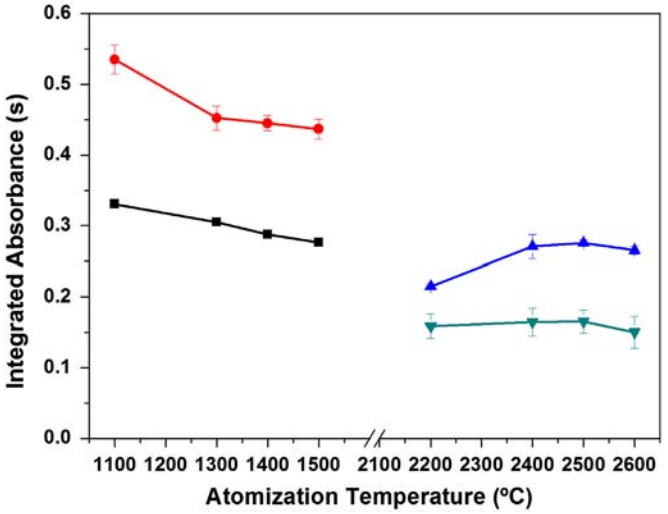

Fig. 3. Atomization curves for Cd (T_{pyr}=400 °C) and Cr (T_{pyr}=400 °C and 1500 °C); -■-25 pg Cd and -▲-6 ng Cr, both in aqueous solution; integrated absorbance signal for -●-Cd and -▼-Cr, both normalized for 0.08 mg sugarcane straw.

that Cd can be atomized efficiently already at a temperature of 1100 °C with a slight decrease in integrated absorbance up to 1500 °C; Cr exhibits essentially a plateau between 2400 °C and 2600 °C. A pyrolysis temperature of 400 °C and atomization temperatures of 1500 °C for Cd and 2600 °C for Cr have finally been chosen, based mainly on the well-defined absorbance signals obtained for the two analytes under these conditions, which are shown in Fig. 4a and b. This figure also shows that the continuous background absorption, which is inevitable in the case of biomass samples and a pyrolysis temperature of only 400 °C, is perfectly corrected, and there is not any structured background visible. In the case of Cr, the atomization stage of Cd acts as a second pyrolysis stage that removes the matrix efficiently.

The final temperature program for the sequential determination of the two analytes is shown in Table 1; the second pyrolysis stage before the atomization of Cr would not be really necessary from an analytical point of view, but it is compulsory due to the configuration of the software of the instrument.

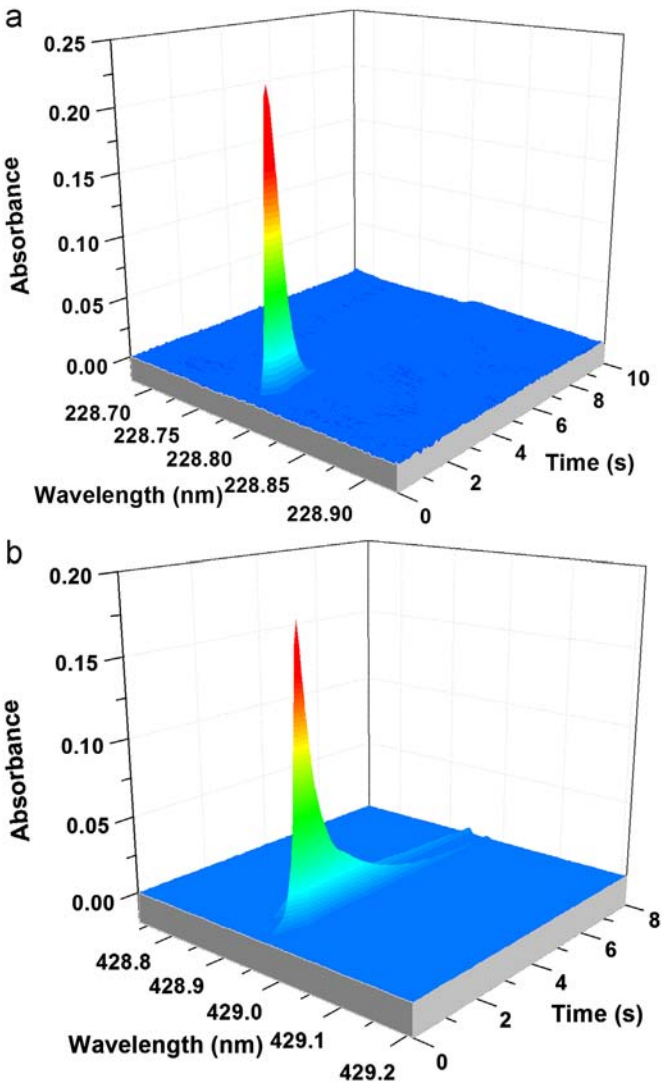

Fig. 4. Time- and wavelength-resolved absorbance signals for (a) Cd (T_{atom}=1500 °C) and (b) Cr (T_{atom}=2600 °C) in 0.1 mg sugarcane straw.

