TRAPPING AND IDENTIFICATION OF OXIDIZED MERCURY SPECIES IN FLUE GAS

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ABSTRACT

Current methods for speciation of vapor-phase mercury do not distinguish the inorganic forms of oxidized mercury. The assumption that Hg(II) is HgCl₂ or HgO for modeling behavior of oxidized mercury is unwarranted. Advances in cryogenic and solvent trapping of oxidized mercury species and their analysis by mass spectrometry led to the conclusion that surface reactions of elemental mercury with flue gas components result in more complex chemistry. Recent research demonstrated that in a simulated flue gas stream containing NO₂ and SO₂, the volatile form of the mercury emitted from the sorbent after breakthrough was determined to be mercury (II) nitrate hydrate, Hg(NO₃)₂·H₂O. Improvements in the sampling and analysis allowed for examination of other reaction products. Mercuric chloride and mercuric nitrate hydrate are separated by gas chromatography and identified by mass spectrometry. The eventual goal of this effort is a definitive speciation technique for determination of oxidized mercury in combustion flue gas.

INTRODUCTION

Much attention is currently focused on the air emission of trace amounts of toxic inorganic compounds during combustion of fossil fuels and incineration of waste materials. Mercury is of particular interest, owing to the high volatility of mercury and certain mercury compounds, the biological pathways that result in its concentration in fatty tissues, and its potential neurotoxic effect. To understand the complexities of its emission during combustion and dispersion throughout the environment, it is necessary to identify the mechanisms for its transformations, including capture on sorbents, scrubbers, or other control devices and release from these devices. Understanding these mechanisms in turn requires identification and quantitation of the forms of mercury compounds involved. Previous and ongoing identifications or speciations of trace mercury are based mainly on distinguishing oxidized from elemental mercury forms. Often it is assumed that oxidized mercury in the gas phase is mercuric chloride, since that is the most well-known volatile mercury salt. Predictions based on this implicit speciation could be erroneous if one uses the thermodynamic stabilities of mercuric chloride to represent the behavior of oxidized mercury.

Characterization of trace amounts of solid-phase mercury has progressed further, especially with the application of XAFS. Mercury forms sorbed on three types of activated carbon sorbents were recently examined (1). The results for mercury chemisorbed on a lignite-derived activated carbon were consistent with a form with either a mercury-sulfur bond or a mercury-chlorine bond. This more explicit speciation is valuable in determining the nature of the sorption reactions.

For understanding mercury transformations between the gas and solid phases, a definitive speciation of mercury compounds is needed. Perhaps HgO could form in certain atmospheric conditions as a combustion gas cools, but it is unlikely that HgO desorbs from a solid phase, since the heat required to decouple the mercury-oxygen bonds in the polymer is too high; thus elemental mercury is more likely released. That simply points to a need for a method to identify not only HgO in the gas phase but also many other mercury species containing nitrogen, sulfur, oxygen, and chlorine.

Previous research at the Energy & Environmental Research Center (EERC) was successful in cryogenically trapping oxidized mercury forms from a gas stream (2). Selective desorption could separate elemental mercury from oxidized forms, but the desorption of oxidized forms was not accompanied by a selective identification method.

Recently, the EERC reported the trapping and identification of the oxidized mercury species that is released from an activated carbon sorbent after breakthrough in a simulated flue gas stream containing both SO₂ and NO₂ (3). In an extensive matrix of mercury sorption experiments with flue gas components (4), early breakthrough was observed only when NO₂ and SO₂ were both present in the gas phase. Many years ago, the reaction of NO₂ with Hg was shown to form HgO on the container surface (5). This reaction is consistent with the high sorption capacity observed on carbons.
in a gas containing NO\textsubscript{2} and not SO\textsubscript{2}. Later, Freeman and Gordon (6) presented evidence for mercuric nitrate and mercurous nitrate in solid products from the reaction. To understand the early breakthrough interaction when SO\textsubscript{2} is added to experiments, identification of the volatile oxidized mercury species was required. This was established by trapping the effluent gas in a cold organic solvent, evaporating part of the solvent, and analyzing by GC–MS. This high-confidence technique demonstrated that the released mercury product formed in the NO\textsubscript{2}–SO\textsubscript{2} mixture was mainly mercuric nitrate hydrate (3). Both MnO\textsubscript{2} and catalytic carbons behaved similarly.

In other environments, species such as HgCl\textsubscript{2} could also be present and detectable. Work in an earlier CATM project established that HgCl\textsubscript{2} could be trapped cryogenically and subsequently desorbed readily as an oxidized mercury species, presumed to be the original HgCl\textsubscript{2} (2).

Transformations of the oxidized species in the flue gas to other oxidized species are anticipated as a result of gas-phase or gas–solid reactions. Methods for distinguishing these species, mixtures of these species, and other oxidized species are needed to understand the interactions occurring on sorbents, ash particles, and duct or filter bag surfaces.

Whether other oxidized mercury species are present in sorbent breakthrough emission or flue gas emissions in general is unknown. It is important to determine the definitive speciation of all emitted oxidized species in order to understand the reactions that occur on the sorbent that lead to inferior mercury sorbent performance in flue gas component mixtures. These interactions between mercury and gas components are also very important in understanding speciation of mercury in combustion flue gases and similar interactions that may occur on ash particles.

Organomercury compounds, as well as HgCl\textsubscript{2}, have been separated and determined by GC; however, the trapping and identification of a nonhalogenated vapor-phase oxidized mercury species is a novel breakthrough in mercury research. The goal of present research is to develop cryogenic trapping and desorption methods for oxidized mercury species and to develop and apply high-confidence MS methods for identification and quantitation of oxidized mercury species.

