

1 **Application of thermal desorption for the identification of**
2 **mercury species in solids derived from coal utilization**

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14 **Abstract**

15 The speciation of mercury is currently attracting widespread interest because the
16 emission, transport, deposition and behaviour of toxic mercury species depend on its
17 chemical form. The identification of these species in low concentrations is no easy task
18 and it is even more complex in coal combustion products due to the fact that these
19 products contain organic and mineral matter that give rise to broad peaks and make it
20 difficult to carry out qualitative and quantitative analysis. In this work, a solution to this
21 problem is proposed using a method based on thermal desorption. A sequential
22 extraction procedure was employed for the comparison and validation of the method
23 developed. Samples of fly ashes and soils were analyzed by both of these methods, and
24 thermal desorption was found to be an appropriate technique for mercury speciation.
25 Even in the case of low mercury contents, recovery percentages were close to 100%.
26 The main mercury species identified in the samples studied were HgS and, to a lesser
27 extent, HgO and HgSO₄. In addition, although the presence of mercury complexes
28 cannot be demonstrated, the desorption behaviour and sequential extraction results
29 suggest that this element might be associated with the mineral matrix or with carbon
30 particles in some of the solids.

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32 **Keywords:** mercury speciation; solid samples; thermal desorption; sequential extraction

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37 **1. Introduction**

38 Mercury is a naturally occurring element that is found in air, water and soil. Exposure to
39 mercury can affect the human nervous system and harm the brain, heart, kidneys, lungs,
40 and immune system. The toxicity of mercury is known to be strongly dependent on its
41 chemical form. Generally, organomercury is more toxic than inorganic mercury and, of
42 the latter, elementary mercury and insoluble HgS are the least toxic (Morita et al.,
43 1998).

44 Mercury emitted to the air can travel thousands of kilometres in the atmosphere before
45 being deposited, making this element an issue of world-wide concern. Elemental
46 mercury (Hg^0) has a lifetime in the atmosphere of up to one year, while oxidized forms
47 of mercury (Hg^{2+}) have lifetimes of a few days because of the higher solubility of Hg^{2+}
48 in atmospheric moisture. Elemental mercury can thus be transported over long
49 distances, whereas Hg^{2+} and the mercury species present in particles, particulate
50 mercury (Hg^p), are deposited near the source of emission (Keating et al., 1997; Stein et
51 al., 1996).

52 Mercury is found in many rocks including coal. When coal is burned, mercury is
53 released into the environment, making coal-burning power plants one of the largest
54 anthropogenic sources of mercury to the air. In Europe, 30.5 tons of mercury
55 compounds were emitted in 2010 with a share of 53.9 % coming from thermal power
56 stations (E-PRTR, 2010). During combustion, all the mercury in coal is vaporized as
57 Hg^0 . As the gas cools after combustion, oxidation reactions may occur, which will
58 reduce the concentration of Hg^0 by the time the post-combustion gases reach the stack
59 (Galbreath, and Zygarlicke, 2000; Gale et al., 2008). The adoption of pollutant control
60 technologies in power plants has changed the behaviour of mercury with the possibility

61 of new unexpected interactions between mercury and solid by-products (Park et al.,
62 2008; Cao et al., 2008; Ochoa-González et al., 2011). This has made the prediction of
63 the fate of mercury more difficult.

64 The identification of mercury species in solids contributes to an understanding the
65 mercury behaviour and fate of mercury in the environment and the toxicity of by-
66 products in industrial processes. This knowledge is crucial for the design and
67 improvement of mercury control and remediation technologies. However, mercury
68 speciation in solid samples is still a difficult task. Various methods of analysis have
69 been tested, one of the most promising of which is desorption (Bloom et al., 2003; Reis
70 et al., 2010; Biester et al., 1997; Shuvaeva et al., 2008; Reis et al., 2012; Rumayor et
71 al., 2013; Kim et al., 2003). Nevertheless, this method still needs to be validated and the
72 scientific community involved in the analysis of mercury has yet to demonstrate that the
73 method is reproducible for any solid matrix. Until now, sequential and selective
74 extraction procedures (Bloom et al., 2003; Reis et al., 2010; Biester et al., 1997), have
75 been the conventional way to determine mercury speciation in solids. This method
76 identifies mercury species on the basis of the chemical leaching of the complex
77 substrate. Although selective extraction is handicapped by problems associated with re-
78 adsorption, background contamination or losses of volatile mercury provide useful
79 information on the mobility of mercury in solids. Other methods are being evaluated to
80 determine the speciation of mercury in solid samples, including thermo-desorption (TD)
81 (Biester et al., 1997; Shuvaeva et al., 2008; Reis et al., 2012; Rumayor et al., 2013),
82 and X-ray adsorption fine structure spectroscopy (EXAFS) (Kim et al., 2003), although
83 both of these methods need to be further optimized and validated. Because these
84 methods are based on the volatility of mercury compounds (TD) and the properties
85 related to the atomic structure (EXAFS), the results are less likely to be affected by the

86 substrate matrix than those obtained by the sequential and selective extraction method
87 which is based on chemical interactions in the complex substrate. EXAFS has a high
88 limit of detection ($>100 \text{ mg kg}^{-1}$) making this method useful only for relatively high
89 mercury concentrations. In contrast TD can be used to analyze a wide variety of
90 samples due to its lower limit of detection ($0.03 \text{ mg}\cdot\text{kg}^{-1}$).

