

Application of Mercury Temperature Programmed Desorption (HgTPD) to ascertain mercury/char interactions

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Abstract

This work investigates the scope of a Mercury Temperature Programmed Desorption (HgTPD) technique for identifying mercury species in solids. The specific objective of this study was to clarify the mechanism of mercury retention by chars used as sorbents in coal combustion in air and oxy-combustion atmospheres based on the identification of the mercury species retained. Different mercury species were identified by HgTPD depending on the flue gas composition and the type of char. The results lead to the conclusion that depending on these conditions the main mechanism of mercury retention will be the interaction of mercury with organic matter, or the interaction of mercury with sulfur to form HgS. In a few particular cases $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was produced on the char surface. It was found that HgTPD is a highly useful technique for investigating the different mechanisms of mercury/char/gas interactions.

Keywords: mercury; chars; biomass; gasification; combustion

1. Introduction

The high toxicity of mercury and the effects of this element on human health are well known problems [1]. Likewise, it is generally acknowledged that coal-fired power plants are one of the largest anthropogenic sources of mercury emissions to the environment [2]. As an example, in Spain 1 ton/year of mercury was emitted from coal combustion plants in 2012. This represents 40% of the total amount of mercury emitted in this country [3], with coal contributing nearly 20% to the energy supply in this year. The seriousness of this problem has led governments to establish standards of mercury emissions [4-6], and has encouraged the scientific community to develop cost-effective technologies to reduce these emissions.

The most commonly used method for mercury retention in conventional coal combustion is the injection of activated carbons (ACs) in the flue gas [7]. The efficiency of this technology depends on the speciation of the mercury. Mercury in combustion flue gases may be bound to particulate matter (Hg_p), which is mainly retained in particle control devices, or it may remain in the vapor state as oxidized (Hg^{2+}) or as elemental (Hg^0) [8-9]. Although the proportion of these species will depend, among other factors, on the combustion flue gas composition, mercury speciation in conventional coal combustion in air is relatively well known compared to oxy-combustion where the behavior of mercury still requires considerable research. Oxy-combustion is one of the promising emerging technologies for performing coal combustion with CO_2 capture. The basic concept of oxy-combustion is to replace combustion in air by combustion in a mixture of oxygen and recycled flue gas and/or water for temperature control. In this way, the remaining flue gas, rich in CO_2 and water vapor, can be easily separated to yield a stream of CO_2 ready for utilization or sequestration. Oxy-combustion implies,

therefore, a reduction in CO₂ emissions from coal-fired power plants which is a necessary pre-requisite for controlling and limiting global warming.

Although ACs are well-proven sorbents with a mercury removal efficiency of up to 90%, further advances are still necessary in AC technology to reduce costs and to limit the balance-of-plant impacts associated with its use [7,10]. In their search for high-quality and low-cost alternatives some researchers have focused on the use of industrial or agricultural wastes as sorbents for mercury or as precursors for obtaining mercury sorbents [11-14]. Previous studies carried out by the present authors [15-16] have demonstrated that some chars obtained from gasification of biomass particularly from paper and plastic wastes, show similar mercury retention capacities to that of Filtracarb D47/7+S, a commercial activated carbon especially designed for the capture of Hg⁰. The main advantage of using these chars, apart from the revalorization of an industrial waste, is that the chars do not have to be pretreated or impregnated, which in itself implies a reduction in costs. Char sorbents were therefore used in this study in oxy-combustion conditions and compared with previous results obtained in conventional air combustion atmospheres. Mercury behavior in oxy-coal combustion is of major concern because not only does it cause serious environmental problems but it can also damage the aluminum components of the CO₂ compression units. Although several coal chars and biomass chars have already been tested in a variety of conditions for mercury adsorption [14,17-20], and has been shown that the surface functionality of chars and chlorine and sulfur species play an important role in mercury retention, no mechanism for mercury adsorption has been clearly established. In this study an attempt is made to explain mercury/char interactions in gases produced in different coal combustion systems. To achieve this goal, identification of the mercury species present on solids is a necessary prerequisite.

