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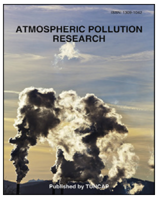

A pilot study of different materials applied for active sampling of gaseous oxidized mercury in the atmospheric air

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ABSTRACT

Samplers made with different materials were tested for the quantitative collection and recovery of mercury halides from the atmospheric air. The tested adsorbent materials included zirconia (ZrO_2), titania (TiO_2), melted SiO_2 (quartz wool) and potassium chloride (KCl). Different processes affecting the sampler efficiency were investigated specifically: breakthrough during sampling because of the surface passivation and loss of already collected mercury halides due to spontaneous reduction or due to the reaction with ozone. Reduction of mercury because of reaction with the atmospheric ozone appeared to be the major cause of the sample loss and it was inherent in all tested materials at a comparable extent. We hypothesized the zirconia layer covered on a ceramic substrate (patented) to be less sensitive to the ozone-caused reduction, inert to gaseous elemental mercury and completely insensitive to atmospheric humidity. In addition, zirconia samplers were highly resistant to heating and they could be used for multiple adsorption/desorption cycles avoiding degradation in the atmospheric air. Key results of the zirconia sampler tests with mercury halides were: the collection efficiency of >98%; reduction with 50 ppb ozone in the first 4 min of exposition to the atmospheric air – 6% ±1%; spontaneous reduction at 50 °C in the first 4 min after spiking – <0.6%. Along with the above experimental results, some insights into the possible mechanism of interaction of ozone with mercury halides have been provided.

1. Introduction

Gaseous oxidized mercury (GOM) compounds in the atmosphere are important as they are toxic, short-lived and reactive, ready to quickly enter ecosystems by wet or dry deposition (Landis et al., 2002). Mercury (II) chloride ($HgCl_2$) is probably the oldest known and most investigated representative of the atmospheric GOM. Mercury (II) bromide ($HgBr_2$), mercury (II) oxide, sulfate, nitrate and others have also been widely discussed recently (Huang et al., 2015; Jones et al., 2016).

However, low atmospheric concentrations of the above compounds make the proper collection (preconcentration) of the sample a crucial analytical task. Larjava et al. (1990), Larjava (1993) proposed to selectively trap $HgCl_2$ using KCl–coated quartz denuders for flue gas analysis. Xiao et al. (1997) proposed applying a similar technique for $HgCl_2$ analysis in the atmospheric air. In these experiments KCl denuders were analyzed for mercury by using wet chemistry. The inventors Frank H. Schaedlich and Daniel R. Schneeberger proposed to thermally desorb and at the same time to convert GOM to the elemental form by heating the KCl denuders to 500 °C as described in the patent “Apparatus for and method of collecting gaseous mercury and differentiating between different mercury components” (Tekran Inc., 2002).

It remained to prove the reliability of the method and apparatus under the field conditions. A group of authors (Landis et al., 2002) reported that their studies were conducted under a range of extreme conditions from the Florida Everglades in summer to the Arctic in winter and samples were collected over land, water, and from the aircraft. The authors also informed that their laboratory and field evaluations of the denuders showed the RGM (reactive gaseous mercury) collection efficiency to be >94% and the mean

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collocated precision to be <15%.

However, as it appeared later, serious biases of the method were observed even under regular atmospheric conditions, to say nothing of the aforementioned extreme ones. The method was not calibrated against all species of GOM, as it was pointed out by Gustin et al. (2013, 2015). The ozone effect on KCl denuders with mercury halides became known due to the investigation by Lyman et al. (2010). The latter researchers found that both KCl-coated and uncoated quartz denuders loaded with $HgCl_2$ and $HgBr_2$ lost 29–55% of these compounds, apparently as elemental mercury, when exposed to ozone (range of 6–100 ppb). This effect was also observed for denuders loaded with gaseous oxidized mercury at a field site (3–37% of oxidized mercury was lost). The authors tested two mercury halides, $HgCl_2$ and $HgBr_2$, which were collectively called HgX_2 and we will further follow this notation.

More recently, other researchers (McClure et al., 2014; Huang and Gustin, 2015) noted that humidity might be the subject under consideration as well. KCl-coating has disadvantages of being quite short-lived, hygroscopic and virtually reactive to different atmospheric gaseous compounds and therefore it needs to be replaced about every two weeks during the analyzer continuous operation.

On the other hand, the KCl denuders have the advantage that they are convenient to use both manually and in automated instruments, because they need to be just heated to desorb the collected GOM and to convert it to GEM (gaseous elemental mercury) for analysis. Moreover, the fresh KCl coating has been recognized as extremely inert for elemental mercury vapor. Cation exchange membranes (CEM) feature an excellent collection efficiency for GOM but they are prone to positive interference with humidity and they require liquid chemistry for analysis of the collected GOM. Recently suggested nylon membranes (Huang et al., 2013a) have the same advantage of being analyzed by thermal desorption, but they seem to suffer from negative humidity interference (surface passivation) (Huang and Gustin, 2015) and it is not excluded that they can suffer from the ozone-caused HgX_2 reduction either. Quartz denuders of the etched surface without any coating were also tested and they were found to suffer from the ozone-caused Hg halide reduction to a similar extent as KCl (Lyman et al., 2010).

