



DEVELOPMENT OF SAMPLING AND ANALYTICAL TOOLS TO ASSESS MERCURY SPECIATION

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Project Description

This project focused on the development of sampling and analytical methods to appropriately collect and definitively determine the species of oxidized mercury Hg^{2+} compounds in a flue gas stream. Current methods for speciation of vapor-phase mercury do not distinguish the inorganic forms of Hg^{2+} . This information is needed to understand and accurately model the behavior of mercury in flue gas and in a control device. Development of methods for cryogenic and solvent trapping of certain volatile Hg^{2+} and their analysis by mass spectrometry (MS) continued. The analysis of mercuric chloride and mercuric nitrate by gas chromatography (GC) and identification by MS is now better understood, and the unusual behavior of mercuric nitrate on the chromatograph was documented in a refereed publication. A method for transferring mercuric chloride from the initial cryotrap to the GC-MS was further developed, but problems were encountered in its application in high-moisture flue gas. Improvements were made in the construction and use of a continuous vapor source for mercuric nitrate. These insights in the behavior of the oxidized mercury species have advanced the development of a model for the chemisorption of elemental mercury (Hg^0) on a carbon sorbent surface. Subsequent improvement will lead to quantitative speciation methods with high levels of confidence for the major volatile oxidized mercury species.

Goal

The goal of the project is to develop methods and instrumentation for accurate and reliable speciation of oxidized mercury compounds in flue gas that distinguish the inorganic forms. Specific project objectives are as follows:

- Develop methodology for isolation and separation of oxidized mercury species using selective cold trapping and desorption.
- Demonstrate cryogenic trapping and a desorption device for oxidized mercury.
- Develop high-confidence (MS) method for identification and quantitation of oxidized Hg species.
- Investigate oxidized species transformations occurring in sampling and analytical methods.
- Perform sampling and analyses for oxidized Hg emissions during bench sorbent testing and pilot combustion runs.

Rationale

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 potent toxicity in the nervous system. To understand the complexities of mercury emission during combustion and its dispersion in the environment, it is necessary to identify the transformation mechanisms that govern its capture on sorbents, scrubbers, and other control devices or its release from these devices. Understanding these mechanisms, in turn, requires identification and quantitation of the forms of mercury compounds involved. Previous identifications or speciations of trace mercury were based mainly on distinguishing oxidized from elemental mercury forms. Often it was assumed that oxidized mercury in the gas phase was mercuric chloride, since that is a well-known volatile mercury salt. Models based on this *implicit speciation* could be erroneous if one uses the thermodynamic stabilities of mercuric chloride to represent the behavior of oxidized mercury. Galbreath and Zygarlicke recently discussed a number of speciation models for coal combustion and the speculation upon which these models draw [1].

For understanding mercury transformations between the gas and solid phases, a *definitive speciation* of mercury compounds is needed. HgO may form under certain atmospheric conditions as combustion gases cool, but it is unlikely that HgO desorbs from a solid phase, since the heat required to break the mercury–oxygen bonds in the polymer is too high. Hg⁰ is more likely to be released. Methods are needed to identify not only possible HgO in the gas phase, but also many other mercury species containing nitrogen, sulfur, oxygen, and chlorine.

Previous work at the EERC was successful in cryogenically trapping HgCl₂ from a gas stream [2]. Selective desorption could separate Hg⁰ from oxidized forms, but the desorption of oxidized forms was not accompanied by a selective identification method.

Recently, results were reported for the trapping and identification of the oxidized mercury species 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 that was observed on carbons in a gas containing NO₂ and not SO₂. Later, Freeman and Gordon [6] presented evidence for mercurous nitrite and mercurous nitrate in solid products from the reaction. To understand the early breakthrough interaction when SO₂ is added, 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. The GC retention time and the mass spectrum of the released mercury product formed on the spent (broken-through) sorbent in the NO₂–SO₂ mixture (no HCl) matched that of mercuric nitrate hydrate [3]. Both MnO₂ and catalytic carbons behaved similarly. Further research was needed to elucidate the nature of the eluting peak in the GC–MS analysis and whether the chloride, nitrate, and other oxidized species that are trapped in these experiments can be distinguished by these methods.

Approach

The approach to developing the desired methodology for mercury speciation is based on coupling the cryogenic trapping that successfully isolated the mercury compounds from the flue gas stream with a spectroscopic method that identifies the compounds that are desorbed from the trap. The trapping device was described in the previous two annual reports [7, 8]. The current approach is to find an appropriate method for interfacing the cryotrap with the MS.

MS methods are highly sensitive and give characteristic molecular ion peaks for each molecular component of a mixture. They also give compound-specific mass spectra for each molecular species that is separated and fragmented. Identifications and quantitations are especially reliable when combined with another separation technique, such as GC. Thus a high confidence level is achieved for identifications of molecular compounds. For example, mercuric chloride (HgCl_2) gives a set of molecular ion peaks corresponding to the various combinations of mercury isotopes and chlorine isotopes, as well as other peaks resulting from breakdown of the molecular ions. Hg^0 gives a set of ions corresponding to the mercury isotopes.

