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Programmable thermal dissociation of reactive gaseous mercury – a potential approach to chemical speciation: results from a field study

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Abstract

The use of programmable thermal dissociation (PTD) as an approach to investigating the chemical speciation of reactive gaseous mercury (RGM, Hg^{2+}) has been explored in a field study. In this approach RGM is collected on a denuder and analyzed using PTD. The denuder is placed in an oven and the dissociation of the RGM is measured, as a function of temperature, by monitoring the evolution of elemental mercury (GEM, Hg^0) in real time using laser-induced fluorescence (LIF). The technique was tested in a field campaign at a coal-fired power plant in Pensacola, Florida. Uncoated tubular denuders were used to obtain samples from the plant's stack exhaust gases and from the stack plume, downwind of the stack using an airship. The PTD profiles from these samples were compared with PTD profiles of $HgCl_2$.

1 Introduction

The specific chemical speciation of mercury in flue gas emitted from coal-fired power plants (CFPPs) has important implications for its impact on the environment. The rate of wet and dry deposition and any potential atmospheric reactivity will depend both on the oxidation state of mercury and also on the specific chemical form of any oxidized mercury. The importance of understanding chemical speciation has been highlighted by work that suggests that oxidized mercury may be reduced to elemental mercury in power plant plumes.

The first observations of in-plume reduction were reported by Edgerton et al., (2006) who measured gaseous elemental mercury (GEM, Hg^0), reactive gaseous mercury (RGM, Hg^{2+}), and fine particulate mercury (Hg-P) at three sites in the southeastern United States (US), using simultaneous measurements of SO_2 and NO_y to identify plumes from CFPPs. Their measurements suggested that total-Hg (i.e., GEM + RGM) was essentially conserved from the point of emission to the sampling site; however GEM was the dominant component with less than 20 % present as RGM. This contrasted strongly with speciation estimates obtained from EPRI-ICR model equations for CFPPs that burn bituminous coal. The EPRI-ICR model (EPRI, 2000) is an empirical correlation model developed with ICR (EPA Information Collection Rule) coal analysis data and stack test data and it predicted that RGM should be the dominant component of the total mercury in the observed plumes.

Lohman et al. (2006) simulated nine power plant plume events with a reactive plume model that included a comprehensive treatment of plume dispersion, transformation, and deposition. Their study focused on observations at one of the sites, Yorkville, GA, used in the Edgerton et al. (2006) study. The EPRI-ICR model was used to predict the speciation of the mercury emitted from the CFPP's in the vicinity of the Yorkville site. The reactive plume model was then used to examine any change in the speciation of mercury as a result of in-plume chemistry. The model simulations failed to reproduce any depletion in RGM that could rationalize the observations of Edgerton et al. (2006) and, as possible explanations, they modeled RGM reduction to GEM in the plume by unknown chemistry, rapid reduction of RGM on ground surfaces, and/or an overestimation of the RGM fraction in the power plant emissions by the EPRI-ICR model. The incorporation of either a pseudo-first order decomposition of RGM or reaction with SO_2 as possible in-plume reduction processes produced better agreement with the observations.

In this context, the Electric Power Research Institute (EPRI) and the United States Environmental Protection Agency (USEPA) sponsored a major field campaign at CFPP Crist in Pensacola, Florida. The objectives of the campaign were, by making simultaneous measurements of both GEM and RGM in the boiler stack and in the stack emission plume, to A) determine if significant reduction of RGM was occurring in the plume; and B) investigate the rate of reaction if significant reduction was observed (Landis et al., 2009). If GEM/RGM ratios in the plume were observed to be significantly higher than those ratios within the stack, then this would be evidence of such conversion occurring. The stack measurements were made using both a mercury continuous emission monitoring system (CEMS) and the Ontario Hydro method to inter-compare methods and provide confidence in the measured stack concentrations. The plume measurements were made using an airship that could maintain the sampling instrumentation within the plume and measure at a variety of distances from the stack to follow the evolution of the plume chemistry. The plume measurements were designed to incorporate both a CEMS system that was identical to the stack system, avoiding instrumental bias, together with manual denuder measurements of RGM. In addition, a variety of ancillary measurements were made both in the stack and plume.

The chemistry of mercury in combustion emissions has been reviewed in detail by Schofield (2008) who concluded that heterogeneous processes are responsible for mercury oxidation in flue gas with homogeneous gas phase chemistry playing no role. This explains both the variability in the fraction of total mercury that is oxidized in CFPP and the inability of combustion models to predict this variability. Prior work on the speciation of mercury in CFPP flue gas has attempted to quantitatively measure the concentrations of GEM and total RGM. It is currently assumed that mercuric chloride, $HgCl_2$, is the major component of oxidized mercury in the combustor (Galbreath and Zygarlicke, 1996; Schofield, 2008), and hence the major component of the oxidized mercury in the exhaust plume; however, no direct measurements of $HgCl_2$ in either stack or plume gases have confirmed this. Identification of the specific chemical components of RGM would improve our understanding of the mercury oxidation chemistry within power plant combustion systems and allow us to better understand the fate of RGM after it exits the power plant stack and interacts with the ambient atmosphere. Preliminary studies in our laboratory (Donohoue, 2008) suggested that collection of RGM on denuders coupled with analysis using programmable thermal dissociation (PTD) could provide information on the specific chemical speciation of RGM. As a result, PTD measurements were included as a speculative component of the Plant Crist campaign, but precluding any additional characterization of the PTD approach prior to the field campaign. In this sense the field measurements were an attempt to characterize the potential of PTD analysis applied to samples collected in a realistic combustion environment. It was in effect a "proof of concept" experiment. The results, although preliminary in nature, are of value because of the unique nature of this field experiment, with simultaneous sampling in the stack and the stack plume.

2 Experimental approach

2.1 Conventional denuder sampling

Since PTD is not a commonly used analytical method, it is useful to contrast the PTD technique with “conventional denuder sampling” as a route to the measurement of total RGM concentrations. The use of denuder sampling coupled with thermal dissociation has been described by Landis et al. (2002) and forms the basis of a commercially available RGM measurement system, the Tekran Model 1130 Mercury Speciation Unit (Tekran, 2010). In this instrument air is pulled through a KCl coated annular denuder that captures RGM but transmits elemental and particulate mercury. After a period of sampling the denuder is flushed with zero air and the denuder is heated to 500 °C. The RGM is thermally decomposed producing elemental mercury that desorbs from the denuder surface and is then captured by a Tekran 2537 Mercury vapor analyzer. In the Tekran 2537 the elemental mercury is collected by amalgamation on a gold cartridge during a sampling phase. The instrument is then flushed with argon and the mercury desorbed by heating the gold cartridge. The desorbed gas phase mercury is detected by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS).

