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SAMPLING AND ANALYTICAL METHODS

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Project Summaries

CATM[®] is committed to developing, improving, and testing new and/or existing sampling and analytical methods for air toxic elements. As described by the following task activities.

Determination of Trace Constituents in Biological Tissues of Low Mass (<10 mg) Using Microdigestion/ICP-MS. During the past few years, the EERC has expanded into health-related research. Current projects funded by CATM Program Area 4 (Health Issues) and related programs are investigating Se-Hg interactions in laboratory animals. As a result, several animal tissue samples (i.e., brain, blood, hair, and pituitary) are being generated that require accurate determination of Hg, Se, and other potentially important metals. Some of these tissues pose analytical challenges in terms of sample preparation and instrumental analysis. The proposed activities will address these challenges and develop an accurate and reproducible method for the determination of Hg, Se, and other elements in biological matrices. A microdigestion procedure will be developed to accommodate the extremely small sample size, and modifications will be made to an inductively coupled plasma-mass spectrometer (ICP-MS) to minimize interferences associated with the determination of Se.

Evaluation of a Chlorine Species Continuous Emission Monitor for Coal Combustion Flue Gases. Last year, the EERC demonstrated that gaseous hydrogen chloride (HCl) and molecular chloride (Cl₂) could be selectively sampled and analyzed using infrared (IR) spectroscopy (Thermo Electron Model 15C HCl analyzer). A chiller/condensation drying system was used to selectively remove HCl from a simulated coal combustion flue gas, whereas a Perma Pure gas dryer removed H₂O without affecting HCl and Cl₂ concentrations. Cl₂ was converted to HCl for analysis by passing the chiller/condensation-treated gas stream through a hydrogen (H₂) torch. The EERC is proposing to test a chlorine species continuous emission monitor (CEM) on an actual coal combustion flue gas generated by a pilot-scale combustion system.

Improved Method for the Determination of Low-Level Halogens in Coal. This project will supplement information that is being generated in an ongoing CATM project entitled “Measurement of Halogens.” Because of the sensitivity associated with current analytical methods, this project is using established standard methods for detecting halogen concentrations >100 ppm and instrumental neutron activation analysis (INAA) for concentrations <100 ppm. Samples being generated under the currently funded project that require INAA will be sent to the University of Missouri for analysis. It is the goal of this activity to develop a reliable method at the EERC with existing equipment that is as sensitive as INAA. Existing methods will be modified for determining Br and Cl in coal that use combustion preparation procedures followed by ion chromatography separation and analysis. The challenge is to develop a preparation procedure that significantly increases the sample size while minimizing possible instrumental interferences. Samples will include those that are being analyzed by INAA under the current CATM project. Additional coals will be added to include all ranks and a broad concentration range of Br and Cl.

Spiking and Measurement of Carbon Sorbent Traps to Meet Appendix K Requirements. Based on discussions at a recent mercury measurement workshop sponsored by the Electric Power Research Institute (Research Triangle Park, Raleigh, North Carolina, September 7, 2005) and at the EERC–U.S. Department of Energy–CATM-sponsored Air Quality V Conference, there is concern regarding the reliability of the 40 Code of Federal Regulations, Part 75, Appendix K (Sorbent Traps) mercury-sampling method. The problem has been the low recoveries obtained in the mercury-spiked portion of the carbon trap, resulting in data rejection and costly analyses. Therefore, this effort will undertake further development of the mercury-sampling procedure. The first task will be to develop and test two different sorbent trap spiking methods; the second will be to evaluate the use of an instrumental measurement method (Ohio Lumex RA-915+). Analytical results will be compared to analysis done by another method at Frontier Geosciences, Inc., and the EERC.

Improving Laser Spectroscopic Techniques for Mercury Determination. Advances in laser diode technology and the need for improved techniques for measuring mercury in the environment and fossil fuel combustion systems have prompted an investigation into a two-photon laser-induced mercury measurement technique. Initial investigations have tested two excitation schemes. Parameters included laser excitation wavelengths and gas matrix. Further development of this technique is warranted because previous data suggest that it should be possible to lower method detection limits by modifying key experimental components.

Development of an As, Se, and Hg Sampling and Analytical Method for Reducing Flue Gas Environments. A sampling protocol will be developed for sampling arsenic (as arsine gas), selenium (as hydrogen selenide), and mercury (as elemental mercury) including sample-conditioning solutions that will convert the desired species into a form suitable for CEMs.

A more detailed description of each project follows.

Determination of Trace Constituents in Biological Tissues of Low Mass (<10 Mg) Using Microdigestion/ICP–MS

Key Personnel: Jenny Sun (EERC), Carolyn Nyberg (EERC)

Project Description

During the past few years, the EERC has expanded into health-related research. Current projects funded by CATM Program Area 4 (Health Issues) and related programs are investigating Se–Hg interactions in laboratory animals. As a result, several animal tissue samples (i.e., brain, blood, hair, and pituitary) are being generated that require accurate determination of Hg, Se, and other potentially important metals. Some of these tissues pose analytical challenges in terms of sample preparation and instrumental analysis. The project described herein is addressing these challenges and developing an accurate and reproducible method for the determination of Hg, Se, and other elements in biological matrices. A microdigestion procedure is being developed to accommodate the extremely small sample size, and modifications are being made to an inductively coupled plasma–mass spectrometer (ICP–MS) to minimize interferences associated with the determination of Se. The development of a reliable method for measuring trace element concentrations in biological matrices will enhance the success of health-related research proposed under CATM.

Goal

The overall goal is to develop a suitable method for analyzing biological samples of very low masses. Specific objectives include the following:

- Review the literature for applicable sample preparation and analytical techniques for biological tissues.
- Validate digestion procedures and analytical techniques such as ICP–MS and cold-vapor atomic absorption spectroscopy (CVAAS) with suitable biological standard reference materials.
- Apply procedures to samples generated from separate health-related studies.

