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3 **A NEW APPROACH TO MERCURY SPECIATION IN SOLIDS USING A**

4 **THERMAL DESORPTION TECHNIQUE**

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Abstracts

Identification of the chemical form of mercury in coals and during the entire combustion process is essential for successfully controlling mercury emissions. However, the speciation of mercury in coal and, in general, in carbonaceous samples has so far proved elusive because of the limitations of current analytical techniques as a consequence of the detection limits of the equipment or interferences originating from the matrix. In this work a new device based on temperature programmed desorption (HgTPD) has been developed to identify mercury species in carbonaceous materials. The samples studied were coals of different rank obtained from around the world and activated carbons that had previously been used as mercury sorbents in simulated coal combustion atmospheres. The mercury species present in both types of sample were identified without any interference from the matrix. This achievement is extremely important as it will contribute to a better understanding of (i) the behavior of mercury species in coal in coal utilization processes and (ii) the retention mechanisms and subsequent stability of the mercury species captured by carbon sorbents.

Keywords: mercury; speciation; coal; thermal analysis

1. Introduction

Mercury is a global pollutant because it can be transported over long distances through the atmosphere. The ability to determine the chemical form of mercury in a contaminated and industrial environment is the key to predicting its solubility, transport, behavior and bioavailability as well as for designing effective control and remediation technology.

The current interest in the analysis of mercury species in coals and activated carbons is a consequence of the need to control mercury pollution from coal combustion processes. Mercury is a naturally occurring element in coal. Although the speciation of this element has often proved elusive due to the limitations of the instruments designed for this task, it is believed that mercury can be present in coals as sulphides (HgS), selenides (HgSe), in forms associated with pyrite and sphalerite (HgFeS_2), organically bound to coaly matter (HgOM), or even as metallic mercury (Hg^0) [1, 2]. The concentrations of mercury in coal generally range from 0.02 to 1.0 $\mu\text{g}\cdot\text{g}^{-1}$ [1, 2]. However, the huge amount of this combustible consumed for power generation makes coal combustion power plants one of the largest sources of mercury emissions to the atmosphere. 475 tons of mercury were emitted in 2010 to the air from these utilities [3]. The reduction of mercury emissions from coal combustion can be tackled in different ways. It can be achieved by cleaning the coal [4-7] or by thermal drying [8] as a previous step to its combustion, by optimizing control systems used for other pollutants [9], or by developing specific mercury control strategies such as the retention of the mercury present in the flue gas by solid sorbents [10, 11]. In the case of the pre-combustion methods, the mode of occurrence of mercury in the coal will determine the

efficiency of the process. In the same framework, the speciation of mercury in sorbents used for mercury retention is also necessary to understand the interactions that occur between the mercury species in gas phase and the material used for its retention.

With the analytical equipment now available, determination of the total mercury content in solid samples at $\mu\text{g}\cdot\text{g}^{-1}$ and even at $\mu\text{g}\cdot\text{kg}^{-1}$ levels can be easily and cost-effectively carried out. The most sensitive and accurate techniques are based on using atomic absorption spectrophotometry and atomic fluorescence detection [12]. However, it is still difficult to identify the mode of occurrence of mercury in all types of solids. X-ray adsorption fine structure spectroscopy (EXAFS) [13, 14], sequential extraction (SE) [15, 16] and temperature programmed desorption (HgTPD) [17-22] are the techniques usually employed to identify mercury species in solids. However, all of them have their limitations especially when they are applied to samples with a high content of carbonaceous matter and low concentrations of mercury. The high detection limit in the case of EXAFS, the low selectivity and inability to extract individual mercury species of SE and the interferences caused by volatile matter in HgTPD are the main problems that arise in carbon materials analysis. For these reasons, it is necessary to develop sensitive and selective methods of analysis that are free from interference and applicable to any material. In the case of HgTPD, optimization of the technique entails solving the problems associated with the matrix effects and especially those related to carbonaceous matter.

The aim of the present study is to identify mercury species in solids with a high carbon content using a novel thermal desorption technique. For this purpose, a commercial thermo-desorption device was modified to oxidise the volatile matter produced by carbon materials without interfering with the evaporated mercury species. The samples studied were coals with different characteristics and activated carbons

previously used as mercury sorbents in simulated coal combustion and oxy-combustion atmospheres.