2.2 Programmable Thermal Dissociation

In PTD, RGM is sampled on a denuder and during the thermal analysis we monitor the extent of RGM decomposition as a function of temperature in real time by measuring the evolution of GEM produced during decomposition. PTD could be considered to be somewhat analogous to thermogravimetric analysis. However, in PTD the evolution of a gas phase product is monitored, rather than monitoring the decrease in the weight of the sample. The sample gas is pulled through a quartz or pyrex tube that acts as a denuder and captures RGM but transmits elemental and particulate mercury. The collection efficiency of the denuder is not known and PTD is not designed to produce a quantitative measurement of RGM concentration. After a period of sampling the denuder is transported to a laboratory, flushed with He and then heated in a series of temperature ramps in an oven. As the denuder temperature increases, RGM dissociates and the GEM product is desorbed from the denuder wall. The GEM evolution is monitored in real time using laser-induced fluorescence (LIF). Comparison of the PTD profiles of unknown samples with profiles of known oxidized mercury compounds may provide information on the chemical identity of the sample. Since PTD is an indirect technique and different compounds can have identical or very similar decomposition properties it is unlikely to provide a definitive molecular identification. However, it should be possible to indicate whether the PTD profile of a sample is consistent with a particular molecular species or class of species. $HgCl_2$ is widely assumed to be a major component of the RGM in the stack gas of CFPP's and in the ambient atmosphere (Landis et al. 2002), and in this work PTD is used to see if observations are consistent with that assumption.

2.3 Denuder sampling

2.3.1 Sampling during the Crist campaign

Field sampling at CFPP Crist took place between 18 February and 1 March 2008. The plant has four coal-fired units, two of which were operational during the campaign. The operational units, #6 (320 MW) and #7 (500 MW) shared a common stack and mercury continuous emissions monitoring systems (CEMS) were located at the output of each unit prior to discharge into the stack. In addition to the mercury CEMS, independent measurements of mercury concentration were made using the Ontario Hydro method and sorbent traps. NO_x, SO_2 and CO_2, were measured by the Crist CEMS instrumentation. Mercury emissions were dominated by the exhaust from unit #7, which typically contained 5–7 $\mu g\,m^{-3}$ of mercury, more than 90 % of which was present as RGM. The unit #6 exhaust typically contained less than 1 µg m^{-3} of mercury and contained equal amounts of GEM and RGM. As a consequence, mercury in the stack gas was largely in the form of RGM. The Ontario Hydro and CEMS RGM stack measurements showed good agreement although the agreement between the GEM measurements was more problematic, reflecting the much lower concentrations of elemental mercury in the stack gas (Landis et al., 2009).

A preliminary laboratory assessment of the utility of PTD on KCl coated annular denuders is described by Donohoue (2008). Due to time constraints we were not able to perform additional experiments to characterize the best types of denuders to use or the optimal sampling and analysis configurations. Based on the prospect of sharper PTD profiles, together with time and cost limitations, uncoated tubular denuders were selected for PTD analysis during the campaign. A total of 17 quartz and Pyrex tubular denuders approximately 2.5 cm diameter and 50 cm long were used during the sampling campaign. Both quartz and Pyrex and etched and unetched denuders were used in order to assess the utility of the material and the utility of the surface area enhancement that is produced by the URG etching process. Denuders designed for use on the airborne platform had #30 screw ends, as described by Landis (2002), to ensure compatibility with the URG Corporation filter and sampling system designed by the EPA investigators. Two of these denuders were constructed of quartz and eight were constructed of Pyrex. One of the quartz tubes and three of the Pyrex tubes had a 10″ central section that was etched by URG Corporation to enhance the surface area. This etching is similar to that found in the KCl coated annular denuders described by Landis et al. (2002). The remaining tubes were constructed of Pyrex and had o-ring ends for compatibility with the Ontario Hydro stack sampling system. Two of these tubes had etched 10″ central sections. Denuders were prepared by rinsing with concentrated KOH, followed by distilled water, 10 % nitric acid solution, distilled water and finally methanol. They were dried in air without heating.

It was necessary to analyze the denuders and then clean them for additional sampling, making on-site analysis desirable. Analysis was performed at the University of

West Florida (UWF), located approximately 7 miles from Plant Crist and 5 miles from Pensacola Airport, the base of operations for the airship. Denuder sampling experience prior to the Crist campaign had been a limited set of laboratory studies and high levels of RGM in the stack and blimp samples that could be analyzed using single photon LIF were anticipated.

During the sampling campaign the dye laser that was used to excite fluorescence showed short term drift, due to a damaged output coupler that had been degrading the Nd-Yag pump laser over the course of the two week sampling period, and possibly also due to temperature variation in the laboratory at UWF. This short-term drift produced background shifts in a number of the dissociation profiles.

2.3.2 Stack sampling

All stack sampling was performed by personnel from the Energy and Engineering Research Center (EERC), University of North Dakota in conjunction with their measurements of GEM and RGM using the Ontario Hydro method. For stack sampling the gas was pumped from the stack and diluted to prevent condensation. Most of the samples were obtained with a quartz particle filter in the sampling line. The filter was located in the stack and had a capture efficiency of 99.95 % for 0.3 µm particles. Typical sampling times were 1–30 min at the stack at 5 SLPM total flow (4.5 SLPM dilution air + 0.5 SLPM stack gas). Typical stack gas temperatures at the sampling point were ∼150 °C and the gas had cooled to ∼25 °C before reaching the denuder. After sampling, the denuders were capped, and once sampling was completed for the day they were transported to UWF for analysis. Denuders were stored in the analysis laboratory at room temperature and typically analyzed the day following sampling.

2.3.3 In-plume sampling

As described by Landis et al. (2009), an airship was used to sample the exhaust plume with the objective of holding the sampling modules within the centerline of the plume at approximately the same position for an extended period of time. The sampling PVC modules were suspended 60 feet below the airship's gondola and connected by umbilical tubes that included sample lines connected to pumps in the gondola. In addition to denuders and filters located in the sampling modules, a dual TEKRAN system located in the gondola ran in parallel and measured total gaseous mercury (RGM+GEM) and GEM separately at 2.5 min intervals. In addition, SO_2, NO_y, and CO_2 were measured continuously and used as plume-detection tracers.

The in-plume sampling was performed by EPA personnel. The sampling module for the PTD denuders pulled air directly from the plume at ambient temperature and this was drawn though the denuder at 3.5 SLPM. After a sampling period of typically one hour the module was pulled up into the airship's gondola, the denuder was removed and capped, a fresh denuder loaded into the module, and the module lowered back into the plume for another period of sampling. After the airship landed the denuders were transported to UWF for analysis. A total of 20 uncoated tubular denuder samples were obtained on six days during the campaign. The airship's sampling protocol involved taking one sample upwind of the stack to establish background conditions followed by a sample downwind and close to the stack, and then a final sample further downwind in-plume; referred to as "close-in" and "further-out", respectively.