Rationale

During the past few years, the EERC has expanded into health-related research. Current projects funded by CATM Program Area 4 (Health Issues) and other related programs are looking at Se–Hg interactions in laboratory animals and invertebrates. As a result, several animal tissue samples (i.e., brain, blood, hair, and pituitary) are being generated that require accurate determination of Hg, Se, and other potentially important metals. Some animal tissues and organs are extremely small (<10 mg) and pose an analytical challenge regarding sample preparation (digestion) and low instrument detection limits. Although ICP–MS offers extremely low detection limits, the determination of Se in complex matrices can be difficult because of the presence of molecular interferences. However, these interferences can be minimized by applying collision cell technology (CCT) which introduces a collision gas such as hydrogen into the analyzing chamber. Argon, which is typically used as a carrier gas in ICP–MS, forms many interfering molecular species in the analyzing chamber. One of these species is $^{80}\text{Ar}_2$ which has the same mass (80) as the predominantly measured isotope of Se (^{80}Se). CCT works by bombarding the interfering

species with an alternate gas which causes the interfering molecular species to disassociate. This approach is also beneficial in reducing molecular species that interfere with the determination of other elements such as As, Cr, and Co.

Approach

A new hot block heater and supplies to digest extremely small samples have been purchased. A literature survey is being performed to obtain relevant information regarding preparation procedures for the determination of metals in biological matrices. It is anticipated that applicable methods will need to be scaled down to accommodate extremely small samples (5–20 mg). Biological standard reference materials are being obtained to validate suitable digestion procedures. Suggested materials to be used for validation are listed in Table 1. Ultraclean labware and certified trace metal-grade reagents are being used for all sample preparation procedures to eliminate or minimize contamination. Reagent and method blanks are being prepared with each set of experiments. Prepared samples and blanks are being analyzed using an ICP–MS protocol described below.

An existing ICP–MS is being combined with CCT that minimizes molecular interferences associated with the determination of selenium and other elements.

The samples and standard reference materials will be analyzed using this instrumental technique for the determination of Se and other elements of interest as indicated in related research projects. CVAAS will be used for the determination of Hg since it offers a slightly lower detection limit than ICP–MS. Precision, accuracy, and detection limits will be determined for Se and other select elements using the combined microdigestion–ICP–MS method

Table 1. Biological Standard Reference Materials

Standard Reference Material:	IAEA-086 Trace Elements in Human Hair Reference Value, mg/kg	UTAK-44522 Metals in Whole Blood Reference Value, ng/mL	DORM-2 Dogfish Muscle – Trace Metals Reference Value, mg/kg	BCR 414 Trace Elements in Plankton Reference Value, mg/kg
Hg	0.573 ± 0.039	15	4.64 ± 0.26	0.276 ± 0.018
Se	1.00 ± 0.20	201	1.40 ± 0.09	1.75 ± 0.10

Experimental Apparatus

The analytical work will be performed in the Analytical Research Laboratory (ARL) at the EERC. The ARL is equipped for routine and specialized analyses of inorganic and organic constituents, which are performed using classical wet-chemistry and state-of-the-art instrumental procedures. Established analytical techniques enable the chemical characterization of a variety of environmental sample types, including fossil fuels, biomass, geologic materials, fine particulate matter, groundwater, and wastewater. Particular attention is directed toward trace element analysis, including mercury. The staff follows EPA, ASTM (American Society for Testing and Materials) International, and other standard methods for the analysis of samples. Analytical methods are routinely monitored for precision and accuracy with certified reference materials from the National Institute of Standards and Technology, the South African Bureau of Standards, the International Atomic Energy Agency, the Commission of the European Communities Community Bureau of Reference, and other sources.

The ARL supports mercury and other trace metal research at the EERC. The ARL has developed improved digestion techniques and lowered instrument detection limits on graphite furnace atomic absorption spectroscopy and ICP-MS.

The ARL analyzes certified parameters annually in a water pollution study acquired from a NIST/National Voluntary Laboratory Accreditation Program-accredited provider. Additional external quality assurance is maintained by participating in interlaboratory studies and proficiency programs such as the Coal and Ash Sample Proficiency Exchange™ (CANSPEX™) Program. This participation allows the ARL to demonstrate competence in methods of analysis by comparing analytical results and techniques with other laboratories throughout the United States and Canada.

Progress

A literature search was conducted to obtain information relevant to the preparation and analysis of biological materials of low mass. Several promising journal articles and methods were acquired and are being reviewed (1–7). Project equipment and supplies have been purchased including a hot block digestion system, standard reference materials, and ultrapure reagents.

Trial experiments have been completed with two of the standard reference materials listed in Table 1: DORM-2 and IAEA-086. Method blanks were also included. These experiments were conducted to evaluate the purity of the method reagents and digestion vessels and also to increase proficiency with the new digestion system. The digested solutions from these experiments will be analyzed by ICP-MS to help evaluate calibration ranges, matrix effects, and approximate detection limits. Definitive results are not yet available.

Quality Assurance/Quality Control

Quality Objectives

The key quality control measure for this project will be reproducible recovery of analytes in selected standard reference materials. Acceptable recovery limits are 85%–115% of reported values, and acceptable precision is <10% relative standard deviation. Standard reference materials that are appropriate for this project are listed in Table 1.

Measurement/Data Acquisition

Animal tissues and standard reference materials will be prepared and analyzed using techniques developed in this project. Since the goal of this project is to develop a new procedure that applies to extremely small samples, standard methods will be modified to meet the objectives of the project. Methods that will be modified include EPA SW846 6020A – Trace Metals by ICP–MS and EPA SW846 7471A-Hg by CVAA. The ICP–MS with CCT that will be used for the Se analysis has a calculated detection limit of 0.1 µg/L (10× less than what is expected in reference materials), and the CVAAS that will be used for the Hg analysis has a calculated detection limit of 0.05 µg/L (10× less than what is expected in the reference materials). These limits were discussed with the CATM researchers who require Hg and Se determination in biological tissues, and they agreed that these limits would be sufficient for their studies.

There is a concern that very small samples (<50 mg) are not representative of the tissue that is being analyzed; however, some tissues, such as rat pituitaries, have a total mass of 5–10 mg. Therefore, the entire sample will be analyzed.

