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METHODS TO IMPROVE MEASUREMENT OF MERCURY AND CHLORINE IN COMBUSTION FLUE GASES

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Project Description

The EERC is striving to improve the mercury measurement results obtained with impinger-based methods, such as ASTM International Method D6784-02 (Ontario Hydro), and continuous mercury monitors (CMMs) (e.g., Semtech Hg 2000, PS Analytical [PSA] Sir Galahad, Tekran). They are investigating potential sources of analytical bias including:

- The removal of CO_2 from flue gas by a $SnCl_2$–NaOH solution that also captures acid gases and reduces gaseous mercurous and mercuric compounds ($Hg^{1+,2+}$) to Hg^0 positively biases total mercury concentration measurements.

- Mercury–fly ash interactions occur on the filter medium (i.e., glass fibers) and promote the formation of $Hg^{1+,2+}$ and/or particle-associated mercury forms (Hg[p]), thus negatively biasing Hg^0 measurements.

Tests will be conducted to determine the rate of CO_2 uptake by $SnCl_2$–NaOH based on gas and liquid flow rates and CO_2 and NaOH concentrations. A prototype miniature electrostatic precipitator (ESP) was evaluated as an alternative to glass fiber filters for removing fly ash and Hg(p) from coal combustion flue gases. An existing ESP was redesigned and modified to enable periodic online cleaning, thus reducing particulate buildup on the collecting surfaces during continuous sampling. In addition, the ESP was made larger to enable higher potentials for improving particulate collection efficiency.

The EERC is also striving to use a recently purchased Model 15C HCl analyzer combined with chiller and Perma Pure gas drying systems and a Cl_2–H_2 reaction chamber to quantify Cl_2 and HCl in coal combustion flue gas and other gas streams on a nearly continuous basis. The capability to monitor Cl_2 and HCl together with the EERC's mercury species monitoring capabilities would be very beneficial for investigating mercury chlorination reactions. In addition, Cl_2 and HCl monitors are needed to optimize wet and dry scrubber control strategies for various industrial activities (e.g., pharmaceutical processing, semiconductor manufacturing, coal combustion, and municipal solid waste and hazardous waste incineration).

Goal

A goal is to improve the mercury measurement results obtained with impinger-based methods, such as ASTM Method D6784-02, and CMM by determining the amount of CO_2 absorbed as functions of varying $SnCl_2$, NaOH, and CO_2 concentrations and gas and liquid flow rates and by minimizing mercury speciation biases that result from the presence of fly ash in sampling systems. An overall project goal is to develop a correction factor for use with the wet-chemistry mercury conversion/conditioning systems. A specific objective is to determine CO_2 absorption rates as functions of:

- NaOH concentration in the $SnCl_2$/NaOH and KCl/NaOH solutions.
- CO_2 concentration.
- Gas flow rate through the bubbler.
- Solution flow rate in to the bubbler.

Another goal is to develop a system for monitoring Cl_2 and HCl concentrations in gas streams on a nearly continuous basis. To achieve this goal, the following objectives must be met:

- Demonstrate that mixtures of Cl_2, HCl, and water vapor can be successfully transported to the Model 15C HCl analyzer.

- Demonstrate the selective and quantitative removal of HCl by a chiller.

- Demonstrate that low concentrations of Cl_2 can be converted to HCl by reacting with hydrogen in the presence of UV light or at 250°C.

- Determine and document the specificity, sensitivity, bias, and precision of the Cl_2/HCl monitoring system using simulated and real coal combustion flue gases.

Rationale

All instruments currently used to measure mercury in a combustion flue gas stream require a conditioned gas sample. Conditioning generally involves the removal of moisture and acid gases and the conversion of $Hg^{1+,2+}$ to Hg^0. Conditioning systems have employed an acidic $SnCl_2$–HCl solution for this purpose. Although this solution is effective, problems have occurred because of sulfur plating on glassware and limited solution shelf life. As recommended by PSA, this acidic solution was replaced with a basic $SnCl_2$–NaOH solution. This solution, however, also has limitations, including CO_2 absorption from the sample gas. CO_2 can account for as much as 15% of a flue gas stream, thus removing CO_2 will positively bias total mercury measurements. Therefore, it is imperative to know how much CO_2 is removed. SO_2 and other acid gases are also removed in the $SnCl_2$–NaOH solution, but their removal does not greatly affect sample volume. The amount of CO_2 removed is dependent on solution pH that varies with gas and liquid flow rates in the conversion system and with changes in acid gas concentrations.

