

Research Article

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Temperature stability of mercury compounds in solid substrates

Abstract: The major aim of the newly adopted Mercury Convention is to reduce global mercury (Hg) emissions to the environment. In high temperature industrial processes, including coal combustion, Hg compounds present as impurities in solid materials are decomposed and evaporated leading to the emission of Hg to the atmosphere. The behaviour of different Hg compounds and their mixtures during heating have been the subject of numerous studies, and is the topic of the present work. Controlled heating can be used to fractionate Hg compounds in solid substrates, offering the possibility of identification and quantification of Hg compounds. In the attempt to develop a method for temperature fractionation of Hg, experiments were conducted with pure Hg compounds, and the compounds mixed with different substrates (SiO_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), for calibration purposes. Detection was performed by two methods, namely Cold Vapour Atomic Absorption Spectrometry (CV AAS) with Zeeman background correction, and Nier-type Mass Spectrometry with a Knudsen cell (MS). Further investigation is in process.

Keywords: mercury compounds, temperature fractionation, substrate, CV AAS, mass spectrometry.

DOI: 10.1515/chem-2015-0051

received February 10, 2014; accepted August 28, 2014.

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1 Introduction

Hg, as a global pollutant, originates from natural and anthropogenic sources, mainly by unintentional release into the environment. Industrial processes, such as burning of fossil fuels, the cement industry, oil refining, gold mining and others represent the biggest anthropogenic Hg sources, emitting more than 2000 tons per year, which represents around 30% of the total amount of Hg entering the atmosphere each year [1]. Due to the global nature of Hg pollution a new legally binding convention was adopted in 2013 with the main aim of reducing anthropogenic Hg emissions [2].

Hg in the environment exists in different forms such as elemental Hg(0), oxidized Hg(I) and Hg(II), or Hg associated with particulate matter, Hg(p) [3]. In the environment the formation of monomethylmercury (MeHg) is of concern because of its toxicity and bioaccumulation and biomagnification in aquatic and terrestrial food webs. Transformations between these forms are the basis of complex biogeochemical cycling of local and global relevance [2]. In solid matrices and industrial samples, Hg can be found as e.g. HgS (cinnabar, metacinnabar), HgCl_2 , HgO, HgSO_4 , with different degrees of solubility and temperature stability [4–8].

The method of temperature fractionation could be used to verify the decomposition temperatures of different Hg compounds and to identify Hg species in solid samples. Decomposition/sublimation temperatures of some Hg compounds are shown in Table 1.

Some methods involving different approaches have been tested by Biester and Scholz [4], Shuvaeva *et al.* [12], Lopez-Anton *et al.* [13], Rallo *et al.* [14], Luo *et al.* [15], Bollen *et al.* [16], Iwashita *et al.* [17], Wu *et al.* [18], Coufalik *et al.* [19,20] etc. However, no procedure for temperature fractionation of Hg has been validated or standardized yet, and therefore its comparability is questionable due to procedural differences. Validation of the method is necessary for further comparison of results and identification of Hg compounds.

Hence the aim of this work was to investigate the performance of the pyrolysis method based on CV

Table 1. Accessible literature data about the temperature characteristics of mercury compounds.

Mercury compound		Temperature of decomposition or sublimation
Mercury(I) chloride	Hg ₂ Cl ₂	383°C – sublimation ^[9]
Mercury(II) chloride	HgCl ₂	277°C – melting point, 304°C – boiling point ^[10]
Mercury(I) oxide	Hg ₂ O	100°C – decomposition ^[9]
Mercury(II) oxide	HgO	500°C – decomposition ^[10]
Mercury(II) sulfide – (Red)	HgS	344°C – transforms to black HgS ^[9] , 584°C – sublimation ^[10]
Mercury(II) selenide	HgSe	Sublimation ^[9]
Mercury(I) sulfate	Hg ₂ SO ₄	335 – 500°C – decomposition ^[11]
Mercury(II) sulfate	HgSO ₄	450°C decomposition ^[9] , 500°C decomposition ^[11]
Mercury(I) fluoride	Hg ₂ F ₂	570°C – decomposition/ sublimation ^[9]
Mercury(II) fluoride	HgF ₂	645°C – decomposition ^[9]

AAS detection, which is frequently used in various laboratories [4,8-20]. A comparative method based on mass spectrometry was used to better understand the temperature stability and reaction mechanisms of different Hg compounds in solid materials. The long-term goal of this work was to develop a methodology for the identification of Hg compounds in environmental and industrial solid materials and their transformation on heating.

2 Methods

2.1 Preparation of Hg compounds with substrates

Nine different Hg compounds (Table 2) were selected for examination (HgS, HgSe, HgO (red and yellow), HgSO₄, Hg₂SO₄, HgF₂, HgCl₂ and Hg₂Cl₂).

These compounds were “diluted” by mixing the pure compound with two different substrates: SiO₂ or CaSO₄ • 2H₂O powders. The first is frequently used for “diluting” pure Hg compounds for calibration purposes, while the second resembles gypsum from the wet desulfurization in coal burning power plants. Each pure Hg compound (1-4 mg when mixing with SiO₂, and 10-12 mg when mixing with CaSO₄ • 2H₂O) was added to 5 g of substrate powder. The mixtures were carefully homogenized by mixing in a zirconium container that was placed in a planetary mill (Fritsch planetary mill Pulverisette 7). The bulk homogeneity of the prepared mixtures was checked by six independent analyses of total Hg. A sample of weight between 80-140 mg was acid digested and Hg was determined by CV AAS after the reduction with SnCl₂ [21].

Table 2. Type of mercury compound, suppliers and purity.

Mercury compound	Supplier	Declared purity of mercury compound
Hg ₂ Cl ₂	Sigma-Aldrich Co. LLC.	≥ 99.5%
HgCl ₂	Kemika d.d., Zagreb	99%
HgO – Red	Sigma-Aldrich Co. LLC.	≥ 99.5%
HgO – Yellow	May & Baker Ltd.	≥ 99.5%
HgS – Red	Mallinckrodt Chemical Works	99%
HgSe	Sigma-Aldrich Co. LLC.	99.9%
Hg ₂ SO ₄	Sigma-Aldrich Co. LLC.	98%
HgSO ₄	Sigma-Aldrich Co. LLC.	≥ 99%
HgF ₂	Sigma-Aldrich Co. LLC.	97%

2.2 Experimental Apparatus for Temperature Fractionation

2.2.1 Apparatus 1

An RA-915+ Mercury Analyser with a PYRO-915+ pyrolysis unit was used for the detection of Hg. The instrument was developed for direct determination of the total Hg by combustion of samples and cold vapour atomic absorption detection (CV AAS) with Zeeman background correction [22].

The apparatus used for temperature fractionation was a home-constructed device, presented in Fig. 1. It consisted of a gas tank (1) for the supply of carrier gas, a flow meter (2) for flow adjustment and quartz tubes. The first quartz tube was placed in the 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. The second quartz tube was packed with quartz wool (5)

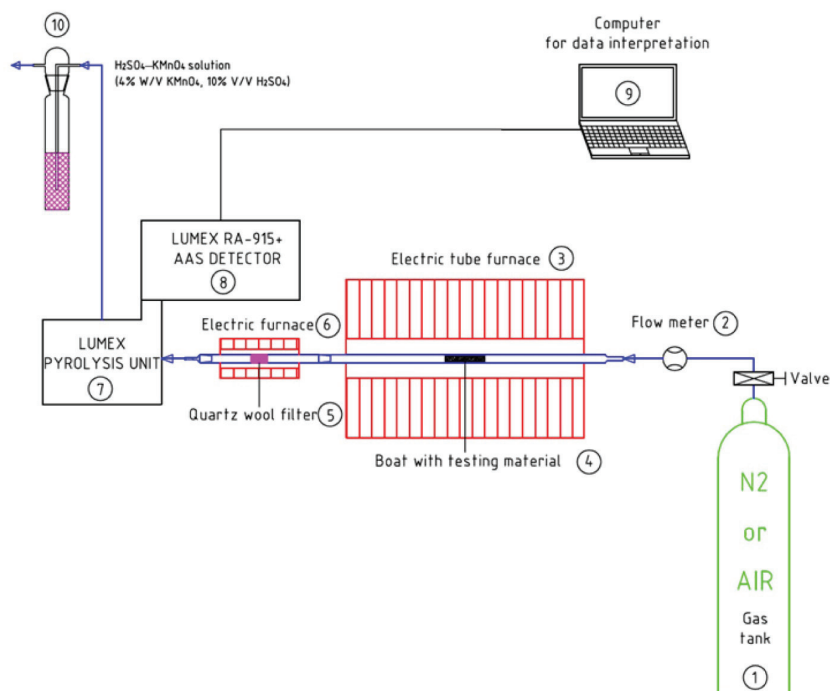


Figure 1: Scheme of the measuring line.

and heated to 800°C by a small electric furnace (6) to ensure the transformation of all volatile Hg compounds to elemental Hg and to retain any particles that might be released from the sample. The Lumex Pyro 915+ pyrolysis unit (7) ensured additional decomposition of any remaining volatile compounds of Hg that might interfere with the atomic absorption measurement [22]. Elemental Hg was detected by the Lumex Ra-915+ atomic absorption detector with Zeeman correction (8), which was connected directly to a computer (9) for data collection. An impinger containing H_2SO_4 - KMnO_4 solution (10) was connected to the exhaust from the Lumex Ra-915+ to retain Hg(0) in solution by oxidation.