2.4 Analysis by Programmable Thermal Dissociation (PTD)

Analysis was performed using PTD, heating the denuders in a series of steps and monitoring the evolution of GEM as a function of time using single photon LIF. Analysis was performed in He buffer to enhance detection sensitivity for GEM. For analysis the denuders were placed in a clamshell furnace and flushed with He at 0.45 L/min to remove all ambient gas and this flow was maintained for the full heating cycle. Two thermal cycles were used and are subsequently referred to as "oven 1" or "oven 2". In the "oven 1" cycle the temperature was raised to 100 °C and then increased in five 25 °C ramps up to 225 °C with each ramping cycle taking 5 min. Finally, the oven temperature was rapidly increased to 500 °C and held at this temperature for 5 min. In the other cycle "oven

2” the oven temperature was increased to 100 °C, 175 °C, 200 °C, four 10 °C ramps to 250 °C and then rapidly increased to 500 °C. Again each ramping step took 5 min. The “oven 1” profile was similar to the profile used in the analysis of the coated annular denuders described by Donohoue (2008) and was designed to capture species that dissociated at a significantly lower temperature than the mercuric halides. The “oven 2” profile, which began with a much steeper initial ramp from 100 °C to 170 °C and then with smaller increments to 250 °C, was designed to try and distinguish between compounds with similar decomposition temperatures in the 170–250 °C range. Throughout the initial flushing and the heating cycle the gas that left the denuder passed through a fluorescence cell and the concentration of GEM was monitored by single photon LIF. After the heating cycle was complete the LIF signal was calibrated by injecting a known amount of GEM into the gas flow through a septum as described below.

2.5 GEM detection

GEM was detected by single photon, resonance LIF using excitation of the 6^3P_1-6^1S_0 transition at 253.7 nm. A frequency doubled dye laser pumped by the third harmonic of a Nd-Yag laser was used to generate the excitation beam. Resonance fluorescence was observed using a Hammamatsu 1P28 photomultiplier tube with a 253 nm filter. In this approach the detection PMT detects both LIF and laser scatter and thus sensitivity is limited by the ratio of intensity of the LIF signal to the laser scatter. Since the 6^3P_1 level is efficiently quenched by both O_2 and N_2 the thermal analysis was performed in He buffer gas to achieve good detection sensitivity. The PTD profiles of all the samples collected during the Crist campaign used uncoated tubular denuders and the analysis used single photon LIF.

2.6 Calibration of absolute Hg^0 concentration

The LIF signal was converted into an absolute Hg^0 concentration by injecting known amounts of GEM into the detection cell through a septum. A saturated calibration gas was obtained by taking a sample of GEM and allowing it to equilibrate at 6 °C for over 24 h before initial use. The elemental mercury was kept in a Pyrex vial capped with a septum in Ar bath gas. The transfer syringe was at room temperature and the saturated gas was withdrawn from the vial and directly injected slightly upstream of the fluorescence cell. The GEM concentration was calculated assuming saturation, correcting for the temperature difference between the syringe and the vial, and using the temperature dependence of the vapor pressure given by the Dumarey equation (Dumarey et al., 2010).

2.7 $HgCl_2$ calibration profiles

After the completion of the sampling campaign at Plant Crist, thermal dissociation profiles of $HgCl_2$ were measured for comparison with stack and plume samples. Samples were obtained by flowing N_2 over powdered $HgCl_2$ and passing the gas mixture through denuder tubes that were then analyzed using the "oven 1" or "oven 2" cycles. Calibration profiles from samples deposited at N_2 flows of 520 sccm and 135 sccm were measured although there were large fluctuations in the deposited amounts of $HgCl_2$ presumably as a result of fluctuating gas phase concentrations during sampling and variations in denuder collection efficiency. 6 PTD profiles were measured using samples deposited at 135 sccm and 2 PTD profiles at the 520 sccm deposition flow using the "oven 1" thermal ramp sequence. A single "oven 2" profile was measured, using a sample deposition flow of 520 sccm.

2.8 Characterization of the oven temperature distribution

After the completion of the Plant Crist campaign and the laboratory $HgCl_2$ calibration experiments we analyzed the temperature distribution along a denuder tube by attaching thermocouples at the ends and center of the inside of a tube and at the center on the outside of the tube. With the oven controller reading at 190 °C the temperature at the center of the denuder was 212 °C on the outside and 204 °C on the inside. The active heating section of the oven was 30 cm long and the temperature differential over the central 18 cm section was 30 °C with a maximum at the center, a drop of 10 °C at 9 cm downstream i.e. in the direction of gas flow, and a drop of 30 °C at 9 cm upstream at the point where cool gas is entering. The differential then increased considerably and was 30 °C cooler 12.5 cm upstream and 50 °C cooler at the 12.5 cm downstream point. The ability of the oven controller to produce reproducible temperature ramps was limited with the temperature typically overshooting the set point.

3 Results: plant Crist field campaign

3.1 Laboratory $HgCl_2$ PTD profiles

Laboratory PTD profiles of $HgCl_2$ were obtained after the completion of the Crist field experiment. As noted in section 2.4, analysis of stack samples used two thermal ramping schemes that we denote as “oven 1” and “oven 2”. Figures 1 and 2 show the individual and averaged calibration profiles obtained at the two deposition flows for the “oven 1” thermal cycle. The single calibration profile obtained for the “oven 2” profile is shown in Fig. 3. The $HgCl_2$ PTD profile in Figs. 5–7 shown for comparison with stack and plume samples analyzed using “oven 1” cycles is the average of the 6 PTD profiles obtained at the 135 sccm flow rate. Figure 1 also gives a sense of the reproducibility of 6 PTD profiles obtained by depositing pure $HgCl_2$ under nominally identical conditions. As noted in Sect. 2.7, the $HgCl_2$ loadings varied considerably presumably as a result of gas phase concentration fluctuations and variations in denuder collection efficiency. In subsequent work we have found that it is extremely difficult to develop stable sources of $HgCl_2$ for calibration purposes and this represents a major challenge in this type of experiment.