91 In the present study a TD method was developed to identify mercury species in coal
92 combustion products, which is key for understanding and developing efficient control
93 options, such as sorbent capture. This is not an easy task due to the fact that these
94 products contain organic and mineral matter that give rise to broad peaks and make it
95 difficult to carry out a qualitative and quantitative analysis. The results obtained will
96 contribute to a better understanding of the behaviour of this toxic element in processes
97 involving coal and to a more accurate evaluation of its mode of occurrence in solid coal
98 by-products. However, the most important achievement of this study is the analytical
99 progress that has been made as a result of which the way is now open for performing
100 analyses of solid substances.

101 **2. Material and methods**

102 *2.1. Thermal desorption procedure for mercury speciation*

103 A continuous mercury analyzer (RA-915) coupled to a furnace (PYRO-915), both from
104 Lumex, were used for the TD procedure. The analyzer operates on the basis of
105 differential Zeeman atomic absorption spectrometry and the high frequency modulation
106 of light polarization. The PYRO-915 furnace consists of two chambers in series. The
107 first chamber serves to pyrolyze the solid samples. In this chamber mercury compounds
108 are released from the solid matrix in a controlled heating mode. The second chamber,
109 kept at approximately 800°C , serves to reduce the mercury compounds to elemental

110 mercury and to eliminate interference compounds. The temperature of the first chamber
111 is continuously monitored. One of the novel aspects of this work is the possibility of
112 carrying out an optimum control of the temperature and heating rate. A four-step
113 program was set up. The temperature rate was kept at $40\text{ }^{\circ}\text{C min}^{-1}$ for 575 s. Then the
114 heating velocity was increased up to $50\text{ }^{\circ}\text{C min}^{-1}$ where it was held for 200 s and then
115 up to $80\text{ }^{\circ}\text{C min}^{-1}$ where it was held for a further 125 s. The temperature was controlled
116 by a thermocouple placed in the boat sample. The parameters for the selective
117 desorption were previously optimised (Rumayor et al., 2013), additionally, Hg(II)
118 complexed by humic acids (Hg-HA) has been prepared and used as reference sample in
119 this work. Hg-HA was prepared according to the method described by Terzano et al.,
120 2010. The mercury species were identified on the basis of the temperature range in
121 which they were released. The main temperature points used to identify the species were
122 i) the temperature at which thermal release started, ii) the maximum temperature of
123 release and iii) the temperature at which desorption returned to the baseline. The
124 thermograms of the samples were compared with the reference thermograms of fifteen
125 pure mercury compounds (Rumayor et al., 2013) (Table 1). About 100 mg of sample
126 was used for each analysis. Overlapping peaks were deconvoluted using Origin 6.0
127 software.

128 *2.2. Sequential extraction procedure for mercury speciation*

129 A sequential extraction procedure based on a simplification of the US Environmental
130 Protection Agency Method 3200 (US EPA Method 3200) was employed. The method
131 consists of three sequential extraction steps which yield three mercury fractions as a
132 function of the solubility of each species in different solutions (Table 2). A Vac Elut 20
133 Manifold (Varian) unit was used for the extractions. Each sample (0.5 g) was introduced
134 into a 6mL glass reservoir and then the different extraction solutions were sequentially

135 added. The solid residue was rinsed between each sequential step, and each fraction was
136 filtered and analysed by means of a mercury analyzer (LECO AMA 254). All the
137 extraction reagents were prepared with mercury-free chemicals.

138 *2.3. Reference materials*

139 The method was validated using the following certified reference materials i), an
140 agricultural soil (NIST-SRM 2709) ii) a soil sample from a slightly contaminated site
141 (RTC-CRM026-050), and iii) a soil sample from a contaminated carbonisation site
142 (LGC6138). The total certified mercury contents of these materials were 1.40 ± 0.08
143 $\text{mg}\cdot\text{kg}^{-1}$; $2.42\pm 0.32 \text{ mg}\cdot\text{kg}^{-1}$ and $1.5\pm 0.2 \text{ mg}\cdot\text{kg}^{-1}$, respectively. Although the mercury
144 speciation was not certified the sum of the species was compared with the total mercury
145 value to validate the effectiveness of the recovery of the tested methods. The precision
146 of the analysis was estimated as the relative standard deviation.

147 *2.4. Samples*

148 Several fly ash samples taken from electrostatic precipitators (ESP) and soils sampled
149 from areas related to coal utilization processes were studied. These samples had been
150 thoroughly characterized in previous studies (López-Antón et al., 2011, 2007a, 2007b).
151 Their chemical compositions and Hg contents are presented in Table 3. Elements such
152 as sulphur, chlorine and selenium are included because they are thought to be involved
153 in reactions with mercury (López Antón et al., 2007b).

154 The nine fly ash samples analyzed in this study came from different origins. Samples
155 CTA, CTSR and CTL were obtained from a pulverized coal power plant in which high
156 rank coals, high volatile bituminous coal and bituminous coals, respectively, are burned.
157 Samples CTP, CTP2, FA14b, FA15b, FA16b and FA17b were taken from a fluidized
158 bed combustion plant that burns blends of coal and coal wastes with a high mineral

159 matter content. In this plant limestone is used in the bed. Samples CTP and CTP2 are
160 representative of whole fly ashes obtained in two different sampling campaigns from
161 the same power plant and FA14b, FA15b, FA16b and FA17b are fractions of CTP2
162 sampled from consecutive hoppers in the ESP.

