

## Study of mercury in by-products from a Dutch co-combustion power station

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### Abstract

Fly ashes and gypsum are one of the main wastes produced in coal-fired power stations which may be sent to landfills for their disposal. In this work, leaching and speciation of mercury in fly ashes and gypsum from a modern co-combustion power plant equipped with a selective catalytic reduction (SCR) unit in the Netherlands were studied. The mercury leachable contents were checked against different regulations, including Dutch, German and the Council Directive 2003/33/EC. The speciation of mercury in coal combustion products is essential not only to determine the risk when the wastes are finally disposed but also to understand the behaviour of mercury during combustion and therefore to select the appropriate mercury removal technology. A temperature programmed decomposition technique was used in order to identify and quantify which mercury species are associated with coal combustion products. The main mercury species identified in fly ash samples was mercury sulphate, whereas in the gypsum sample the mercury present was mercury chloride. The quantitative mercury results carried out using the thermal desorption method may be considered accurate. The results obtained show that fly ash and gypsum samples from this power plant can be acceptable at landfills as a non-hazardous waste.

**Keywords:** mercury speciation, fly ashes, gypsum, co-combustion

## **1. Introduction**

Approximately 54 and 27% of the electricity produced in the United States and the European Union (EU 15), respectively, is generated by coal [1-2]. Specifically in the Netherlands, the coal based power is approximately 30% [3]. The burning of coal and the cleaning of flue gases produce a large volume of material or residue, called coal combustion by-products (CCBs). CCBs include fly ash, bottom ash, boiler slag and flue gas desulfurization (FGD) material. It is estimated that over 70 million tons of fly ash and 29 million tons of FGD material were generated in the United States in 2004 [4]. While 43% were used beneficially, nearly 70 million tons were disposed of [5]. In the European Union (EU 15) approximately 64 million tons of CCBs were produced in 2005 [6] with the utilisation for fly ash being around 48% (road construction, cement replacement material) and for FGD-gypsum (wallboard manufacture, cement industry) around 66% [6]. As previously mentioned, a significant proportion of these materials can be employed as a landfill material in mine reclamation or sent to landfills for its disposal. In such cases the potential leaching of elements of environmental concern must be controlled according to the Council Decision 2003/33/EC [7] presently in force. This Council Decision establishes the criteria and procedures for the acceptance of waste at landfills and its application is compulsory from 16 July 2005 by EU Members States. In the Netherlands, the Decree on Soil Quality (DSQ) was published in 2007 [8]. From 1 July 2008, the decree held for application of building materials. In Germany, the regulation LAGA 2003 [9] has established leaching limit values for the application of mineral by-products, specifically for ashes. The German EWC (European Waste Catalogue) [10] gave a proposal for leaching limit values in order to classify the waste on

leaching characteristics. Actually, the limit values are the same as those in the Landfill Directive [7]. These values have no legal status yet, but possibly they will form the basis for European limit values for the EWC.

Mercury is one of the most toxic elements in coal. Due to its high toxicity, a tendency to bio-accumulate and a series of difficulties that impede its control, strict policies for control/reduction of mercury emissions are being established [11-13]. Although the concentration of mercury in CCBs is relatively low, the large volumes of CCBs produced annually are potential risk when they are disposed of in landfills. Leaching test of fly ash and FGD products have found that, at least in some cases, mercury mobility is limited [14]. Alvarez-Ayuso et al., [15] found that the leachable contents for mercury in FGD gypsum samples remained below the required limit values for wastes to be accepted at landfills for non-hazardous wastes. However, in the last years, cleaning devices are being installed in coal-fired power plants to reduce the emissions of particulates, SO<sub>2</sub> and NO<sub>x</sub> which can affect the behaviour of mercury. At the same time, the co-combustion of biomass is increasing and it is important to check whether this has any effect on the quality, applicability and toxicity of the by-products.