Assessment and Validation

Several measures are being used to assess the accuracy, precision, and validity of the analytical procedures developed during this project. Some of these measures include replicate sample analyses, certified reference material analyses, matrix spikes, and method blanks.

Status

This project is approximately 40% complete. The literature search is nearly completed, and the project supplies and equipment have been purchased. Once the instrument calibration methods have been established, additional reference materials and project samples will be prepared with two or three different digestion methods, using the information obtained from the literature and equipment manufacturers. These digestion procedures will be fully evaluated based on method blanks, replicate samples, analyte recovery, and matrix spikes. After a suitable method is established, it will be applied to samples generated from other CATM research projects.

Potential Applications and Benefits

Potential Users and Real-Life Applications

Current health-related projects within the CATM program that focus on physiological studies of trace elements will benefit from the methods developed in this project.

Technology Transfer

Results of this project will be transferred through periodic CATM review meetings and CATM annual and technical reports.

Environmental and/or Health Benefits

The success of this project will support other CATM studies that relate to Hg–Se interactions, which will ultimately provide information to health researchers and environmental regulatory agencies about the behavior of these elements.

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Evaluation of a Chlorine Species Continuous Emission Monitor for Coal Combustion Flue Gases

Key Personnel: Kevin Galbreath (EERC), Blaise Mibeck (EERC)

Project Description

Last year, the EERC demonstrated that gaseous hydrogen chloride (HCl) and molecular chloride (Cl_2) could be selectively sampled and analyzed using infrared (IR) spectroscopy (Thermo Electron Model 15C HCl analyzer). A chiller/condensation drying system was used to selectively remove HCl from a simulated coal combustion flue gas, whereas a Perma Pure gas dryer removed H_2O without affecting HCl and Cl_2 concentrations. Cl_2 was converted to HCl for analysis by passing the chiller/condensation-treated gas stream through a hydrogen (H_2) torch. This project will test a chlorine species continuous emission monitor (CEM) on an actual coal combustion flue gas generated by a pilot-scale combustion system.

Goal

The goal is to evaluate a system for monitoring Cl_2 and HCl concentrations in coal combustion flue gases on a nearly continuous basis. To achieve this goal, the specificity, sensitivity, bias, and precision of the Cl_2 /HCl-monitoring system must be determined with an actual coal combustion flue gas.

Rationale

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. Continuous Cl_2 and HCl measurements are essential for understanding time-dependent reactions, such as fluctuations in Hg 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.

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).

Approach

Initially, the HCl content of a coal combustion flue gas will be monitored using a Perma Pure gas- (GASS-II™) drying system and Model 15C HCl analyzer during pilot-scale testing. The chlorine content of the coal will be determined and used in mass balance calculations, assuming that all chlorine reacts with water vapor to form HCl, to estimate HCl recovery. The coal combustion flue gas will also be dried using a chiller/condensation system to remove HCl and then treated with an H₂ reaction torch to convert any Cl₂ to HCl so that it can be analyzed using the Model 15C HCl analyzer. Known Cl₂-HCl mixtures will be introduced through a stack probe of the system to evaluate sample recoveries. Relatively high Cl₂ spike concentrations (e.g., 50 ppmv) will be used to evaluate whether GASS-II-dried flue gas can be delivered directly to the H₂ torch for determining Cl₂ concentrations.

Experimental Apparatus

The EERC has a Model 15C HCl analyzer, chiller/condensation and GASS-II gas-drying systems, and a Cl₂-H₂ reaction torch needed to perform chlorine species measurements on a nearly continuous basis. A VICI Medtronics Dynacal 190 Cl₂ permeation source will be used for spiking purposes. Pilot-scale (7- or 150-kW) coal combustion systems are periodically used at the EERC for various types of testing. Chlorine species monitoring will be conducted during several of these tests.

Test Plan

As demonstrated in Figure 1, the EERC has the capability to monitor HCl, total gaseous mercury (Hg[g]), and elemental mercury (Hg⁰) in coal combustion flue gases on a nearly continuous basis. The HCl measurements are performed with a Model 15C HCl analyzer combined with a GASS-II gas-drying system. The Model 15C analyzer uses IR spectroscopy to achieve an HCl detection limit of 0.2 ppmv (5-min integration time). The Model 15C analyzer measures only HCl because Cl₂ is not IR active. However, it is possible to scrub HCl from an airstream using a chiller/condensation drying system without removing Cl₂; and then Cl₂ in the scrubbed gas stream can be converted to HCl by reacting with H₂ in a torch (Figure 2), as demonstrated in Figures 3 and 4, respectively. The selective HCl scrubbing and Cl₂-to-HCl conversion process may be used to measure HCl and Cl₂ concentrations in coal combustion flue gas streams on a nearly continuous basis. Alternatively, the GASS-II-conditioned flue gas containing HCl and Cl₂ may be analyzed upstream and downstream of the hydrogen torch to evaluate HCl and Cl₂ concentrations by difference, assuming that the Cl₂ concentration is relatively high in comparison to the HCl concentration.

Progress

Several experiments with Cl₂ mixed with nitrogen from either a calibration gas cylinder or Cl₂ permeation device were used to test the Cl₂-to-HCl conversion system pictured in Figure 5. Table 1 and Figure 6 compare the expected and observed HCl concentrations.