To develop a quantitative method, several steps are required:

1. Determine the volatility and stability of the mercury compounds of interest. A set of standard mercury compounds must be prepared and vaporized and then detected with conventional fluorescence methods. This will test thermal response, flow rate response, response to thermal conversion, and trapping.
2. Develop coupling hardware for interfacing the traps to the MS. Specific hardware must be designed and constructed as necessary. Standards will be introduced into the MS by placing nanogram amounts in the traps and desorbing through a capillary into the MS to obtain usable spectra.
3. Evaluate methods for dealing with moisture. The presence of moisture will likely be a problem for the MS, but it can be separated from the gas component mixture either prior to or during introduction to the MS.
4. Test cryotrap–MS interface. Tests were conducted by generating vapors of standards, cryotrapping, and desorbing to the MS. Derivatization methods will need to be evaluated.

Progress

In the course of the project, progress was made in the following areas (relevant publications are noted):

- Mercuric nitrate volatilization, trapping, and analysis
 - Elucidated the chemistry occurring in the GC–MS analysis of mercuric nitrate by demonstrating that, after injection of the solution, the highly reactive mercuric nitrate reacted with the siloxane column phase to give a chromatographical methylated species (CH_3HgCl) that gives the characteristic mass spectrum [9–12].
 - Demonstrated the uniqueness of mercuric nitrate in the GC–MS analysis [12].
 - Determined sorption and desorption temperature profile for $\text{Hg}(\text{NO}_3)_2$ in anhydrous, hydrated, and basic salt forms.
 - Developed improved standard source for $\text{Hg}(\text{NO}_3)_2$ vapor.
 - Developed hardware and performed successful cryogenic trapping of $\text{Hg}(\text{NO}_3)_2$ vapor from a source and desorbed into atomic fluorescence spectroscopy (analyzed as Hg^0).

- Determined that gas-phase transfer and direct GC–MS of $\text{Hg}(\text{NO}_3)_2$ without derivatization is not feasible for quantitation owing to high reactivities with moisture films and column phases, but transfer and analysis via derivatization may be feasible.
- Mercuric chloride volatilization, trapping, and analysis
 - Performed successful high-confidence GC–MS trapping, separation, and identification of vapor-phase HgCl_2 by trapping HgCl_2 from the vapor in the cryotrap, transferring sorbed HgCl_2 to a vial, and desorbing from the vial into the MS to give the unique HgCl_2 spectrum [11].
 - Performed successful high-confidence GC–MS separation of HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ mixture in acetonitrile solution, giving unique spectra for identification of these species [11].
 - Developed improved high-sensitivity GC–MS method for HgCl_2 using derivatization with diazomethane [10]. The peak shape for the bischloromethylmercury product was sharp, whereas HgCl_2 exhibits extreme tailing and poor calibration characteristics.
- Model for mercury speciation in flue gas–sorbent interactions
 - Based on insights into volatilization and chemistry of oxidized mercury species developed in this project and other CATM projects, a model for speciation of mercury on sorbents has been developed [13].

Status

A feasible design approach for the collection and transferring devices is beginning to emerge. Problems still need to be resolved in going from high-volume, high-velocity collection to very small, high-vacuum MS instrumentation. Additional issues result from the high reactivity of $\text{Hg}(\text{NO}_3)_2$ vapor with moisture and surfaces such as the GC column phase. Because of the different sorption and desorption behavior of HgCl_2 and $\text{Hg}(\text{NO}_3)_2$, the likely configuration for oxidized mercury speciation now appears to be a double-trapping system where HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ are trapped and transferred to the MS independently. Transfer of oxidized mercury species from the cryotrap to a vial for derivatization and GC–MS analysis was hindered by plugging of the transfer tube with moisture and ice at the low temperatures. Larger tubes and better insulation will be utilized in future tests.

Calibration of HgCl_2 by derivatization and MS analysis were completed, but detection limits were not as low as expected. Changes to the GC inlet system will be investigated to reduce the decomposition of the HgCl_2 in the inlet and maximize the amount injected. Novel methods for $\text{Hg}(\text{NO}_3)_2$ analysis via derivatization will continue to be investigated. Trapping and analysis of samples from sorbent testing in simulated flue gas in the sorbent test unit and conversion and environmental process simulator unit are currently being conducted and planned.

Potential Users/Technology Transfer

The methods, techniques, and instrumentation developed under this project will benefit researchers in understanding mercury transformation and emission measurements for particular mercury species. Results will be applied in the development of control technologies and in understanding the transport and fate of mercury species in the atmosphere.

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