

Stability of mercury compounds at high temperatures

Matej Sedlar^{1,3}, Majda Pavlin^{2,3}, Sani Bašič¹, Milena Horvat^{2,3}

¹ Esotech, d.d.

² Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia

³ Jožef Stefan International Postgraduate School, Ljubljana, Slovenia

milena.horvat@ijs.si

Abstract. Combustion of fossil fuels is the main anthropogenic source of mercury. The efficiency of methods for removing mercury from coal syngas or flue gases mainly depends on the chemical forms of mercury. Despite the fact that temperature fractionation is a common approach to defining mercury species in solid samples, the accuracy of known results is still questionable.

For developing the method of temperature fractionation, a home-made apparatus was used, in which known mercury compounds, pure or mixed with SiO₂, were heated by a slow increase of temperature (approximately 2.2 °C min⁻¹) to 800 °C in a flow of either nitrogen or air. Released elemental mercury was detected by an atomic absorption spectrometry technique. The results showed that not only the type of carrier gas, but also the substrate affected the number and size of the peaks and the temperature at which elemental mercury was released.

Keywords: Mercury, temperature fractionation, speciation, pure mercury compounds

1 Introduction

Mercury is a global pollutant that originates from both natural and anthropogenic sources. The greatest anthropogenic source of mercury is industry, where approximately 45 % of global anthropogenic mercury emissions come from fossil fuel combustion [1]. Due to the global nature of mercury pollution, a new legally binding convention will be adopted in 2013 with the main aim of reducing anthropogenic emissions [2]. Considerable measures have already been taken to remove mercury from flue gases of coal combustion or gasification [3]. Until now, no efficient method has been implemented in industry to remove mercury from flue gas at elevated temperatures due to the instability of mercury, its compounds and of its trapping or complexation at higher temperatures.

Generally mercury can occur in flue gas in three different forms, namely as elemental mercury ($\text{Hg}(0)$), particulate (Hg_p), and oxidized mercury (Hg(I) , Hg(II)) [4]. Mercury is found only as $\text{Hg}(0)$ at temperatures above 650 °C. However, when the temperature begins to decrease, mercury is transformed to the oxidized state (Hg(I) , Hg(II)). This form of mercury reacts with other molecules in the gas to form different mercury compounds; the dominant mercury compound depends on the temperature of the gas itself. A knowledge, of which mercury compounds are present during the cooling of gases, is necessary to develop a process for the efficient removal of mercury.

The aims of this study were to observe and understand the behaviour of different mercury species at higher temperatures, exposed to different conditions, and to discover at which temperatures mercury is released from specific mercury compounds. With this in view, sets of experiments were conducted based on the pyrolytic technique. This served to calibrate the method for subsequent comparison with other solid samples, observed in further experiments.

Up to the present, much work has been done to develop an optimal method for mercury fractionation. Different methods for mercury fractionation [5],[6], [7], have resulted in varying results. Taking these inconsistencies into consideration, we developed a method for mercury fractionation which would provide reliable results for the temperatures at which different forms of mercury are released from solid

samples. To calibrate the method two sets of experiments were conducted: the first set included only pure mercury compounds, while the second set included different pure mercury compounds mixed with quartz powder. This served for comparison to other more complex matrixes that will be studied in future work.

2 Methods and materials

Apparatus: The apparatus used for temperature fractionation was a home-made device. As presented in Figure 1, it consisted of a gas cylinder (1) for a supply of carrier gas (nitrogen or air), a flow meter (2) for flow adjustment normally about 1 L min⁻¹, and a quartz tube, which was placed in an electric tube furnace (3). The quartz boat used for samples (4) was carefully positioned in the first quartz tube in the middle of the electric tube furnace which was linearly heated from room temperature to 800°C at a heating rate of approximately 2.2 °C min⁻¹. The second quartz tube was filled with quartz wool (5) kept heated at 800 °C by a small electric furnace (6) to ensure the transformation of all volatile Hg compounds to elemental mercury and to retain any particles that might be released from the sample. A Lumex pyrolysis unit (7) (Pyro 915+) provided additional decomposition of any remaining volatile mercury compounds that could interfere with the atomic absorption measurements [8]. Elemental mercury was detected by a Lumex Ra-915+ atomic absorption detector, based on Zeeman correction (8), which was connected directly to a computer (9) for data collection. A trap containing H₂SO₄–KMnO₄ solution (10) was connected to the exhaust from the Lumex Ra-915+ to retain Hg(0) in solution by oxidation and to quantitatively trap recover mercury released from the sample. This was used to assess the mass balance. Two parameters were controlled; the temperature of the sample at which the maximum of the mercury release peak was obtained, and the peak height/area.

