



ELSEVIER

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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

Alvaro T. Duarte^a, Morgana B. Dessuy^a, Maria Goreti R. Vale^{a,b,*},
Bernhard Welz^{b,c}, Jailson B. de Andrade^b

^a Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, 91501-970 Porto Alegre—RS, Brazil

^b Instituto Nacional de Ciência e Tecnologia do CNPq—INCT de Energia e Ambiente, Universidade Federal da Bahia, 40170-115 Salvador—BA, Brazil

^c Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis—SC, Brazil

ARTICLE INFO

Article history:

Received 6 February 2013

Received in revised form

10 April 2013

Accepted 15 April 2013

Available online 19 April 2013

Keywords:

High-resolution continuum source AAS

Direct solid sample analysis

Sequential determination of two elements

from the same sample aliquot

Cd and Cr in biomass and ash

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.

© 2013 Elsevier B.V. All rights reserved.

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 CO₂, the main goal of the Kyoto protocol, since the burning of biomass does not release more CO₂ 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

* Corresponding author at: Universidade Federal do Rio Grande do Sul, Instituto de Química, Av. Bento Gonçalves, 9500, 91501-970 Porto Alegre, Rio Grande do Sul, Brazil. Tel.: +55 51 3308 6278; fax: +55 51 3308 7304.

E-mail addresses: mgrvale@ufrgs.br, mgrvale@gmail.com (M.G.R. Vale).

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, $CP \pm 1$) has been used for signal evaluation, corresponding to a spectral interval of 4.6 pm ($CP \pm 1$) for Cd and 2.3 pm (CP) for Cr at 428.972 nm, or 6.0 pm ($CP \pm 1$) 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 $18 \text{ M}\Omega \text{ cm}$, 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 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.

Download English Version:

<https://daneshyari.com/en/article/7681535>

Download Persian Version:

<https://daneshyari.com/article/7681535>

[Daneshyari.com](https://daneshyari.com)