3.2. Figures of merit

The figures of merit for the sequential determination of Cd and Cr using HR-CS GF AAS are presented in Table 2. The limits of detection (LOD) and quantification (LOQ) have been calculated for a sample mass of 0.15 mg as three and ten times, respectively, the standard deviation of ten measurements of the blank, divided by the inclination of the calibration curve. The blank measurements were carried out according to the "zero mass response" principle [41] by repeatedly inserting an empty solid sampling platform into the graphite furnace and executing the entire temperature program shown in Table 1. The most sensitive line of Cr at 357.869 nm, with three pixels for evaluation, has only been used for the determination of this analyte in the CRM Tea; for the determination of Cr in all the samples and the CRM Sandy Soil A, the less sensitive line at 428.972 nm has been used with only one pixel for evaluation and a gas flow of 0.1 L min^{-1} during atomization in order to adapt the sensitivity to the concentration of Cr in the samples. The determinations of Cd have all been carried out at the main resonance line at 228.802 nm with three pixels for evaluation and the gas flow stopped in the atomization stage.

The calibration curves have been established using a blank and six calibration solutions in the concentration range 0.50–6.00 μg L^{-1} Cd (5.0–60 pg Cd) and 2.5–30.0 μg L^{-1} Cr (25–300 pg Cr) for measurements at the 357.869-nm line, or 100–600 μg L^{-1} Cr (1.0–6.0 ng Cr) for measurements at the 428.972-nm line.

The figures of merit obtained in this work are in agreement with the values reported in the literature for Cd [25,27–29] and Cr [28,33,37] using direct analysis of solid samples by GF AAS with line or continuum sources. The LOD reported in the literature are between 0.2 μg kg^{-1} and 4.2 μg kg^{-1} for Cd [25,27–29] and between 0.05 mg kg^{-1} and 1.1 mg kg^{-1} for Cr [28,33,37]. There are only two papers that report the determination of Cd by HR-CS SS-GF AAS, one of them in coal samples [36] and another one in bean and soil samples [25]; in both, the authors calculated the LOD and LOQ using the zero mass response. The LOD reported for the two matrices was the same: 2.0 μg kg^{-1}. This value is higher than that found in this work, 1.1 μg kg^{-1}. Regarding Cr determination by HR-CS SS-GF AAS, there is a paper that reports the analysis of charcoal and carbon black with a LOD of 50 μg kg^{-1} [37] and another about medicinal plants with a LOD of 3.3 μg kg^{-1} [38]; both used the analytical line at 357.869 nm and CP ± 1 for signal evaluation.

Table 2
Figures of merit for the sequential determination of Cd and Cr in biomass and ash using HR-CS GF AAS, T_{pyr}=400 °C, T_{atom}=1500 °C (Cd) and 2600 °C (Cr).

Parameter	Cd (CP ± 1) λ=228.802 nm	Cr (CP ± 1) λ=357.869 nm	Cr (CP) λ=428.972 nm
LOD* (μg kg^{-1})	1.1	21	90
LOQ* (μg kg^{-1})	3.7	70	300
Ar gas flow-rate (L min^{-1})	0	0	0.1
m_o (pg)	0.4	2.5	72
Linear regression equation	A_{int}=0.0056+0.0105 m_{Cd} (pg)	A_{int}=0.0065+0.0018 m_{Cr} (pg)	A_{int}=0.0009+0.0444 m_{Cr} (ng)
Correlation coefficient	0.9993	0.9972	0.9966

* LOD and LOQ calculated for 0.15 mg of sample for both analytes.

3.3. Analysis of CRM and samples of biomass and their ash

Two CRM were analyzed in order to validate the accuracy of the proposed method, 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 Cd and Cr in these materials is much higher than that in the samples investigated here, so that the proposed method could not be applied without modification. As the ash of the biomass samples was rich in silicates, the sandy soil CRM has been considered appropriate for the purpose. The results of the determination of Cd and Cr in the two CRM are shown in Table 3. The results are not significantly different from the certified values, based on a Student *t*-test on a 95% confidence level, proposing that the results obtained with the proposed method are accurate.

The results obtained for the two analytes in three biomass samples, sugar cane straw, rice husk and peach pit, and in the ash that remained after the biofuel production, are shown in Table 4. The values found for Cd in the biomass samples varied between less than 1.1 μg kg^{-1} for the peach pit and 789 μg kg^{-1} for the sugar cane straw. As expected for a volatile element, the concentration found in the ash was lower than in the biomass; the values were between less than 1.1 μg kg^{-1} for the ashes of sugar cane straw and peach pit and 6.3 μg kg^{-1} for rice husk ash.