RESULTS

In order to develop a method for determination of oxidized mercury compounds in the gas phase by cryogenic trapping coupled with desorption into a GC–MS, the volatility and stability of the mercury compounds of interest must be understood. The volatility behavior of mercuric chloride is better known, and the application to trapping and desorption appeared straightforward (2). Other mercury halides are less well understood. A recrystallized standard of Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O was prepared and vaporized in a gas flow as a source of Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O vapor. The gas flow was trapped cryogenically, and the concentration was determined by desorption, conversion to elemental mercury in a heated tube, and detection with a conventional atomic fluorescence spectrometer. This gave reproducible peak area responses. This established that a constant source for vapor phase Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O could be utilized for loading traps with this species and that trapping and desorption of this compound are feasible.

Conditions for GC–MS analysis of HgCl\textsubscript{2}–Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O mixtures were investigated. Previous studies indicated that acetonitrile solutions of Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O could be injected in a standard inlet operated under splitless conditions, and the Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O eluted as a fairly sharp peak at 5.4 minutes through a nonpolar (DB5) 30-meter column. A unique mass spectrum corresponding to Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O was observed for this peak. Injection of HgCl\textsubscript{2} in acetonitrile resulted in elution of a HgCl\textsubscript{2} peak with its characteristic mass spectrum. The HgCl\textsubscript{2} peak eluted later than the Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O and was very broad. This indicates that HgCl\textsubscript{2} interacts much more strongly with the column phase than does Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O, as one would expect.

During the chromatography of Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O, some elemental mercury forms in the GC injector from decomposition of the Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O on the injector surfaces and elutes very early in the chromatogram. It is also likely that some mercury is vented from the inlet. Thus, there is no response for Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O not as high as hoped, but standard injection in a solvent is probably not the ideal way to introduce these compounds to the mass spectrometer. In fact, the injection temperature had to be lowered to get a better response for the HgCl\textsubscript{2}. Except for the elemental, no other Hg-containing peaks, such as an acetonitrile complex or product resulting from decomposition, were observed.

When mixtures of Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O and HgCl\textsubscript{2} in acetonitrile were injected at an intermediate temperature, two peaks were observed at their characteristic retention times in the chromatogram (Figure 1b). Reconstructed selected ion chromatograms for the isotopic cluster at m/z 250–254 representing the Hg(NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O peak and at m/z 270–274 representing the HgCl\textsubscript{2} peak are shown.
Figure 4c and 4d, respectively. The mass spectrum of Hg(NO₃)₂·H₂O representing one scan in the Hg(NO₃)₂·H₂O peak is shown in Figure 4a. The base peak is at m/z 252 with a characteristic pattern for the mercury isotope ions (3). The molecular ion is very small for this compound and cannot be seen in the mass spectrum for this scan.

While it is clear that optimization of the inlet configuration and chromatography conditions are needed, these experiments establish the feasibility of observing at least two oxidized mercury species as they elute from a GC column. These two compounds appear to have no difficulty transferring through the coated columns that are necessary to maintain the vacuum conditions. Of course, other mercury compounds may not survive inlets, columns, or desorption conditions and may convert to these and other species.

Replacement of the standard GC inlet with a 1-mL glass vial for introducing oxidized mercury species was investigated. The vial was fitted with a small septum through which an inlet capillary (from the injector assembly) and outlet capillary (the GC column) were inserted through the septum. The vial was loaded with a mixture of HgCl₂ and Hg(NO₃)₂·H₂O by injecting 1μL of the standard acetonitrile solution of HgCl₂ and Hg(NO₃)₂·H₂O and allowed to evaporate for a minute. The septum cap was replaced and the vial placed in the GC oven. The GC oven temperature program was initiated and mass spectral data accumulated. The HgCl₂ and Hg(NO₃)₂·H₂O were successfully desorbed from the vial into the column. Initially, a very short column (3 meter) was used, and both mercury compounds desorbed and eluted into the MS in a broad unresolved peak. The spectra of both the HgCl₂ and Hg(NO₃)₂·H₂O were evident, but the ion trap was not operating under high vacuum with the short column, so the spectra and reconstructed chromatogram were noisy, owing to excessive space charging. Use of a longer column resolved the peaks and allowed a better vacuum resulting in better spectra. The peaks were not as sharp as those obtained with a normal GC injector.

The vial was then loaded from a gas stream containing Hg(NO₃)₂·H₂O. The vial was cooled in an ice salt bath, and the Hg(NO₃)₂·H₂O was loaded using the source described above. The vial was then transferred to the GC oven and attached to the column as described above with the septum cap. Again, the Hg(NO₃)₂·H₂O peak was observed in the accumulated mass spectral data. Some decomposition to elemental mercury was evident. The reproducibility of this method has not yet been established, and further research in materials and techniques is needed. Of major concern is how to deal with trapped moisture that is eluted into the MS.

CONCLUSION

GC–MS methods were used to separate a mixture of two volatile oxidized mercury species, HgCl₂ and Hg(NO₃)₂·H₂O, and give characteristic mass spectra for the two components. The separation and analysis can occur with materials trapped from the gas phase into a solvent and subsequent injection into the GC–MS injection port or by desorption from a solid phase in a small trapping vial. Thus definitive identification and quantitation of these two species are feasible. Present efforts are focused on developing coupling hardware for interfacing larger traps to the GC–MS.

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REFERENCES

Figure 1a. Mass spectrum for Scan 329; 1b, total ion chromatogram; 1c, selected ion chromatogram for m/z 250-254; and 1d, selected ion chromatogram for m/z 270-274.