2.2.2 Procedure 1

Testing was conducted with pure Hg compounds and those mixed with SiO_2 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. An amount of up to 0.2 mg of the sample was directly weighed into a quartz boat and tested without any pre-treatment for the pure Hg compounds. The Hg compounds homogeneously mixed with SiO_2 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and the sample weight varied from 9 to 30 mg. The sample boat (4) (Fig. 1) was carefully positioned in the middle of the quartz tube which was heated at room temperature of up to 750°C with a linear heating rate of approximately 2.2°C min⁻¹. Nitrogen or air

was used to flush Hg vapour released from the sample through the measurement train at a flow rate of 1 L min⁻¹.

2.3 Mass spectrometry

2.3.1 Apparatus

As a measuring device, a Nier – type mass spectrometer was used, initially designed for Knudsen Effusion Mass Spectrometric measurements, known as the KEMS method. The current sample was not loaded into the Knudsen cell; instead it was loaded into a semi-closed quartz inlet tube 10 cm long with 3 mm inner diameter, with the opened end tightly inserted into the circular hole drilled in a block of the ionization chamber of the Nier ion source. Such an arrangement provided for all desorbed species to be entered into the ionization volume and significantly improving the sensitivity compared with standard KEMS. The typical amount of mercury necessary to obtain a reliable thermodynamic spectrum is 100 ng contained in up to a 5 mg sample. The closed end of the inlet tube with a sample, positioned outside the spectrometer, was heated resistively with the temperature ramp of 10°C min⁻¹, using a EUROTHERM regulator. Ni/CrNi thermocouple was used for the temperature measurement. The desorbed atomic and/or molecular species were ionized by an electron of

35 eV energy and a 10 μ A trap current. Ions were extracted from the ionization space through an extraction slit, accelerated with -2 kV and analysed by a 60 degree magnetic separator according to their m/z ratio. Ions were finally detected by the ETP electron multiplier operating in counting mode and registered on counts per second base using an acquisition computer, together with temperature information.

It should be noted that desorption in MS experiments takes place at high vacuum conditions (better than 10^{-5} Pa). Species once desorbed are instantly detected by the detection system, within milliseconds. Thus, any change in the desorption process is instantly observed. The interaction between desorbed species and inner walls is low, compared with the transpiration method (CV AAS). It should be mentioned, that the rather turbulent flow of the carrier gas might blur the possible fine structure of thermodynamic curves due to the mixing effects.

In principle, the use of a mass spectrometer enabled us to detect any molecular species involved during the desorption process. However, in this work we were preferably interested in the shapes of thermodynamic curves to answer whether or not their shapes could be used for mercury speciation. For this reason, we were mainly concerned regarding the mercury that contained ions and/or their precursors. Since HgO, HgS, HgSe, Hg_2SO_4 and HgSO_4 are thermally unstable compounds, only atomic Hg could be expected as the desorption species. On the contrary, HgCl_2 and HgF_2 are according to the literature data stable upon heating, and ions such as HgCl_2^+ , HgCl^+ , HgF_2^+ and HgF^+ might be found in mass spectra.

2.3.2 Procedure

Only Hg compounds mixed with SiO_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were used. In this procedure the heating of the samples was conducted at a heating rate of $10^\circ\text{C min}^{-1}$ from room temperature to 550°C in a low pressure atmosphere. The reason for the heating to only 550°C was due to the material of the measuring line having a higher melting temperature.

In the series of measurement in which SiO_2 was used as a substrate for Hg compounds, the measurement method was adjusted by enlargement of the effusion orifice and the reduction of the amount of sample due to its binding to the surface of the substrate. This caused a reduction in the sample so that the intensity of the signal could not cope with the exponential function of the temperature. This resulted in a desorption peak. Despite the fact that in such conditions the saturation vapour pressure was not

reached, the possibility of a re-adsorption of Hg species still existed before they left the Knudsen cell. A second series of measurements on Hg compounds where $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was used as the substrate. Samples were inserted directly into the ionization area of the spectrometer through a quartz tube. This method differed from the first one by ensuring the introduction of every single desorbed molecule to the ion source, causing a significant amplification of the detection sensitivity. Additionally, the larger orifice reduced the possibility of re-adsorption. This made a substantial impact on the structure of the dynamic thermal curves. With this method, the pressure inside the insertion tube was much lower than the saturation pressure due to the faster outflow of gas, as compared to the velocity of the desorption process.

3 Results

3.1 Temperature fractionation results

The results are shown as graphs (thermograms) of temperature versus the relative intensity of Hg peaks to allow a comparison of the thermograms from different compounds. Thermograms are described for each Hg compound separately below.

The results for each Hg compound are presented in three figures. The first two present results obtained with CV AAS and the third with MS. Three sets of experiments were conducted using CV AAS; the pure Hg compound was followed by the Hg compound mixed with SiO_2 or with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The three thermograms obtained by CV AAS are presented in two separate figures for each Hg compound. The first was obtained in a flow of nitrogen and the second in a flow of air. Results were obtained as an average of at least two replicates. The third figure in each set of experiments represents the results obtained by MS.

In general, the comparison of the thermograms obtained by CV AAS and MS shows that the temperatures at which Hg peaks appear differ. In most cases the peak maxima appear at higher temperatures for the CV AAS method compared to MS due to different conditions regarding a low pressure atmosphere of the MS method procedure. The comparison of the results obtained by CV AAS indicated that the parameters of the experimental set-up, such as carrier gas, heating rate, flow rate and substrate may have played an important role in Hg release during heating, and therefore constant conditions had to be maintained during repetitive experiments.

3.1.1 Hg₂Cl₂:

The thermograms obtained by CV AAS are shown in Figs. 2 and 3. The shape of the thermogram of pure Hg₂Cl₂ was smooth and ranged between 50 to 300°C with a major peak of 75°C and 78°C for nitrogen and air as carrier gases, respectively. The pure compound mixed with SiO₂ resulted in wider peaks at 165°C and 146°C for nitrogen and air, respectively. It is assumed that the larger surface area provided by the substrate affected the release of Hg during heating. Three main peaks could be seen for CaSO₄ • 2H₂O as a substrate. The first peak ranged between 50 to 140°C with peak maxima of 93°C and 87°C for nitrogen or air as carrier gases, respectively. The shape and the temperature were similar to the peaks obtained for pure Hg₂Cl₂. The second peak was much broader compared to the other peaks and ranged from 140 to 500°C with peak maxima of 273°C and 223°C when purged with nitrogen or air, respectively. It was assumed that two or more peaks were hidden by the wide peak. The third sharp peak appeared at a much higher temperature, with peak maxima of 680°C and 623°C for nitrogen and air respectively.

The appearance of the second and third peaks was clearly attributed to the presence of CaSO₄ • 2H₂O which decomposed and probably reacted with Hg.

During heating, Hg₂Cl₂ disproportionate to Hg(0) and HgCl₂ (Eq. 1) decomposed to elemental Hg and Cl₂ (Eq. 2) [13].



The vapour pressures of the gaseous products HgCl₂ and Hg were the same (130 Pa at 136°C), and for that reason both gaseous products were released at the same temperature [18] resulting in one main peak (Figs. 2 and 3). Interestingly, in recent work Lopez-Anton et. al., reported two major peaks for Hg₂Cl₂ mixed with SiO₂ [13]. In our case, another small peak was also visible at lower temperatures (at 90°C when purged with nitrogen) when SiO₂ was used as the substrate. This could be explained by a possible decomposition of Hg₂Cl₂ to Hg(0) and HgCl₂ which could have been caused by exposure to the light [10].

The appearance of the third peak at temperatures above 600°C is difficult to explain as no theoretical background exists. The sharp shape of this peak suggests that the appearance of this peak might be due to an experimental artefact induced by breakdown processes during heating and the subsequent formation of less volatile Hg compounds that could be adsorbed on cooler surfaces of

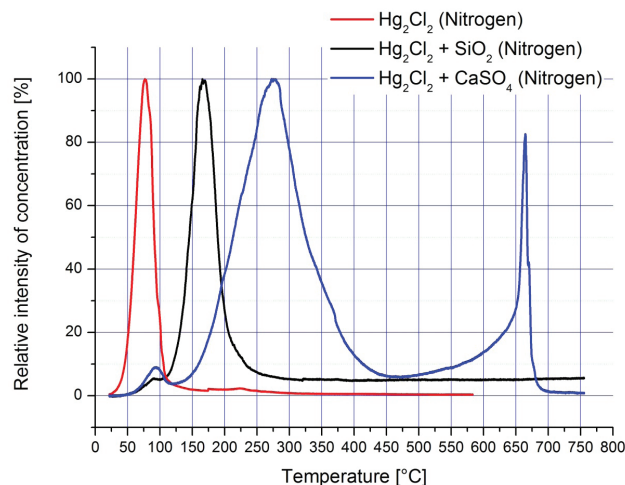


Figure 2: Thermograms of Hg₂Cl₂, purged with nitrogen.