Fly ash–mercury interactions during sampling are a major source of mercury species measurement bias. A current method of minimizing this bias is to use an Apogee probe that is based on inertial impaction (1). Alternatively, a miniature ESP can be used to capture fly ash upstream of impinger-based and CMM systems. Preliminary testing of such an ESP in November 2001 demonstrated the feasibility of this approach for minimizing fly ash–mercury interactions during flue gas sampling. However, additional effort is needed to optimize the ESP system for performing mercury species measurements.

In addition to mercury, chlorine species (e.g., Cl, Cl_2, and HCl) are among the 188 hazardous air pollutants identified in the 1990 Clean Air Act Amendments. Consequently, there is significant need to measure and control Cl, Cl_2, and HCl emissions. The EPA-recommended method for Cl_2 and HCl emission analysis, EPA Method 26A, is based on impingement. This approach is adequate for determining an average total chlorine concentration in a coal combustion flue gas over an extended period of time but cannot provide information about continuous changes in Cl_2 and HCl concentrations (2). Continuous Cl_2 and HCl measurements are essential for understanding time-dependent reactions, such as fluctuations in mercury chlorination caused by kinetic and equilibrium processes. Regardless of whether Cl_2 and HCl are produced as a by-product of a manufacturing process or combustion/incineration, they are generally controlled through wet scrubbing. HCl is very water-soluble even under relatively low pH conditions, whereas Cl_2 typically requires a caustic scrubbing solution. Scrubber optimization has economic and environmental implications.

Recently, the EERC purchased a Model 15C HCl analyzer from Thermo Environmental that uses infrared (IR) spectroscopy to achieve an HCl detection limit of 0.2 ppmv (5-min integration time). The Model 15C analyzer measures only HCl because Cl_2 is not IR active. However, it should be possible to scrub HCl from a gas stream without removing Cl_2, and then Cl_2 in the scrubbed gas stream can be converted to HCl by reacting with hydrogen in ultraviolet light or at 250°C for subsequent IR spectroscopy analysis. The proposed selective HCl scrubbing and Cl_2 to HCl conversion process may be used to measure HCl and Cl_2 concentrations in gas streams on a nearly continuous basis.

The solubility of Cl_2 in water is between that of the slightly soluble gases, such as oxygen and hydrogen, and the exceedingly soluble gases, such as HCl and NH_3. Theoretically, only about 0.7% Cl_2 can be dissolved in water at 20°C. Practical solubility, which requires considerable mixing and time, is about half this value (3). Chiller/condensation systems are commonly used in extractive-type sampling systems to remove water vapor from a gas stream prior to introduction into analyzers. Chillers typically provide a chamber cooled to 4°C using thermoelectric or other devices. Water vapor in the stack gas condenses providing a sample with a 4°C dew point. This condensation process occurs rapidly so that insoluble compounds, such as Cl_2, pass through with insignificant loss, whereas highly soluble compounds (e.g., HCl, NH_3) are removed with water (4).

In contrast to chiller/condensation systems, the Gas Analysis Sampling System (GASS™) from Perma Pure Inc. utilizes a Nafion® gas dryer to selectively absorb water vapor from gases. Nafion is a corrosion-resistant fluoropolymer that functions as a semipermeable membrane to water vapor, thus enabling water to permeate out of the sample gas stream into a countercurrent purging flow of dry N_2 (5); Cl_2 and HCl will not react with N_2. Arnó (6) demonstrated using mass spectrometry and Fourier transform-IR (FT-IR) spectroscopy that the GASS selectively removes water without affecting low concentrations of Cl_2 and HCl in water vapor-saturated gas streams. The GASS also improved IR spectroscopy HCl detection limits (6). Galbreath and Zygarlicke (7) demonstrated that the GASS Model 15C HCl analyzer could accurately and precisely measure HCl in a simple heated air mixture by comparing results to those obtained using EPA Method 26A. More recently, the EERC has used the Model 15C analyzer to monitor HCl concentrations in coal combustion flue gases.