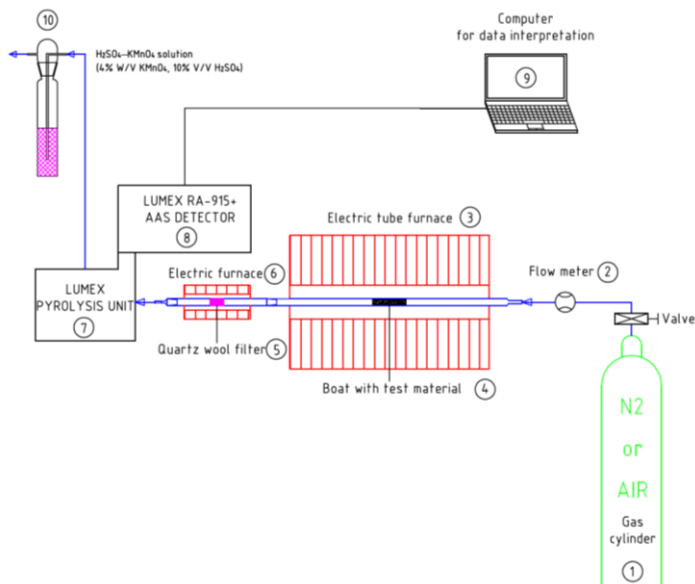


Figure 1: Scheme of the measuring line.

The RA-915+ Mercury Analyser with PYRO-915+ pyrolyser was developed for direct mercury determination (no pre-treatment procedures required). Using the RA-915+ spectrometer with background correction and the PYRO-915+, two-chamber catalyst atomizer allows direct mercury analysis of complex-matrix samples [8].

Sample preparation: Nine different mercury compounds were chosen; HgCl₂, Hg₂Cl₂, HgS, Hg₂SO₄, HgSO₄, HgSe, HgF₂, HgO-Red and HgO-Yellow. Experiments were performed with pure mercury compounds and mercury compounds mixed with SiO₂ powder. In the latter case the compounds (1-4 mg) were mixed with about 5 g of SiO₂ powder. The mixture was carefully homogenized by mixing in zirconia containers in a planetary mill with zirconia balls. Homogenization was done in three sequences, each of 10 min, in order to prevent heating of the contents. The homogeneity of the prepared mixtures was checked by acid digestion of 10 mg sub-aliquots, followed by cold-vapour atomic absorption spectrometry (CVAAS) based on reduction with SnCl₂ [9]. Six independent analyses were made and it was shown that the homogeneity was better than 2.5 %, except for HgSe and HgCl₂ which were approximately 6 and 8 %. After the homogenization

process a sample aliquot 9-30 mg mixture with SiO₂, was transferred to the quartz boat.

In the case of pure substances, pre-treatment was not required. Samples were weighed (< 200 µg) on a Mettler Toledo AE 240 S micro balance, with uncertainty of 0.01 mg. A mass balance assessment by trapping and analysis of mercury in the permanganate solution was made to evaluate the completeness of mercury release during heating.

3 Results and discussion

For better comparison of the experiments, results are shown as graphs of temperature versus the relative intensity of the released mercury. The mercury compounds were intercompared according to the type of carrier gas and the temperature at which mercury was released as a peak from the pure compound and from its mixture with SiO₂.

The thermograms of mercury compounds can be divided into three groups, depending on the number of peaks observed. The first group contained mercury compounds with only one thermal peak. These were HgS, Hg₂Cl₂, HgCl₂, and both HgO compounds (red and yellow). The second group consisted of mercury compounds that formed more than one peak, depending on the conditions (HgF₂, Hg₂SO₄ and HgSO₄). The third group consisted of the mercury compound HgSe which showed no effect on released peak depending of experimental conditions.