The speciation of mercury in by-products can provide very valuable information to understand the behaviour of mercury during the coal combustion and its mobilization in water and land. A method employed to speciate mercury in solid samples is thermally induced desorption. This method has been applied to identify mercury compounds in soil contaminates, sediment samples, iron-based sorbents [16-18] and even in mercury lamp wastes [19]. However, there is a lack of a similar knowledge concerning the speciation of mercury in coal combustion products [20]. Feng et al. [21] showed that Hg<sup>0</sup>, HgCl<sub>2</sub>, HgO

and HgS species exist in airborne particulate matter at detectable levels using thermal desorption. At the same time, Feng et al. [21] used a standard of coal fly ash (NIST 1633b) to verify the quantitative analysis and suggested that the mayor species of mercury in this standard was HgCl<sub>2</sub>. Milobowski et al. [22] conducted a study on samples from wet flue gas desulfurization processes. The samples showed two thermal decomposition curves. In the first curve was difficult to distinguish between HgS and HgO whereas the second curve corresponded well with HgSO<sub>4</sub>. The thermal desorption method for mercury species has been developed by the authors [23], showing that the temperature appearance range can be arranged in increasing order as HgCl<sub>2</sub><HgS<HgO<HgSO<sub>4</sub>. The aim of this study is (i) to evaluate the concentration and leachable content of mercury in fly ash and gypsum samples and (ii) to determine the mode of occurrence or speciation in these CCBs which may contain multiple compounds.

## **2. Experimental**

### **2.1. Samples**

Samples from a Dutch co-combustion power station were used. The power station (426 MW) is equipped with SCR (Selective Catalytic Reduction) type of DeNO<sub>x</sub>, high efficiency ESPs (Electrostatic Precipitators) and wet FGD (Flue Gas desulphurization) unit. Approximately 30% (m/m) of biomass waste from the food processing industry was co-fired. This waste is a mixture of three biomasses: cacao pellets, palm kernel chips and sheanut pellets. Four fly ash samples (PFA1-4) were sampled from four successive

hoppers of one row from one electrostatic precipitator (ESP) and one gypsum sample (FGD-gypsum) from the FGD unit. The samples were stored in closed containers of polyethylene.

## 2.2. Physical and chemical characterization

Cold Vapour Atomic Fluorescence spectroscopy (CV-AFS) was used to determine the mercury concentration in the samples. The equipment consists of a modified reactor vessel where reduction of  $\text{Hg}^+$  and  $\text{Hg}^{2+}$  ions takes place [24]. The reduced mercury in vapour phase is carried in a stream of argon to an atomic fluorescence detector, (PS Analytical Merlin). The loss of ignition (LOI) was determined by the combustion of the organic matter in air at 815°C. BET surface area was determined by volumetric adsorption of nitrogen at 77K, using a Micromeritics ASAP 2010 analyser (Accelerated Surface Area and Porosimetry). For the particle size characterization, “Malvern Mastersizer-S” particle size analyzer was used. The measurements were performed by using approximately 0.2 g of fly ash dispersed in 50 ml of 2-propanol, IPA ( $\text{C}_3\text{H}_8\text{O}$ ) and 0.2 g of gypsum in 50 ml of water.

## 2.3. Leaching tests

Leaching tests were performed according with the following regulations: the Dutch Building Materials Decree (BMD), its successor, the Decree on Soil Quality (DSQ) [8], the German LAGA requirements for application of ashes [9], the proposed German AVV requirements for class H-13 of the European Waste Catalogue (EWC) [10] and the Landfill Directive [7] for waste disposal. The tests were carried out using a

column at a L/S ratio of 10 l kg<sup>-1</sup> and batch leaching tests at L/S=2 and L/S=10 l kg<sup>-1</sup>. Mercury content in the leachates were analysed by CV-AFS.