Despite the enormous usefulness of analytical techniques able to identify the mode of occurrence of low concentrations of mercury species in solids, the progress made so far has not been very satisfactory. Techniques such as X-ray absorption finestructure spectroscopy (EXAFS) [21, 22] and X-ray absorption near edgestructure (XANES) [23], are able to produce a characteristic spectra for each mercury compound. However, these techniques often present interference; the data processing is complex and the detection limits (100 ppm) are not usually appropriate for the analysis of the majority of the solid samples. Another technique is sequential chemical extraction (SCE) [24-27] which is based on the different solubilities of mercury compounds. The main drawbacks of this method are its low selectivity because the complete extraction of each fraction depends on the time; not all mercury species can be distinguished and it is a tedious method with many sources of uncertainty. In this work the identification of mercury species in the char samples used for mercury capture is carried out by means of a thermal desorption procedure (HgTPD). This technique of identifying mercury species is based on the temperature at which they are released [28-31]. The method has proven to be a relatively simple and selective procedure for the identification of mercury species in concentrations lower than 10 ppm. The identification of mercury species can be expected to play a key role in the development of the most appropriate solid sorbent for each particular case.

2. Experimental

Two previously characterized chars [15] were employed as mercury sorbents for this study. The chars were by-products of the gasification of wood wastes (WW) and a mixture of paper and plastic wastes (PW). They were tested under a simulated flue gas

of coal combustion and oxy-combustion and then subjected to thermal desorption (HgTPD) for the purpose of identifying their mercury species.

The experimental device used to retain the mercury consisted of i) a glass reactor containing the sorbent bed (50 mg of char (40-60 μm) mixed with 650 mg of sand (200-300 μm)), ii) a permeation tube for the generation of elemental mercury in gas phase, the mercury concentration in gas phase being 100 $\mu\text{g m}^{-3}$ iii) a gas blending station in which the two atmospheres were prepared (Table 1) and iv) a continuous mercury analyzer (VM-3000) that monitored the Hg^0 . The Hg^{2+} was captured by an ion exchanger resin (Dowex 1x8), suitable for the selective extraction of Hg^{2+} species [32]. The resin was conditioned with a solution of $\text{HCl:H}_2\text{O}$ (1:1) at 90°C for 30 minutes and then filtered and dried. The resin was placed prior to the Hg^0 continuous analyzer in such a way that the total mercury concentration was balanced. The Hg^{2+} in the resin at the end of the experiments and the mercury retained in the sorbent were determined by means of an automatic mercury analyzer (AMA 254). The temperature of the sorbent was kept at 150 °C and the flow rate through the sorbent was 0.5 L min^{-1} . The duration of the mercury experiments was the time needed for the samples to reach maximum retention capacity, i.e. the maximum amount of mercury that a sorbent can retain until it reaches its point of saturation, expressed as micrograms of mercury per g of sorbent. Maximum retention capacity is represented by the mercury adsorption curves obtained using a continuous VM-3000 analyzer.

The experimental device employed to identify the mercury species in the post-retention chars consisted of an advanced RA-915 Mercury analyzer coupled to a PYRO-915 furnace (Ohio Lumex). 20 mg of sample was introduced in the first chamber of the PYRO-915. Inside this chamber the mercury compounds were released from the solid matrix under a controlled heating mode. The parameters for the selective desorption of

the mercury had previously been optimized by the authors [31]. A four-step program was set up. The temperature rate was kept at $40\text{ }^{\circ}\text{C min}^{-1}$ for 575s. Then the heating velocity was increased up to $50\text{ }^{\circ}\text{C min}^{-1}$ where it was held for 200s and then again up to $80\text{ }^{\circ}\text{C min}^{-1}$ where it was held for a further 125s. Air was used as carrier gas at 1 L min^{-1} . In the second chamber of the PYRO-915 kept at a temperature of 800°C , the desorbed mercury compounds were reduced to elemental mercury which was detected by atomic absorption spectrometry. The mercury species were identified from the temperature range in which they were released. This range comprises the temperature at which thermal release starts, reaches its maximum point and then returns to the baseline. The desorption profiles of the samples were compared with the reference desorption profiles of fifteen pure mercury compounds obtained in a previous work [31]. Two new mercury compounds were added to this reference database: HgS black and Hg-OM (mercury bound to organic matter). The Hg-OM species had not been considered in a previous desorption study with char samples [20]. The mercury standard for organic matter was prepared from a humic acid [33]. The humic acids contain COOH, OH and CO groups and, although the evolution of these groups depends on the rank of coal, this mercury compound was chosen as being representative of organic groups in coals [34-35].