3.2 Stack PTD profiles

Figure 4b shows PTD profiles for several stack samples analyzed using the “oven 2” thermal cycle. An “oven 2” PTD profile for pure $HgCl_2$ is shown for comparison in Fig. 4a. The stack profiles show a sharp onset of RGM dissociation at ~200 °C. GEM continues to evolve as the temperature increases, with a spike in RGM dissociation as the oven temperature is ramped to 500 °C. The profiles are similar to the $HgCl_2$ profiles although the onset of dissociation occurs at a slightly lower temperature in the $HgCl_2$ profile. The shape of these profiles is a function of the deposition pattern of RGM on the denuder, the very significant temperature gradient along the denuder during the heating cycle and the direction of buffer gas flow during both sampling and analysis. During the Crist measurements RGM was sampled over the whole denuder surface including the ends that are located outside of the oven and the direction of gas flow was not noted during sampling. As discussed in Sect. 2.8, we have found that during the heating cycle the center portion of the denuder heats most rapidly and the initial production of GEM reflects dissociation of RGM in this section of the denuder. The temperature in the PTD profile figures is the temperature as read by the oven thermocouple and most closely reflects the temperature of the central section of the denuder; the ends of the denuder are significantly cooler. As the temperature increases RGM deposited further from the center reaches decomposition temperature and the final ramp produces decomposition over most of the length of the tube. The oscillations in the PTD profiles appear to be the result of this effect in conjunction with the “ramp and hold for 5 min” sequence that we used for temperature ramping at Crist. In addition, RGM deposition appears to be a function of flow direction, presumably maximum deposition occurs as the flow enters the denuder and decreases as the RGM concentration is depleted as the gas flows down the denuder. The flow-effect becomes more significant as the RGM loading increases. One consequence of the flow-effect is that dissociation profiles are more reproducible if the direction of gas flow through the denuder is the same during sampling and analysis. Since the direction of the sampling flow was not noted during stack sampling, this variation, together with a lack of reproducibility in the oven cycling, contributes to variation in the PTD profiles. Nevertheless, the profiles shown in Fig. 4 are quite similar and consistent with the $HgCl_2$ calibration profile and the onset of RGM dissociation was quite consistent. The observation that these profiles are consistent with the $HgCl_2$ profiles is not intended to imply that this constitutes a definitive identification of $HgCl_2$.

Figure 5b shows PTD profiles of stack samples analyzed with the "oven 1" cycle together with an averaged "oven 1" PTD profile of $HgCl_2$ shown in Fig. 5a. The "oven 1" profiles have a slower temperature ramp between 100 and 200 °C, however we saw no evidence for any RGM species with a lower peak decomposition temperature. The "oven 1" PTD profile for pure $HgCl_2$ shows measurable decomposition at 100 °C and typically peaks at ∼200 °C. In the "oven 1" PTD profiles of stack samples, decomposition begins at a slightly higher temperature but the peak decomposition temperatures of the majority of the stack PTD profiles are consistent with $HgCl_2$ being the sampled component of the deposited RGM. Again we should emphasize that this does not identify or prove that the compound is $HgCl_2$, however we do not see any evidence for a species with a peak decomposition temperature that is significantly lower and could clearly be identified as not being consistent with $HgCl_2$.

As we have noted above, the variation and reproducibility of the PTD profiles is a function of the deposition pattern, the temperature gradient, reproducibility of oven temperature cycling, and the direction of gas flow during both sampling and analysis. During stack sampling it is reasonable to assume that a variety of compounds that are present in the stack gas are being co-deposited on the denuders and this may have some impact on the decomposition temperature. It is also possible that chemical reactions can take place on the surface of the denuder between deposited RGM and other components of the stack gas. In-situ spiking of the stack gas with $HgCl_2$ could address the impact of co-deposition effects.

3.3 In-plume sampling

Figure 6b shows profiles from 28 February, providing evidence of a correlation between sampling in the stack and plume. The "close in" sample shows a well-defined thermal dissociation profile that is similar to the stack profile of the morning of the 29th, as seen in Fig. 5, burning an identical coal mixture. The airship profiles show a GEM signal that occurs prior to the heating cycle. This preheat mercury signal was observed in all of the airship samples including those that were not able to detect any plume RGM. No preheat mercury signal was observed in any of the stack samples. This could be a result of a contamination problem in the adapters used to plumb the screw end denuders into the analysis gas flow system but its origin was not identified. Figure 7 shows the PTD profiles of $HgCl_2$, the "close in" blimp sample and the stack sample from the morning of the 29th. The similarity between the PTD stack and blimp profiles and their similarity to the $HgCl_2$ profile suggest that the species sampled from the stack and the plume are the same and are consistent with the chemical speciation of the sampled RGM being $HgCl_2$. The coal that was used during this sampling period contained the highest level of chlorine seen during the Crist campaign, constituting 97 % of the total halogens with a bromine content of 0.16 % and fluorine as the balance. Comparing PTD profiles of $HgCl_2$ with the PTD profiles of the stack and plume samples suggests they are consistent with $HgCl_2$ as the specific chemical speciation of sampled stack RGM but, as discussed above, this does not prove that the stack RGM is $HgCl_2$. It could also consist of other oxidized mercury compounds that have a similar PTD profile to $HgCl_2$. One possible explanation of the observations of Edgerton et al. (2006) would be a component of the RGM that undergoes slow thermal decomposition at ambient temperatures. No evidence for a significant component of the RGM sample that has a significantly lower decomposition temperature than $HgCl_2$ was observed.

3.4 Denuder sampling efficiencies

The objective of this component of the Crist study was to investigate the potential of PTD for chemical speciation of RGM. As noted above, the collection efficiency of the denuder is not known and PTD will not give a quantitative measurement of RGM concentration under these conditions. However the PTD profiles were also calibrated for Hg^0 as discussed in Sect. 2.6. This provides an approximate measure of the total amount of RGM collected on the denuder. Since the RGM stack concentrations were measured independently, we can obtain an approximate measure of the sampling efficiency of the denuders as a check on the integrity of the measurements. For example, a sampling efficiency in excess of 100 % would imply major problems with denuder contamination. All denuder sampling was performed under laminar flow conditions and a theoretical sampling efficiency can be estimated using the Gormley–Kennedy equation (Gormely and Kennedy, 1949). This assumes laminar flow and a sticking coefficient of 1 and requires a tube diameter and a flow rate, which are known, and a diffusion coefficient for the species of interest, which is not known. If a diffusion coefficient of $0.1\,\text{cm}^2\,\text{s}^{-1}$ is assumed, a typical value for molecules in air, we calculate a sampling efficiency of ∼60 % for the stack sampling and ∼70 % for plume sampling. If we assume that the chemical identity of the RGM is $HgCl_2$, we can estimate a diffusion coefficient of $0.04\,\text{cm}^2\,\text{s}^{-1}$ using the mass relationship from Schwarzenbach et al. (1993), and this would give calculated sampling efficiencies of 35 % and 43 % at the stack and plume sampling flow rates. To estimate the actual denuder sampling efficiencies, the total amount of RGM that was sampled was calculated from the stack RGM concentrations as measured by the CEMS instrumentation and sampling flow rate through the denuder. The RGM that was actually deposited on the denuder was taken from the total calibrated PTD profiles and included the final peak obtained during the temperature increase to 500 °C. The RGM actually deposited on the denuder was then divided by the calculated total sampled amount based on the flow and stack concentrations. This then gives an estimate of the denuder sampling efficiency, i.e. the amount of RGM collected on the denuder compared with the total amount of RGM that was sampled from the stack and then flowed through the denuder, but did not necessarily deposit on the walls. These sampling efficiencies are estimates since some RGM was deposited on the ends of the denuders and was not measured. It is also possible that some of the deposited RGM evaporated before decomposition to Hg^0 and this would not have been measured. The efficiencies for stack profiles shown in the figures are given in Table 1. A total of 28 stack profiles were analyzed with sampling efficiencies that ranged from ~1 % to 55 %. Sampling efficiencies from samples obtained with the particle filter in place were typically much lower than estimated from the Gormley-Kennedy equation, ranging from ~1 to 30 %. Three PTD stack profiles were obtained without the particle filter in the sampling stream and the calculated sampling efficiencies were 50 %, 55 % and 37 %, much closer to the estimated values so it appears that the presence of the filter significantly reduced the sampling efficiency. This does not appear to be due to collection of particulate mercury when the filter was removed. These samples were obtained downstream of the electrostatic precipitator and Ontario Hydro measurements found that the concentration of particulate mercury was below detection limits. The shape of the PTD profiles without the filter was consistent with those collected with the filter in place.