There exist some contradicting accounts regarding the Quartz wool. Some researchers reported the capture efficiency of GOM by Quartz wool as being limited and inconsistent (Huang et al., 2013a), whereas the others reported a successful use of Quartz wool to retain GOM altogether with particulate-born mercury (e.g., for the UW-DOHGS mercury analyzer at the University of Washington Bothell, USA). We have recently inquired the creators of the UW-DOHGS analyzer about their usage of Quartz wool for the sampling of GOM and the possible effect of ozone. They informed us that their quartz wool still suffered from the ozone-caused reduction to a minor extent (10–20%), while it suffered much more from the high relative humidity. They informed us that for these reasons they moved away from using Quartz as the GOM collection surface and have switched to the cation exchange membranes (CEM). (Prof. Daniel A. Jaffe, personal communication, 2015, with reference to Ambrose et al., 2013).

We were interested in identifying a material that could be efficient in collecting GOM and sufficiently inert to GEM, whereas sufficiently robust mechanically and thermally to high temperatures and could be used repetitively for a long time of automated operation without replacing or re-coating. By spiking $HgCl_2$ and $HgBr_2$ on a lab scale, for comparison we tested such compounds/coatings as zirconia, titania, Quartz wool and potassium chloride. In each case we investigated the collection efficiency and the possible biases caused by ozone and humidity.

2. Material and methods

2.1. Sampling site

The air for tests was sampled through a 3 m-long, a ¼" o.d. PFA tubing, the inlet of which was located 2 m aside from the building, 7 m above the ground, and with no high buildings nearby (next to the forest). The sampling site was located in the suburbs of Vilnius city (540 thousand inhabitants, no major industrial factories) and with no point sources of mercury nearby, also at least a few kilometers from the main flows of the city transport, with the observed average concentration of gaseous elemental mercury of 1.5 ng/m^3 and little fluctuations. In all cases, the air was prefiltered from aerosol particles with a 0.1 μm pore size PTFE filter, prior to entering the analytical equipment. The location of the sampling site provided us free access to the lower troposphere which can be characterized as a mid-latitude suburban site.

Having in mind the sufficient length (3 m) of the non-preheated PFA tubing, we did not expect any detectable amounts of HgX_2 to reach the equipment from the atmosphere. We explain this by general difficulties in transmission of mercury halides through even a short, e.g. 15 cm preheated PFA line with the zero-air, as observed by ourselves and also reported by Jones et al. (2016). Meanwhile, our 3 m – long non-preheated sampling line was open to the atmospheric air containing ozone. Under these conditions any mercury halides present at the line inlet would be completely decomposed to Hg (0) at the outlet. Moreover, our spiked amounts of HgX_2 at the sampling line outlet were rather high, by two to three orders of magnitude higher than typical background atmospheric values of GOM. Therefore, the atmospheric input of GOM, if even present in any of its chemical form other than mercury halides and able to pass the sampling line, would not have great influence on the process analysis and calculations for our experiments. Actually, we used the atmospheric air merely as the matrix for the experiments for GOM capture, desorption and analysis, whereas the GOM itself (in the form of mercury halides $HgCl_2$ and $HgBr_2$) was introduced by ourselves. In comparison to rather high spiked GOM doses (e.g., 200 pg for 4 L sample resulting in app. 50 ng/m^3 effective concentration), even the GEM background values of 1.5 ng/m^3 (on average) from the atmospheric air were minor, which were easy to monitor and to eliminate from the final results.

However, it should be noted that the used relatively high (when compared to atmospheric background) GOM concentrations were still extremely low from the point of view of analytical chemistry. For example, a spike of 200 pg (as Hg) of $HgCl_2$ would occupy only 0.06 mm^2 as the monoatomic layer on a plain surface. This is a negligible amount compared to the dimensions of our sampling system, and also the spiked resulting concentrations (in the range of ppt) were low compared to the concentration of criteria atmospheric pollutants (range of ppb), thus the saturation effects might never have occurred. Therefore, we expect that our findings could be successfully extrapolated to the actual low atmospheric GOM concentrations, although, of course, this should be confirmed by the experiment.

Instead of using artificially generated ozone or other gaseous constituents, we employed the natural atmospheric air, whereas the concentration of ozone, humidity and temperature were measured outdoors. Ozone was detected with the Horiba GmbH ozone analyzer APOA370 and the relative humidity was detected with the Campbell Scientific Ltd. sensor HMPC45C. Data on atmospheric CO, SO_2 and NOx were obtained from the nearby meteorological station.

The semi-automatic experiments including about 80 episodes were performed under different weather conditions in summer - autumn - winter from July 2014 to January 2015.

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