#### 2.4. Analysis of mercury species by thermal desorption method (TDM)

A thermal dissociation rig (PS Analytical Thermogram model 50.042) coupled to a mercury analyser (PS Analytical Sir Galahad Mercury Analyser model 10.525) was used for the thermal decomposition tests. The mercury compounds present in a portion of solid sample (0.2 g max.) are carried through the oven tube at 10°C min<sup>-1</sup> in a stream of argon carrier gas of 250 ml min<sup>-1</sup>. The commercial unit was previously modified by the authors to improve the temperature distribution along the work-tube between the programmed dissociation furnace and the “cracker” furnace, where the volatilized mercury compounds are fully dissociated prior to detection as elemental mercury. In the case of the gypsum sample a water trap of silica gel (particle diameter 1.0-3.0 mm) was integrated in the system just before the Sir Galahad detector. Different heating programmes, called Procedure 1, 2 and 3, were employed in the dissociation furnace. In the heating programme 1, the temperature rises linearly from room temperature to 650°C at 10°C min<sup>-1</sup>. The heating programme 2 consists of three steps at 10°C min<sup>-1</sup> with isothermal intervals of 10-15 minutes. The procedure 3 increases the temperature from 40 to 450°C at 45°C min<sup>-1</sup>.

The calibration test was performed by injecting different known quantities of mercury. A standard fly ash (NIST 1633b) was used in this study to verify the quantitative analysis.

### 3. Results and discussion

The mercury content of the fly ash samples ranges from  $0.3 \mu\text{g g}^{-1}$  to  $1 \mu\text{g g}^{-1}$ , while FGD gypsum presents a mercury concentration of  $0.005 \mu\text{g g}^{-1}$  (Table 1). The standard deviation was used to measure how the values are spread out in a data set. The mercury concentration was analyzed by CV-AFS and thermal desorption method (TDM). The results by TDM will be discussed in the section 3.2.2. Loss of ignition (LOI), surface area, porosity and particle size are also presented in Table 1. As it was expected, fly ashes particle size decreases from the first hopper (PFA1) to the last one (PFA 4) of the ESP.

The results show a direct relationship with the sampling collection point at the power plant in terms of mercury and particle size. The fly ash with the highest mercury content ( $0.95 \mu\text{g g}^{-1}$ ) is the sample with the lowest particle size ( $4.9\mu\text{m}$ ) and the highest porosity ( $4.9 \text{ nm}$ ) (Table 1) [25-27]. Not significance differences were found in LOI and surface area values for fly ash samples, being approximately LOI 6-7% and BET  $7 \text{ m}^2\text{g}^{-1}$ . These results are similar to those found for fly ashes from firing only coal [27-29].

#### 3.1. Leaching tests

The results obtained for mercury concentration in eluates from all leaching tests are shown in Tables 2-3. L/S ratio is defined as follows: for the batch tests it is defined as the amount of water added to the dry mass, while in the column tests it is defined as the percolate to the amount of dry mass. Dry mass was determined in a separate procedure [30]. The column is normally filled with the wet mass, therefore, the real L/S ratio in the column test is higher than in the batch test. This could lead to more leaching in the column test because at same L/S more water contact has already taken place. Not

significant differences were found in leaching results at similar L/S ratios using column or batch test for fly ash (PFA1) (Table 2) and FGD-gypsum (Table 3). For this reason, the leaching tests were only carried out in batch for the rest of the fly ash samples (PFA2-4). Similar mercury contents ( $<0.0006$ ) were found for the fly ash samples (Table 2). The relative leaching percentage is calculated as the amount of a component leached/total amount in solid sample. The relative leaching was calculated at L/S=2 and L/S=10 (column test) for PFA1 and FGD-gypsum. Relative leaching from fly ashes is lower ( $<0.11$  %) than relative leaching from gypsum ( $<7$  %) (Tables 2-3).

Tables 4-5 show the mercury leaching values of the co-firing ashes and FGD gypsum according to the BMD, DSQ, LAGA and AVV EWC Class H13 regulations and Council Directive 2003/33/EC. The leaching values for mercury are below the limit values for all regulations. Therefore, the co-firing ashes from this plant can be used in the form in which they are being applied, i.e. fly ash with insulation (Table 4). Taking into account that the study was restricted to mercury, co-firing biomass would not imply a negative effect on the application possibilities. According with the mercury leaching tests, fly ash and gypsum samples could be acceptable at landfills as non-hazardous waste (Table 5).