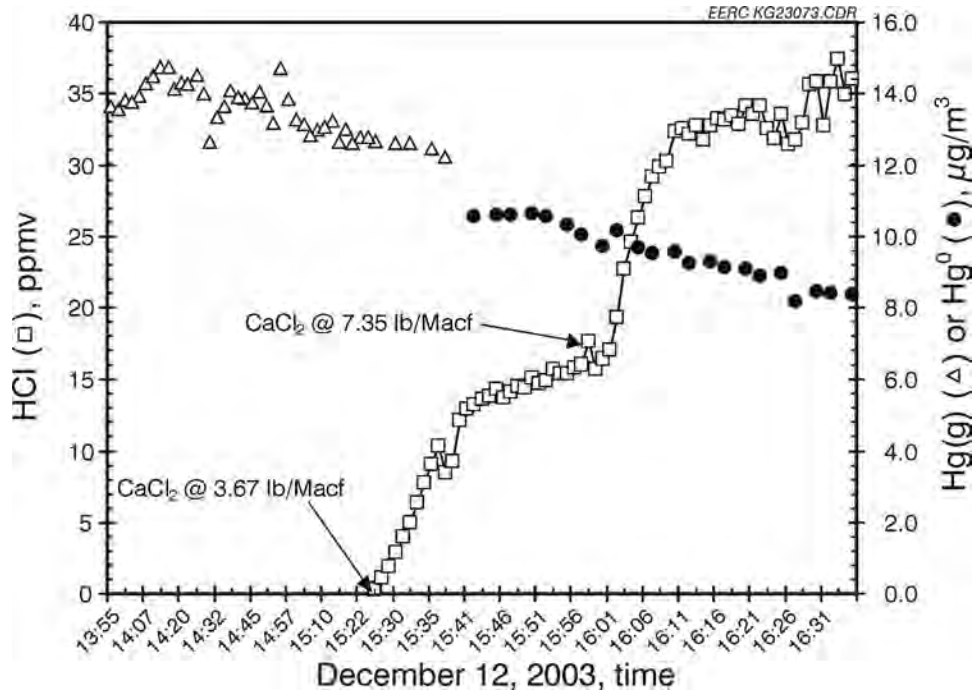


Figure 1. Temporal variations in spray dryer inlet HCl and fabric filter outlet Hg(g) and Hg⁰ concentrations during CaCl₂ additions to the Center lignite coal.

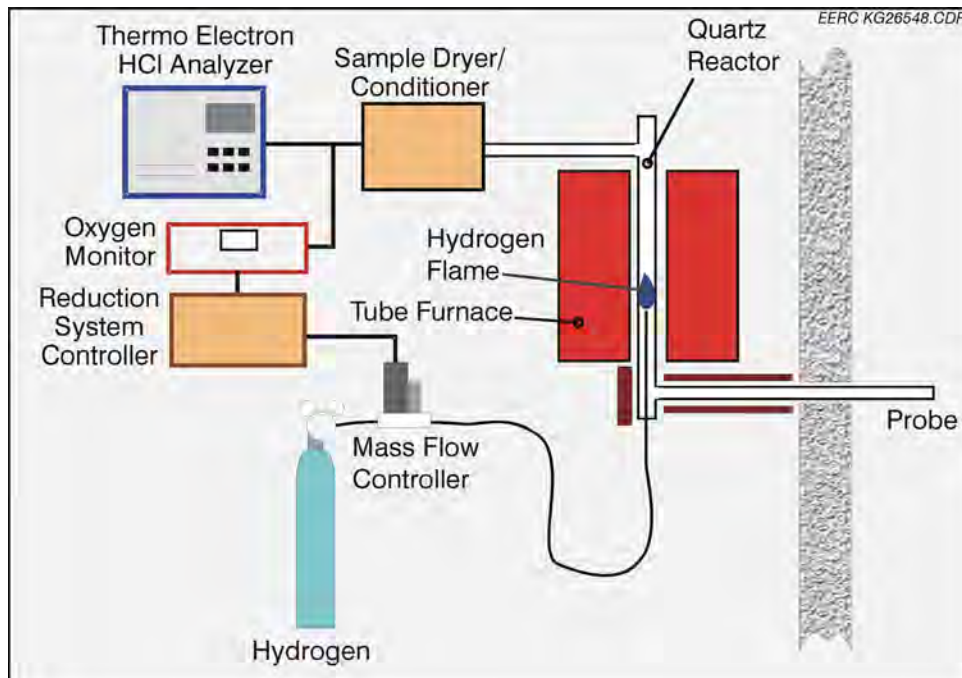


Figure 2. Schematic of the Cl₂-to-HCl conversion system.

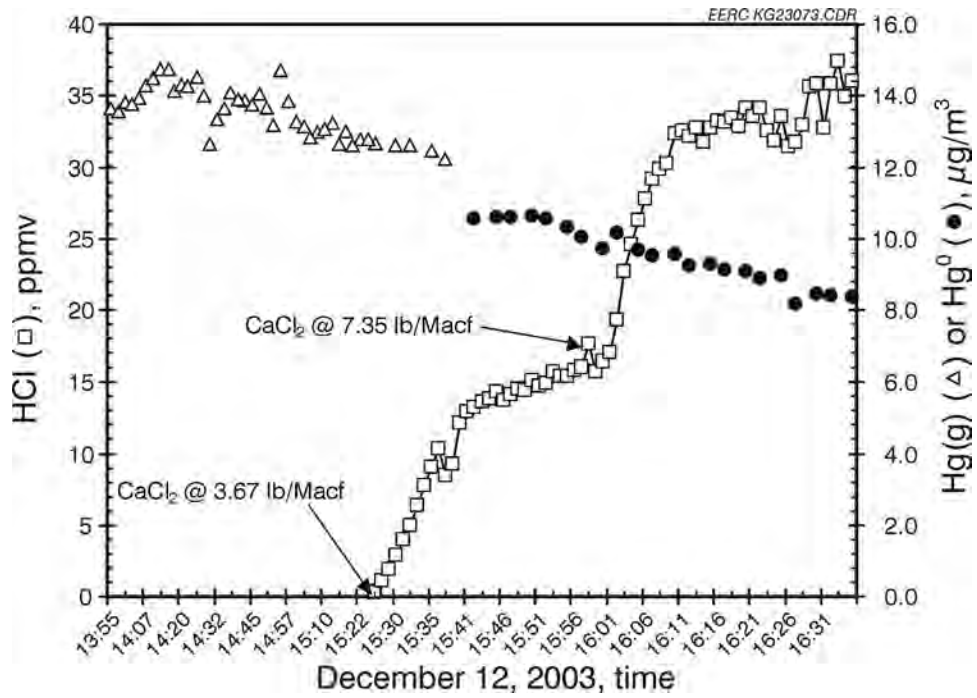


Figure 3. Continuous HCl-monitoring results demonstrating the removal of a 50-ppmv HCl spike from a simulated coal combustion flue gas using a chiller/condensation drying system.

