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A comparison of devices using thermal desorption for mercury speciation in solids



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ABSTRACT

The goal of this work is to emphasize the reliability of the thermal desorption technique in identifying mercury species. The analysis of mercury species in solids is essential for assessing the risk of disposal or re-use of mercury-contaminated materials. This study evaluates the accuracy and reliability of thermal desorption as a technique for identifying mercury species by means of different thermo-desorption devices. For this purpose, mercury species present in samples related with coal utilization processes were identified. Three devices were compared for analyzing samples free of carbon or with a low carbon content (fly ashes, gypsums and soils), and a new equipment was developed to analyze samples with a high carbon content (coal). In spite of the fact that the first three devices employ different experimental conditions (i.e., heating rate, gas flow and carrier gas), the mercury species identified in the samples were comparable in all cases. The need for new equipment for mercury speciation in materials containing carbon was a consequence of interferences produced from the pyrolysis products of the organic matter. The new device consists of two furnaces and two gas inlets to allow thermal oxidation of organic pyrolysis products and the identification of mercury species in carbonaceous samples. This new approach offers the application of thermal desorption to mercury speciation in all types of materials contaminated with mercury.

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1. Introduction

Mercury (Hg) is a metal with unique characteristics. Its high vapor pressure and surface tension facilitates its distribution in the atmosphere, causing widespread contamination. Although Hg is found in nature in the form of cinnabar (red HgS), metacinnabar (black HgS), livingstonite (HgSb₄S₇), coloradite (HgTe), tiemannite (HgSe) and calomel (Hg₂Cl₂), human activity has changed the global Hg cycle and increased the amount of mercury that people can be exposed to. Mercury entering water, soil and atmosphere from anthropogenic emissions is in the form of elemental mercury (Hg⁰), inorganic mercury (between Hg²⁺ and Hg⁺) and organic mercury. Inorganic mercury is linked to sulfide, chloride, nitrate, oxide or sulfate. Depending on the source and the environmental conditions, mercury can be transformed into different forms that show distinct behaviors, bioavailability and toxicity. Therefore,

it is essential to know the chemical form of this element in order to be able to predict its behavior in the ecosystem and find suitable remediation methods for its control.

Coal combustion is the main anthropogenic source of mercury emissions, followed by metal smelting, cement production and waste incineration [1–3]. The emissions of mercury from thermal power stations and other combustion installations account for 55.4% of the total amount of mercury emitted in Europe in 2012 [4]. Coal fired power plants also generate Hg-loaded solid wastes [5], such as fly ashes and gypsum. These sub-products are disposed of in landfills or re-used as raw materials, with the consequent risk of being released to water or to the atmosphere. The environmental impact of mercury depends on the mode of occurrence in these solids.

Mercury speciation in solids can be measured via different techniques. X-ray absorption Spectroscopy (EXAFS) is a powerful technique that provides detailed information about the form and neighboring atoms of Hg. However, EXAFS is generally effective in samples with concentrations of Hg higher than 1 mg kg⁻¹.

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Table 1
High peak desorption temperatures of mercury compounds obtained in different solid matrices and experimental conditions.

Hg species	High T (°C)	Solid matrix	Heat rate (°C/min)	Carrier gas (ml/min)	Detector	DL (mg kg ⁻¹)
Hg ₂ Cl ₂	160	Soil	10	N ₂ (100)	AAS [33]	0.03
	225–350	Phosphorus powder	33	N ₂ (200)	AAS [19]	–
	190	–	5	N ₂ (2000)	CVAAS [34]	0.05
	148 and 240	gypsum	10	N ₂ (400)	AAS [22]	0.002
HgCl ₂	263	Soil	10	N ₂ (100)	AAS [33]	0.03
	275	Phosphorus powder	33	N ₂ (200)	AAS [19]	–
	120	Fly ash	50	Ar (1000)	ICP-MS [35]	0.000005
	100–220	Sand	30	Ar (500)	AAS [36]	0.5
	145	–	5	N ₂ (2000)	CVAAS [34]	0.05
	212	Gypsum	10	N ₂ (400)	AAS [22]	0.002
	260–350	Sand	30	Ar (500)	AAS [36]	0.5
Hg-HA (Hg-OM)	100–240	Aluminum oxide	–	Air	AAS [13]	0.02
	250	Quartz sand	10	N ₂ (250)	AAS [24]	–
Black HgS	180–350	Silica	–	He	[37]	–
	350	Quartz sand	10	N ₂ (250)	AAS [24]	–
Red HgS	250–430	Sand	30	Ar (500)	AAS [36]	0.5
	350	Fly ash	50	Ar (1000)	ICP-MS [35]	0.000005
	250–400	Silica	–	He	[37]	–
	290	–	5	N ₂ (2000)	CVAAS [34]	0.05
	350	Gypsum	10	N ₂ (400)	AAS [22]	0.002
	300	Soil	10	N ₂ (100)	AAS [33]	0.03
HgO	400	Phosphorus powder	33	N ₂ (200)	AAS [19]	–
	500	Fly ash	50	Ar (1000)	ICP-MS [35]	0.000005
	540	–	5	N ₂ (2000)	CVAAS [34]	0.05
	200–380	Silica	–	He	[37]	–
	145–225	Gypsum	10	N ₂ (400)	AAS [22]	0.002
Hg ₂ SO ₄	400	Gypsum	10	N ₂ (400)	AAS [22]	0.002
	580	Silica	–	He	[37]	–
HgSO ₄	580	–	5	N ₂ (2000)	CVAAS [34]	0.05