An estimate of the collection efficiency of the in-plume samples requires a comparison between sampled RGM and that predicted using the measured stack concentrations and calculated plume dilution ratios. Dilution ratios were based on the measured concentrations of three tracer gases, SO_2, NO_y and CO_2, which were measured in stack and also in the airship. Fig. 8 shows the "background corrected" concentrations of SO_2, NO_y and CO_2 as measured by the airship's sampling system during the 75 min "close in" sampling run on February 28th. The background correction was obtained by subtracting the concentrations measured upstream of the plume. The concentrations shown in Fig. 8 reflect the increase in the concentration of these gases over ambient as the plume gases mix with ambient air. There was little variation in the stack concentrations during the sampling period and the observed variations reflect the difficulties of keeping the airship's sampling system in the plume. The measured airship concentrations of SO_2, NO_y and CO_2 can be used to calculate the dilution of the plume gases as the plume evolved and mixed with ambient air. Because of the variation in concentration, the dilution ratios were calculated for 2.5 min coincident time bins for each tracer gas. The calculated dilution ratio for each tracer gas was then multiplied by the stack RGM concentration measured by the CEMS instrumentation to calculate the mass of RGM sampled by the denuder during each 2.5 min bin. This was summed to calculate the total mass of RGM sampled by the denuder during the 75 min sampling period based on each tracer dilution ratio. Table 2 shows the calculated total amount of RGM sampled by the denuders at the "close in" and "further out" positions. These amounts are calculated from the RGM concentration measured in the stack by the CEMS instrument and the calculated dilution ratio from each tracer. The difference between the values calculated using the three tracers reflects the fact that the three tracers give different integrated dilution ratios, an indication of the difficulty of the measurement.

The observation of the early Hg^0 signal and the drifting baseline complicate the analysis of the dissociation profiles in Fig. 5. The "close-in" profile shows a well-defined dissociation profile between 150–225 °C and a larger area in the final ramp to 500 °C. Taking the total integrated sample gives ∼1.3 ng of Hg^0, 0.61 ng in the structured profile and 0.66 ng in the final ramp to 500 °C. If we take the 0.08 ng from the upwind sample as our field blank we calculate 0.13 ng of RGM deposited on the "further-out" denuder and 1.19 ng deposited on the close in denuder. If we then compare this with the total RGM sampled by the denuders, as calculated from dilution ratios, we find sampling efficiencies of 67 % and 55 % using the SO_2 and NO_y dilution ratios and 100 % from the CO_2 dilution ratio. For the "Further out" denuder we calculate sampling efficiencies of 32 %, 18 % and 32 % respectively. Given the large uncertainty in the dilution ratios these efficiencies suggest that the RGM sampled in-plume is consistent with the levels measured by the CEMS instrument in the stack. This, together with the PTD profiles of the stack and plume samples shown in Fig. 6 suggests that it is possible to use PTD to measure a component of RGM in the stack and follow its evolution in the plume.

3.5 Further development of the PTD approach

In continuing development of the PTD approach focus was on the use of uncoated quartz tubular denuders with an etched central area. The control of the oven ramping temperature is critical for reproducible PTD profiles and we have eliminated the use of a PID temperature controller and the type of "ramp and hold" cycles that were used during the Crist campaign. In addition by using an etched central portion of the denuders it is possible to completely eliminate the large peak that is associated with the final temperature ramp. Typically we now use 5 min of preheating at 50 °C and then a constant ramp from 50–500 °C. Supplement Fig. S1 shows PTD profiles of $HgCl_2$ deposited on etched quartz denuders that are obtained using this 50–500 °C ramping sequence. The mass of $HgCl_2$ deposited varies between 20–50 pg i.e. more than an order of magnitude lower than deposited during the Crist campaign. The profiles are quite reproducible and eliminate the "final ramp" peak and oscillations that are particularly evident in the "oven 1" profiles. The PTD profiles of $HgCl_2$ and $HgBr_2$ were compared and are identical on uncoated tubular denuders. However, this is not relevant to the Crist work because chlorine was the dominant halogen component of all the coal that was burned during the Crist campaign. In contrast, solid samples of HgO and a compound deposited from the heterogeneous reaction of mercury and ozone have PTD profiles that decompose at significantly higher temperature than $HgCl_2$. In other work from this laboratory (Bauer et al, 2012), uncoated quartz denuders with an etched central surface were used to sample from a small aircraft over Mississippi and the Gulf of Mexico. Several samples show evidence for an RGM species that decomposes at a significantly lower temperature than $HgCl_2$ or $HgBr_2$ together with samples that decompose at temperatures that are consistent with the PTD profiles of these mercuric halides. Examples of two such profiles are shown in Supplement Figs. 2 and 3. Supplement Fig. S2 shows a PTD profile of a high altitude sample with a total mass of 58 pg. Supplement Fig. S3 shows a PTD profile of a sample taken at 500 ft in the marine boundary layer over the Gulf of Mexico with a total mass of 56 pg. In both cases the PTD profiles of the flight blanks are shown. These observations are significant in that they may imply there is a form of atmospheric RGM with a PTD profile which is not consistent with speciation as either $HgCl_2$ or $HgBr_2$.

4 Conclusions

Measurements of the chemical speciation of RGM represent a significant analytical challenge. Lack of information on the chemical speciation is perhaps the single biggest obstacle to developing a detailed understanding of the chemical cycling of mercury in the atmosphere. A "proof of concept" experiment as a component of a major field campaign was conducted to test the use of PTD to chemically speciate RGM in a working combustion environment. Thermal dissociation profiles for RGM were obtained in both stack and in-plume samples that suggest that it is possible to track a specific chemical form of RGM from the stack and follow its evolution in the stack plume. The PTD profiles of the stack and plume samples are consistent with $HgCl_2$ being the chemical form of the sampled RGM. It is also possible that the RGM consists of some other oxidized mercury species with a similar decomposition temperature. An example would be $HgBr_2$ but the absence of a significant amount of bromine in the feed coal makes this unlikely.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/33291/2012/acpd-12-33291-2012-supplement.pdf.