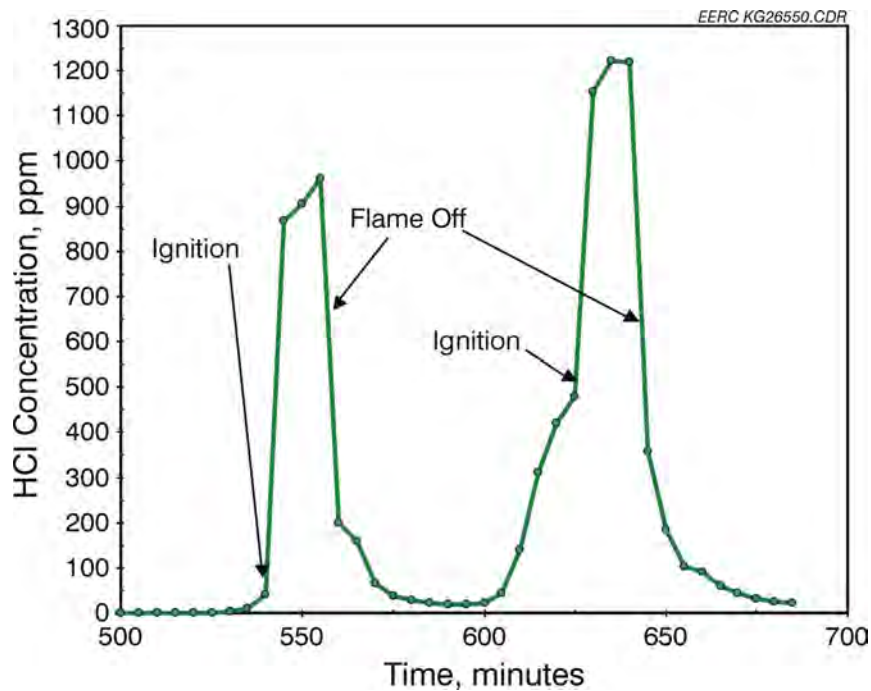


Figure 4. Continuous HCl-monitoring results demonstrating the conversion of Cl₂ to HCl using an H₂ torch.

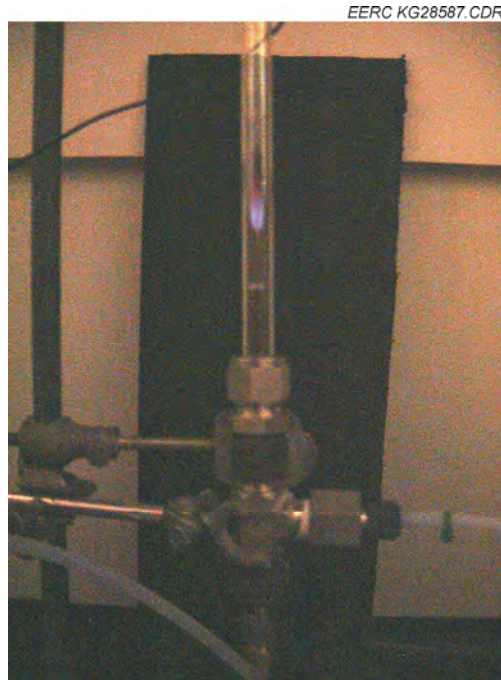


Figure 5. Apparatus for flame conversion of Cl_2 to HCl .

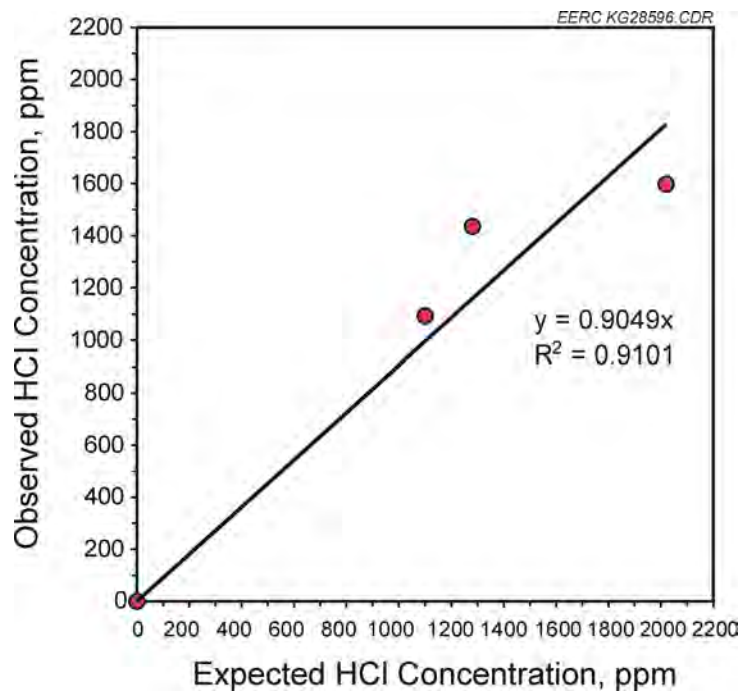


Figure 6. HCl linearity during conversion tests.

Table 1. Comparison of Expected and Measured HCl Concentrations

Expected HCl, ppm	Measured HCl, ppm	Difference, %
0	0–5	
1100	1093	–0.6
1280	1436	12.2
2020	1598	–20.9

Quality Assurance/Quality Control**Quality Objectives**

The quality objective is to accurately and reproducibly measure HCl and Cl₂ in coal combustion flue gas using a newly developed flue gas-conditioning system and CEM. The quantitative objective is to attain Cl₂ and HCl spike recoveries of ≥90%. The measured results in Table 1 are not within the 90% spike recovery goal; thus additional modifications to the flame conversion system (Figure 5) are being made in an effort to improve conversion efficiency.

Measurement/Data Acquisition

A Model 15C HCl analyzer was used as a CEM. The analyzer is based on the principal of IR spectroscopy to achieve an HCl detection limit of 0.2 ppmv (5-min integration time).

