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Leachability and analytical speciation of antimony in coal fly ash

Ricard Miravet, José Fermín López-Sánchez*, Roser Rubio

Departament de Química Analítica, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

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Abstract

The present study assesses the single extraction of Sb from two coal fly ashes with aqueous solutions at a range of pHs (1–12) and with citrate 1 mol L^{-1} at pH 5, in order to obtain preliminary information about Sb leaching from this matrix. Speciation analysis of the coal fly ash extracts by HPLC-ICP-MS and HPLC-HG-AFS was carried out in order to identify the presence of individual Sb species. Sb(V) was the main Sb species in the leachates, although minor amounts of Sb(III) were also detected in some extracts. Citrate at pH 5 gave the best extraction efficiency for both samples whereas Sb species were also fairly soluble in aqueous solutions at acidic pHs. Analysis by HPLC-ICP-MS provided the most accurate results in some extracts (aqueous solution at pH 1 and citrate at pH 5) when both coupled techniques used were compared. The presence in these leachates of higher content of interfering metal ions (Ca, Fe and Pb) than those obtained for the Sb species reduced stibine generation in the HPLC-HG-AFS analysis. The proposed methodology can be considered reliable and useful for antimony speciation in environmental studies.

Keywords: Antimony speciation; Coal fly ash; Leachability; Hyphenated techniques

1. Introduction

Fly ash is produced in large quantities by coal-fired power stations and industrial waste incinerators, and is widely distributed in the environment [1]. Fly ash particles are inhomogeneous, highly diverse, dispersed in a broad range of sizes, and have differing morphologies [2]. Fly ash contains high levels of potentially toxic elements that can be leached from the matrix and may be transported to soils, freshwater, seawater or groundwater and eventually taken up by organisms [3]. The potential toxicity of fly ashes is more closely related to the leachable fraction of contaminants, since the total toxic amount of fly ash is not extractable under natural environmental conditions [4]. Thus, the mobility of heavy metals from fly ash has been studied extensively and found to depend on their intra- and inter-particle distribution [5]. Various tests are available to measure the amounts of metals leached by single extractions with selective mild extractants [6–8], or by using sequential extraction schemes [9–12]. Such studies together with analyses of different ash fractions after separation shed light on the way these elements are distributed among the different ash components [13]. Although large variations have been found between both the extraction procedures tested and the analysed ashes, generally, the most mobile trace elements show an affinity for calcium oxide and sulfates (As, B, Cd, Mo, S, Se and Sb) and unburned carbon (Se). Less mobile are those with an affinity for iron oxides (Co, Cr, Cu and Ni) and the elements with the lowest mobility show an affinity for the glass fraction (Cr, Cu, Pb, V and the rare earths) [6].

Considering the most mobile metals, Sb is a potential toxic element of increasing environmental significance, given the diversity of its commercial and industrial uses and the number of different sources of Sb present in the environment [14]. As a chalcophile element, Sb is commonly enriched in coal and vaporised during fossil fuel combustion, resulting in the largest single source of anthropogenic Sb to the global atmosphere [15]. After condensation, Sb is found mainly in the fly ashes on sub-micrometre size class particulates [16]. However, there have been remarkably few studies regarding the leachability of Sb in fly ashes beyond the determination of Sb digested under harsh acidic conditions. Seames et al. [11] analysed different coal fly ashes and reported that Sb was partially soluble at pH 5.0 whereas its solubility increased at more acidic pHs. Otherwise, Nugteren et al. [6] leached Cr, V and Sb from one alkaline coal fly ash with water and several chelating agents and confirmed that these extracting reagents could lead to the removal of substantial amounts of these trace elements.

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* Corresponding author. Tel.: +34 93 403 4873; fax: +34 93 402 1233.
E-mail address: fermin.lopez@ub.edu (J.F. López-Sánchez).

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Apart from the distribution of the trace elements in ash, for some of them the oxidation state influences both mobility and toxicity. The analytical speciation of these pollutants is necessary to understand their mechanisms of transport and thus their environmental impact. Among other elements, there is increasing interest in the assessment of antimony species in environmental, biological, and geochemical samples. The on-line combination of separation techniques with suitable element-specific detectors has been used for such a purpose [17–25]. However, there have been few reported studies of extraction and subsequent speciation of Sb species in fly ash leachates [12,26,27]. Such studies require an extraction procedure that provides a successful removal of the analyte from coal fly ash solid without changing its oxidation state or chemical form. Moreover, the extraction conditions should be representative of the environmental risk in spite of the conditions imposed by more aggressive extraction methods. The few studies reported presented widely varying results, since different extracting procedures (single or sequential extraction) were used. Moreover, the major Sb species were found to be Sb(III) or Sb(V), depending on the fly ash sample.