The mercury compounds in the first group showed one distinctive mercury peak. The carrier gas and the presence of matrix (SiO₂), have a great impact on the release temperature. Pure mercury compounds show variations in their thermograms solely due to the use of a different carrier gas. It was evident that the maximum of the release peak usually occurred at a lower temperature when purging mercury compounds with nitrogen. A similar situation was found when testing mercury compounds mixed with SiO₂. The most important finding was that mercury compounds from first group mixed with SiO₂, displayed their maximum peak at

different temperature from the pure compound. This reflects the effect of the substrate on these mercury compounds, probably by chemical interaction.

The most typical characteristic of this group of mercury compounds is the HgS thermogram, where nitrogen was used as carrier gas (Figure 2). On this thermogram, the peaks were separated into two temperature ranges. The first range of temperature at which release of mercury occurred extends from 150 to 350 °C with the peak maximum at a temperature of around 300 °C, while the second extends from 225 to 500 °C with a peak maximum temperature of around 340 °C. The difference in temperature behaviour was due to the substrate SiO₂ mixed with HgS in the case of the first temperature range. Evidently quartz affected the temperature at which mercury was released from the HgS sample.

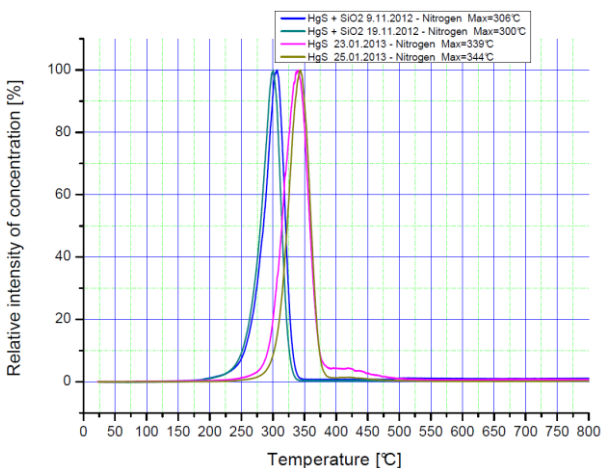


Figure 2: Thermogram of HgS, purged with nitrogen

As we have already mentioned above, the second group of results consisted of mercury compounds mixed with SiO₂ and those without (pure mercury compounds) that showed more than one peak when purged with nitrogen or air. The pure compounds of this group formed much smoother peaks than the same compounds mixed with SiO₂. This indicated that SiO₂ has some interaction with mercury compounds, just like with those from the first group. When comparing pure HgSO₄ to its mixture with the substrate, it was noticed, that the pure compound released

only one main peak while HgSO_4 mixed with quartz released several, no matter which carrier gas was used.

In general, mercury compounds released peaks earlier when purged with nitrogen, except for pure Hg_2SO_4 , which displayed its maximum peak at about the same temperature when purged with nitrogen and air.

The thermogram of HgF_2 where nitrogen was used as carrier gas is presented as an example (Figure 3). As seen on the thermogram, pure HgF_2 formed repeatable peaks at around 480 °C. Peaks also occurred at lower temperatures, but the temperatures of these peaks were not so repeatable. The most repeatable was the range of temperature in which mercury was released. This range extended from 170 °C to 550 °C for all samples of pure HgF_2 . When observing HgF_2 mixed with SiO_2 a degree of repeatability could also be noticed. Peaks of mercury from HgF_2 samples mixed with silica substrate could be observed in the range from room temperature to 370 °C. From this data, interactions of HgF_2 with the silica are clearly evident.

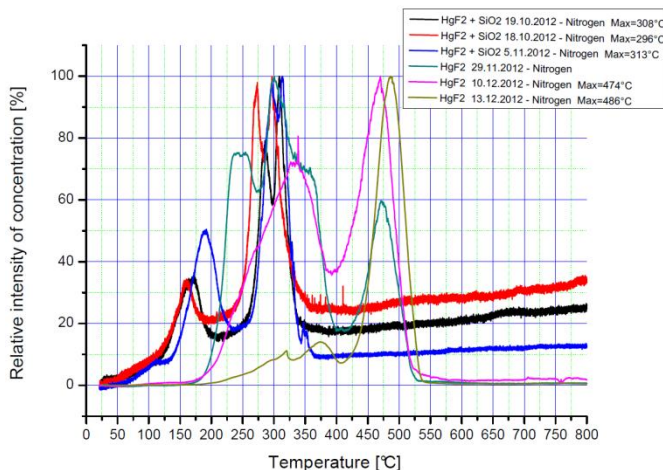


Figure 3: Thermogram of HgF_2 , purged with nitrogen

In the third group, only one mercury compound could be found, which showed no effect of carrier gas or substrate on the peaks released at elevated temperatures. This mercury compound is HgSe .