163 Four soil samples collected from the surrounding area of a coking plant (Diaz-Somoano
164 et al., 2012) were also analyzed. These have different mercury contents (Diaz-Somoano
165 et al., 2007). FAR2 was sampled from the area farthest away from the plant; TDIST1
166 and TDIST2 from an area contaminated with mercury (Table 3), while PUSH3 was
167 collected from the area of greatest activity near to the coking furnaces.

168 **3. Results and discussion**

169 *3.1. Mercury speciation by thermal desorption*

170 In a previous work (Rumayor et al., 2013) a database was established for the
171 identification of mercury species by means of thermal desorption by recording the
172 thermograms of several pure commercial compounds. Table 1 summarises their
173 characteristic peak temperatures that serve as footprints for the identification of the
174 mercury species, additionally Hg-HA was prepared in this study and added to the
175 database.

176 Fly ash CTA exhibits maximum desorption temperatures at 290 and 410 °C,
177 corresponding to pure HgS and HgO (Table 1). A shoulder is also present at 200°C, the
178 possibility that it may also have been due to mercury bound to solid matrix or unburned
179 particles forming complexes cannot be discarded (Biester et al., 1997; Shuvaeva et al.,
180 2008; Reis et al., 2012), this peak could correspond with the desorption of Hg(II) bound
181 to organic matter (Hg-OM). The formation of HgS may be attributed to the interaction
182 between the sulphur present in the carbonaceous matrix of the fly ash (Martinez-

183 Tarazona et al, 1996) and gaseous mercury. This phenomenon has been observed by
184 other authors and proposed as the mechanism of mercury interaction with S-
185 impregnated activated carbons [Graydon et al., 2009; Korpiel et al., 1997]. The
186 desorption profiles obtained for the CTSR and CTL samples are similar (Figures 1b-c)
187 possibly due to the fact that the ashes originated from coals with similar characteristics.
188 The profiles of CTSR and CTL show a main peak around 310-320 °C, shifted to slightly
189 higher temperatures than the desorption temperature of the HgS species, and a small
190 shoulder at 410 °C, indicating a lower amount of HgO (Table 1). The CTP desorption
191 profile shows peaks at 190, 295 and 630 °C (Figure 1d), the last two corresponding to
192 HgS and HgSO₄ (Table 1). The peak at 190°C can be assigned to Hg-OM. The
193 desorption profile of CTP2 shows peaks at 210°C and 280°C (Figure 1e), which are
194 assigned to the desorption of Hg-OM and HgS respectively. The peak at 630°C in the
195 thermogram of CTP2 has a much lower intensity than in the case of CTP. Both of the
196 fly ashes, that were sampled in different campaigns but in the same fluidized bed power
197 plant, were produced by burning combustibles of similar but not identical
198 characteristics. This might explain the differences in the proportions of each species.

199 The four samples collected from the hoppers of the ESP (FA14b, FA15b, FA16b and
200 FA17b), have similar desorption profiles. The intensity of their peaks differs(Figure 2),
201 reflecting the increase in mercury content from FA17b to FA14b (Table 2). The highest
202 mercury contents correspond to the ashes with largest carbon contents (López-Antón et
203 al., 2011). The enhancement of carbon particles was found to be directly related to the
204 surface area (5.71, 6.62, 9.05 and 9.13 m²·g⁻¹), but inversely to the particle size (Table
205 3). The amount of HgS (300°C), increases with decreasing particle size, the most intense
206 peak corresponding to FA14b and FA15b. In this series of samples the amount of

207 mercury bound to organic matter (190°C) and HgSO₄ (630°C) increases with increasing
208 particle size.

209 The desorption profiles of the soils FAR2, TDIST1, TDIST2 and PUSH3, show two
210 high peaks at 200 and 300°C, that are assigned to Hg-HA and HgS respectively (Figure
211 3). The intensity of each peak varies depending on the soil and the proportions of
212 mercury species present in each case. The presence of a peak of lower intensity at 120°C
213 in the thermogram of FAR2, corresponds to HgCl₂, while the peak at 420°C in PUSH3
214 is consistent with the presence of HgO. The proportions of HgS and Hg-HA are similar
215 in FAR2, TDIST1 and TDIST2. However, a lower percentage of HgS and a higher
216 amount of matrix-bound mercury were found in PUSH3 compared to the others. The
217 sample of PUSH3 was collected from the area of main activity and contained a high
218 proportion of coal. The high affinity of Hg for S-containing groups of organic
219 molecules and the presence of Hg-HA, Hg-Cl and Hg-S compounds including HgCl₂
220 and cinnabar has been frequently found using X-Ray absorption spectroscopy
221 techniques (Xia et al., 1999, Terzano et al., 2010).

