Title: Programmable Thermal Dissociation of Reactive Gaseous Mercury, a Potential Approach to Chemical Speciation: Results from a Field Study.

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Additional Reply to Referee 1.

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From review 1.

My key concerns are as follows:

1. Large variability in recovery of RGM (table 1 and 2).

2. Large variability in PTD profiles for a single compound (HgCl2),

3. No comparisons with other compounds so we are left to qualitatively compare a PTD for HgCl2 with highly variability PTD from ambient samples. If the point is to show this method can identify HgCl2, then it is essential that other compounds be shown.

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From the paper:

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.

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We have looked at the variability in greater detail. Based on a total of 24 samples taken with the filter the mean and standard deviation of the RGM / m^3 is 0.46±0.66 ug / m^3, taking only etched samples we obtain 0.25±0.19 ug / m^3 and those analyzed using the oven 2 cycle 0.35±0.24 ug/ m^3. For the samples taken without the filter the average is 2.7±1.0 ug / m^3. It is clear that the presence of the quartz filter significantly reduced the collection efficiency and we have no explanation for this. The significant variability is also clear and it does not appear to correlate with analysis i.e oven program, or tube etching.

It is important to also recognize that the measured RGM in the stack gas was variable and there was disagreement of up to 40% in the stack RGM measurements using different approaches.

It is clear that the filter reduced sampling efficiency but there is no evidence that it had any impact on the speciation of RGM and this is surely the critical issue here.

If one examines Fig. 7: Panel (A): Calibration profile obtained from average of six PTD profiles using Oven 1 program for denuder loaded with pure HgCl2. Panel (B): Dissociation profiles obtained using Oven 1 program for “close in” airship sample collected February 28, 2008. Panel (C) Dissociation profiles obtained using Oven1 program for stack sample collected February 29, 2008. It is clear that these profiles are not consistent with oven 2 profiles. The onset of dissociation at approximately 125-150 C is clearly not compatible, as we discussed below, with other mercuric compounds. In spite of the variability it is reasonable to conclude that these profiles could be the same compound.

In relation to point 3, lack of comparison with other compounds we've now discovered several papers using programmable thermal desorption on solid samples containing mercury compounds. For example

Biester and Scwartz Environ. Sci. Technol. **1997**, 31, 233-239

They used AA detection of Hg(0). Desorbed/ dissociated sample was passed through 800 C quartz before analysis, however they saw no difference if the pyrolizer was removed. They examined contaminated soils and solid mercuric compounds generating standards by mixing pure compounds with powdered quartz. They ramped the temperature at 0.5 C / sec.

They noted appearance temperatures of:

very sharp “Hg(0)” at 100 C

HgCl2 starts at ~100 C peaks at 200 C

HgS peaks at 300 C

Feng et al. Anal Bioanal Chem (2004) 380: 683–689:

In this work thermograms are based on icp-ms detection of Hg(0), i.e. this does not distinguish between desorbed/sublimed RGM decomposition to produce Hg(0).

Several mercuric compounds when mixed with fly ash and ramped at 50 C /min

They noted appearance temperatures of:

