



DEVELOPMENT OF MERCURY SAMPLING AND ANALYTICAL TECHNIQUES

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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 coal combustion 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 (HgCl_2) 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 HgCl_2 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 Hg^{2+} 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 Hg^{2+} species.

Goal

The goal of the project is to develop methods and instrumentation for accurate and reliable speciation of Hg^{2+} compounds in flue gas that distinguish the inorganic forms. Specific project objectives are as follows:

- Develop methodology for isolation and separation of Hg^{2+} species using selective cold trapping and desorption.
- Demonstrate cryogenic trapping and a desorption device for Hg^{2+} .
- Develop high-confidence (MS) method for identification and quantitation of Hg^{2+} species.
- Investigate oxidized species transformations occurring in sampling and analytical methods.
- Perform sampling and analyses for Hg^{2+} 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 Hg^0 forms. Often it was (and still is) assumed that Hg^{2+} in the gas phase was HgCl_2 , 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 HgCl_2 to represent the behavior of Hg^{2+} . 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. Mercuric oxide (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. Hg^0 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 Energy & Environmental Research Center (EERC) was successful in cryogenically trapping HgCl_2 from a gas stream [2]. Selective desorption could separate Hg^0 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 Hg^{2+} species released from an activated carbon sorbent after breakthrough in a simulated flue gas stream containing both SO_2 and NO_2 [3]. In an extensive matrix of mercury sorption experiments with flue gas components [4], early breakthrough was observed only when NO_2 and SO_2 were both present in the gas phase. Many years ago, the reaction of NO_2 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 NO_2 and not SO_2 . 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 SO_2 is added, identification of the volatile Hg^{2+} 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 NO_2 – SO_2 mixture (no HCl) matched that of mercuric nitrate hydrate [3]. Both MnO_2 and catalytic carbons behaved similarly. Further research is 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 previous 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, 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.
- HgCl_2 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.
- Developed new trapping method on diazo-coated resin. Obtained definitive GCMS evidence for trapping HgCl_2 on diazo-coated resin. The method is definitive for any mercury halide or organomercury halide. Development of quantitation method is in progress.
- Model for mercury speciation in flue gas–sorbent interactions
 - Based on insights into volatilization and chemistry of Hg^{2+} 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. Transfer of Hg^{2+} 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. 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 Hg^{2+} speciation now appears to be a resin system where HgCl_2 and $\text{Hg}(\text{NO}_3)_2$ are trapped, derivatized, and transferred to the MS independently.

If the resin trapping experiments in simulated flue gas are successful, the method will be calibrated by exposure to the HgCl_2 source for different periods to accumulate known amounts of $\text{Hg}(\text{II})$ to be plotted with the MS peak areas. The method will then be evaluated for use in flue gas using known HgCl_2 levels in synthetic flue gas on the bench-scale unit. A subsequent experiment with an elementary mercury source and a spent sorbent to furnish $\text{Hg}(\text{II})$ species will be performed on the bench-scale unit. Finally, the method will be tested on a pilot-scale combustor fired with a bituminous coal which is expected to produce a high percentage of Hg^{2+} in the flue gas.

Quality Assurance/Quality Control

An organizationwide quality management system (QMS) is in effect that governs this project. The EERC QMS complies with the requirements of American National Standards Institute/American Society for Quality Control E4, “Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs.”

Quality Objective

Although high recovery and reproducibility are feasible in vapor-phase Hg^0 analyses, Hg^{2+} compounds are notoriously “sticky” on surfaces and easily change forms by hydrolytic and other chemical transformations. Despite these problems and the lack of previous viable methods for these analyses, optimistic goals for achieving success in developing methods for analyses of vapor-phase Hg^{2+} compounds were set. The quality objective was to distinguish the two volatile mercury species proposed for flue gas ($\text{Hg}[\text{NO}_3]_2$ and HgCl_2) and determine their amounts with the degree of accuracy and reproducibility stated in the following discussion.

Measurement/Data Acquisition

The research developed new methods for mercury vapor analysis based on trapping techniques coupled with calibrated GC–MS instrumentation to achieve high confidence levels for identification and quantitation of HgCl_2 in a gas sample. High confidence identification of HgCl_2 in a trapped sample by its characteristic mass spectrum was achieved early in the project. In contrast, the identification of $\text{Hg}(\text{NO}_3)_2$ was problematic and required considerable effort to understand the transformations that occur in the analysis and how this relates to the identification.

Assessment and Validation

Quantitative Analysis

The trapping and GC–MS method without derivatization of the sample was demonstrated to give high-confidence identification, but unsatisfactory quantitative results were obtained, owing to the very broad peak shape of the analyte. This problem was solved in the course of the project by employing a derivatization method to determine the HgCl_2 . This method also gave unequivocal identification for the HgCl_2 as its derivative, but also met the target quantitative objectives. By cryotrapping or solvent trapping and conversion of HgCl_2 to bischloromethylmercury, the target relative standard deviation and percentage accuracy of 10% was achieved while maintaining the definitive identification. Thus the methods were validated by reproducing the earlier cryotrap results with HgCl_2 and atomic fluorescence spectroscopy detection, based on a calibrated HgCl_2 permeation tube source (dry system). In a surrogate flue gas trapping experiment, the method failed to achieve quantitative results, owing to reactions occurring in the trapped aqueous medium. New methods based on a resin-supported reagent are expected to overcome this difficulty and achieve the desired quantitative objectives in the current year project.

Owing to the high reactivity of $\text{Hg}(\text{NO}_3)_2$ to moisture and surfaces, the quantitation objectives were not attained, and methods are currently being considered for solving the problems. A successful permeation source for $\text{Hg}(\text{NO}_3)_2$ was, however, constructed. This will go a long way toward solving the quantitation problems for $\text{Hg}(\text{NO}_3)_2$.

Testing in Actual Flue Gas (42-MJ/hr unit)

This portion of the work has not been completed owing to the unavailability of an actual flue gas containing a high proportion of Hg^{2+} . A surrogate flue gas cryotrap system test was conducted; however, the methods were not validated owing to reactions of the $\text{Hg}(\text{II})$ in the trap. A flue gas $\text{Hg}(\text{II})$ test will be conducted with the resin-supported reagent for derivatization at temperature about the condensation point of the flue gas to avoid excess water (and sulfite) in the trapped sample.

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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