2. Material and methods

2.1. Samples

Eighteen coal samples of different origin were chosen for the identification of mercury species by a modified thermal desorption method (Table 1). The coal ranks included lignites (4 samples), sub-bituminous (1 sample), bituminous (11 samples) and anthracites (2 samples).

Moreover, two commercial activated carbons (Norit RB3 and RBHG3), previously used as mercury sorbents in simulated coal combustion and oxy-combustion atmospheres [23], were analysed by the same method. RBHG3 was prepared by impregnating RB3 with sulphur compounds to be used for mercury retention at low temperatures [24].

2.2. Experimental device for mercury speciation

For this study a specially designed procedure based on thermo-desorption was developed and optimized for mercury speciation in carbonaceous materials [25] (Figure 1). The speciation device employed was a modification of a commercial device described by the authors elsewhere [21]. The main components of the commercial apparatus are a furnace (PYRO 915) and a mercury analyzer (Lumex RA-915). In this equipment, mercury is evaporated from the solid during combustion and decomposition in the oven where reduction to elemental mercury also takes place. The elemental mercury (Hg^0) in gas phase is transported to the analyzer where it is detected as $\text{Hg}^0(\text{g})$. This apparatus records temperature versus mercury and is not only able to determine the

total concentration of mercury in the solid samples but also to identify the species of mercury. For this purpose, it was first necessary to analyze different mercury standards with different temperatures of decomposition. By comparison it would then be possible to identify the mercury species in the solid samples. Commercial devices usually work with air or oxygen to facilitate the total decomposition of the solids. However, these gases can interfere with some of the mercury species. To overcome this problem a new device was developed. The modified device was set up by coupling a second thermo-desorption furnace to a commercial PYRO 915 furnace and then connecting these to a commercial continuous mercury analyser (Lumex RA-915).

The novelty of this set-up is that the desorption of the mercury species takes place in an inert atmosphere (N_2) in the new furnace at the beginning of the process to avoid interferences and undesired reactions, while at the same time O_2 is introduced into the commercial furnace PYRO in order to oxidize the volatile matter emitted by the carbon material. The new furnace contains two chambers, in the first of which the desorption of the mercury species occurs, while the second chamber ensures that the temperature is maintained so as to avoid cool zones and the condensation of the mercury until it enters the PYRO furnace. The new furnace also contains two temperature controllers that allow the heating ramp and the temperature in the zone between the new and PYRO furnace to be optimized. First the sample is weighed and then introduced into the new thermo desorption furnace. The temperature of the sample is continuously controlled by a thermocouple situated inside a quartz sample boat. In the new thermo-desorption furnace the mercury compounds are released from the solid matrix in a flow of nitrogen of $500\text{ mL}\cdot\text{min}^{-1}$ under a controlled heating mode of $50\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The PYRO 915 unit is kept at $800\text{ }^{\circ}\text{C}$ in a flow of oxygen of $500\text{ mL}\cdot\text{min}^{-1}$. This unit serves to decompose volatile matter and to reduce the mercury compounds to elemental mercury. Finally, the

Hg⁰ is determined using a RA-915+ analyser based on differential Zeeman atomic absorption spectrometry.

The mercury species are identified from the high peak temperature at which they are released. To this end, the desorption profiles are compared with the desorption profiles of the reference mercury compounds that are the most likely species to form in coals [HgS, HgSe Hg-OM, (organic matter) and Hg-FeS₂]. The presence of HgO and HgCl₂ was also considered to be possible in coals and activated carbons. The reference compounds for mercury sulfide, mercury selenide, mercury oxide and mercury chloride were prepared from commercially pure HgS, HgSe, HgO and HgCl₂, respectively, which were blended with silica and carbon matrices in mercury concentrations of up to 10 mg·kg⁻¹. The mercury standard for organic matter (Hg-OM) was prepared from a humic acid [26]. Humic acids contain COOH, OH and CO groups and, although the presence of these groups will depend on coal rank, a similar environment for the mercury linkages in humic acids and carbon materials can be considered as likely. On the basis of this premise, mercury bound to humic acid was chosen as being representative of organic groups in coals [1, 27]. Finally, a sample of natural pyrite (FeS₂) was used as the reference compound for mercury associated to pyrite (Hg-FeS₂).