222 *3.2. Mercury speciation by means of a sequential extraction procedure*

223 The mercury speciation results obtained by means of the sequential extraction procedure
224 in the fly ashes are presented in Figure 4. Most of the mercury in fly ashes CTA, CTSR
225 and CTL was extracted from the semi-mobile fraction which is consistent with the
226 occurrence of mercury in complexes or amalgamates (Table 2). In the two fly ashes
227 taken from the same power plant CTP and CTP2 mercury was mainly found in the non-
228 mobile fraction in the form of mercury stable compounds like HgS, or Hg₂Cl₂. These
229 results agree with those inferred using the thermal desorption procedure. Similarly, the
230 results for the samples collected from the ESP hoppers (FA14b, FA15b, FA16b and

231 FA17b), indicate that most of the Hg was extracted in the non-mobile Hg fraction,
232 corresponding to stable mercury compounds such as HgS, HgSe and Hg₂Cl₂. In these
233 fractions some mercury in the semi-mobile fraction was also found, assignable to
234 mercury complexes (Figure 4) (Table 2). The mobility of mercury, which increases as
235 the particle size of the solid decreases, is in some way predictable because a higher surface
236 area implies a higher reactivity. In fact, the percentage of mobile plus semi-mobile
237 mercury is highest in FA14b, the fly ash of the lowest particle size. A correlation
238 between the content of unburned carbon in the fly ashes and the percentage of mercury
239 extracted in the semi-mobile fraction was also established (Figure 6). Fly ash CTSR
240 with the highest unburned carbon content (7.2 %LOI) has the highest percentage of
241 mercury extracted in the semi-mobile fraction (78.2%), which suggests there is a bond
242 between the mercury and the carbon particles.

243 Analysis of the soil samples by the sequential extraction procedure revealed the
244 presence of HgS, HgSe or Hg₂Cl₂ (Figure 5). FAR2 has the highest percentage of
245 mobile mercury (28%) while PUSH3 has the highest percentage of mercury in the semi-
246 mobile fraction (28%). This sample is the soil with the highest carbon content (Table 3),
247 confirming the strong affinity of mercury for carbon (Bloom et al., 2003). The
248 behaviour of mercury during the sequential extraction of TDIST1 and TDIST2 was
249 found to be similar, a large proportion of mercury being analysed in the non-mobile
250 fraction.

251 *3.3. Comparison of results obtained by both methods*

252 The results obtained by both methods are complementary and they show good
253 agreement for most samples. The occurrence of HgS in CTP, CTP2 and CTA, identified
254 by the peak at 300°C in the desorption thermograms was confirmed by the 73.1; 47.3

255 and 38.0% of mercury extracted in the non-mobile fractions respectively. The presence
256 of mercury complexed by organic particles in CTP, CTP2 and CTA was also
257 corroborated by selective extraction analysis. 24.5, 53.5 and 61.1 % of Hg was extracted
258 in the semi-mobile fraction of CTP, CTP2 and CTA. Moreover, the presence of HgSO₄
259 in CTP and CTP2 was validated by the extraction of 2.42 and 1.12 % in the mobile
260 fraction. In the fly ashes from the combustion of coals of similar rank, CTL and CTSR,
261 the HgO identified by the small shoulder at 410 °C was confirmed by the 7.89 and 2.06
262 %, of mercury extracted in the mobile fraction. Nevertheless, the possible presence of
263 HgS identified by thermal desorption, shifted to a higher temperature in CTL and CTSR
264 could not be refuted by selective extraction. The results of the sequential extractions
265 suggest that in these samples mercury was mainly present in the form of complexes. In
266 CTL and CTSR, the peaks at 310-320°C may indicate that mercury is strongly bound to
267 the solid matrix. Indeed, the high desorption temperatures would suggest the chemical
268 binding of mercury rather than physical adsorption (Cao et al., 2008). Comparison of
269 the results obtained using the thermo-desorption technique and sequential extraction of
270 FA14b-FA17b were consistent, HgS being the main species obtained by desorption as
271 confirmed by the extraction of 63.4, 60.9, 63.1 and 66.8% in the non-mobile fraction for
272 FA14b-FA17b respectively, while lower amounts of matrix-bound mercury, HgSO₄ and
273 HgO were identified as minor species. The peak at 190°C in the desorption profiles
274 assigned to the desorption of mercury complexes or matrix-bound mercury was
275 corroborated by the extraction of 35.3, 38.2, 34.7 and 29.0 % in the semi-mobile
276 fraction. The presence of HgO was also confirmed by the extraction of 1.33, 1.11, 2.19
277 and 4.24 % in the mobile fraction. Furthermore, the FA16b and FA17b ashes were
278 found to contain HgSO₄, as identified by TD. This species was extracted in the mobile
279 fraction together with HgO, contributing to the above mentioned percentages.

280 The presence of HgS as the main species in soil samples was confirmed by the
281 extraction of 52.0, 86.2, 89.2 and 67.1 % in the non-mobile fraction. The occurrence of
282 mercury complexed by humid acids identified by the thermal desorption thermograms
283 was confirmed by the extraction of 20.0, 9.04, 7.69 and 28.7 % from the semi-mobile
284 fraction.