Approach

Evaluation of the Interaction Between CO_2 and $SnCl_2$–NaOH in Flue Gas Mercury Conversion/Conditioning Systems

The original plan was to use a Bacharach Fyrite gas analyzer, employing the well-known "Orsat" method of volumetric analysis that involves the chemical absorption of a gas such as CO_2 to determine the CO_2 concentrations upstream and downstream of a PSA conversion/conditioning system. However, Rousemount CO_2 and NO_x analyzers along with an Ametek SO_2 analyzer have become available and will be used. Independent variables will include NaOH and CO_2 concentrations and sample gas and liquid flow rates. The following simulated flue gas mixture will be used for all of the tests:

- O_2 – 6%
- SO_2 – 1600 ppm
- HCl – 50 ppm
- NO – 300 ppm
- NO_2 – 20 ppm
- H_2O – 8%
- N_2 – 85.8%

CO_2 concentrations will be varied from 5% to 20% and NaOH concentrations from 10% to 20%. Gas flow rates through the bubblers will range from 0.5 to 3 l/min. The flow rate of the solution depends on the peristaltic tubing size and pump RPM. Tests will be conducted to determine CO_2 breakthrough as a function of time in a fixed volume of liquid sample.

ESP Design and Fabrication Modifications

An existing ESP system will be redesigned to accommodate the requirements for sampling flue gas upstream of impinger-based and CMM systems. Design changes included resizing to accommodate the required sample volume, relocating components to minimize gas–solid interactions, and providing a solid removal system to enable long-term operation. The prototype ESP will be used to design and fabricate a new electrostatic flue gas-conditioning module.

Demonstration testing will be performed in an economical manner by taking advantage of existing measurement programs. The ESP gas conditioning unit will be used in applications that are known to contain mercury reactive ashes and where direct comparisons can be made with the techniques that are currently being utilized (e.g., glass fiber filtration upstream of an ASTM Method D6784-02 sampling train). Reductions in measurement bias will be recognized by decreases in Hg(p) and/or $Hg^{1+,2+}$ species concentrations. Examples of potential demonstration sites where EERC research is currently planned include a pilot-scale (550,000-Btu/hr) combustion system and power stations in North Dakota. By combining these existing programs, the testing will be performed at a very low cost and will also benefit these existing programs.

Chlorine and Hydrogen Chloride Monitoring of Coal Combustion Flue Gas and Other Gas Streams Utilizing Infrared Spectroscopy

Initially, known Cl_2–HCl–H_2O mixtures will be generated by diluting certified Cl_2–N_2 and HCl–N_2 mixtures with humidified air. Cl_2 and HCl concentrations will be maintained at about 3 and 50 ppmv, respectively, which are representative of measured values in actual coal combustion flue gases. The Cl_2–HCl–H_2O mixtures will be introduced through the stack probe of the system shown in Figure 1 to evaluate whether 1) mixtures of Cl_2, HCl, and water vapor can be successfully transported to the GASS dryer and Model 15C HCl analyzer; 2) HCl can be removed selectively and quantitatively from the gas stream using a chiller; and 3) Cl_2 can be converted to HCl by reacting with hydrogen in the presence of UV light or at 250°C. Additional tests will be conducted using known Cl_2–HCl mixtures in simulated coal combustion flue gases to evaluate the robustness of the system. Presented in Table 1 are representative simulated flue gas compositions. Assuming that the simulated coal combustion flue gas test results warrant further testing, then similar tests will be conducted in a bench- or pilot-scale coal combustion system using real flue gas.