Overlapping peaks were deconvoluted using Origin 6.0 software. The accuracy and precision of the analysis of the reference mercury compounds was validated by means of 5 analyses of one of the reference samples (HgS). The results showed differences in a range of 15-20% between the total mercury concentrations obtained from calculation of the peak area (experimental) and the expected concentrations, whereas the relative standard deviation (%RSD) was lower than 10%.

3. Results and discussion

3.1. Mercury speciation in coal samples.

The combustibles analyzed in this work are, in most cases, coals or coal blends used to feed thermal power plants. As explained above, this study aims to validate a technique based on thermal desorption for the identification of different mercury species in carbonaceous samples. It is not intended to be an evaluation of the origin of mercury in coal. However, a collateral result of this study is that it does provide useful information about the mode of occurrence of mercury in coals of different characteristics. It is therefore important to take into account some of the characteristics of these samples such as the S, Se and Cl whose contents are presented in Table 1. The affinity of mercury for these elements is well-known. In general, the mercury concentration in the coals ranges from 0.08 to 0.3 $\mu\text{g g}^{-1}$, with the exception of the bituminous coal SB-Jo which contains 1.5 $\mu\text{g g}^{-1}$. The chlorine content is $<150 \mu\text{g g}^{-1}$ with the exception of two bituminous coals (SB-Ca and SB-Mo) and one anthracite (SA-T) whose chlorine contents range between 700 and 950 $\mu\text{g g}^{-1}$. The sulphur content ranges from 0.3 to 5 % while that of selenium ranges from 0.1 to 7 $\mu\text{g g}^{-1}$.

Figures 2-4 show the mercury desorption profiles for all the coal samples grouped according to their rank: lignites (Figure 2), bituminous and subbituminous coals (Figure 3) and anthracites (Figure 4). As can be seen, mercury is mainly released between 100 and 500°C from lignite, bituminous and subbituminous coals and up to 600°C from anthracites. According to the thermal desorption data of the mercury reference compounds (Table 2), the main mercury species in this temperature range can be expected to be mercury bound to organic matter (Hg-OM), mercury associated to pyrite (Hg-FeS₂) and HgS, the most abundant mercury mineral in the Earth's crust. In addition, mercury is also present as HgSe in bituminous coals. Others species such as HgO or even HgCl₂ might also occur in some coals but in lower proportions (Table 3).

The presence of these species could be a consequence of reactions in the environment of the coalfield and transformations brought about by percolated species.

As can be seen in Figure 2 the HgTPD obtained from the lignites shows a double maximum peak between 168 and 220°C. The peak at 169°C corresponds to Hg-FeS₂ whereas the peak at 220°C is assigned to Hg-OM. Moreover in some samples the presence of HgCl₂ cannot be ruled out since a small shoulder is observed at approximately 130°. This species is not abundant but it might be incorporated into coaly matter under favourable environmental conditions.

The presence of organic mercury (Hg-OM) is more probable in low rank coals, where coaly matter contains more functional groups (Figures 2-3), than in more evolved high rank coals (Figure 4), where functional groups have been lost. Indeed, the main peak observed in the anthracites studied (Figure 4) is at approximately 300°C, corresponding mainly to sulphides (Table 1), whereas the peak corresponding to Hg-OM is less significant.

The HgTPD method developed in this work was found to be highly effective for identifying mercury species in coals. Although the number of coals analysed may not represent all the different types of coal, the results obtained do permit a few generalizations. The main species present in lignites is Hg-OM and mercury linked to pyrite (Hg-FeS₂). In subbituminous and bituminous coals there is a contribution by both organic matter and sulphides, where some HgSe is also present in conjunction with a small amount of HgCl₂ and HgO in some cases. Sulphides and HgO are the main mercury species present in the anthracites. It should be pointed out that in the samples evaluated in this work the majority of the mercury species expected to be present in the coals were identified.

3.2. Mercury speciation in activated carbon sorbents

A well-known technology used to control mercury emissions in energy generation from coal combustion is the injection of activated carbon [28]. The efficiency of mercury retention in activated carbons varies depending on the type of carbon, coal and combustion conditions [10, 29].