Leaching tests for PFA1 and FGD-gypsum were carried out at different L/S ratio. The mercury concentration in each specific fraction ( $\mu\text{g g}^{-1}$ ) were calculated for L/S= 0.1, 0.2, 0.5, 1, 2, 5 and 10  $\text{l kg}^{-1}$ . In all cases the mercury was not detected in the leachates above the detection limit ( $0.0001 \mu\text{g ml}^{-1}$ ).

### 3.2. Thermal Decomposition tests



### *3.2.1. Qualitative analysis of mercury species in by-products*

According to studies carried out by the authors [23], the TDM allows to identify different mercury species since each presents a characteristic decomposition temperature. The thermal dissociation temperatures for mercury model compounds are shown in Table 6. Figures 1-2 show the thermal decomposition profiles for fly ash and gypsum samples using the first heating programme (Procedure 1). As it can be observed in Figure 1, the decomposition of fly ashes occurs at temperatures ranging from 200 to 400°C, showing a maximum at approximately 290°C. According to the decomposition temperatures for mercury model compounds (Table 6) the main mercury species present in the fly ashes would be Hg-S species. The thermal decomposition for FGD-gypsum (Figure 2) occurs at low temperature with a maximum peak at approximately 130°C suggesting that HgCl<sub>2</sub> is the mercury species present in the gypsum sample (Table 6). In fact, the limestone slurry used in the FGD unit in this power station is a mixture of limestone and sea water favouring therefore, the formation of HgCl<sub>2</sub>.

For both fly ash and gypsum samples the baseline was the same before and after appearance of the peak, showing congruency and reliability of the technique.

The thermal decomposition of fly ashes presented broad peaks (Figure 1) suggesting that some peaks might overlap. With the aim of improving the resolution between successive peaks, a second programme (Procedure 2) was developed. The intervals in the Procedure 2 were selected in order to allow each mercury compound was completely resolved within its characteristic desorption temperature. Taken into account that temperature of decomposition for the fly ash and gypsum samples range from 90 to 400°C (Figures 1-2, Table 6) the following steps were selected:

- i) a first step at 150° C (decomposition of halogens)
- ii) a second step at 200° C (decomposition of sulphides)
- iii) a final step at 300° C (decomposition of sulphates and red sulphide)

Figure 3 shows the thermal decomposition profile for a fly ash sample using the stepwise temperature programme (Procedure 2). Due to no significant differences found in PFA1-4 samples with Procedure 1, the thermal desorption with the Procedure 2 was only carried out in one PFA sample. As it can be observed in Figure 3, the range of decomposition temperature for the fly ash sample is the same that with Procedure 1 (200-400°C) (Figure 1). However, a sharp peak is now observed at approximately 290°C (Figure 3). This fact suggests that the fly ashes start to decompose at 200 °C (small shoulder) but their completely decomposition is at 290°C, suggesting that mercury may be present mainly as mercury sulphate (Table 6).

### *3.2.2. Quantitative analysis of mercury species in by-products*

The thermal decomposition method can be used to identify mercury species and also to analyze mercury concentrations. For this purpose, a third thermal dissociation program (Procedure 3) was designed. In this way, a quick decomposition represented by a sharp peak is obtained. The range of temperature was selected because the fly ash and gypsum samples decomposed in such interval of temperature (Figures 1-2). Figure 4 shows the external calibration for the different quantities of mercury injected in the thermal dissociation rig. The peak area of each individual mercury peak is computed using a customized data logging programme, written as a Visual Basic extension to an excel spreadsheet. The programme allows acquisition of all relevant data collected during

the temperature-programmed dissociation run and successively converts them for mercury quantification (Figure 4). The quality of the results was evaluated by analyzing a standard sample. Satisfactory results were obtained where the mercury concentration for five analyses of standard NIST 1633b was  $0.17 \pm 0.03 \mu\text{g g}^{-1}$ , being the certified value  $0.14 \pm 0.02 \mu\text{g g}^{-1}$ . The mercury contents for fly ash and gypsum samples obtained with the thermal dissociation rig were compared to the values obtained by CV-AFS (Table 1). Although these results are less precise than those collected from the CV-AFS technique (Table 1), they may be considered as accurate and they give an estimation of the uncertainty of the analyses carried out with the thermal dissociation rig compared to the conventional cold vapor method.