Assessment and Validation

A Model 15C HCl analyzer combined with chiller/condensation and GASS-II gas-drying systems and a Cl₂–H₂ reaction torch should be useful for quantifying Cl₂ and HCl in coal combustion flue gas on a nearly continuous basis. Cl₂ and HCl spike recoveries of ≥90% should be considered an acceptable demonstration of this approach.

Status

A sampling and analysis strategy for measuring Cl₂ and HCl in a simulated coal combustion flue gas and N₂ has been demonstrated. The spiking of Cl₂ and HCl into an actual coal combustion flue gas should be performed to evaluate the robustness of the system. Cl₂ spiking should also be performed to evaluate whether the GASS-II-dried flue gas can be delivered directly to the H₂ torch for determining Cl₂ concentrations by difference (i.e., Cl₂ = total chlorine as HCl – HCl). Follow-on work to perform these additional tasks is being pursued.

Potential Applications and Benefits

Assuming a favorable outcome from an improved flame conversion system, a collaborative effort with analytical equipment manufacturers may be proposed to create a more compact and eloquent Cl₂ and HCl monitor. This technology will enable the characterization of gas-phase components in coal combustion-derived flue gases. In addition, it will provide validation information for Hg and Cl speciation-modeling efforts. Pharmaceutical processing, semiconductor manufacturing, coal-fired power plant, and municipal solid waste and hazardous waste incineration facilities should be interested in using a Cl₂ and HCl monitor to optimize their scrubber removal efficiencies. The EERC is interested in using

online Cl_2 and HCl measurements to optimize mercury oxidation and sorbent enhancement strategies that are being developed for controlling mercury emissions from coal-fired power plants.

Improved Method for the Determination of Low-Level Halogens in Coal

Key Personnel: Carolyn Nyberg (EERC), Jenny Sun (EERC)

Project Description

This project is supplementing information that is being generated in another ongoing CATM project entitled “Measurement of Halogens.” Because of the sensitivity associated with current analytical methods, this project is using established standard methods for detecting halogen concentrations >100 ppm and instrumental neutron activation analysis (INAA) for concentrations <100 ppm. Samples being generated as part of the other CATM projects have been sent to the University of Missouri for INAA analysis. It is the goal of this project to develop a reliable method for determining Br and Cl at concentrations of <10 ppm in coals and ash by-products. Existing methods will be modified for determining Br and Cl in coal that use combustion preparation procedures followed by ion chromatography (IC) separation and analysis. The challenge is to develop a preparation procedure that significantly increases the sample size while minimizing possible instrumental interferences. Samples selected for this project include those that are being analyzed by INAA. Additional coals will be added to include all ranks and a broad concentration range of Br and Cl.

Goal

The overall project goal is to develop and implement a sensitive, reliable, and reasonably priced method for low-level (1–10 ppm) Br and Cl determination in coals and combustion by-products. Specific objectives include the following:

- Evaluate two novel preparation procedures for halogens in coal and related materials followed by IC.
- Compare method results with those obtained from INAA.

Rationale

It is widely accepted by the research community that halogens (i.e., Br and Cl) play a critical role in Hg speciation and control in coal combustion flue gas; however, the majority of lignite and subbituminous coals contain very low concentrations (<10 ppm) of these halogens. As a result, halogenated agents are being used to supplement halogens already present in the fuel to develop Hg control strategies. This is resulting in an increased need for accurate and reliable determination of halogens in coal and combustion by-products. Current methods for determining Br in coal are limited to INAA, bomb combustion/ion selective electrode (ISE), or bomb combustion/IC finish. Although INAA offers the best detection limit (1–5 ppm) over other methods, it is not available in most analytical laboratories. The bomb combustion technique followed by ISE or IC is available in most laboratories; however, it has a high detection limit of >100 ppm and is prone to interferences from other elements. Thus more accurate and less costly methods are needed.

Approach

All the coals are being prepared according to ASTM (American Society for Testing and Materials) International D2013 to pass a 250- μm sieve (No. 60 mesh), and moisture is being determined according to ASTM D3173. The coals are being prepared using two different approaches: sealed combustion followed by ion separation and low-temperature ashing involving a halogen sorbent.

Coals are being combusted in a sealed system, and the volatilized halogens are being trapped in an absorbing solution. This is similar to the oxygen bomb combustion procedure outlined in ASTM Method D4208; however, it is being modified to increase the sample size and reduce the known NO_x interference. After the coal is combusted and the ions trapped in the absorbing solution of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$, ion exchange columns are being used to separate the bromide, chloride, and nitrate ions. After these ions are separated into their respective fractions, they will be concentrated and analyzed using a modified IC technique.

An additional sample preparation approach that is being developed involves the ashing of a large quantity of coal (~10 g) mixed with a Ca–Mg compound that readily absorbs volatile Br and Cl species to avoid potential losses during the ashing process. Different low-temperature ashing procedures are being evaluated, and samples are being spiked with appropriate Br and Cl compounds that closely reflect their concentrations in coal. The ashed samples are being extracted with a minimal amount of deionized water to extract bromine and chlorine from the ash as halide ions in solution. The solutions are being analyzed using an IC that was modified to achieve better detection and peak resolution.

Results obtained from the samples prepared and analyzed using the two different approaches will be compared to those from INAA. It is anticipated that the majority of the samples will be the same materials that are currently being characterized under an ongoing CATM project. Results obtained from all methods will be compared and evaluated. If possible, additional samples will be added to include all ranks and the concentration ranges of Br and Cl will be broadened.

Progress

Approximately 70% of the samples that will be evaluated in this project have been collected. Coal and fly ash samples have been obtained from various CATM and EERC projects. Twelve coal samples have been prepared to –60 mesh and sent to the University of Missouri Research Reactor Center (MURR) for INAA. Results of these samples are pending. A subset of the samples was selected for trial experiments at the EERC to evaluate the feasibility of the other methods discussed above. The first approach involved combusting the coal in a humidified oxygenated system (oxidative hydrolysis) which converts the volatilized halogens to HBr and HCl. These compounds are then trapped in an absorbing alkaline solution where they exist as bromide and chloride ions. Initial separation and extraction procedures for removing interfering ions were unsuccessful. The nitrate ion was interfering with bromide determination by IC, and definitive results were not obtained from these initial experiments.