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Table 1. Estimated denuder collection efficiencies for stack samples shown in figures. All samples were collected on unetched pyrex tubular denuders.

Sample Date	Sampling Time (min)	PTD Oven Profile	Stack RGM* ($\mu g\, m^{-3}$)	Total RGM** sampled from stack (ng)	Actual RGM*** deposited on denuder (ng)	Denuder Collection Efficiency (%)
18/02/2008	3	1	n/a	n/a	4.8	n/a
18/02/2008	10	2	n/a	n/a	1.8	n/a
23/02/2008	3	1	5.3	7.95	0.98	12
27/02/2008	10	2	5.4	27	0.60	2
28/02/2008	10	2	4	20	0.99	5
29/02/2008	10	1	4.5	22.5	1.2	5
29/02/2008	30	1	4.5	67.5	19.8	29

[*] As measured by CEMS instrumentation;
[**] Based on CEMS stack concentration, sampling flow rate, and sampling time;
[***] As determined using PTD technique.

Table 2. Estimated denuder collection efficiencies for in-plume samples obtained 28/02/2008.

Airship sample	Denuder Type	Actual RGM[*] deposited on denuder (ng)	Total RGM[**] sampled by denuder (ng) as calculated from dilution ratios			Denuder Collection Efficiency (%) as calculated from dilution ratios		
			SO_2	NO_y	CO_2	SO_2	NO_y	CO_2
"Close in"	unetched quartz	1.19	1.78	2.16	1.19	67	55	100
"Further out"	unetched pyrex	0.13	0.41	0.73	0.41	32	18	32

[*] As determined using PTD technique;

[**] Based on CEMS stack concentration and calculated dilution ratio for each tracer.

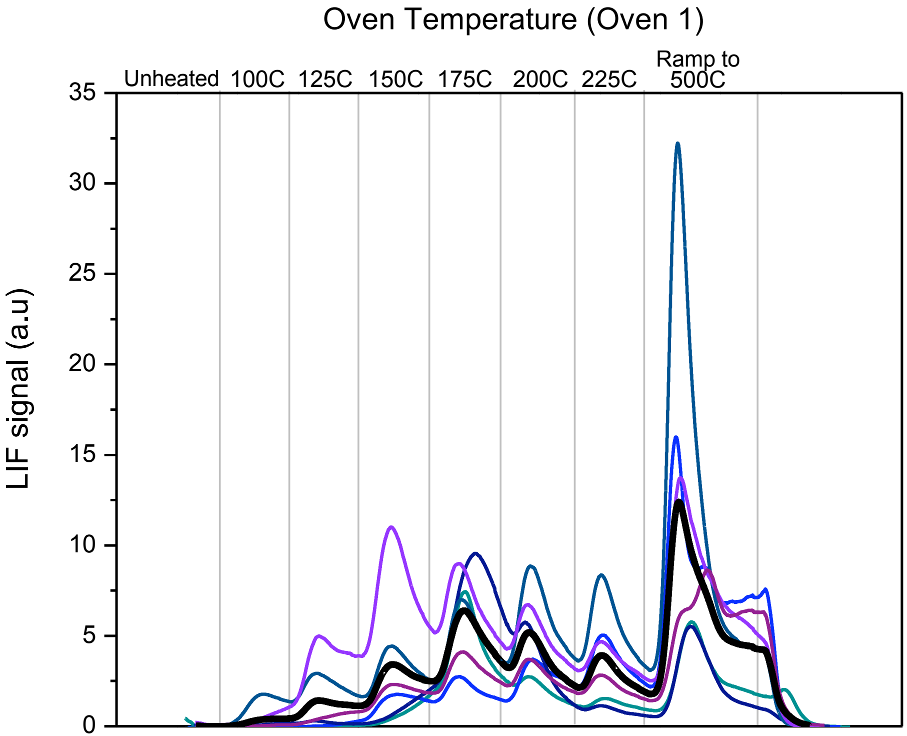

Fig. 1. Six PTD profiles using Oven 1 program for an uncoated tubular denuder loaded with pure $HgCl_2$. Denuders were loaded by flowing N_2 over pure $HgCl_2$ for 1 min at 135 sccm. The average of the six profiles is also shown.

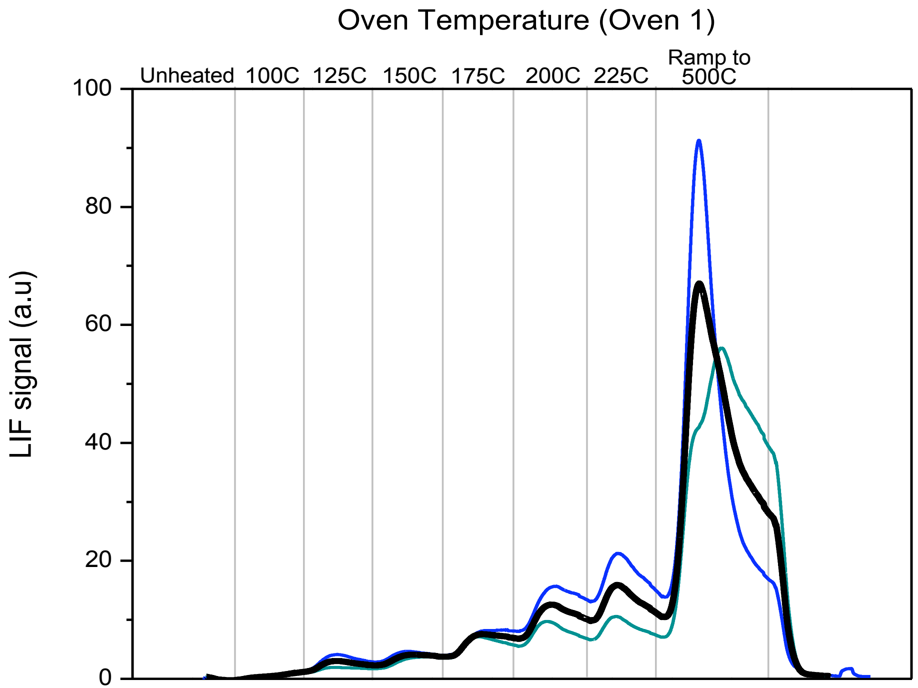

Fig. 2. Two PTD profiles using Oven 1 program for an uncoated tubular denuder loaded with pure $HgCl_2$. Denuders were loaded by flowing N_2 over pure $HgCl_2$ for 1 min at 520 sccm. The average of the two profiles is also shown.