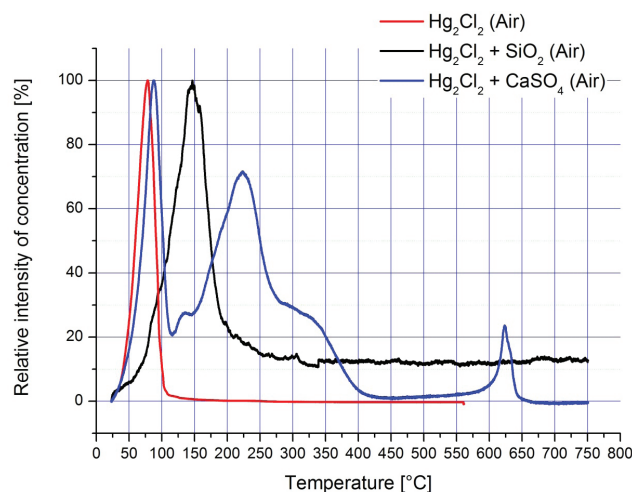


Figure 3: Thermogram of Hg₂Cl₂, purged with air.

the experimental set-up. On increasing the temperature of the carrier gas, these compounds were probably released when the critical temperature was reached. However, the possibility also exists that during the decomposition steps a complex compound was formed.

The results obtained by mass spectrometry are shown in Fig. 4. As mentioned in the experimental part, pure compounds without substrates were not used in the MS experiments. The appearance of the main peaks at temperatures of 84°C and at 110°C was observed for HgCl₂ with SiO₂ and CaSO₄ • 2H₂O as substrates. On the thermogram of Hg₂Cl₂ mixed with CaSO₄ • 2H₂O, a small peak can be seen at the lower temperature of around 80°C. This peak was probably caused by the release of Hg(0) adsorbed on the powder as a result of the decomposition of Hg₂Cl₂ due to exposure to light [10]. Although the thermograms obtained by the CV AAS set-up and MS

seemed different, particularly for Hg_2Cl_2 mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the peak pattern initially followed the same trend with a skew towards higher temperatures. The reason for that can probably be found in the procedure of the MS method which operates in a near vacuum. Therefore the sample almost instantaneously entered the measuring cell after the decomposition of the sample, unlike the CV AAS method where Hg needed to be purged into the measuring cell. Unfortunately the MS system could not be used at a temperature above 400°C to verify whether the appearance of Hg peak above 600°C using CV AAS was associated with an experimental artefact.

3.1.2 HgCl_2 :

The results for HgCl_2 , measured by CV AAS were similar to those for Hg_2Cl_2 (Figs. 4 and 5), although with less smooth peak shapes. The major peak of the pure compound appeared at slightly higher temperatures and completely covered the first peak of the Hg compound mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The second and third peaks of HgCl_2 mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ appeared in the same temperature range as the second and third peaks of Hg_2Cl_2 mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The literature data suggests that HgCl_2 sublimes, but it can also be stabilized by the supporting material due to the adsorption; or it decomposes to elemental Hg when it comes in contact with the surface of the matrix [18]. Other authors also reported one peak only when heating mixed with SiO_2 [4]. It is obvious that the heating rate and flow rate influence Hg release from the substrates [4,13]. Since gaseous HgCl_2 and Hg [18] have the same vapour pressure, only one peak could be seen for the pure Hg compounds. When HgCl_2 was mixed with substrates, the first small peak probably belonged to the elemental Hg as a result of the preliminary decomposition of the compound. It is assumed, that the presence of the substrate could shift the temperature of the decomposition to higher values, as seen in Fig. 5. The presence of a third peak at temperatures of more than 500°C for HgCl_2 mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ could be explained by the artefact phenomenon, or formation of a complex compound, as already mentioned for Hg_2Cl_2 .

The MS thermograms (Fig. 7) were also similar to those of Hg_2Cl_2 . The mass spectrum of HgCl_2 is known. Upon ionization of the HgCl_2 molecule, 60% of HgCl_2^+ , 4% of HgCl^+ and 36% of Hg^+ ions were created [23]. Therefore if Hg was desorbed in the form of HgCl_2 , more HgCl_2^+ than Hg^+ ion should have been found in the mass spectrum. This was not the case, however. The great majority (100/1)

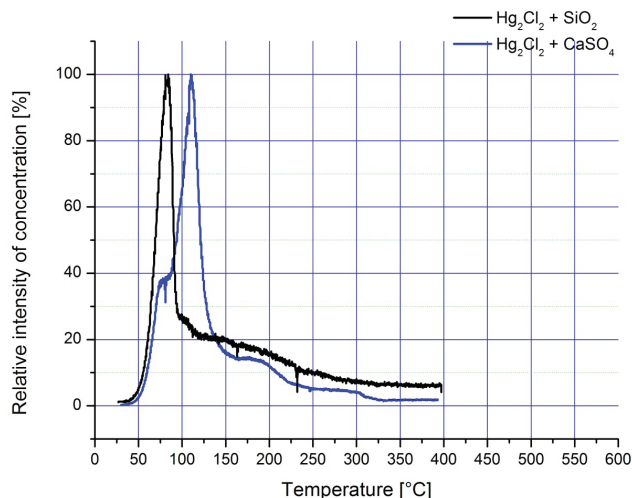


Figure 4: Thermograms of Hg_2Cl_2 mixtures, obtained by MS.

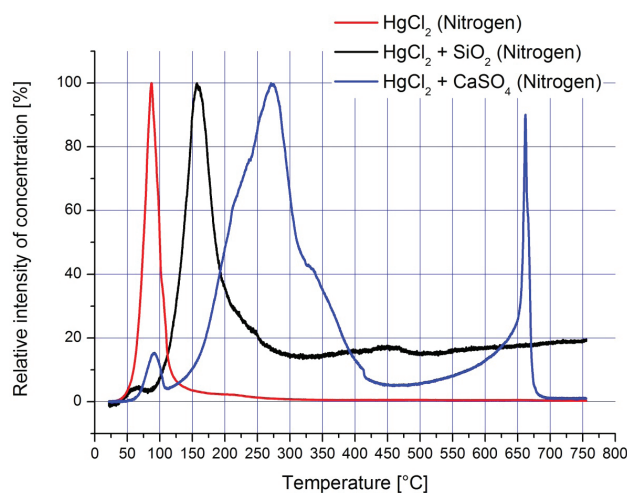


Figure 5: Thermograms of HgCl_2 , purged with nitrogen.

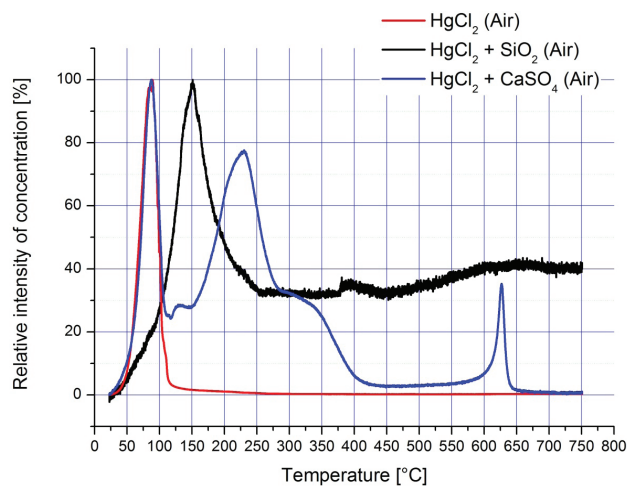


Figure 6: Thermograms of HgCl_2 , purged with air.

of ions in the desorption spectra were observed to be Hg^+ , indicating mostly a dissociative desorption process.

The maximal peak temperature, shown on the thermogram (Fig. 7) was at 92°C whereby SiO_2 was used as the substrate and 130°C for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. As observed from the results of the MS method (Fig. 7), both first peaks probably belonged to elemental Hg due to the decomposition of HgCl_2 during the mechanical treatment or exposure to sunlight, while the second could be related to the interactions or reactions with the substrate.