Table 3
Results for the determination of Cd and Cr in the Tea and Sandy Soil CRM using HR-CS SS-GF AAS and calibration against aqueous solutions; all values are the average of $n=6$ determinations ± sd.

CRM	Cd (μg kg^{-1})			Cr (mg kg^{-1})		
	Certified	Found	RSD (%)	Certified	Found	RSD (%)
Tea	62 ± 4	63 ± 6	10	0.45 ± 0.1	0.43 ± 0.07	15
Sandy soil A*	30	29 ± 4	13	21.5	19.6 ± 2.8	14

* No uncertainty is given for the certified values of Cd and Cr in the CRM sandy soil A.

Table 4
Results for Cd and Cr in biomass samples and their ashes using HR-CS SS-GF AAS and calibration against aqueous solutions; all values are the average of $n=6$ determinations ± sd.

Sample	Cd (μg kg^{-1})		Cr (mg kg^{-1})	
	Found value	RSD (%)	Found value	RSD (%)
Sugar cane straw	789 ± 95	12	36 ± 2	5
Rice husk	30 ± 3.9	13	89 ± 9	10
Peach pit	< LOD*	—	7.9 ± 1.1	14
Ash of sugar cane straw	< LOD*	—	28 ± 3.7	13
Ash of rice husk	6.3 ± 0.7	11	3.4 ± 0.6	17
Ash of peach pit	< LOD*	—	10.2 ± 0.9	8

* LOD for Cd: 1.1 μg kg^{-1}.

The values found for Cr in the biomass samples were between 7.9 mg kg^{-1} for the peach pit and 89 mg kg^{-1} for the rice husk; however, in contrast to Cd, the concentration in the ash did not follow a uniform pattern. While the Cr concentration in the rice husk ash was about a factor of 25 lower than in the biomass, the concentration in the sugar cane straw ash and in the peach pit ash was essentially unchanged, which, however, has to be put into relation with the mass loss of the sample during the pyrolysis stage.

As we had no access to the biofuel produced in this process, which was used for other purposes, we could make only a partial mass balance for the investigated analytes, which is presented in Table 5. The mass of ash obtained for 10 g of biomass sample after the pyrolysis stage at 700 °C, was around 2.5 g for the sugar cane straw, 2.0 g for the rice husk and 2.2 g for the peach pit. In the case of Cd, less than 5% of the original mass present in rice husk is found in the ash, and the content of Cd in the ash of sugar cane straw was less than 1 μg kg^{-1}, i.e., all the Cd was lost in the pyrolysis stage for the production of biofuel. Considering the pyrolysis curve for Cd in Fig. 2, which has been obtained under conditions comparable to the pyrolysis of the biomass for biofuel production with the only exception that nitrogen was used as the inert gas instead of argon, we may assume that almost all of the Cd in the biomass is released to the atmosphere in that stage. In the case of Cr the percentage that goes to the ash is between ~ 1% for the rice husk and ~ 30% for the peach pit. As, again referring to Fig. 2, a loss of Cr due to volatilization at 700 °C is unlikely, we have to assume that all the Cr that is not found in the ash went to the biofuel.

4. Conclusion

A method has been developed for the fast sequential determination of Cd and Cr in biomass samples and their ashes using HR-CS GF AAS and direct solid sample analysis. The use of aqueous standard solutions for calibration further simplified the procedure. It might be expected that other analytes or combinations of analytes could be determined in a similar way.

From an environmental point of view, the fate of potentially hazardous elements in the process of biofuel production is of great importance. Apparently only a small fraction is found in the ashes, although the percentage appears to depend on the type of biomass used. In the case of Cd, volatilization in the pyrolysis stage is the most likely pathway, which clearly is of environmental concern, as most of the Cd contained in the biomass is released to the environment. In the case of Cr volatilization at 700 °C is very unlikely, and the amount that does not appear in the ash , which is between 70% and 99%, inevitably is transferred to the biofuel and has to be considered as a contaminant. 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 process of biofuel production.

Table 5
Mass loss of the biomass samples during the pyrolysis stage, the calculated value for Cd and Cr if all the analyte would be in the ash, the found value in the ash and the calculated transfer of the analytes to the atmosphere and/or to the fuel ("loss %").

Sample	Mass loss (%)	**Cd**			**Cr**		
		Calculated value in ash (μg kg^{-1})	Found (μg kg^{-1})	Loss (%)	Calculated value in ash (μg kg^{-1})	Found (μg kg^{-1})	Loss (%)
Sugar cane straw	75	3156 ± 380	< 1.1	~ 100	144 ± 8	28 ± 4	80
Rice husk	80	150 ± 20	6.3 ± 0.7	> 95	445 ± 25	3.4 ± 0.6	99
Peach pit	78	–	–	–	36 ± 5	10.2 ± 0.9	70

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