#### **4. Conclusions**

Taking into account that the study was restricted to mercury, co-firing biomass would not imply a negative effect on the possible applications for coal combustion by-products. According with the European regulations for mercury, the fly ash and gypsum samples studied in this work could be acceptable at landfills as non-hazardous waste.

The programmed thermal dissociation permits identified mercury species in different by-products. The main mercury species identified in fly ash samples was mercury sulphate whereas in the gypsum sample the mercury present was mercury chloride.

Satisfactory quantitative results were found with the thermal desorption method when they are compared to the CV-AFS where the cost of work and time is higher.

## **Acknowledgments**

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## Captions of Figures

**Figure 1.** Thermal decomposition profiles of (a) PFA1, (b) PFA2, (c) PFA3 and (d) PFA4 fly ash samples obtained with the Procedure 1

**Figure 2.** Thermal decomposition profile of FGD-gypsum sample obtained with the Procedure 1

**Figure 3.** Example of thermal decomposition profile of a fly ash sample obtained with the Procedure 2

**Figure 4.** External calibration (regression line) for different quantities of mercury injected in the thermal dissociation rig.



Table 1. Unburned carbon content (LOI), BET surface area, porosity, particle size and mercury content in the fly ash and gypsum samples

Sample	LOI (%)	BET (m <sup>2</sup> g <sup>-1</sup> )	Porosity (nm)	Particle size (μm)	Hg (μg g <sup>-1</sup> )	
					CV-AFS	TDM
PFA1	5.4	6.7	3.4	22	0.393±0.011	0.319±0.026
PFA2	5.8	6.9	3.4	23	0.330±0.015	0.285±0.031
PFA3	6.4	6.9	4.1	6.6	0.919±0.023	0.856±0.042
PFA4	5.2	6.2	4.9	4.9	0.951±0.032	0.887±0.048
FGD-gypsum	26	18	6.7	56	0.005±0.002	0.006±0.002

Table 2. Mercury concentration in evaluates from absolute and relative leaching tests in fly ashes

	PFA1				PFA2-4	PFA1	
	Absolute leaching (μg g <sup>-1</sup> )					Relative leaching (%)	
	Column		Batch		Batch	Column	
L/S (1 kg <sup>-1</sup> )	2.1	10.3	2	10	10	2.1	10.3
Hg	<0.00008	<0.0004	<0.0001	<0.0006	<0.0006	<0.02	<0.11

Table 3. Mercury concentration in eluates from absolute and relative leaching tests in gypsum

	FGD-gypsum					
	Absolute leaching (μg g <sup>-1</sup> )				Relative leaching (%)	
	Column		Batch		Column	
L/S (1 kg <sup>-1</sup> )	1.8	12.6	2	10	1.8	12.6
Hg	<0.00005	<0.0003	<0.0001	<0.0006	<1	<7

Table 4. Mercury leaching values of fly ash (PFA1) and gypsum samples according to Building Materials Decree (BMD), Decree on Soil Quality (DSQ), German LAGA regulation and European Waste Catalogue Class H13 in AVV

	<b>BMD limit</b>		<b>DSQ limit</b>		<b>LAGA limit</b>	<b>AVV limit</b>	<b>PFA1</b>	<b>FGD-gypsum</b>
	Cat.1	Cat.2	No Insul	Insul				
<b>Hg</b> ( $\mu\text{g g}^{-1}$ )	0.02	0.075	0.02	0.08	0.02	0.2	<0.0006	<0.0006

*Cat.*; category

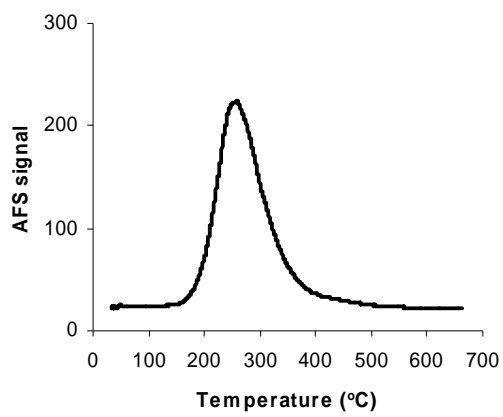
*Insul.*; insulation

Table 5. Mercury leaching values of fly ash (PFA1) and gypsum samples for waste acceptable at landfills according to the Council Directive 2003/33/EC.