3.1.3 HgO:

Red and yellow HgO were investigated. Both have the same orthorhombic crystalline structure, but differ in particle size, with the yellow HgO having a smaller particle size [24]. The thermograms obtained are presented in Figs. 8-12. Those obtained for red HgO purged with nitrogen and air are shown in Figs. 8 and 9. The thermograms are similar for both gases, with the exception of HgO on SiO_2 where the peak appears at a lower temperature. Hg was released in one main peak and some smaller but irregular peaks. Some recent publications reported that the decomposition of pure HgO occurred at around 400°C for the yellow and 460°C for the red form [24], although the detailed study of L'vov [25] suggested a multi-step decomposition; the lowest at $160\text{--}220^\circ\text{C}$, intermediate at $220\text{--}400^\circ\text{C}$ and higher at $400\text{--}500^\circ\text{C}$. L'vov suggested that the primary product of the HgO decomposition was not molecular oxygen as suggested by most papers (Eq. 3), but monoatomic oxygen (Eq. 4) leading to reaction of gaseous Hg with monoatomic oxygen and formation of Hg_2O (Eq. 5). This may explain our results for pure HgO (red curve), where the small peaks at lower temperature correspond to Hg_2O [26] which decomposes at 100°C to HgO and Hg, and the prevailing peak representing the decomposition of HgO (Fig. 8).



The most striking peak was that of HgO mixed with SiO_2 at about 265°C (Fig. 8). It seems that the substrate in this case facilitated the decomposition of HgO at a much lower temperature than for the pure HgO. This trend is the opposite to the other Hg compounds such as HgCl_2 (Fig. 5) between thermograms obtained for pure

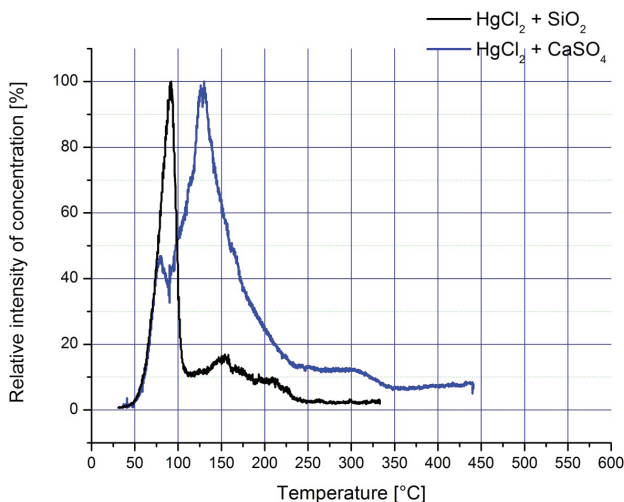


Figure 7: Thermograms of HgCl_2 mixtures, obtained by MS.

compounds and those mixed with SiO_2 . Some recent studies [27,28] suggested that a number of silicate compounds (i.e., HgSiO_3 , $\text{Hg}_6\text{Si}_2\text{O}_7$, etc.) could possibly be formed within cement kiln systems. The decomposition temperature of these compounds was reported to be between 225 and 325°C [29] which would be consistent with our results. In addition, the reaction mechanisms induced by autocatalysis, as suggested by L'vov [25], on the larger surface of SiO_2 may shift the decomposition of HgO through formation of Hg_2O , which is typical of lower temperature range decomposition. As seen on the thermograms (Figs. 8 and 9) the main peak of HgO on SiO_2 corresponded to the lower temperature range decomposition peaks of pure HgO. Further support for this hypothesis was evidenced by a reproducible small peak appearing at a temperature of about 130°C which most probably corresponds to Hg(g) likely resulting in autocatalytic formation of Hg_2O . This mechanism still needs to be better understood.

The mixture of HgO and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ released its major peak at a similar temperature as pure HgO (Figs. 8 and 9). However the peak shape skewed towards lower temperatures indicated the decomposition and subsequent release of Hg at maximum temperatures between 300 to 350°C . Even the shapes were similar, but a slight shift could be seen towards lower temperatures. The lower peak that appeared was relatively greater, compared to samples of pure HgO.

The thermograms obtained by MS are presented in Fig. 10 for red HgO mixed with SiO_2 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ substrates. The first peak appeared ranged between 75 and 125°C and was most probably a result of the release of Hg(0) due to the decomposition of HgO. The temperatures of the second peak differed by around 40°C , where SiO_2

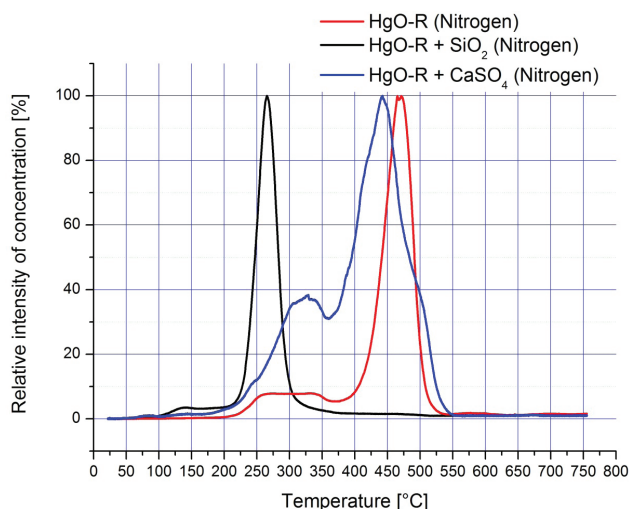


Figure 8: Thermograms of red HgO, purged with nitrogen.

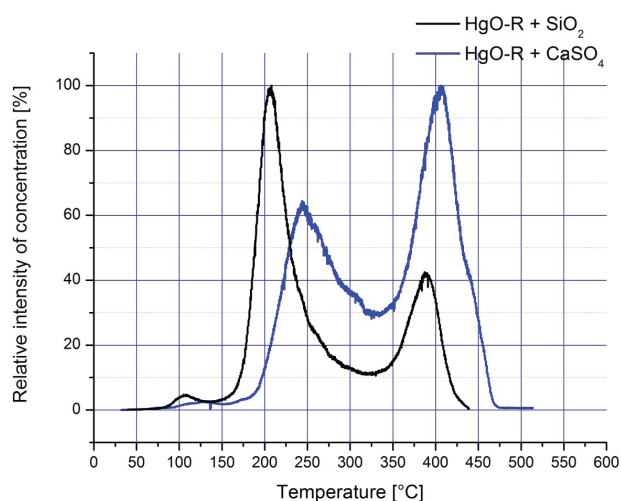


Figure 10: Thermograms of red HgO mixtures, obtained by MS.

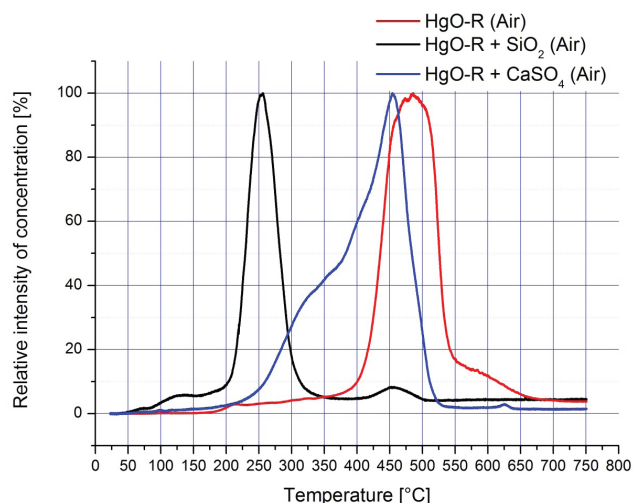


Figure 9: Thermograms of red HgO, purged with air.

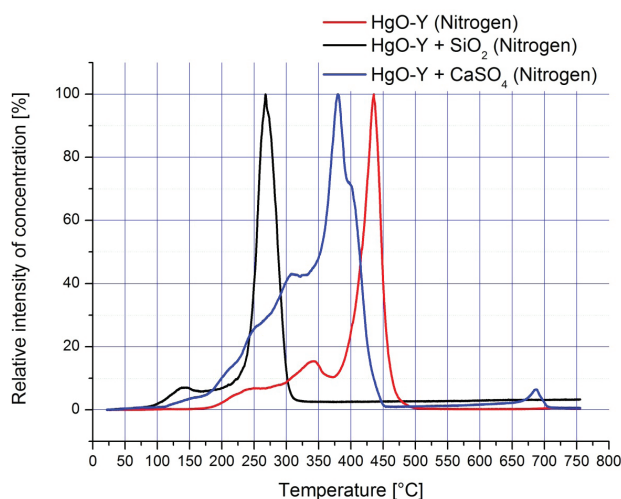


Figure 11: Thermograms of yellow HgO, purged with nitrogen.

caused the earlier release of Hg, shifting it towards a lower temperature (208°C) compared to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (247°C). A similar shift was observed at the release of a third peak as well.

HgO (yellow) (Figs. 11 and 12) has similar characteristics to HgO (red) during the temperature decomposition, when followed by the CV AAS method.