285 *3.4. Validation of the method*

286 In order to ensure the accuracy of the results corresponding to the total Hg content, the
287 sum of the Hg species content was compared with the certified values of total Hg in the
288 reference materials. The values in Table 4 are a comparison of the total Hg
289 concentrations, obtained by means of the two techniques used in this study, with the
290 certified Hg contents for each reference material. Recoveries of $113\pm 13\%$ and $104\pm 5\%$
291 with relative standard deviations of 2-13% and 1-3% were achieved with the thermal
292 desorption and sequential extraction techniques respectively. Although the accuracy of
293 the results obtained was similar for both methods, the main advantage of thermal
294 desorption is that it is possible to identify each individual species, whereas the
295 sequential chemical extraction method identifies groups of species. Furthermore,
296 thermal desorption is a more selective and reproducible method because the potential
297 transformation of the Hg species during the process is avoided. In any case both
298 procedures serve to complement each other until the results of the desorption method
299 can be confirmed and a sufficiently large number of solid samples have been analysed.

300 **4. Conclusions**

301 Thermal desorption is a promising technique for the identification of mercury species in
302 combustion by-products and soils. A good correlation between the results obtained by
303 this method with those obtained by the widely used sequential extraction procedure was

304 achieved. Recoveries of 113 ± 13 % and RSD of 2-13% were attained by thermal
305 desorption.

306 Although Hg bound to unburned particles cannot be ruled out in all the samples studied,
307 HgS was the main Hg species found in the fly ashes taken from a fluidized bed
308 combustion plant that burns blends of coal and coal wastes with a high mineral matter
309 content. However, mercury complexed with unburned particles were the main species
310 found in the fly ashes obtained from pulverized coal power plants fed with different
311 types of coals, HgSO₄ and HgO being found in smaller amounts. In the soil samples
312 HgS and some mercury complexed by humic acids were the main species identified.

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396

397 **Table 1.**

398 Thermal desorption temperatures for pure Hg compounds (Rumayor et al., 2013).

Mercury compounds	High peak T (°C)
HgI ₂	100±12
HgBr ₂	110±9
Hg ₂ Cl ₂	141±7
HgCl ₂	138±4
Hg-HA	200±10
HgS red	305±12
HgF ₂	234±42; 449±12
HgO red	308±1; 471±5
HgO yellow	284±7; 469±6
Hg ₂ SO ₄	295±4; 514±4
HgSO ₄	583±8
Hg(SCN) ₂	177±4; 288±4
Hg(CN) ₂	267±1
Hg(NO ₃) ₂ ·H ₂ O	215±4; 280±13; 460±25
Hg ₂ (NO ₃) ₂ ·2H ₂ O	264±35; 427±19
HgCl ₂ O ₈ ·H ₂ O	273±1; 475±5; 590±9

399

400

401 **Table 2.**

402 Operationally defined mercury fractions

Hg Fractions	Extraction solution	Individual Hg Species
F 1 Mobile Hg	1:1 (v/v) 2% HCl + 10% ethanol	<p style="text-align: right;">HgCl₂ Hg(OH)₂ Hg(NO₃)₂ HgSO₄ HgO Hg²⁺ complexes</p> <p>Inorganic Hg</p> <hr/> <p>Organic Hg CH₃HgCl, CH₃CH₂HgCl</p>
F 2 Semi - mobile Hg	1:2 (v/v) HNO ₃ : Deionized water	<p>Hg⁰ Hg⁰-Metal amalgam Hg²⁺ complexes Hg₂Cl₂ (minor)</p>
F 3 Non - mobile Hg	1:6:7 (v/v/v) HCl:HNO ₃ : Deionized water	<p>Hg₂Cl₂ (major) HgS HgSe</p>

Table 3.

Characteristics of the samples

Sample	Ash (%)	LOI ^a (%)	SiO ₂ (%db)	Al ₂ O ₃ (%db)	Fe ₂ O ₃ (%db)	MgO (%db)	S (%db)	Cl (µg/g)	Se (µg/g)	Hg (µg/g)	SA (m ² /g)	Size (µm)
CTA	-	5.7	56.5	27.2	6.23	1.93	0.12	>20	3.89	0.39	-	32
CTSR	-	7.2	59.9	24.6	5.25	1.64	0.18	160	4.9	1.8	-	11
CTL	-	5.6	59.1	29.2	8.24	0.94	0.08	>20	6.11	0.42	-	29
CTP	-	3.8	54.2	22.8	6.21	1.44	2.05	60	5.18	1.1	-	48
FA14b	-	4.6	43.5	25.6	8.02	1.43	-	-	-	2.16	9.13	-
FA15b	-	4.6	45.2	25.8	7.26	1.40	-	-	-	2.27	9.05	-
FA16b	-	3.1	45.7	24.6	6.05	1.33	-	-	-	1.48	6.62	-
FA17b	-	2.6	45.4	25.4	5.84	1.30	-	-	-	1.07	5.71	-
FAR2	86.8	-	82.4	8.50	5.16	1.18	-	-	0.36	0.14	-	-
TDIST1	88.0	-	81.9	8.74	2.31	1.16	-	-	0.29	19.9	-	-
TDST2	82.8	-	89.1	5.47	1.7	1.02	-	-	0.31	1.25	-	-
PUSH3	24.1	-	-	-	-	-	-	-	2.41	1.33	-	-

^aLOI (%): Loss on Ignition

Table 4.

Total mercury content obtained by means of the sequential extraction and thermal desorption techniques compared to certified values.