The results obtained by HgTPD were compared with those obtained by the method based on sequential extraction. The procedure previously described [36] is a simplification of the US Environmental Protection Agency Method 3200 (US EPA Method 3200), which consists of three sequential extraction steps that split mercury species into three fractions depending on the solubility of each species in each fraction: F1 (mobile Hg (inorganic and organic Hg)), F2 (semi-mobile Hg (mainly Hg^0 , Hg^{2+} complexes) and F3 (non-mobile Hg (mainly HgS)).

2. Results and discussion

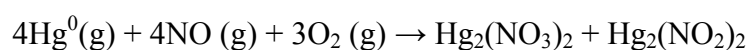
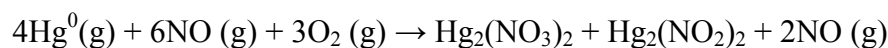
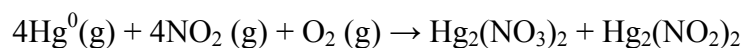
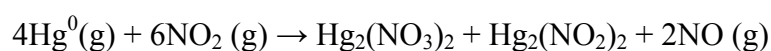
The mercury retention capacities and the mercury adsorption curves for the two chars obtained from the gasification of wood waste (WW) and plastic plus paper waste (PW), under combustion and oxy-combustion atmospheres (Table 1), are presented in Table 2 and Figure 1. The PW char has a higher mercury retention capacity than WW in both atmospheres, as was observed in the previous studies [15-16]. The previous studies were performed in air combustion atmospheres containing the following reactive gases: O₂, SO₂, NO₂, HCl, balanced with N₂. From the effect of the characteristics of the chars on mercury retention it was concluded that the higher retention capacity of the PW chars was mainly due to their higher chlorine content (5%) and/or aluminum content (7%), i.e, elements with which mercury may react or amalgamate. It should be noted that the mercury retention capacities shown in Table 2 are the result of analyzing the sorbent directly by means of the AMA equipment. They represent the total amount of mercury retained in the sorbent (Hg⁰+Hg²⁺). The kinetics of adsorption are reflected in the mercury adsorption curves (Figure 1). The PW chars slowly start to adsorb mercury reaching their maximum retention capacity after approximately 500 minutes, whereas the WW chars quickly reach their maximum retention capacity. The oxidation of Hg⁰ may also be occurring in both chars. It must be remembered that the VM analyzer only detects Hg⁰.

Figure 2 shows the percentages of i) mercury retained in the chars (i.e., Hg_g), ii) the oxidized mercury in gas phase (Hg²⁺), resulting from homogeneous oxidation (gas-gas interaction) plus heterogeneous oxidation (gas-char interaction), and iii) the elemental mercury that was not retained in the sorbent (Hg⁰). The Hg²⁺ at the outlet of the reactor was determined by capturing it in an ion exchanger resin suitable for the selective extraction of Hg²⁺ species [32]. A resin bed was placed after the reactor for each

mercury experiment which was then analyzed by means of the AMA equipment. Hg^{2+} from homogeneous oxidation is the result of an analysis of the resin without the sorbent whereas the Hg^{2+} from heterogeneous oxidation is the Hg^{2+} retained in the resin after the reactor with the sorbent. 30% of the Hg^{2+} was originated by homogeneous oxidation, as established in a previous study using the same oxy-combustion and combustion with air atmospheres [37]. In the present study, similar mercury retention capacities and mercury species distributions were obtained with the char from the gasification of wood waste (WW) in both atmospheres. However, in the case of the char obtained from the gasification of plastic and paper waste (PW) not only was a higher mercury capture achieved under oxy-combustion conditions but also a higher heterogeneous mercury oxidation (30%). As can be seen in Figure 1, whereas WW shows similar mercury adsorption curves for both atmospheres, PW shows a different kinetic behaviour, indicating that the gas composition plays a role in the retention mechanism. These results suggest that different mercury species are retained or formed in the PW chars due to interactions with the gases in the atmosphere. It is therefore essential to be able to identify the mercury species in the sorbents in order to understand the mechanism of adsorption of mercury.