It is evident that for pure Hg compounds mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, air had a large influence on the release of Hg, probably due to interactions with the substrate. Despite the fact that the release of Hg began at around 100°C, the structural changes caused by air as the carrier gas accelerated the release of Hg. This could be the reason why the peaks of the Hg compound mixed with $\text{CaSO}_4 \cdot$

$2\text{H}_2\text{O}$ differed in pattern compared to the thermograms of the same compound in a different carrier gas.

Thermograms of HgO (yellow) obtained by MS are presented in Fig. 13, indicating a similar pattern of Hg release from HgO on both substrates. Three peaks can be seen, of which the main appears at 190–220°C. A slight temperature shift towards lower temperatures was observed with HgO on SiO_2 as the substrate. The small peak appearing in the temperature range of 75–125°C probably belongs to Hg(0). As seen in the MS thermograms of both HgO compounds, the pattern of peaks was similar. Multistep decomposition was present and comparison shows that particle size plays an important role in the release of Hg.

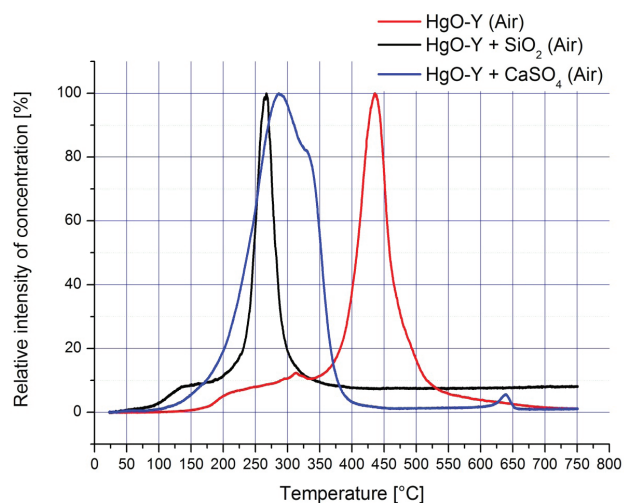


Figure 12: Thermograms of yellow HgO, purged with air.

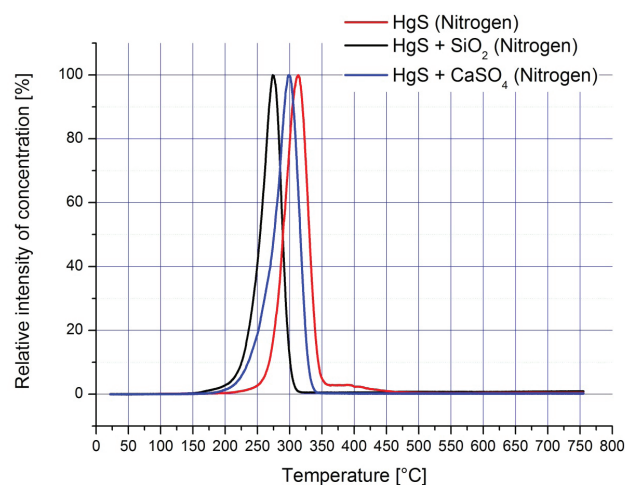


Figure 14: Thermograms of HgS, purged with nitrogen.

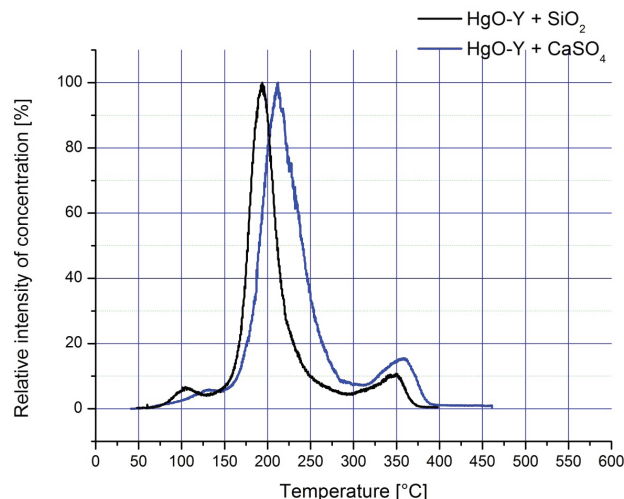


Figure 13: Thermograms of yellow HgO mixtures, obtained by MS.

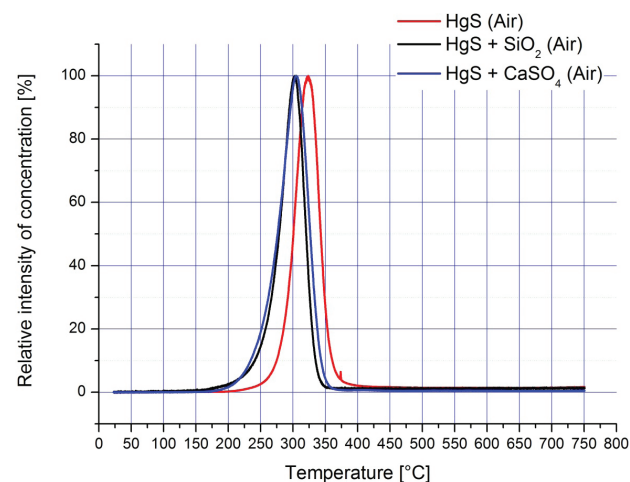


Figure 15: Thermograms of HgS, purged with air.

3.1.4 HgS and HgSe:

Mercury(II) sulphide (Figs. 14 and 15) gave only one main peak when measured by CV AAS. For pure HgS the temperature of the maximum peak is at 313°C and 324°C when purged with nitrogen and air, respectively. For HgS mixed with SiO₂, the maximum in the peak was reached at a temperature that was 20°C lower when purged with air and 40°C when purged with nitrogen. When HgS was mixed with CaSO₄ • 2H₂O, the peak maximum occurred at around 298°C and 303°C in nitrogen and air, respectively. In general, these temperatures were similar to the results obtained by other authors [4,13]. According to the literature data HgS decomposes at 585 °C which is a numerically determined date, where the fugacity effect

is not considered [30]. If also considering fugacity effects, the reaction rate may be significant at lower temperatures [30]. As the authors claim, HgS decomposes before melting by a process also referred to as reactive sublimation which proceeds according to Eq. 6 [30]. It also seems that the flow rates and substrates have minor effects on the temperature at which the decomposition of HgS is detected.



When O₂ was present in the carrier gas, the evolution of SO₂ was observed by Wu *et al.*, though the thermogram was almost identical to that in the absence of O₂ [18].



When considering the literature data, the existence of an intermediate HgSO_3 is also possible, but true identity of HgS decomposition is still not proven [18].

Thermograms for HgS obtained by MS exhibited one peak only (Fig. 16). When mixed with SiO_2 , Hg was released at 242°C , but when $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was used as the substrate, the temperature of release was 251°C .

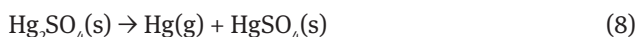
Similarly to HgS , HgSe shows one peak at about 265°C , regardless of substrate and carrier gas (Figs. 17 and 18).

Fig. 19 presents the thermograms of HgSe mixed with SiO_2 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, measured by MS. The peaks were released at 200°C when SiO_2 was used as the substrate, and at 240°C when $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was used.

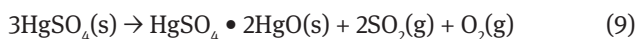
Interestingly, HgSe mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ showed a small peak appearing at a higher temperature of around 280°C . This smaller peak appeared at almost all conditions (substrate, carrier gas), so the effect of the substrate could not have been the cause.

3.1.5 Hg_2SO_4

The CV AAS thermograms for pure Hg_2SO_4 (Figs. 20 and 21) showed three peaks, the first at 296°C , the second at 375°C , and the third at 510°C for nitrogen as the carrier gas. The maximum temperatures were similar for air. The three peaks could not be easily explained. According to literature data [11] the decomposition of Hg_2SO_4 involves three steps. The first stage is disproportion at lower temperatures (Eq. 8) as follows:



In the second stage, the decomposition of mercury(II) sulphate results in the formation of the basic sulphate, Schuetteite ($\text{HgSO}_4 \cdot 2\text{HgO}$), SO_2 and O_2 (Eq. 8):



In the third stage $\text{HgSO}_4 \cdot 2\text{HgO}$ decomposes producing volatile elemental Hg :



The first peak on the thermogram could be associated with the first reaction (Eq. 8), but the subsequent peaks are difficult to interpret. According to the reactions above (Eqs. 8, 9, 10), Tariq and Hill reported two peaks for mercury(I) sulphate, where the heating rate showed almost no influence [11]. It is believed that the intermediate peak in our case may have represented the

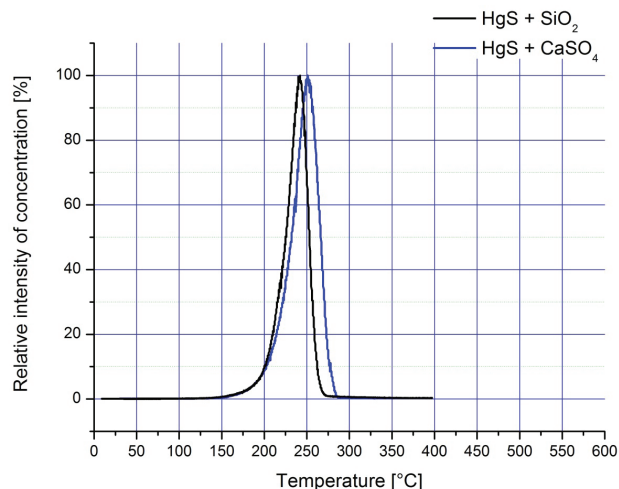


Figure 16: Thermograms of HgS mixtures, obtained by MS.