The same alkaline solutions that were analyzed by IC were also analyzed by inductively coupled plasma–mass spectroscopy (ICP–MS). Although this technique was not initially proposed for this project, preliminary results show that it can achieve a very low detection limit for bromine. Other researchers have found similar results when using an alkaline extraction procedure followed by ICP–MS (1–3). The detection limit for Br in coal using oxidative hydrolysis followed by ICP–MS is estimated to be $<1 \mu\text{g/g}$; however, Cl cannot be determined by conventional ICP–MS at levels below $500 \mu\text{g/g}$. Further evaluation is planned to determine if one preparation and analysis procedure can obtain low concentrations (1–10 $\mu\text{g/g}$) for both elements.

*Quality Assurance/Quality Control***Quality Objective**

The quality objective is to accurately and reproducibly measure Br and Cl in coal and combustion by-products using a newly developed method.

Measurement/Data Acquisition

The following measurement and data acquisition methods will be employed:

- Coal and combustion by-products will be analyzed for low levels (<100 ppm) of Br and Cl using INAA at the University of MURR.
- Coal will be prepared using newly developed techniques involving sealed combustion and ion trapping or low-temperature ashing and ion extraction.
- The extraction solutions will be analyzed by both IC and ICP–MS.
- Combustion by-products will be analyzed using deionized water extraction followed by IC and ICP–MS.

Assessment and Validation

The quality control activities used to assess Br and Cl measurements are listed in Table 1. The availability of certified reference materials for halogens in coal is extremely limited (only one available from the National Institute of Standards and Technology); thus the key quality control measures for this project will be reproducible recovery of spiked analytes in the coal matrix and acceptable agreement with INAA values when sample analysis is complete and results compiled. Acceptable recovery limits will be 85%–115% of expected values, and acceptable method agreement will be <20% difference.

Table 1. Quality Control Activities

Quality Control Activity	Performance Characteristic Measured
Replicate Sample Collection	Total variability associated with sampling, preparation, and analysis
Replicate Sample Analysis	Analytical variability associated with instrument performance
Reference Materials	Method accuracy measured by analyte recovery in appropriate matrices
Analytical Control Samples	Instrument performance, including detector response, calibration drift, and analyte recovery
Matrix Spiking	Analyte recovery in actual sample matrix
Method Blank	Blank effects associated with the method, including reagents and labware

Status

Preliminary experiments produced inconclusive results for samples analyzed by IC; however, promising results for Br were obtained when samples were analyzed by ICP–MS. With some modifications to the extraction process and the IC, it is expected that both Br and Cl can be determined in

one preparation and analysis procedure. However, the detection limits may not be suitable for all coals. If increased sensitivity for Br is needed, ICP-MS is an excellent option. Future experiments using a subset of the project samples will focus on improving IC detection limits and perfecting operating parameters for the ICP-MS. When reasonable results are obtained, the full set of samples collected for this project will be prepared and analyzed with the newly developed techniques. Sample results will be compared to those obtained by INAA.

Potential Applications and Benefits

Potential Users and Real-Life Applications

Developers of Hg control technologies who rely on definitive coal quality parameters, including Br and Cl levels, will use this information to help in the decision-making process for determining the appropriate technologies for coal-fired power plants.

Technology Transfer

Results of this project will be transferred through periodic CATM review meetings and CATM annual and technical reports.

Environmental and/or Health Benefits

The successful development of a sensitive and reliable analytical technique for low-level halogen determination will result in quality data that can be used to develop and improve control technologies to reduce Hg emissions.

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Spiking and Measurement of Carbon Sorbent Traps to Meet Appendix K Requirements

Key Personnel: Dennis Laudal (EERC), Carolyn Nyberg (EERC)

Project Description

Based on discussions at a mercury measurement workshop sponsored by the Electric Power Research Institute (Research Triangle Park, Raleigh, North Carolina, September 7, 2005) and at the EERC–U.S. Department of Energy–CATM-sponsored Air Quality V Conference, there is concern regarding the reliability of the 40 Code of Federal Regulations, Part 75, Appendix K (Sorbent Traps) mercury-sampling method. Under certain sampling conditions, particularly for long sampling times in a high-SO₂/SO₃ flue gas environment, spike recoveries have been very low, and breakthrough has been observed from the first section of the trap to the second. To improve the Appendix K mercury-sampling procedure, bench- and pilot-scale tests are being done using EERC-modified sorbent traps. The scope of work is divided into two tasks. The first task is to complete bench-scale tests using simulated flue gas for proof of concept and to optimize the sample traps. The second task is to perform pilot-scale tests under actual flue gas conditions over a longer sample period.

Goal

The overall goal of the project is to further refine the use of the Appendix K measurement procedure for sampling mercury from coal-fired utilities by developing a sorbent trap that provides spike recoveries that meet the requirements of the Clean Air Mercury Rule (CAMR). The initial objectives of the project were to focus on methods of spiking and analysis of the current sorbent traps; however, it became clear that for Appendix K to be a viable option for compliance sampling, a different sorbent material was needed in certain flue gas environments. Although the overall goal of the project has not changed, the specific objectives of the project have. The current objectives are to 1) perform proof-of-concept bench-scale tests of the new sorbent material and 2) demonstrate the sorbent traps under actual flue gas conditions.

Rationale

EPA included Appendix K as an alternative method to continuous mercury monitors (CMMs) for monitoring vapor-phase mercury emissions from coal-fired electric utilities for regulatory purposes. However, there are questions and concerns regarding the reliability of this procedure in various sampling environments. One of the main concerns has been the low recoveries obtained from the mercury-spiked portion of the carbon trap, resulting in data rejection. Because the recovery of the spiked sample is used to correct and report the total mercury measured in the sorbent traps, it is essential that this part of the procedure yield consistent and reliable mercury recovery values.