Mercury compounds were identified in the post-retention chars using the thermal desorption procedure (HgTPD) optimized by the authors in a previous study [31]. For this purpose, the desorption profiles of the mercury species present in the chars were compared with the desorption profiles of the mercury reference compounds (Figures 3-4). Table 3 summarizes the high peak temperatures of the reference compounds likely to be found in post-retention chars. Similar mercury desorption curves were obtained for WW in the atmospheres of coal combustion (WW-CO) and oxy-combustion (WW-OX), the area below the curve being slightly lower in WW-CO due to the lower mercury

retention. The mercury species retained in these atmospheres can be expected to be the same. The main mercury species identified were Hg-OM and $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Figure 3) in both atmospheres. Where there is a large amount of organic matter, mercury can be expected to be bound to it. In fact, the loss of ignition (LOI) values which is an estimation of carbon content are 55% and 51% for PW and WW chars, respectively [15]. The formation of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ can be explained by the fact that the gas compositions contain a relatively high concentration of NO_x (Table 1). Reactions between the NO_x species and the Hg^0 in gas phase may give rise to different mercury nitrates that might condense on the surface of the char sorbents. The formation of the different mercury nitrates could then occur via the following reactions [16]:



These mercury species, mainly $\text{Hg}_2(\text{NO}_3)_2$, crystallize from slightly acidified aqueous solutions (the formation of $\text{HNO}_2(\text{aq})$ and/or $\text{HNO}_3(\text{aq})$ has been confirmed in atmospheres containing NO_x and H_2O [37]), in the form of dehydrate. When the overlapping peaks are deconvoluted, the desorption curve for WW shows a shoulder at 150°C and another between $250\text{-}370^\circ\text{C}$ a little higher than the peak corresponding to $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Figure 3). The maximum temperature of decomposition for HgCl_2 and HgS red is approximately at 140 and 300°C , respectively [31] and so the possible formation of these species cannot be ruled out. In addition to these species, it needs to

be taken into consideration that HgS black decomposes at 190°C and may overlap with the curve corresponding to Hg-OM (220°C) (Table 3).

In order to verify the mercury species identified in the chars, a series of extractions were carried out by sequential extraction [36] and then analysed by HgTPD (Figure 4). The results after the extraction of F1 (inorganic compounds such as mercury nitrates and mercury chlorides) in WW confirm the formation of mercury nitrates and HgCl₂, the latter in a low concentration (Figure 4a). As can be seen, the main peaks that remain in the char after the extraction of F1 correspond to Hg-OM and/or HgS (F2-F3). HgTPD analysis of fraction F3 confirms a) the presence of HgS red in WW by the peak at 300°C and b) that the peak at around 200°C corresponds effectively to Hg-OM and not to HgS black since Hg-OM was extracted from the semi-mobile fraction F2.

The desorption profiles of PW (Figure 5) show different distributions of mercury species retained in coal combustion with air and oxy-combustion which might explain the differences in mercury retention capacities (Table 2). Whereas HgS red (peak centered at 300°C) is the main species in coal combustion in air, in the oxy-combustion atmosphere Hg-OM is the principal species. As in the case of WW, in PW the presence of HgS black and HgCl₂ cannot be ruled out. It is important to bear in mind that not only is HCl present in the gas composition but also that the chars from plastic and paper waste contain a high amount of chlorine [15]. The formation of mercury nitrates might also occur in PW in same way as it does in WW. However, when the mercury retention is as high as in PW the main interactions are between mercury and sulfur and between mercury and organic matter in combustion and oxy-combustion conditions, respectively (Figure 5).