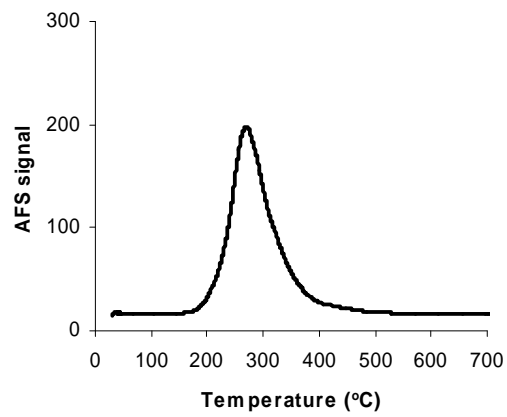
	<b>Non-hazardous waste</b>	<b>Hazardous waste</b>	<b>PFA1</b>	<b>FGD-gypsum</b>
L/S ( $1 \text{ Kg}^{-1}$ )	10	10	10.3	12.6
<b>Hg</b> ( $\mu\text{g g}^{-1}$ )	0.2	2	0.0004	0.0003

Table 6. Thermal dissociation temperatures for mercury compounds.

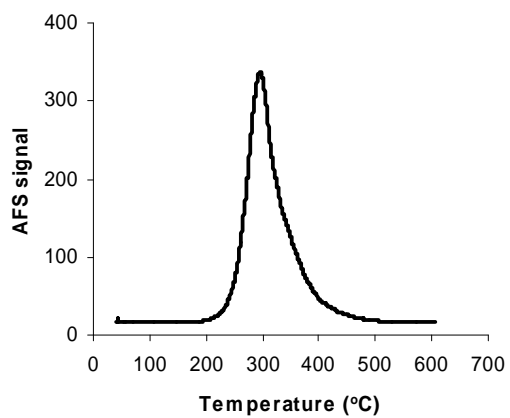
Mercury compounds	High Peak T $^{\circ}\text{C}$	Start of Peak T - End of Peak T $^{\circ}\text{C}$
HgCl <sub>2</sub>	120±10	70-220
Hg <sub>2</sub> Cl <sub>2</sub>	80±5;130±10	60-220
HgBr <sub>2</sub>	110±5	60-220
HgS metacinnabar (black)	205±5;245±5	170-290
HgS cinnabar (red)	310±10	240-350
HgSO <sub>4</sub>	540±20	500-600
Hg <sub>2</sub> SO <sub>4</sub>	280±10	120-480
HgO	505±5	430-560



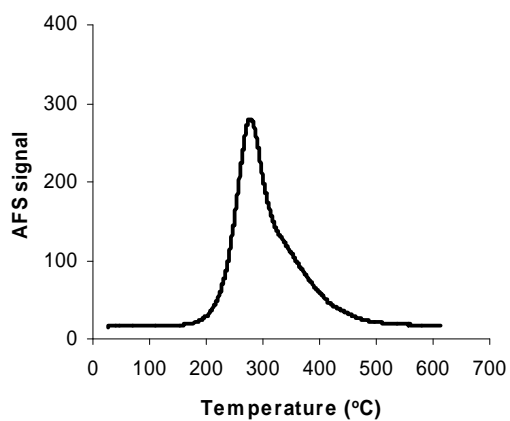
(a)



(b)



(c)



(d)