Moreover, accessibility to this equipment is usually limited [6–8]. The Sequential Chemical Extraction (SCE) procedure which uses sequentially arranged solvents to extract Hg species into different liquid fractions has low detection limits. However, the main drawback of this method is the possible chemical alteration of the sample by the solvents, which decreases the selectivity of the method [9–11].

A promising technique with low detection limits is that based on thermal programmed desorption (HgTPD) [12–14]. Moreover, HgTPD is an easily accessible technique which can be implemented without the need for complicated instrumentation or for the time-consuming sample pre-treatment required by EXAFS and SCE. HgTPD is based on the low stability of Hg compounds at low temperatures, which allows mercury species to be identified by their characteristic temperatures of decomposition or desorption. Table 1 shows desorption temperatures for the main mercury compounds as described in the literature, obtained by using different experimental devices and conditions. The technique has been tested on a wide variety of solids, which include; sediments and soils [15–18], waste lamps [19], fly ashes [18,20], gypsum [21–23] and sorbents from Hg retention [24,25]. However, the validity of the method must remain open to doubt until the influence of several instrumental parameters upon the results has been clearly established. It should also be considered that, unlike EXAFS, HgTPD does not provide quantitative results for the different Hg phases present in samples. Some of the questions concern the overlapping of peaks, possibly related to the flow rate and heating rate, and the selection and preparation of the mercury reference compounds regarding the possible effects the matrix might have upon them.

To clarify these matters and to evaluate the robustness and reliability of the thermal desorption method for identifying mercury species in solids, this study evaluates the results provided by three HgTPD devices under different conditions using several types of solids from coal utilization processes. Once the reliability

of the thermal desorption technique for identifying mercury species in samples free of carbon matter was verified, a new device capable of avoiding the interferences produced by carbon was included in the evaluation sequence. The new device is a modification of a commercial device already evaluated.

2. Method and materials

2.1. Samples

The samples studied were sub-products from coal combustion processes (fly ashes and gypsums), contaminated soils from the coal industry and a coal. The fly ashes, namely CTL, CTA and CTP, were obtained from two pulverized coal power plants and a fluidized bed combustion plant, respectively. The characteristics of these fly ashes have been described elsewhere [18]. Two samples of gypsum (Gypsum A and Gypsum Z) were collected from the Wet Flue Gas Desulfuration Plants (WFGD) of two 1200 MW power stations. These gypsum samples have been previously characterized by the authors [21]. The soil samples were collected from the surrounding area of a coking plant [26]. PUSH3 and FAR2 were taken from points close to, and outside, the area of greatest activity of the plant, respectively, whereas TDIST1 was sampled at the point of maximum mercury concentration [27]. The coal sample (CL-Sb) was a low rank coal.

Eight commercial Hg compounds (HgCl₂, Hg₂Cl₂, black HgS, red HgS, Hg-HA (humic acid), HgO, Hg₂SO₄ and HgSO₄) were blended by successive dilutions with different materials (silica flour, sand, fly ash, gypsum and a soil) in order to simulate different matrices until mercury concentrations of up to 10 mg kg⁻¹ were obtained. Homogenization of the pure mercury compounds and the matrix was carried out by grinding the sample in a mortar to homogenize the particle size, and then using a rotary shaker to blend the solids. These blends were used as reference samples. It must be

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