Progress

Evaluation of the Interaction Between CO_2 and $SnCl_2$–NaOH in Flue Gas Mercury Conversion/Conditioning Systems

These tests are scheduled to be completed the first part of January 2005. The analyzers are being set up, and the tubing for the peristaltic pumps is being calibrated.

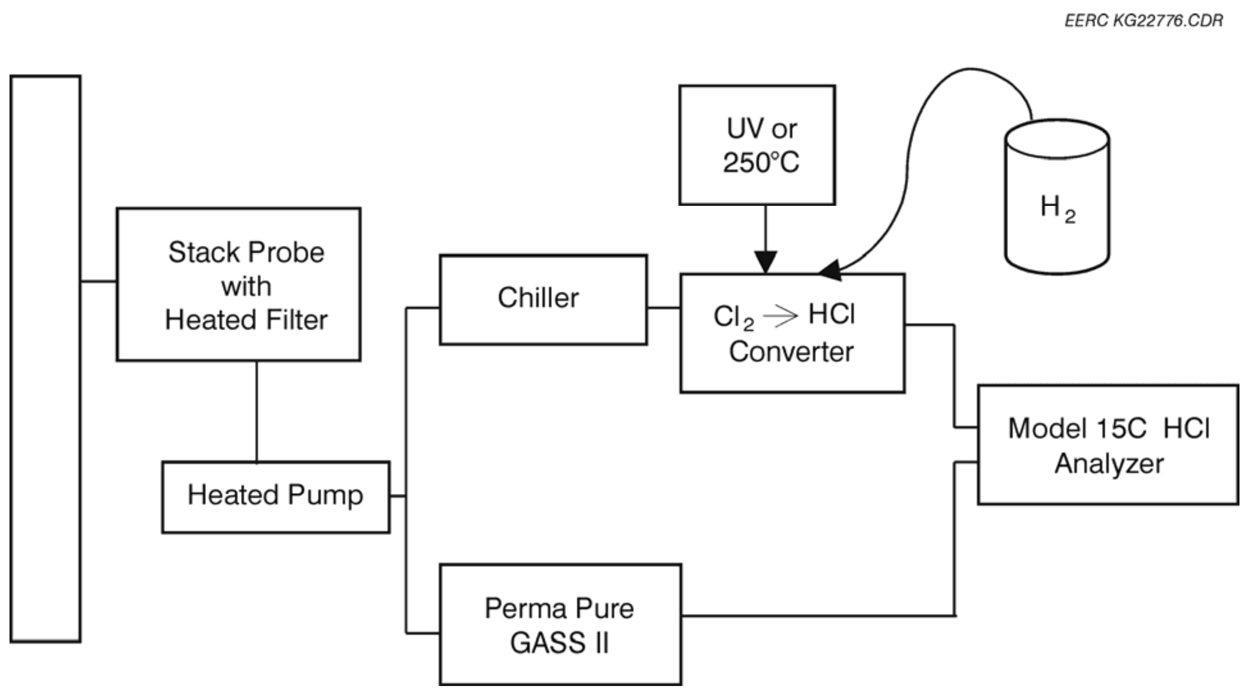

Figure 1. Block diagram of HCl/Cl_2 stack monitoring system.

Table 1. Potential Simulated Flue Gas Compositions

Component	Concentration, ppmv
HCl	5, 25, and 50
Cl_2	1 and 3
NO	1500
SO_2	2500

ESP Design and Fabrication Modifications

The design of the second-generation ESP and the acquisition of building materials will be completed in February 2005. Construction of the ESP should be initiated in February 2005 and completed in March 2005.

Chlorine and Hydrogen Chloride Monitoring of Coal Combustion Flue Gas and Other Gas Streams Utilizing Infrared Spectroscopy

The development of a HCl/Cl_2 stack-monitoring system has been delayed because of safety concerns associated with the direct combination of H_2 and Cl_2. In addition, access to the flue gas simulation apparatus has been limited because of a recent increase in the amount of mercury-related sorbent testing research being conducted at the EERC. Research on the HCl/Cl_2 stack-monitoring system is anticipated to begin early in 2005.