Figure 1

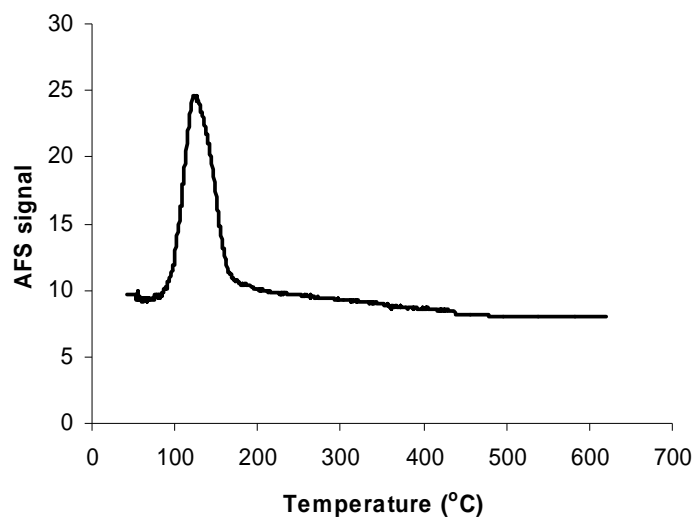


Figure 2

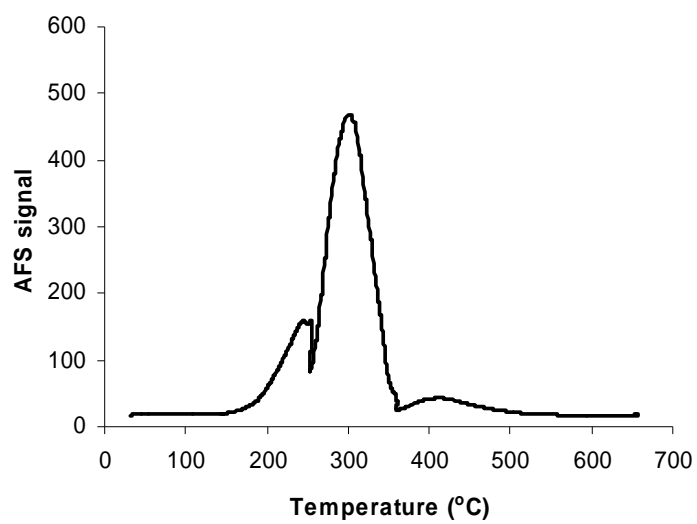


Figure 3

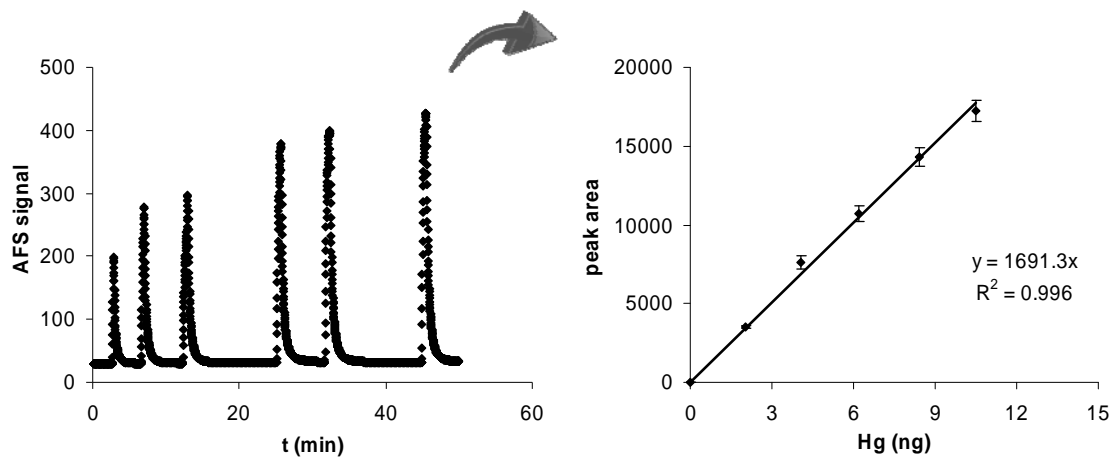


Figure 4