The results obtained from the HgTPD analysis of the residues after sequential extraction of PW-OX verify the formation of Hg-OM. After the extraction from F1 of HgCl₂ and mercury nitrates, and from F2 of Hg-OM, the only peak remaining is the one corresponding to HgS red (300°C) (Figure 4b). The HgTPD analysis of the sample after total extraction, (F4), confirms that HgS red is the other main species present in PW (Figure 4b) since the peak at 300°C has disappeared.

Because in oxy-combustion conditions a high concentration of H₂O is present, H₂SO₄ may form from SO₂/SO₃ [37]. Sulfuric acid would favour the adsorption of Hg⁰ on the surface of the organic matter [38] which would explain the formation of the Hg-OM species. Moreover, H₂SO₄ might favor mercury oxidation on the carbon surface [38] of PW which would accord with the higher heterogeneous oxidation observed in PW under oxy-combustion conditions (Figure 2). This different behavior is not observed in WW. Although both chars have similar LOI contents, the BET surface of WW is lower (2 m²·g⁻¹) than in PW (65 m²·g⁻¹) [15], and the interactions between mercury and organic matter are less likely. The predicted concentrations of each species obtained via peak integration using Origin 6.0 software are shown in Figure 6 where a summary of the percentages of each species found in the post-retention chars is presented.

3. Conclusions

The chars from the gasification of paper and plastic wastes showed high mercury retention capacities in conditions of conventional coal combustion with air and oxy-combustion. In oxy-combustion conditions the chars also demonstrated a high heterogeneous oxidation capacity.

Different mercury species were identified on the chars by HgTPD technique after they had been used as sorbents depending on the composition of the flue gas and the type of char. This analysis was the key to interpreting the results. In an atmosphere enriched in CO₂ and H₂O the main mechanism of mercury retention in the chars with the highest retention capacity was the interaction with organic matter, while in an atmosphere with less CO₂ and H₂O, such as that of conventional coal combustion, Hg-S associations were mainly responsible for mercury capture. The principal mercury species identified in the char with the lowest mercury retention capacity (wood waste), was mercury bound to organic matter and Hg₂(NO₃)₂·2H₂O in both conditions. With the HgTPD technique it was also possible to identify other minority mercury species such as HgCl₂.

Acknowledgments

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Table 1. Composition of the combustion and oxy-combustion atmospheres studied

Compounds	Combustion	Oxy-combustion
CO ₂ (%)	16	64
N ₂ (%)	74	20
H ₂ O (%)	6	12
O ₂ (%)	4	4
SO ₂ (ppm)	1000	1000
NO (ppm)	1000	1000
NO ₂ (ppm)	100	100
HCl (ppm)	25	25

Table 2. Mercury retention capacities of the char samples under combustion and oxy-combustion atmospheres

Sample	Combustion Hg (μg/g)	Oxy-combustion Hg (μg/g)
WW	38±5	49±6
PW	185±10	234±12

Table 3. High desorption temperature of pure reference mercury compounds

Reference Hg compounds	High peak T (°C)	Start T- End T decomposition peak (°C)
Hg ₂ Cl ₂ ²⁰	119±9	60-250
HgCl ₂ ²⁰	138±4	90-350
Hg-OM	220±5	150-300
HgS black	190±11	150-280
HgS red ²⁰	305±12	210-340
HgO red ²⁰	308±1; 471±5	200-360; 370-530
HgO yellow ²⁰	284±7; 469±6	190-380; 320-530
Hg ₂ SO ₄ ²⁰	295±4; 514±4	200-400; 410-600
HgSO ₄ ²⁰	583±8	500-600
Hg(NO ₃) ₂ ·H ₂ O ²⁰	215±4; 280±13; 460±25	150-230; 230-375; 375-520
Hg ₂ (NO ₃) ₂ ·2H ₂ O ²⁰	264±35; 427±19	100-375; 376-500

Figure captions

Figure 1. Mercury adsorption curves for WW and PW in coal combustion with air (CO) and oxy-combustion (OX) atmospheres.

Figure 2. Percentages of mercury retained in the char samples (Hgp), oxidized mercury (Hg^{2+}) and elemental mercury (Hg^0) in coal combustion with air and oxy-combustion atmospheres.

Figure 3. Mercury thermal decomposition profiles of mercury standards and post-retention char WW in coal combustion with air and oxy-combustion.