Quality Assurance/Quality Control

Evaluation of the Interaction Between CO_2 and $SnCl_2$–NaOH in Flue Gas Mercury Conversion/Conditioning Systems

Curves will be generated for the removal of CO_2 from the sample gas stream based on CO_2 concentration, NaOH concentration, sample gas flow rate, and NaOH flow rate. Breakthrough curves will also be generated and used to develop correction factors for mercury concentration. In addition, the data from the NO_x and SO_2 analyzers will be plotted as a function of time.

The CO_2 concentration at the outlet of the wet conversion system will be measured at each test condition with a Rosemount NGA 2000 MLT4 gas analyzer to determine the uptake of CO_2. The NGA 2000 has a detection limit of $\leq$1% of full scale and measurement ranges from 0–5 ppm to 0–100%. The analyzers will be zeroed and spanned daily using calibration gases with known concentrations. The gas delivery components of the mercury bench-scale system include mass flow controllers for each flue gas constituent. The mass flow controllers are periodically calibrated with a Gilibrator, which is a primary standard for flow measurement.

ESP Design and Fabrication Modifications

Comparative Hg measurements will be made using accepted continuous Hg monitoring and wet-chemistry methods utilizing sampling filters to separate particulate from the flue gas stream. Measurable differences in the biases related to particulate capture/conversion of Hg will be evaluated. Reductions in measurement bias will be recognized by decreases in Hg(p) and/or $Hg^{1+,2+}$ species concentrations. Reduction in bias relative to state-of-the-art particulate separation techniques for Hg measurements will be deemed successful. Long-term sampling stability may also be evaluated relative to existing methods of particulate separation.

Chlorine and Hydrogen Chloride Monitoring of Coal Combustion Flue Gas and Other Gas Streams Utilizing Infrared Spectroscopy

A Model 15C HCl analyzer combined with a thermoelectric chiller and Perma Pure GASS gas drying systems and a Cl_2–H_2 reaction chamber will be evaluated for quantifying Cl_2 and HCl in simulated coal combustion flue gas on a nearly continuous basis. Cl_2 and HCl spike recoveries of 90% will be considered an acceptable demonstration of this approach.

Status

Evaluation of the Interaction Between CO_2 and $SnCl_2$–NaOH in Flue Gas Mercury Conversion/Conditioning Systems

These tests are scheduled to be completed the first part of January 2005. The analyzers are being set up, and the tubing for the peristaltic pumps is being calibrated.

ESP Design and Fabrication Modifications

This activity will be initiated in January 2005.

Chlorine and Hydrogen Chloride Monitoring of Coal Combustion Flue Gas and Other Gas Streams Utilizing Infrared Spectroscopy

Research on developing a HCl/Cl_2 stack-monitoring system will begin early in 2005.

Potential Users/Technology Transfer

Evaluation of the Interaction Between CO_2 and $SnCl_2$–NaOH in Flue Gas Mercury Conversion/Conditioning Systems

All users of mercury analyzer sample-conditioning systems that utilize a NaOH solution will benefit from the results of this project. In order to report correct mercury concentrations, the amount of CO_2 removed from the sample gas stream must be known. The results from these tests will be used to develop correction coefficients based on CO_2 concentration, NaOH concentration, sample gas flow rate, and solution flow rate. These results will be published in the CATM annual report and shared with other CMM users.

ESP Design and Fabrication Modifications

The goal of this design is to provide long-term particulate removal for use with continuous Hg monitoring. If successful, this technology could be adopted by CMM vendors or used as an alternate method to vendor-supplied particulate filtering systems for Hg measurement.

Chlorine and Hydrogen Chloride Monitoring of Coal Combustion Flue Gas and Other Gas Streams Utilizing Infrared Spectroscopy

The capability to monitor Cl_2 and HCl together with the EERC’s mercury species monitoring capabilities would be very beneficial for investigating mercury chlorination reactions. In addition, Cl_2 and HCl monitors are needed to optimize wet and dry scrubber control strategies for various industrial activities (e.g., pharmaceutical processing, semiconductor manufacturing, coal combustion, and municipal solid waste and hazardous waste incineration).

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