The activated carbons employed in this study for the identification of mercury species (RB3 and RBHG3), have been tested previously in various conditions and have been used as reference materials for mercury capture [23, 24, 30]. On the basis of the knowledge acquired about the characteristics of these activated carbons and their behavior as mercury sorbents, the HgTPD method can now be used to identify the mercury species formed in the retention process under several conditions. The identification of the species present in these sorbents after mercury retention will contribute not only to our understanding of the mercury retention mechanism in activated carbons but also explain the leaching of mercury species from activated carbon wastes.

The commercial activated carbons used for this study had been previously tested in a laboratory scale reactor by our group [23]. The sorbents were employed in three different atmospheres; an inert atmosphere (N_2) and under simulated oxy-combustion and air combustion flue gas flows. When the sorbents after retention are analyzed by HgTPD, the different mercury species retained in the N_2 , oxy-combustion and air combustion atmospheres may be identified and the effect of the gas composition may be evaluated. The results of mercury retention capacities were presented in a previous work [23], the main conclusions of which were as follows: i) in the N_2 atmosphere, RBHG3 retained Hg^0 with an efficiency of almost 100%, whereas RB3 showed a negligible Hg^0 retention capacity; ii) in the oxy-combustion atmosphere, the mercury retention capacity

of RBHG3 was lower (4%) than that observed in the N₂ atmosphere and similar to that of RB3 (6%); and iii) in the air combustion atmosphere, the mercury retention capacities of RB3 and RBHG3 were similar to that observed in the oxy-combustion atmosphere, i.e., the concentration of CO₂ and H₂O did not affect the mercury retention capacity as long as the concentrations of the other gases remained the same in the both atmospheres. These conclusions refer to the total amount of mercury retained. The novelty of the present study is that thanks to the HgTPD method developed for this study it was also possible to identify the mercury species formed in the sorbent.

Figures 5-6 show the profiles of mercury desorption for RB3 and RBHG3 in the N₂, oxy-combustion and air combustion atmospheres. According to the high-peak temperatures for the reference compounds (Table 2), the species retained in the activated carbons under oxy-combustion and air combustion conditions was mainly Hg-OM (peak at approximately 200°C), whereas in the N₂ atmosphere the main species identified was HgS (represented by a peak at 300°C). From these results it is inferred that in a N₂ atmosphere, mercury that remains as Hg⁰, reacts with the sulphur present in the carbon to yield HgS. It should be borne in mind that the sulphur contents of RB3 and RBHG3 are 0.4 and 6%, respectively [24]. Thus, the proportion of mercury retained in N₂ in RB3 is insignificant compared to the amount retained in RBHG3.

Mercury retention by RB3 and RBHG3 in the oxy-combustion and air combustion atmospheres occurs via the linkage of mercury to organic matter (desorption peak at 220 °C) (Figures 5-6). This is a consequence of the homogeneous and heterogeneous oxidation of Hg⁰ in these atmospheres and the subsequent linkage of reactive oxidized mercury (Hg²⁺) to the carbon matter. In a previous study carried out by the authors with the same activated carbons [23] at least 80% of the Hg²⁺ resulting from homogeneous and heterogeneous oxidation was observed in both atmospheres. Therefore, the results

obtained by thermal desorption confirm that the main mechanism of mercury retention in both sorbents in the oxy-combustion and air combustion atmospheres is via the oxidation of mercury and its subsequent adsorption onto the carbon surface, whereas in an inert atmosphere, where mercury is as Hg^0 , interaction mainly occurs through the formation of HgS .

4. Conclusions

A new device based on thermal desorption was developed in this work to identify mercury species in carbonaceous samples. The results were found to be very promising for differentiating mercury species in the type of samples chosen for this study. The results confirm that different mercury species are present in coals of different characteristics. The mercury species found in the lignite and bituminous coals were mainly associated to organic matter and/or pyritic sulphur, whereas in the anthracites, the mercury species were mainly associated to sulphur.

Moreover, the mercury thermal desorption technique (HgTPD) was found to be a useful tool for clarifying the mechanism of reaction between the mercury and the activated carbons employed as sorbents in different coal combustion conditions since it served to identify the mercury species retained. In an inert atmosphere, where mercury remains as Hg^0 , this species is captured as HgS , whereas in a combustion atmosphere where a significant proportion of the mercury is oxidized (Hg^{2+}), organic linkage to carbon material is the most frequent form of retention.