Figure 4. Mercury thermal decomposition profiles of the different fractions after sequential extraction for a) WW-OX and b) PW-OX

Figure 5. Mercury thermal decomposition profiles of mercury standards and post-retention char PW in coal combustion with air and oxy-combustion.

Figure 6. Distribution of the mercury species in post-retention chars WW-CO, WW-OX, PW-CO and PW-OX.

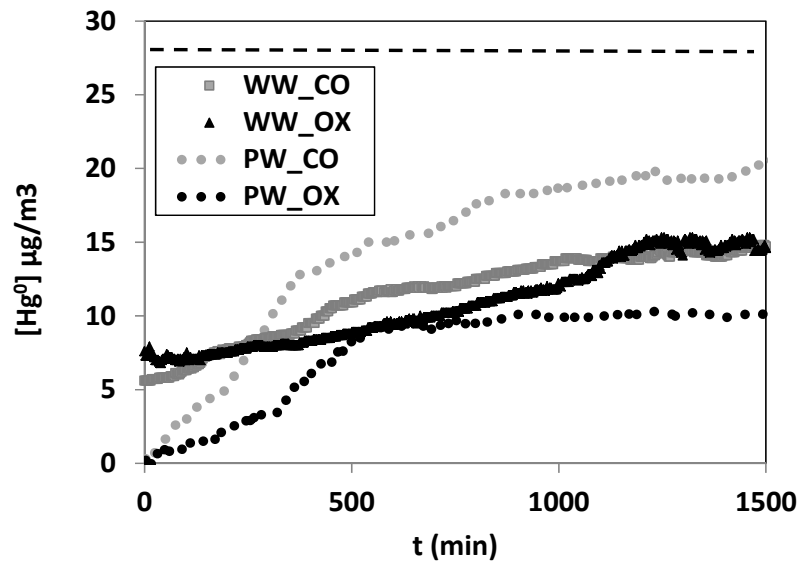


Figure 1

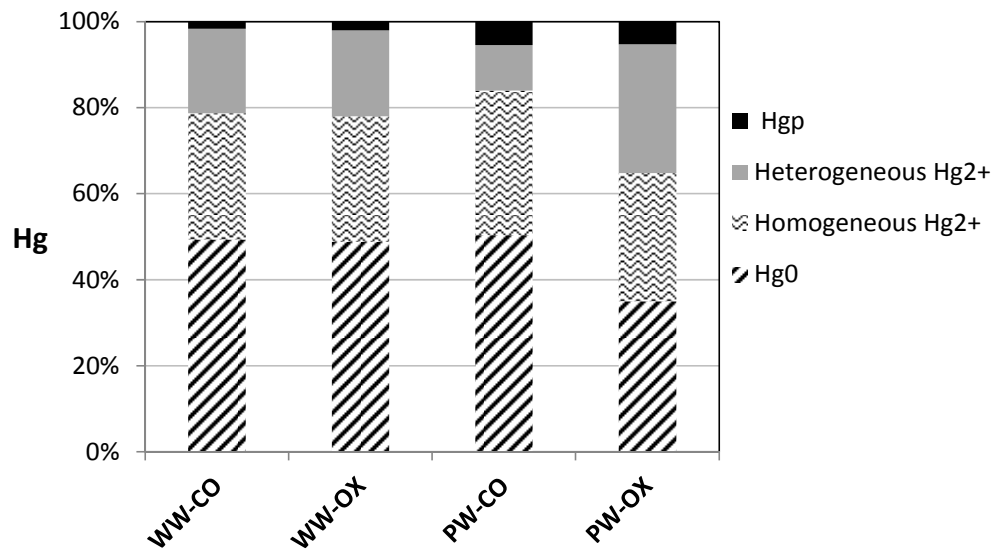