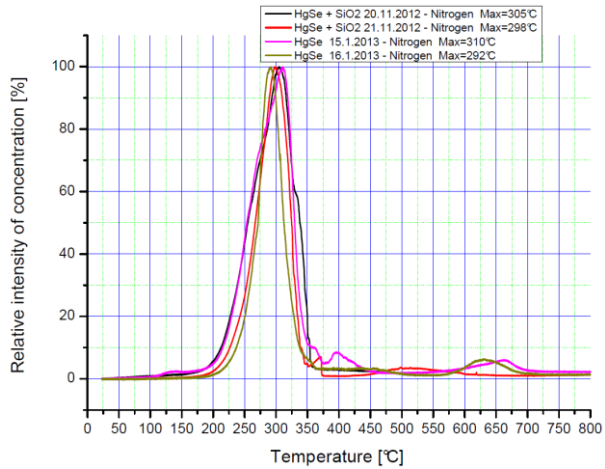


Figure 4: Thermogram of HgSe, purged with nitrogen

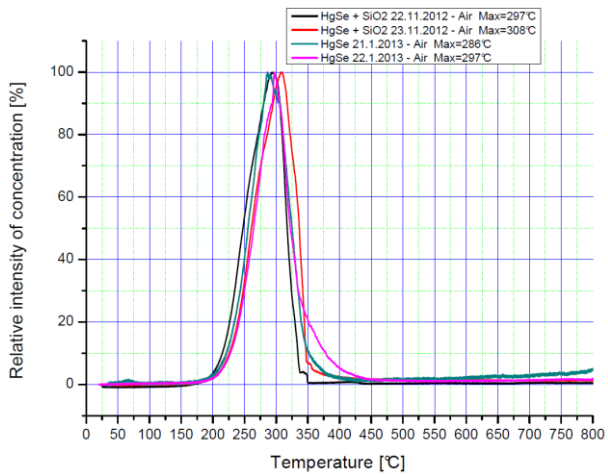


Figure 5: Thermogram of HgSe, purged with air

4 Conclusion

As seen from the experiments conducted during this study, it is necessary to understand the reactions of mercury compounds occurring at higher temperatures. It was shown that the carrier gas and its flow rate, as well as the SiO₂ substrate, and the material that is in contact with the samples affects the release of mercury. This is witnessed in the heights and shapes of the peaks, as well as their number and the breakdown temperature of the mercury compounds. These processes are not fully understood as yet. The mercury compounds most affected by these factors are particularly the sulphates and the fluoride.

Further fractionation experiments will include mixtures of mercury compounds with different substrates, designed to resemble complex matrices such as coal, gypsum, limestone, and materials used for adsorption at higher temperatures. Further investigation of the method's potential for separation and quantification of different mercury compounds in solid materials will be conducted.

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For wider interest

The aim of this study was to calibrate a method for temperature fractionation which would provide an understanding of the chemical reactions of different mercury compounds at elevated temperatures. This would serve as a comparison to other solid samples that contain different mercury compounds, and be applicable to pyrolysis processes involving flue gases and release and trapping of mercury at high temperatures.

The experiments conducted showed that many factors, such as the type of carrier gas, the substrate and the heating rate, affect the release of mercury. These effects can be seen in the temperature of mercury release and in the number of peaks. Our findings raise questions about the decomposition of complex matrices releasing mercury and their temperature comparability with pure mercury compounds.

Further fractionation experiments will include mixtures of mercury compounds with different substrates, designed to resemble complex matrices for which temperature fractionation may provide useful information (for example coal, gypsum, limestone, and materials used for adsorption at higher temperatures). We shall also further investigate the potential of the method for separation and quantification of different mercury compounds (or fractions) present in solid materials, especially coal.