On the other hand, the hydride generation technique for atomic spectrometry offers several advantages, such as improved sensitivity and selectivity of measurement. In spite of this, the interference of metal ions in As, Se and Sb determination by HG-AFS decreases the efficiency of hydride release [28–33].

In the present study, several extraction procedures for Sb species from coal fly ashes were evaluated. Thus, Sb leached from aqueous solutions at different pHs (1–12) and with citrate at pH 5 was investigated in depth. The aim was to obtain reliable information about the leaching behaviour of Sb from this matrix. Next, the speciation analysis of the obtained leachates was carried out by HPLC-HG-AFS and HPLC-ICP-MS in order to identify the stable Sb species present in the extracts. Sb(V) was the main Sb species in the leachates, although minor amounts of Sb(III) were also detected in some extracts. Finally, the presence in the leachates of interfering metal ions (Ca, Fe and Pb) that severely hampered the hydride generation step was assessed by comparing the speciation information obtained by both coupled techniques.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer 250 LC quaternary pump (CT, USA) and a polystyrene-divinylbenzene-based anion-exchange column Hamilton PRP X-100 (Reno, NV, USA) with ammonium quaternary salt with methyl groups as substituents, 10 μm particle size (250 mm × 4.1 mm), were used for the separation of antimony species. The mobile phase consisted of 250 mmol L^{-1} di-ammonium tartrate pH 5.5 and 20 mmol L^{-1} KOH pH 12. A flow rate of 1.5 mL min^{-1} was used. More details about the chromatographic separation are given elsewhere [24]. A Rheodyne 7125 injector (Cotati, CA, USA) with a 200-μL loop was used for sample introduction.

Hydride generation was performed with a Millennium P.S. Analytical (Kent, UK), model 10.055. HCl 2 mol L^{-1} at 9.0 mL min^{-1} and $NaBH_4$ 0.7 (w/v) at 4.5 mL min^{-1} were added for stibine generation. After reaction in a coil the generated stibine was driven by an argon flow (300 mL min^{-1}) to the AFS detector through the Type 'ME' gas–liquid separator. Before detection, the argon stream was passed through a Perma pure drying membrane (Perma Pure Products, Farmingdale, NJ, USA) which prevents droplets being transmitted into the transfer line. N_2 was used as drying gas at a flow rate of 2.5 L min^{-1}. Detection was carried out in a P.S. Analytical model Excalibur Atomic Florescence Spectrometer equipped with a diffusion flame and a Sb Boosted Hollow Cathode Lamp (Super Lamp, Photron, Teknokroma). Peak areas were calculated from custom-developed software running with the Matlab language [34].

A Perkin-Elmer ELAN 6000 inductively coupled plasma mass spectrometer equipped with a "cross-flow" nebulizer was also used for sample analysis. Data acquisition of the FIA peaks was carried out with a microcomputer by using software (ELAN 2.3.1) from Perkin-Elmer. The antimony signal was monitored at mass 121 and 123 without any isobaric or polyatomic interference. Ca, Fe and Pb were monitored at mass 43, 57 and 208, respectively. Rh was used as internal standard.

A Philips PW 2400 spectrometer was used for X-ray fluorescence determination of major elements. The sample pearls measured were obtained from a radiofrequency inductive oven (Perle'X-2).

2.2. Reagents and standards

All of the chemicals and reagents used in this study were of analytical-reagent grade or higher purity and de-ionized water obtained from a MiliQ System (USF PURELAB Plus, Ransbach Baumbach, Germany, 18.2 MΩ cm^{-1}) was used throughout.

Stock standard solutions (1000 mg L^{-1}, as Sb) were prepared by dissolving appropriate amounts of potassium antimonyl tartrate (Fluka, Neu-Ulm, Switzerland) and potassium hexahydroxyantimonate (Riedel de-Haën, Seelze, Germany) in water and diluting to 100 mL. All stock standard solutions were stored in polyethylene bottles in a refrigerator held at 4 °C. These solutions were standardised using a standard reference material (NIST 3102a, antimony standard solution) by ICP-AES measuring at three emission lines of antimony (206.8, 217.6 and 231.2 nm). Working solutions were prepared daily by diluting the stock standard solutions.

Sodium borohydride solutions were prepared daily from $NaBH_4$ 97% "purum" (Fluka) and stabilized in $NaOH{\cdot}H_2O$ "suprapur" (Merck, Darmstadt, Germany) 0.1 mol L^{-1} aqueous solution. Solutions of HCl were prepared from fuming HCl Pro-analysis 37% (Merck).

Potassium hydroxide ("pellets" 99.99%, Aldrich) and di-ammonium tartrate (Fluka) buffer solutions were prepared by dissolving in water. All the buffer solutions assayed were filtered off through a 0.22 μm nylon membrane before use.