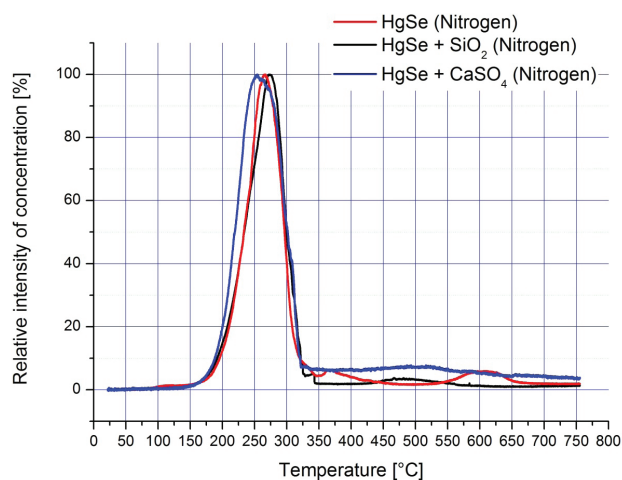


Figure 17: Thermograms of HgSe , purged with nitrogen.

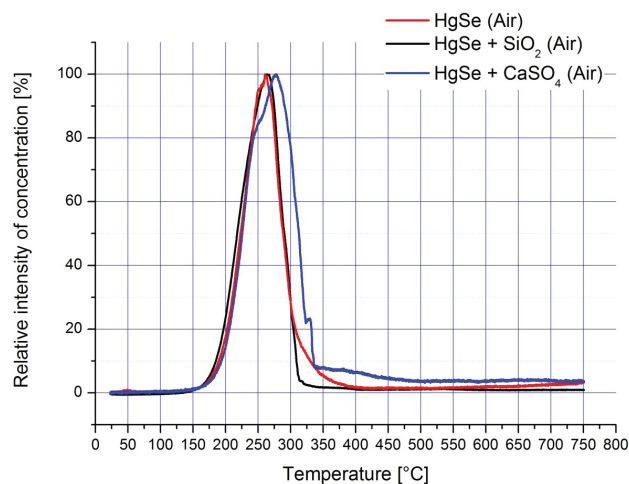


Figure 18: Thermograms of HgSe , purged with air.

temperature instability of $\text{HgSO}_4 \cdot 2\text{HgO}$ at a much slower heating rate.

The thermograms showed a stepwise Hg release from room temperature up to about 350°C with a maximum at 257°C when purged with nitrogen for Hg_2SO_4 mixed with SiO_2 . Regarding the air, a slight shift towards higher temperature was observed. These results are comparable with the thermograms published by Lopez-Anton *et al.* with their results differing for about 20°C towards higher temperature, although they used a much faster heating rate [13]. The substrate clearly affected the release of Hg by lowering the temperature of the major peak.

Four peaks could be seen (Figs. 20–22) for Hg_2SO_4 mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Three of these peaks were quite consistent with the peaks shown by pure Hg_2SO_4 , with a slight downward shift of about 20°C of the peak maximum towards a lower temperature when purged with nitrogen. When purged with air the peak maximum appeared at almost the same temperature as the peak maximum of pure Hg_2SO_4 . Besides the major peak, two other peaks could be observed, the first at a temperature of about 260°C and the second at a temperature of 330°C . The small peak which could be seen in the range of 25°C to 100°C regardless of carrier gas used, probably represented unbound $\text{Hg}(\text{O})$ that could be released from the Hg compound during the mechanical pre-treatment of the sample.

Four peaks for Hg_2SO_4 mixed with SiO_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, with a peak maximum at 218°C , were obtained by MS. Smaller peaks appeared at 275°C and at 390°C in the mixture with SiO_2 , while other smaller peaks appeared at higher temperatures (375°C and 435°C) for the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ substrate. In addition to these listed peaks, Hg_2SO_4 with both substrates also had another peak in common at lower temperatures at about $70\text{--}80^\circ\text{C}$. This also occurred in the thermograms of other Hg compounds, most probably related to $\text{Hg}(\text{O})$ formed as a result of the decomposition and subsequent desorption of $\text{Hg}(\text{O})$.

The appearance of multiple peaks can be explained as suggested above for the CV AAS method, with the exception of the first peak which may be related to the presence of $\text{Hg}(\text{O})$ in the samples itself [11].

3.1.6 HgSO_4 :

The thermograms obtained by CV AAS (Figs. 23 and 24), showed large differences in shapes for pure HgSO_4 and those where HgSO_4 was mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or SiO_2 . Pure HgSO_4 showed one main peak at a temperature of 545°C or 565°C for nitrogen or air, respectively. Similar thermograms were obtained for HgSO_4 mixed with

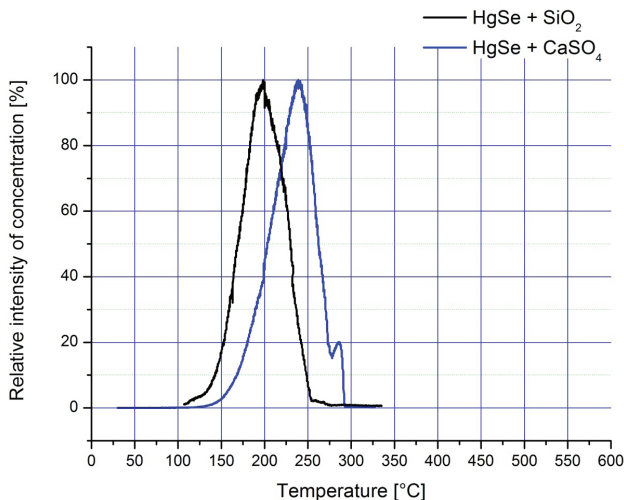


Figure 19: Thermograms of HgSe mixtures, obtained by MS.

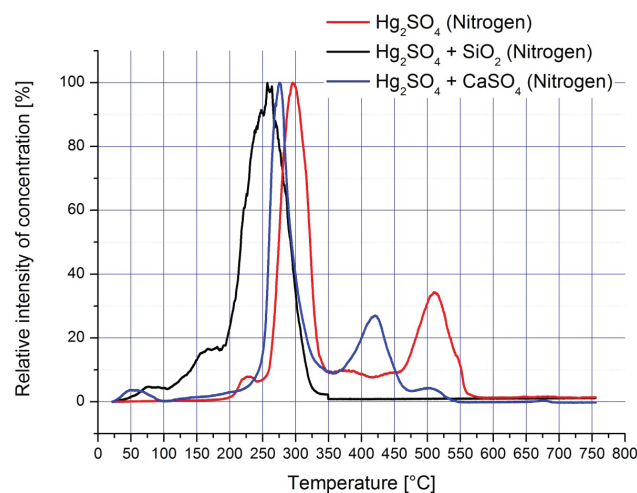


Figure 20: Thermograms of Hg_2SO_4 , purged with nitrogen.

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Small Hg peaks could also be observed in the temperature range between 200 and 470°C . Although one step decomposition was suggested by some authors, it seems more likely that HgSO_4 decomposes through several stages [11,15,20,31] (Eqs. 9 and 10). Collins *et al.* suggested that mercury (II) sulphate may sublime, as confirmed by the detection of a peak in the mass spectra which corresponds to Hg^{2+} [31].

When HgSO_4 was mixed with SiO_2 and purged with nitrogen, a multistage decomposition occurred in the temperature range from room temperature to 570°C with several irreproducible peaks. When air was used as the carrier gas, three main peaks could be seen in the range from 60 to about 600°C . Multiple and irreproducible peaks may reflect unstable intermediate breakdown

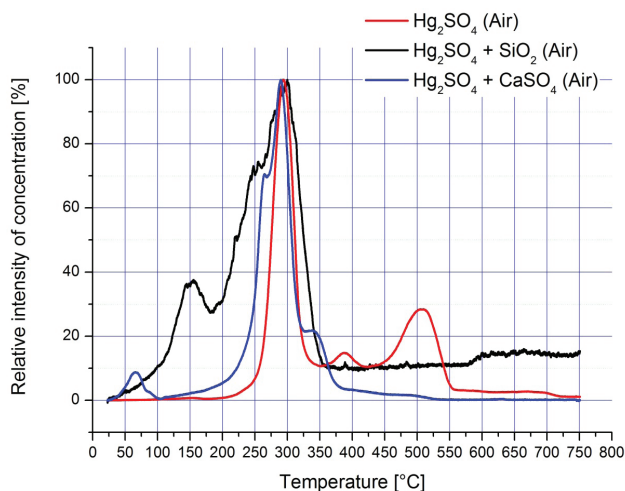


Figure 21: Thermograms of Hg_2SO_4 , purged with air.