“Matrix Hg(0)” 80 C

HgCl2 120 C

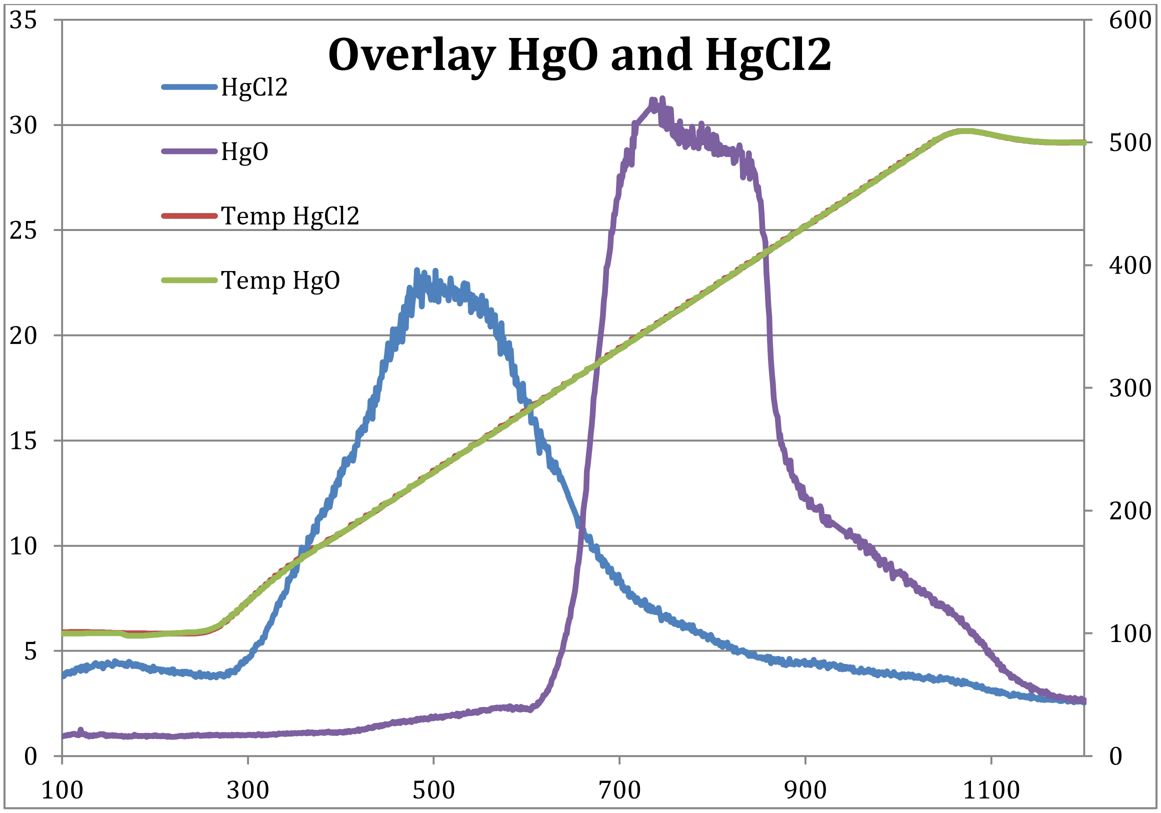
HgS 350 C

HgO 500 C.

Lopez-Anton et al. Fuel 89 (2010) 629–634 used a commercially available thermal dissociation module manufactured by PS Analytical coupled with a CVAFS detector. They used a pyrolyzer prior to analysis would've detected both dissociated and desorbed/sublimed RGM. They examined fly ash and solid mercuric compounds generating standards by mixing pure compounds with powdered quartz. They ramped at 10 C per minute.

They examined both mercurous and mercuric compounds finding that HgS, HgO and HgSO4 all decompose at much higher temperature than HgCl2. The HgCl2 thermogram shows decomposition peaking at 120 C, rather lower than in other work suggesting that the slower ramp temperature may have allowed the HgCl2 to sublime rather than decomposing.

Finally we propose to show supplementary data from our lab showing a comparison of HgCl2 and solid HgO that clearly shows the significant difference between their dissociation profiles. This work, in conjunction with the other cited references suggests that HgCl2 and HgBr2 are the only mercuric compounds that show a dissociation signal below 200 C



We would also like to reiterate an important point about the central thrust of this work.

Referee 2 notes "While this adds weight to the generally held opinion that it is indeed HgCl2 which is emitted from coal fired power plants, it is difficult to describe it as a substantial conclusion.
It is also the only conclusion, and comes with a caveat regarding the fact that HgCl2 and HgBr2 are indistinguishable using this technique."

It is critical to emphasize that the generally held opinion that HgCl2 is the species of RGM emitted from coal-fired power plants is not based on any experimental evidence, or on any reasonable mechanism for homogeneous formation of

HgCl2 in combustion. In spite of the caveats associated with the fact that this was the first attempt to do this kind of sampling and analysis in a working coal-fired power plant, we show experimental evidence, sampling from both stack and plume, that HgCl2 is indeed the emitted form of RGM. To the best of our knowledge this is the only experimental evidence that exists and given the importance of this issue we feel that the work merits publication.