Figure 2

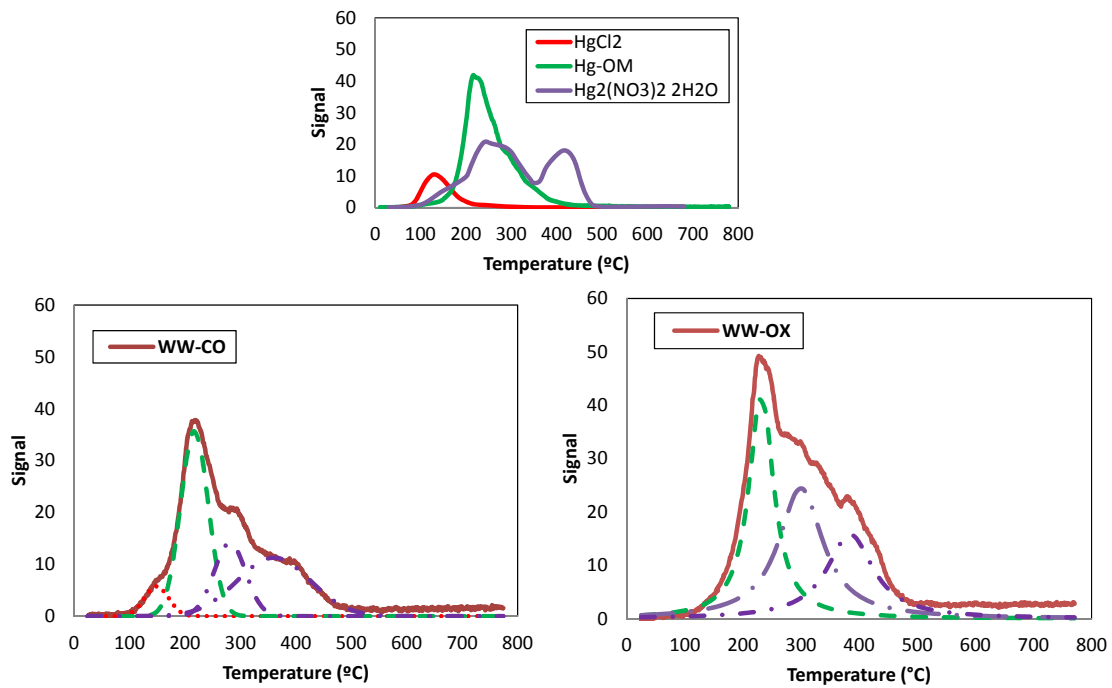


Figure 3

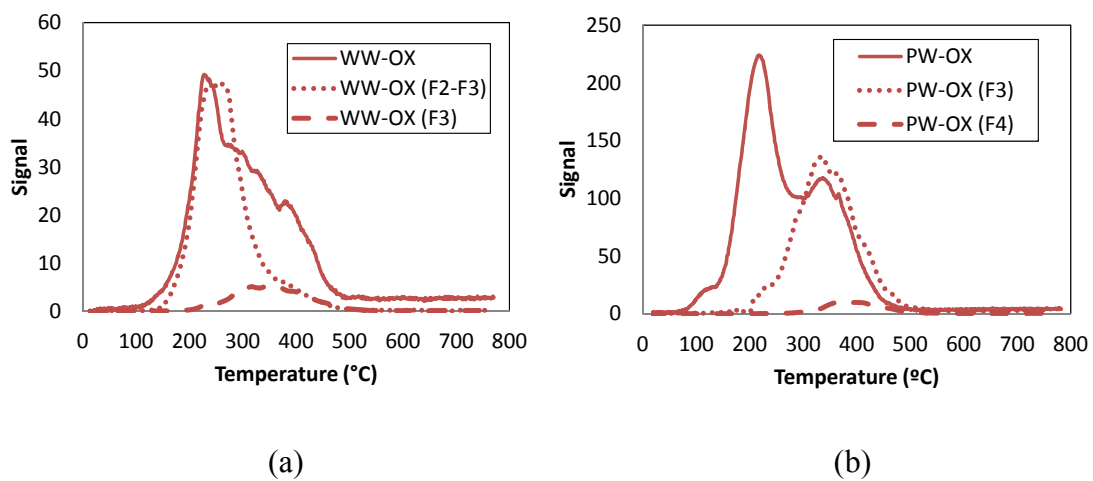


Figure 4

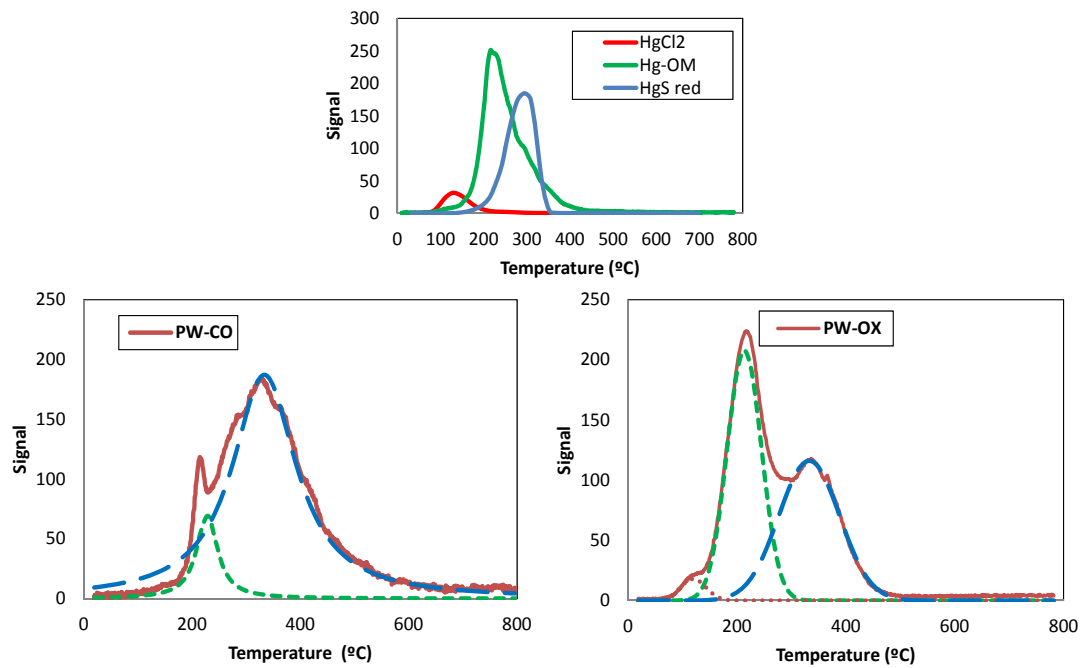


Figure 5

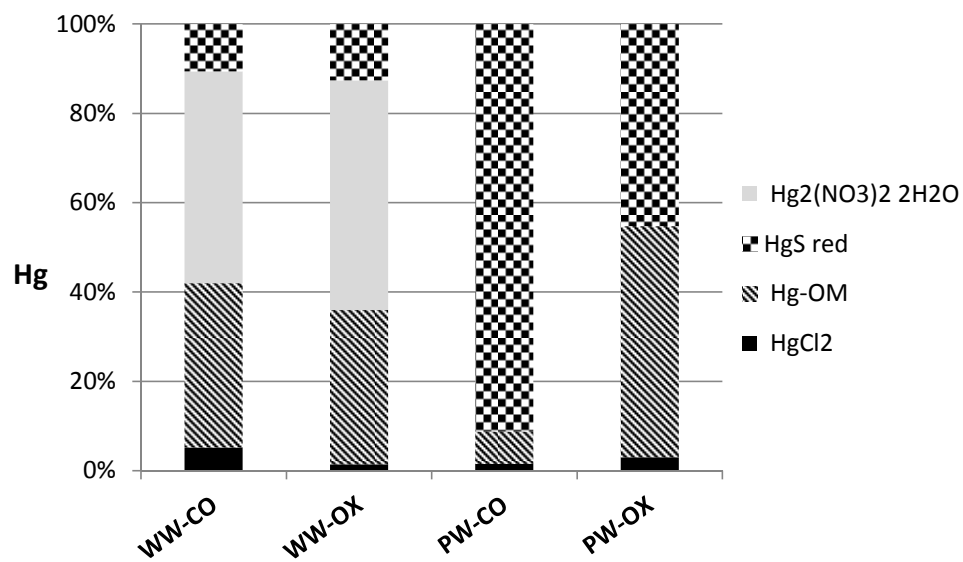


Figure 6