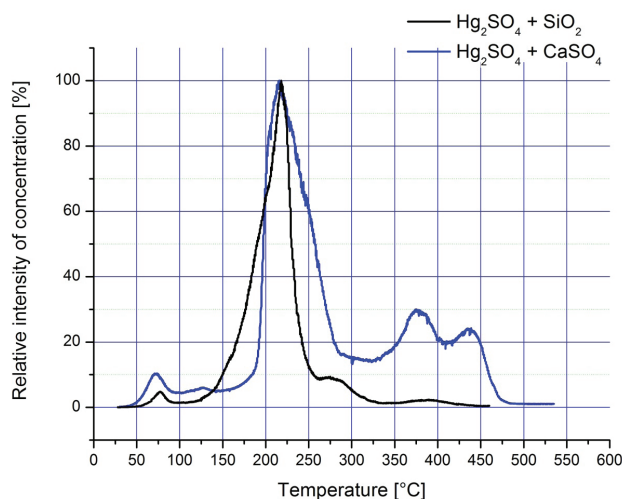


Figure 22: Thermograms of Hg_2SO_4 mixtures, obtained by MS.

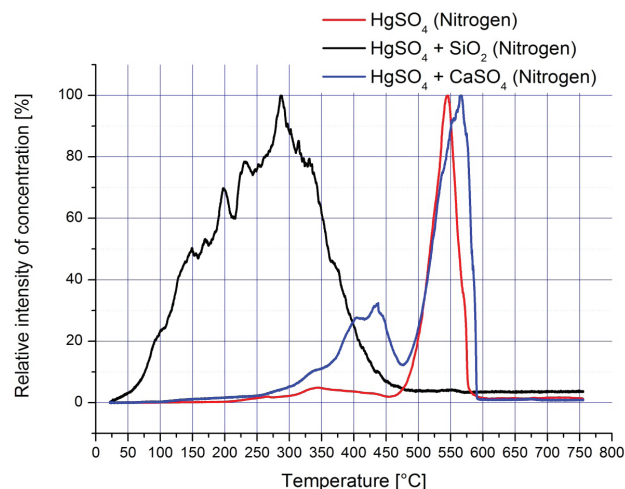


Figure 23: Thermograms of HgSO_4 , purged with nitrogen.

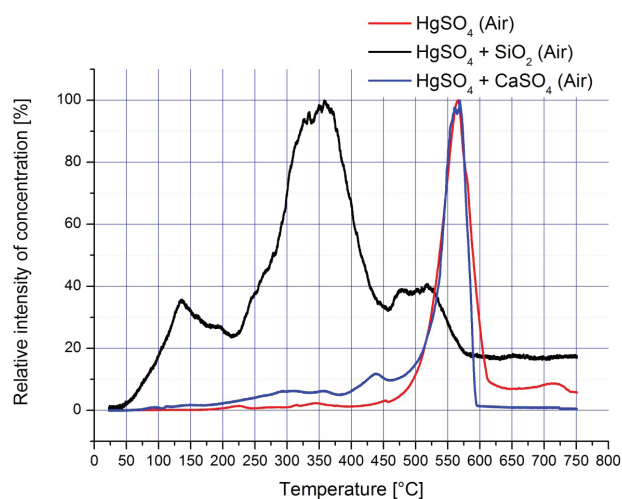


Figure 24: Thermograms of HgSO_4 , purged with air.

processes due to slow heating and/or interactions with the substrate.

A multistep decomposition can be seen in the thermogram of HgSO_4 mixed with SiO_2 (Fig. 25), as mentioned by Collins *et al.* [31], and Tariq and Hill [11], while HgSO_4 mainly showed a single step decomposition when mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, although its decomposition through several stages is more likely (Eqs. 9 and 10) [11]. The explanation for a single peak could be found in the first step of the decomposition without the production of a volatile Hg compound (Eq. 9) [11]. The four peaks that appeared during thermal decomposition of the Hg compound mixed with SiO_2 occurred at 90°C, 280°C and

415°C, with the major peak at 175°C. HgSO_4 mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ displayed a peak at a temperature of 460°C.

In comparison with the CV AAS method, MS revealed a much clearer decomposition when mercury(II) sulphate was mixed with SiO_2 , although the temperature range of Hg release was quite similar (room temperature to 475°C). In comparing the methods for HgSO_4 mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, a similar decomposition could be assumed, although the Hg compound tested with CV AAS method showed a larger second peak than when tested by the MS method. As already evident from the thermograms of the CV AAS method, the substrate and carrier gas significantly affected the release of Hg from HgSO_4 .

3.1.7 HgF₂:

According to the literature data, HgF₂ is not a stable compound, and is usually found as HgF₂ • 2H₂O or HgFOH [32]. Pure HgF₂ could be formed by the disproportionation of Hg₂F₂, when heated above 570°C. HgF₂ then decomposed at 645°C [33].



Compared with other halides, HgF₂ has a very high melting and boiling point due to its ionic structure. This property causes the decomposition (dissociation) of HgF₂ when it is in contact with water and a fast transformation into HgO occurs [33].



However, the experiments with CV AAS and MS indicated that pure HgF₂ and HgF₂ mixed with SiO₂ or CaSO₄ • 2H₂O decomposed through several stages (Figs. 26-29). This could be attributed to the purity of the chemical that probably contained the mixture of the Hg-F species. Humidity in the air also affects the further formation and transformation of compounds during heating. The decomposition of HgF₂ • 2H₂O could release HgO and HF when heated [34]. As already mentioned, released water could cause the transformation of HgF₂ into HgO [32-35]. In general, many similarities were found between thermograms of HgF₂ and HgO described below (Figs. 8-13 and 26-29).

For HgF₂ the major peak appeared at about 450°C or 430°C when purged with nitrogen or air, respectively (Figs. 26 and 27). Pure compound HgF₂ was also placed on a ceramic boat due to the possibility of fluorides reacting with silica (Fig. 28). Only one distinct peak at about 450°C was obtained and was consistent with the major peak of pure HgO (red or yellow). The interactions of HgF₂ with the quartz boat are clearly evident by comparing Figs. 26-28.

HgF₂ mixed with SiO₂ peaks showed a similar pattern in nitrogen or air (Figs. 26 and 27). Two peaks could be seen in both cases, while the second peak was divided into two smaller peaks when purged with nitrogen. SiO₂ caused the shift of released peaks towards lower temperatures. During the heating HgF₂ probably transformed into HgO. Due to the interaction between SiO₂ and HF that was released by the decomposition of HgFX (X = OH, F • 2H₂O), water was formed which could react with HgF₂ and, according to Eq. 12, transformed into HgO. The first small peak probably belongs to Hg(O) formed during the preparation of the sample or the interaction with the substrate and its decomposition.

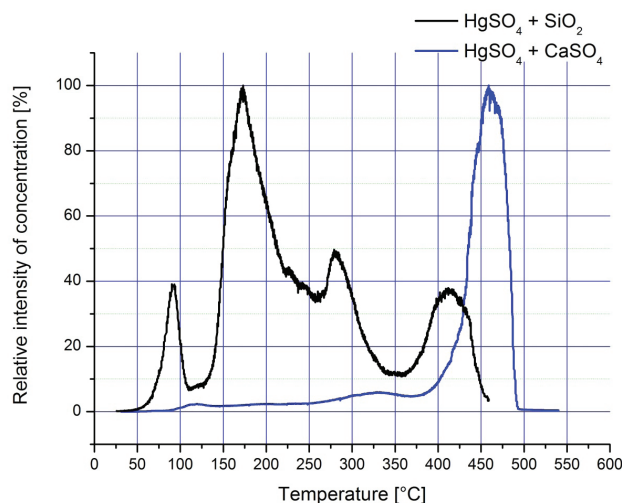


Figure 25: Thermograms of HgSO₄ mixtures, obtained by MS.

When HgF₂ was mixed with CaSO₄ • 2H₂O, one main peak with a temperature of around 215°C could be seen when purged with nitrogen (Fig. 26). When purged with air, three peaks emerged, with the third peak being very low (Fig. 27). The substrate CaSO₄ • 2H₂O contained inbound water which released during the heating process and probably caused the transformation of HgF₂ with CaSO₄ • 2H₂O into HgO. Interestingly, a very small peak could be seen at temperatures of around 430°C which was consistent with the pure HgO compounds (Figs. 8, 9, 26 and 27).