Reference sample	[Hg] mg·kg ⁻¹				Certified value
	Sequential extraction	%RSD	Thermal desorption	%RSD	
SRM 2709	1.53±0.05	3.24	1.8±0.21	12.8	1.40±0.08
RTC-CRM026-050	2.49±0.03	1.42	2.56±0.06	2.52	2.42±0.32
LGC6138	1.49±0.05	3.31	1.57±0.04	2.21	1.5±0.2

Figure Captions

Fig. 1. Thermal decomposition profiles of a) CTA; b) CTL; c) CTSR; d) CTP and e) CTP2.

Fig. 2. Thermal decomposition profiles of a) FA14b; b) FA15b; c) FA16b and d) FA17b.

Fig. 3. Thermal decomposition profiles of a) FAR2; b) TDIST1; c) TDIST2 and d) PUSH3.

Fig. 4. Mercury fractionation in the fly ash samples.

Fig. 5. Mercury fractionation in the soil samples.

Fig. 6. Relation between the content of unburned carbon (% LOI) in the fly ashes versus Hg extracted from the semi-mobile fraction.

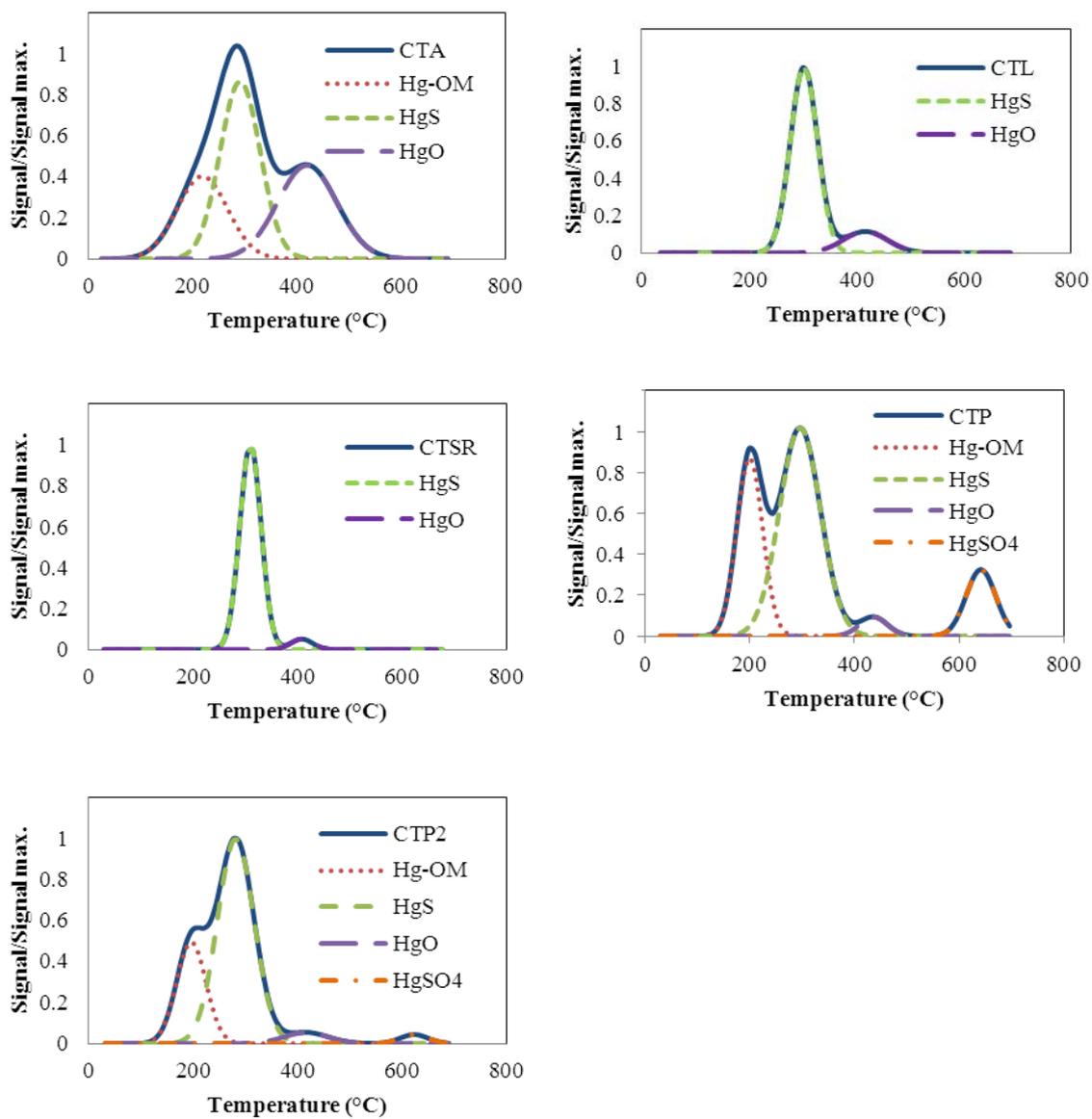


Figure 1

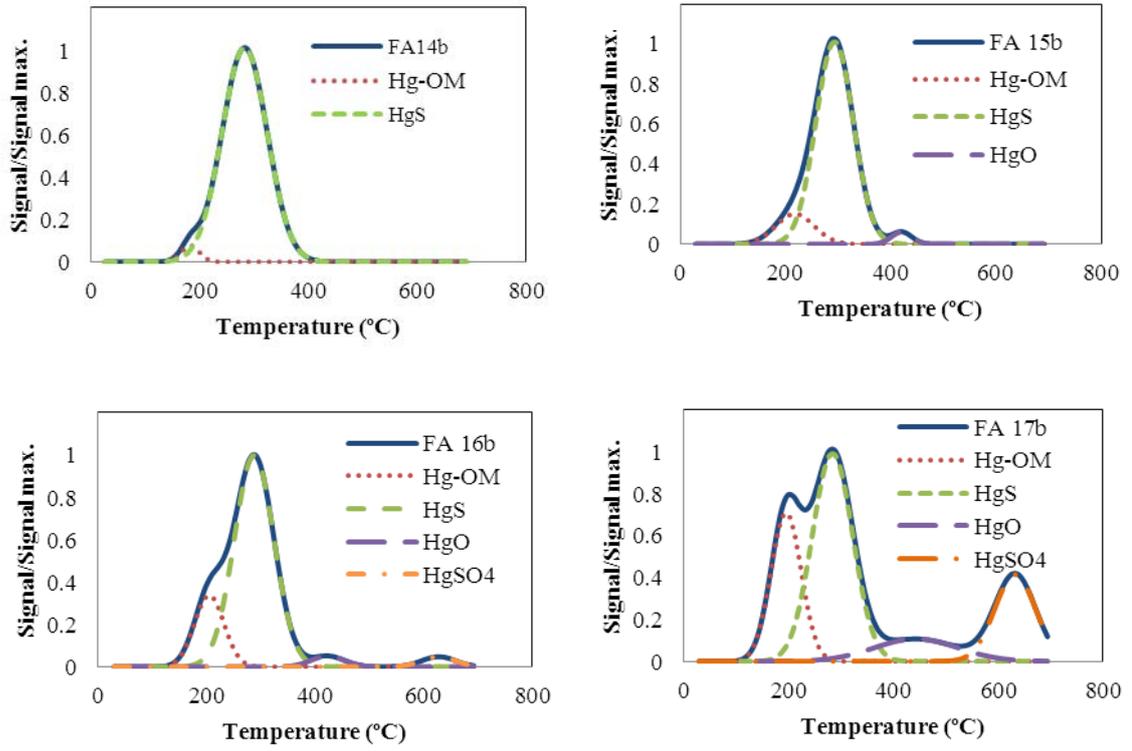


Figure 2

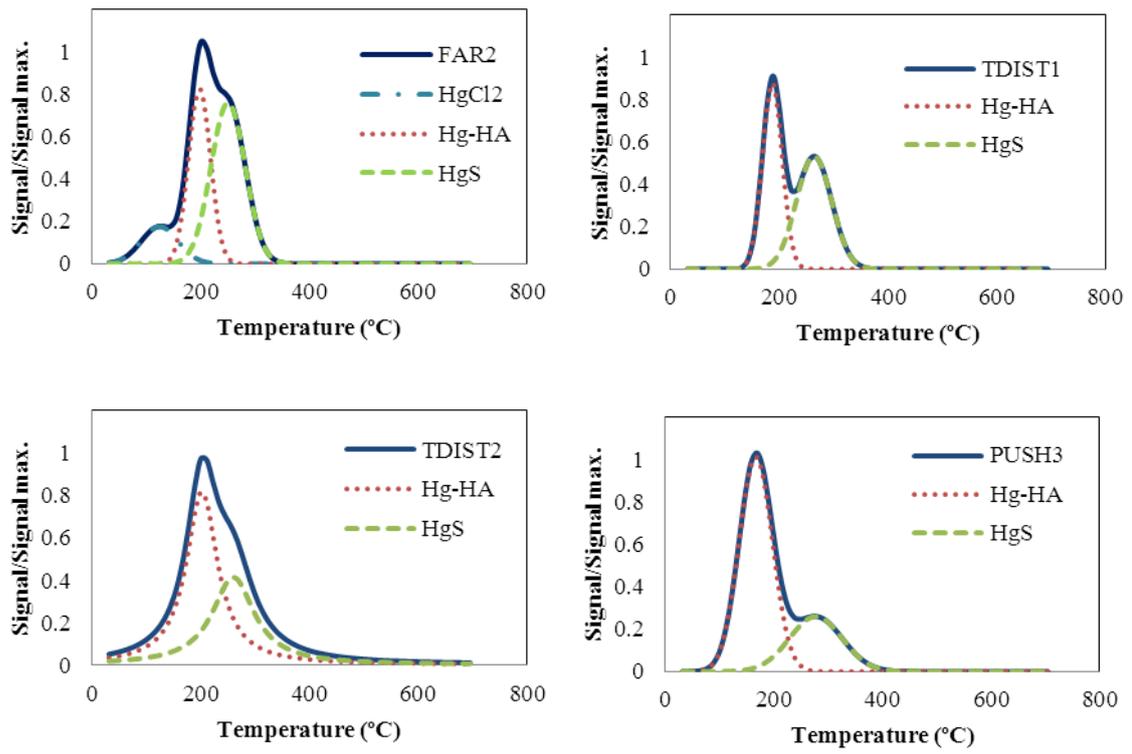


Figure 3

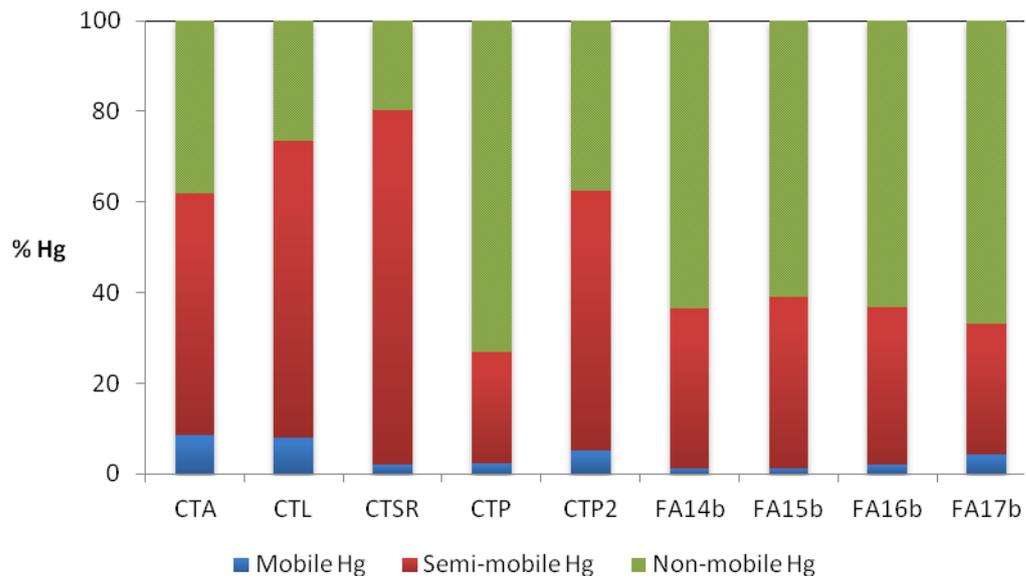


Figure 4

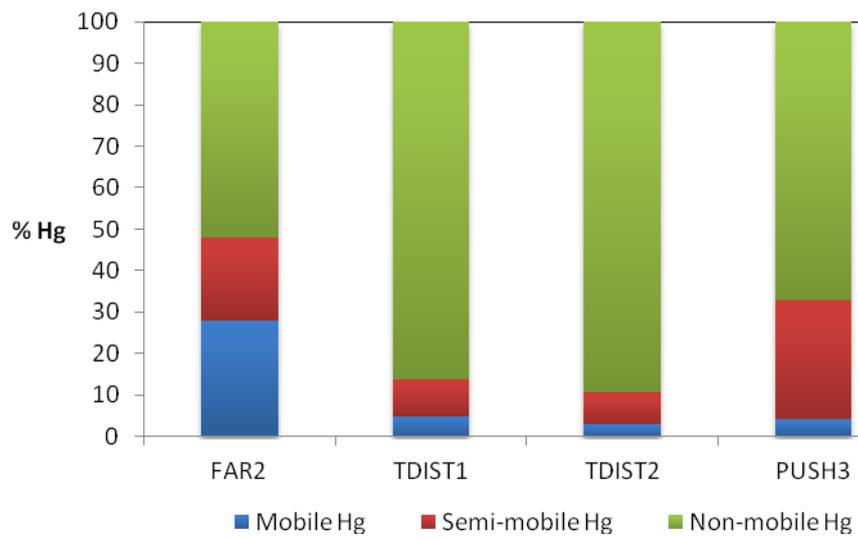
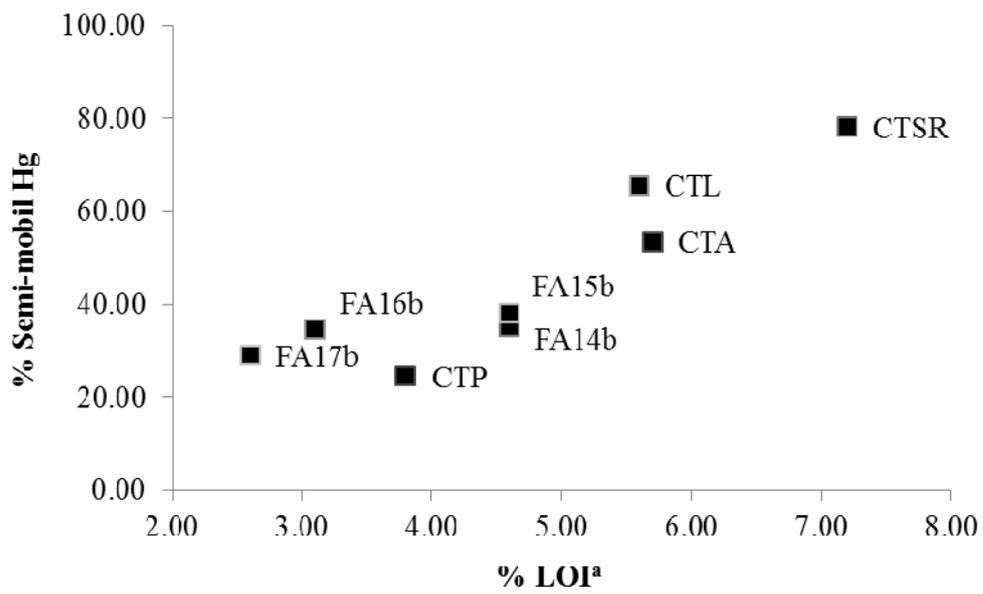


Figure 5



^aLOI (%): Loss on Ignition

Figure 6