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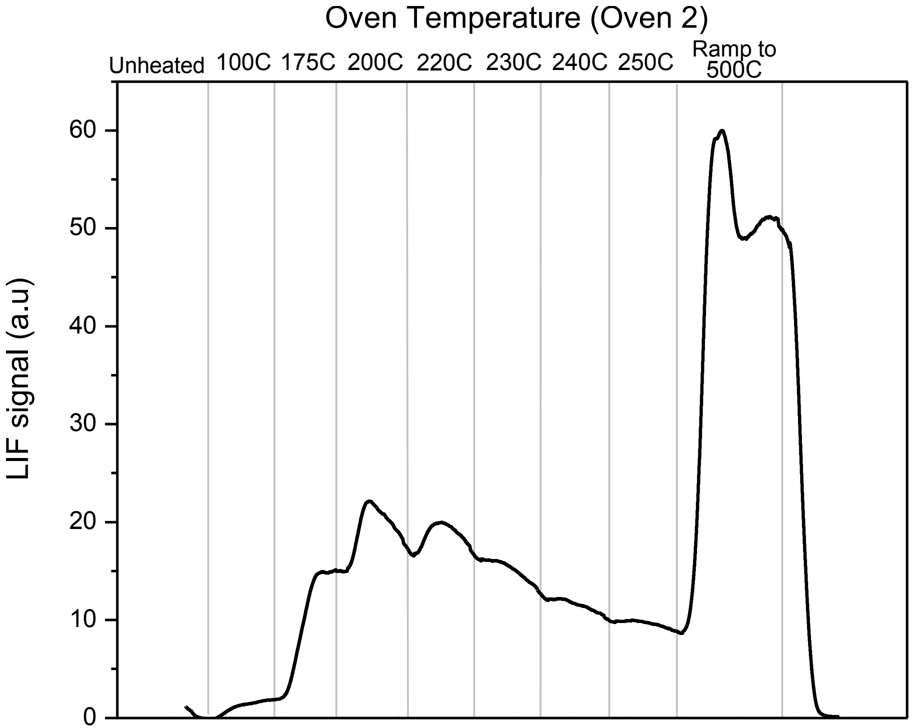

Fig. 3. PTD profiles using Oven 2 program for an uncoated tubular denuder loaded with pure $HgCl_2$. The denuder was loaded by flowing N_2 over pure $HgCl_2$ for 1 min at 520 sccm.

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Programmable thermal dissociation of reactive gaseous mercury

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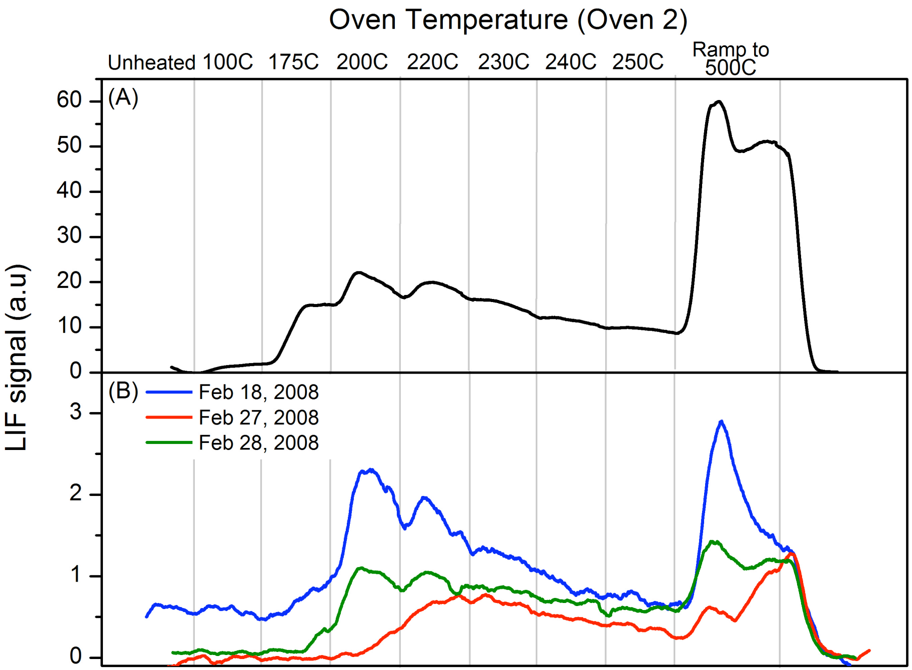

Fig. 4. (A): Calibration profile obtained using Oven 2 program for denuder loaded with pure $HgCl_2$. **(B)**: Dissociation profiles obtained using Oven 2 program for stack samples collected 18, 27, and 28 February 2008.

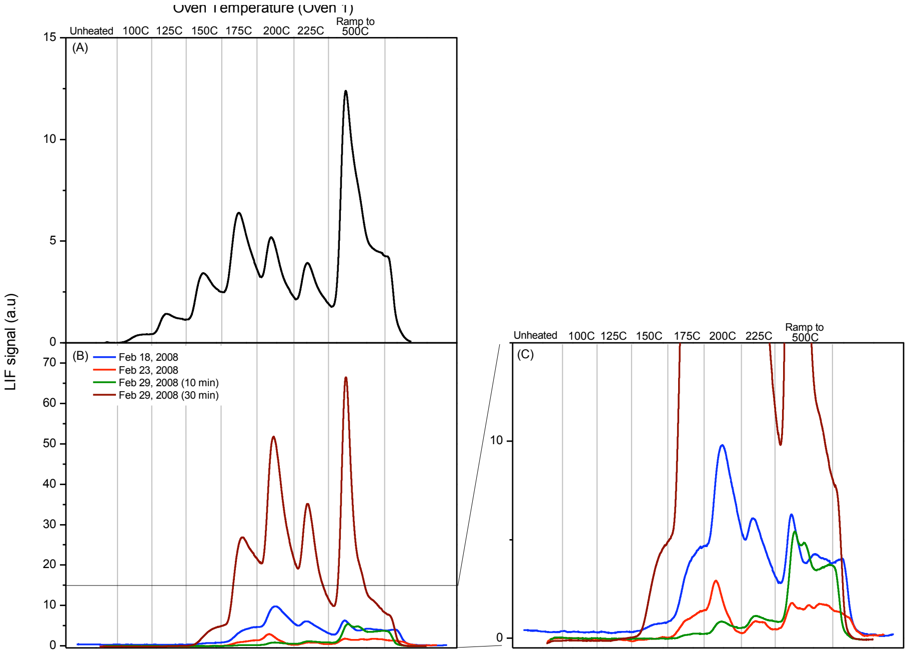

Fig. 5. (A): Calibration profile obtained from average of six PTD profiles using Oven 1 program for denuder loaded with pure $HgCl_2$. **(B)** and **(C)**: Dissociation profiles obtained using Oven 1 program for stack samples collected 18, 23, and 29 February 2008.