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389 **Table 1.** Mercury, sulphur, chlorine and selenium contents of the coal samples

Sample name	Country	Coal	Hg $\mu\text{g}\cdot\text{g}^{-1}$	S %	Cl $\mu\text{g}\cdot\text{g}^{-1}$	Se $\mu\text{g}\cdot\text{g}^{-1}$
HL	Hungary	Lignite	0.21	2.3	34	0.3
CL-Sb	China	Lignite	0.11	0.5	34	2.6
SAL-SAB2	South Africa	Lignite	0.16	0.7	64	0.5
SL-Pe	Spain	Lignite	0.19	3.2	133	7.3
SB-Mo	Spain	Bituminous	0.29	0.9	950	1.4
SB-Mi	Spain	Bituminous	0.27	0.8	130	1.5
SB-Jo	Spain	Bituminous	1.52	2.2	60	2.0
SB-A	Spain	Bituminous	0.11	0.6	44	0.9
SB-C	Spain	Bituminous	0.12	1.7	52	2.2
SB-Ca	Spain	Bituminous	0.14	1.2	840	1.1
RB-Dia	Russia	Bituminous	0.17	0.4	50	0.2
RB-Si	Russia	Bituminous	0.08	0.3	10	0.1
COB-Be	Colombia	Bituminous	0.09	0.7	140	1.6
COB-Pa	Colombia	Bituminous	0.15	0.7	60	1.4
SAB-FB	South Africa	Bituminous	0.11	0.5	110	1.3
CSb-GZ	China	Sub-bituminous	0.28	5.3	ND	1.9
SA-T	Spain	Anthracite	0.21	1.1	703	0.6
SA-F	Spain	Anthracite	0.31	1.1	133	3.0

390 ND: not detected

Table 2. High peak temperatures of mercury compounds used as reference materials

	High peak Temperature (°C)
HgCl ₂	135±5
Hg-FeS ₂	169±5
Hg-OM	217±7
HgSe	260±6
HgS	303±13
HgO	(310±5);462±9
HgSO ₄	580±19

(): minor peak

Table 3. Mercury species present in the coal samples

(%)	HgCl ₂	Hg-FeS ₂	Hg-OM	HgS	HgSe	HgO
HL	5.8	40.9	53.3	-	-	-
CL-Sb	5.2	26.0	36.6	16.1	16.1	-
SAL-SAB2	-	36.7	63.3	-	-	-
SL-Pe	1.1	19.9	45.5	22.1	-	11.4
SB-Mo	-	-	48.7	20.1	23.5	7.7
SB-Mi	-	-	53.9	13.1	30.8	2.2
SB-Jo	-	-	78.1	4.9	10.2	6.8
SB-A	-	-	38.7	26.3	28.2	6.8
SB-C	-	-	67.9	2.8	9.2	20.0
SB-Ca	-	-	54.3	16.2	21.6	7.9
RB-Dia	-	44.6	51.3	-	4.2	-
RB-Si	-	27.9	40.6	14.4	17.1	-
COB-Be	-	30.4	30.6	-	39.0	-
COB-Pa	-	-	100	-	-	-
SAB-FB	-	29.9	32.8	15.8	14.2	7.4
CSb-GZ	-	12.1	30.3	27.2	25.8	4.6
SA-T	-	-	1.8	69.6	-	28.5
SA-F	-	-	3.1	65.6	-	31.3

Figure captions

Figure 1. Configuration of the thermo-desorption device used for mercury speciation in coals.

Figure 2. Thermal profiles of lignites.

Figure 3. Thermal profiles of bituminous and sub-bituminous coals.

Figure 4. Thermal profiles of anthracites.

Figure 5. Thermal profiles of the RB3 activated carbon after it has been used as a mercury sorbent in N₂, oxy-combustion and air combustion atmospheres.

Figure 6. Thermal profiles of the RBHG3 activated carbon after it has been used as a mercury sorbent in N₂, oxy-combustion and air combustion atmospheres.

Figure 1

Figure 2

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Figure 5

Figure 6