Fig. 29 shows a MS thermogram of HgF₂ with different substrates. Although literature data also suggest sublimation of HgF₂ [32], results obtained using both methods (CV AAS and MS) indicate the decomposition through several stages.

A three step decomposition process was observed when HgF₂ was mixed with SiO₂, or CaSO₄ • 2H₂O, although the temperatures at which Hg was released and their relative intensities were different (Fig. 29).

SiO₂ (Fig. 29) shows that the first peak probably belongs to elemental Hg(O), similar to CV AAS. The second and third peak could represent HgO. The comparison of thermograms for pure HgO mixed with SiO₂ and HgF₂ mixed with SiO₂ (Figs. 10, 13 and 29), shows a similar pattern. Thermograms that represent the release of HgO mixed with SiO₂ have the highest second, and the lowest first peak, while the height of the third peak is dependent on the HgO compound, where the red HgO shows a higher peak (Figs. 10 and 13). HgF₂ mixed with SiO₂ shows that the third peak is the highest and probably represents the release of HgO after it has already been fully transformed (Fig. 29).

HgF_2 mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ shows that the first two peaks are higher compared to those thermograms of both HgO mixtures with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, while the third is very low (Figs. 10, 13 and 29). The thermogram (Fig. 29) shows that the first two peaks probably represent released Hg during heating and formation of HgO whereby the third peak represents traces of HgO . Comparing HgF_2 and HgO mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Figs. 10, 13 and 29) shows similarities in the temperature pattern of released Hg .

Thermograms obtained by CV AAS and MS show the connection between HgO and HgF_2 (Figs. 8-13 and 26-29). HgF_2 is very sensitive to the humidity and according to the experiment that was conducted on the ceramic boat (Fig. 28), the transformation into HgO occurred in the presence of air.

4 Conclusion

Experiments conducted during this research showed that the pyrolytic/combustion approach requires an understanding of the reactions of Hg compounds at higher temperatures. However, the mechanisms of such decompositions have not been studied in detail so far. The results of our work suggest that not only the carrier gas, its flow rate and substrate but also the heating rate and the material that is in contact with the samples affect the degradation pattern of Hg compounds. As a consequence, the heights and shapes of the peaks obtained, as well as their number and the temperature at which breakdown products appear, vary significantly for some compounds, particularly for the sulphates and fluoride. These processes are not fully understood as yet.

In the effort of reaching the long-term goal of this work, which was to develop a methodology for identification of Hg compounds in environmental and industrial solid materials, we realized that a number of experimental factors and, in particular the matrix itself, prevent the method to be applied to solid matrices of unknown composition. The spiking of matrices with pure compounds can help in the identification of Hg compounds and understanding the effects of the substrate on mercury temperature stability and Hg appearance in thermograms. The limitations, however, are related to the limited number of pure Hg compounds, which may not be representative of those contained in the solid matrix.

Although the primary goal was not fully achieved, we realized that the methodology developed in this study has a practical value. It provides reproducible and sensitive results of temperature dependent Hg decomposition

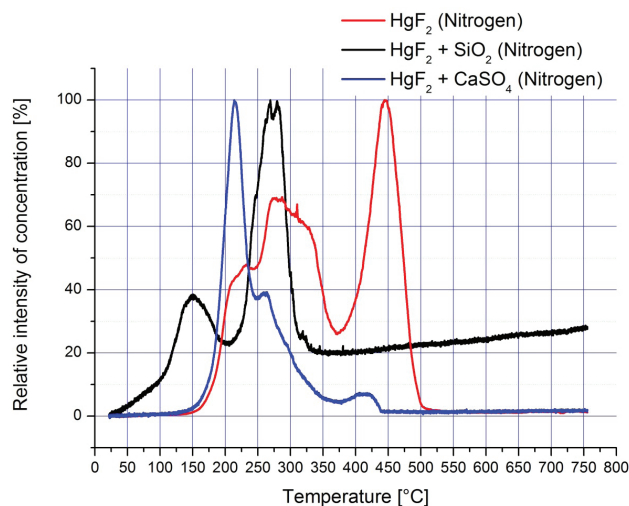


Figure 26: Thermograms of HgF_2 , purged with nitrogen.

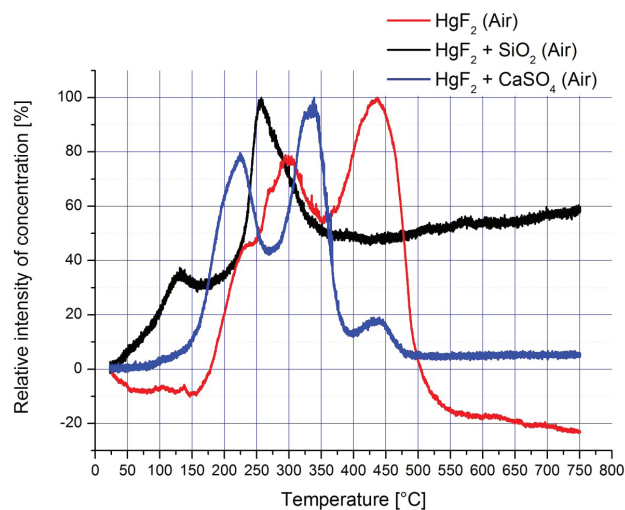


Figure 27: Thermograms of HgF_2 , purged with air.

pattern and can be used for the identification of temperature stability of mercury compounds contained in various substrates/materials. This can be applied in the identification of potential mercury release/emissions from materials subjected to elevated temperature treatments in various industries. Further fractionation experiments will, therefore, include mixtures of Hg compounds with different substrates, intended to resemble complex matrices for which temperature fractionation could provide useful information (for example coal, gypsum from industry, limestone, and materials used for adsorption at higher temperatures).

The potential of the method for separation and quantification of different Hg compounds in solid materials

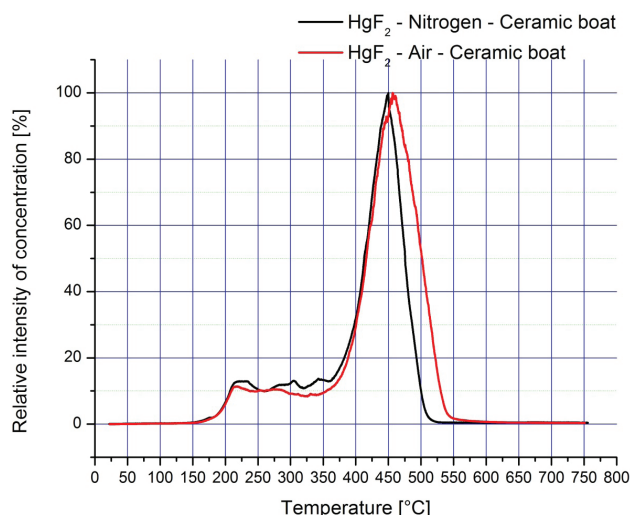


Figure 28: Thermograms of HgF_2 on ceramic boat, purged with air.

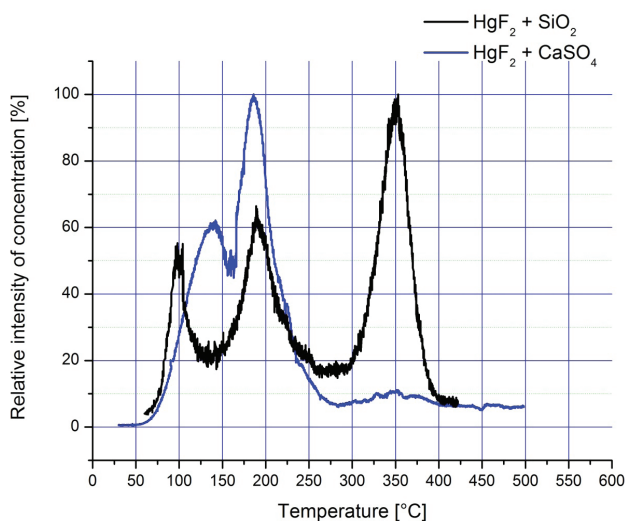


Figure 29: Thermograms of HgF_2 mixtures, obtained by MS.

requires further investigations. Although the literature data available so far is useful, direct comparisons are difficult due to differences in the approaches used and the problems of interpretation when complex mixtures are being considered.

Acknowledgment: This work is supported by the ARRS program P1-0143 and a project J1-4288 and the ARRS young researcher program as well as the program “Young researchers from Industry 2010” partly financed by the European Union, European Social Fund. The project also addresses the WP 4 of the EMRP project ENV02. Thanks are due to dr. A. Stergaršek for useful

discussion and suggestions during the preparation of the manuscript. Linguistic corrections of dr. A.R. Byrne are also acknowledged.

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