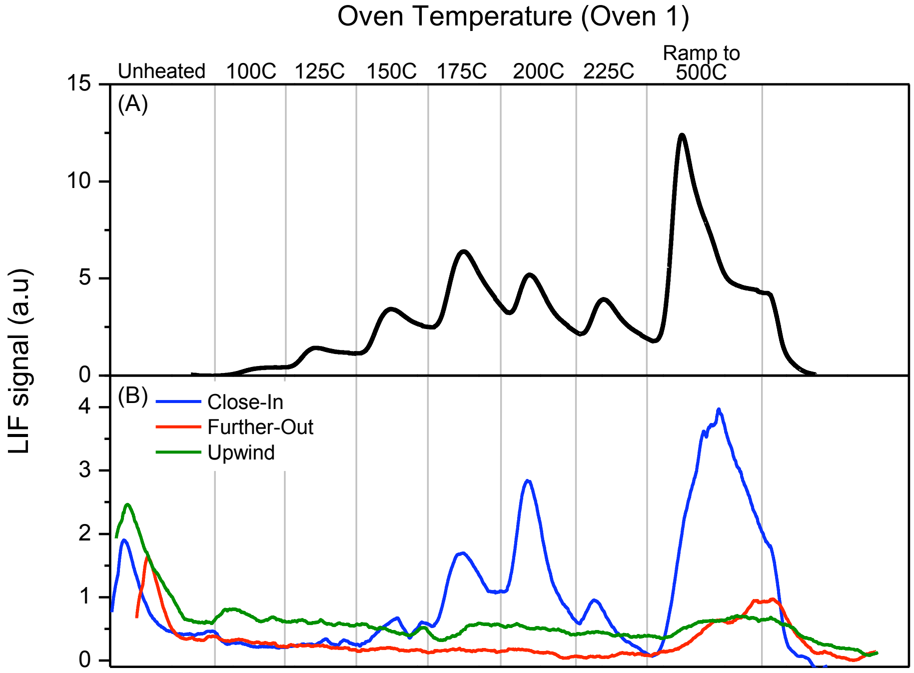

Fig. 6. (A): Calibration profile obtained from average of six PTD profiles using Oven 1 program for denuder loaded with pure $HgCl_2$. **(B)**: Dissociation profiles obtained using Oven 1 program for airship samples collected 28 February 2008.

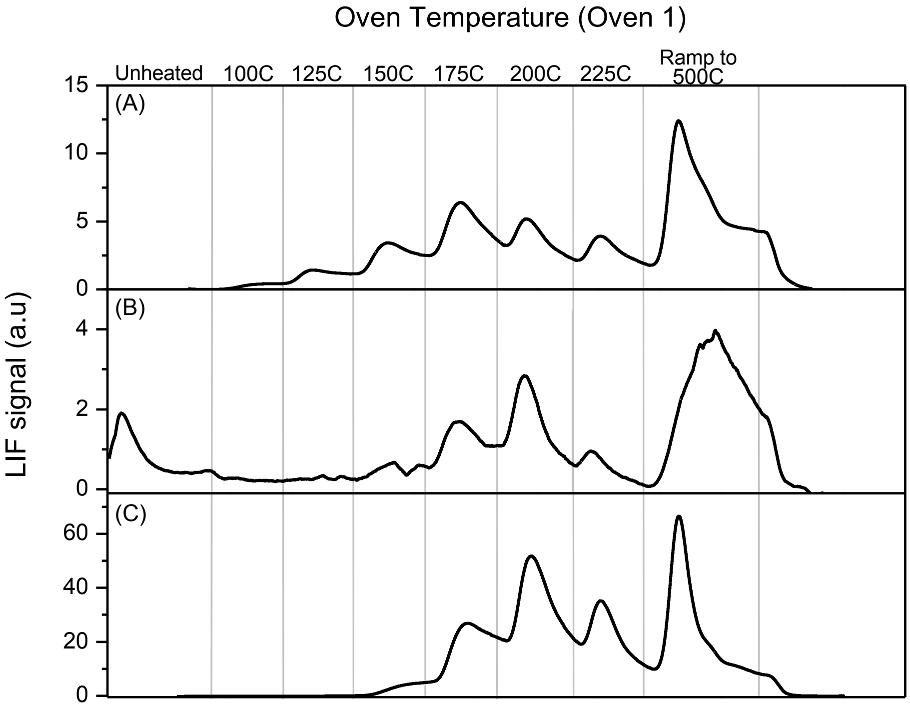

Fig. 7. (A): Calibration profile obtained from average of six PTD profiles using Oven 1 program for denuder loaded with pure $HgCl_2$. **(B)**: Dissociation profiles obtained using Oven 1 program for "close in" airship sample collected 28 February 2008. **(C)** Dissociation profiles obtained using Oven 1 program for stack sample collected 29 February 2008.

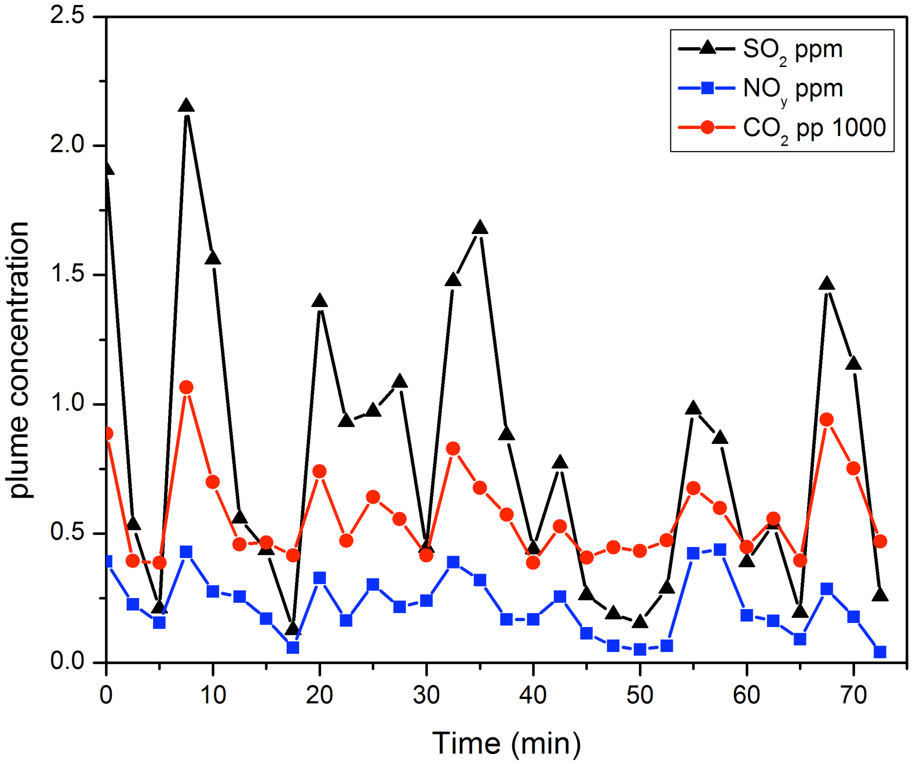

Fig. 8. "Background corrected" Concentrations of SO$_2$, NO$_y$ and CO$_2$ as measured by the airship's sampling system during the "close in" sampling run on 28 February.