Based on previous bench-scale work conducted by the EERC (1), it has been found that SO₂/SO₃ competes with mercury for binding sites on carbon and also can result in the desorption of already captured mercury, especially elemental mercury. This could explain the low recovery of mercury from the spiked sorbent traps that several researchers and sampling teams have observed.

Approach

Blank traps and spiked traps used for testing in this project are being purchased from Frontier Geosciences (FGS). Figure 1 is a schematic of the sample traps, which also includes information regarding the quality assurance criteria required for acceptable mercury measurements.

Task 1 – Proof of Concept for a New Sorbent Trap-Spiking System

To minimize the detrimental effects of SO₂ when using the Appendix K procedure for Hg sampling, the EERC has proposed modified carbon traps containing a mixture of materials. To test these modified traps, fixed-bed bench-scale tests have been designed using the test matrix shown in Table 1. Tests are to be completed using three different sorbents. The first is standard Norit DARCO® carbon for comparison purposes, the second is a treated carbon used by FGS, and the third is a mixture of the FGS carbon and an EERC proprietary material. Following completion of these tests, additional bench-scale tests will be performed to optimize the modified traps.

Task 2 – Pilot-Scale Demonstration

Based on the results of the bench-scale tests, sorbent traps will be prepared using a mixture of FGS carbon and an EERC proprietary material for testing at the pilot-scale level. Spiked traps will be purchased from FGS and modified by replacing the treated carbon in the primary and secondary sections (Figure 1) with a mixture of materials. The spiked section will not be altered. A probe will be built that will allow three traps to be used simultaneously. The modified traps will sample flue gas for three consecutive days, and the samples will be analyzed using an Ohio Lumex instrument.

The coal used in the pilot-scale testing is expected to be a medium-sulfur Illinois No. 6 bituminous coal. If the results are successful and there is enough funding, a second pilot-scale test will be conducted firing a Texas lignite–Powder River Basin (PRB) blend.

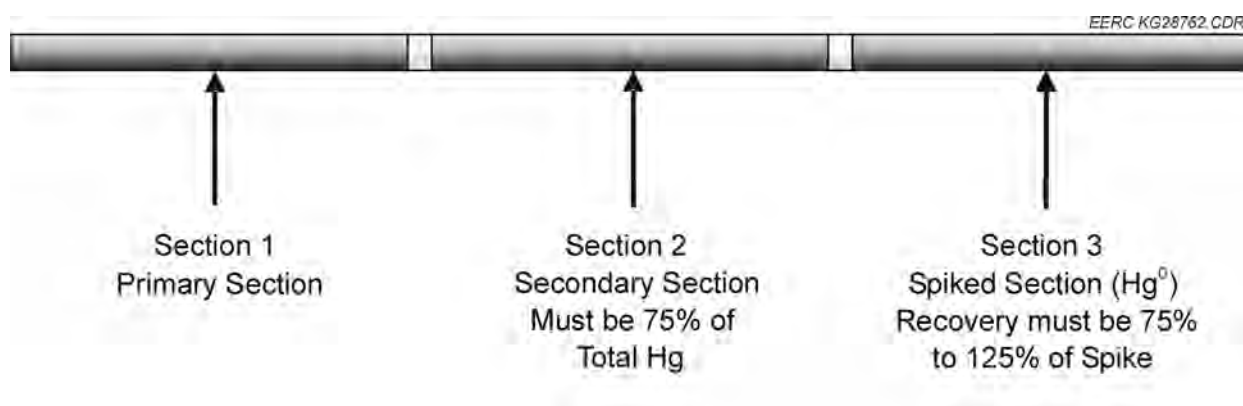


Figure 1. Schematic of Appendix K sorbent trap.

Table 1. Test Matrix for Carbon Sorbent Testing under Simulated Flue Gas Conditions

Test	SO ₂ , ppm	HCl, ppm	NO, ppm	NO ₂ , ppm	H ₂ O, %	O ₂ , %	CO ₂ , %	Hg ⁰ , μg/m ³	N ₂
1	1000	50	400	20	8	6	12	10	Balance
2	0	50	400	20	8	6	12	10	Balance
3	1000	0	400	20	8	6	12	10	Balance
4	0	0	400	20	8	6	12	10	Balance
5	1000	50	0	20	8	6	12	10	Balance
6	0	50	0	20	8	6	12	10	Balance
7	1000	0	0	20	8	6	12	10	Balance
8	0	0	0	20	8	6	12	10	Balance

Progress

Issues related to the reliability of results obtained from Appendix K sampling continue to surface as this project is being carried out. Results and observations from other projects, as well as discussions with other researchers, indicate that the procedure as written may not work for all sampling conditions (2, 3). As stated earlier, issues related to the capture and retention of mercury in sorbent traps, especially in the presence of SO₂/SO₃, needed to be addressed before any spiking experiments could be done.

The first step was to determine what sorbent material may help mitigate the effects of SO₂ on the ability of the carbon sorbent traps to capture and retain mercury. Based on previous testing, it was decided that the treated carbon used by FGS mixed with an EERC proprietary material had potential (1). The results of five of the bench-scale tests are shown in Figure 2. The results show that mercury breakthrough occurred relatively quickly (<1 hour) for the Norit DARCO carbon and the FGS treated carbon at 1000 ppm SO₂. When an EERC modified trap was tested at an SO₂ concentration of 500 ppm, breakthrough did not occur until 4 hours into the test. Bench-scale tests are continuing to improve and optimize the EERC's modified traps.

Quality Assurance/Quality Control (QA/QC)

Quality Objectives

The primary quality objectives and measure of success for the pilot-scale test will be as follows:

- The triplicate sorbent traps should have relative differences ≤10%.
- Spike recoveries should be 75%–125% of the actual value.
- The mercury measured in Section 2 of the trap should be ≤5% of total Hg measured.

If, however, there is more variability, the data will be flagged and evaluated as to the source of the deviation. As a final QA/QC check, an independent laboratory, FGS, will analyze the traps.

Measurement/Data Acquisition

Measurement of mercury will be accomplished at the EERC using the Ohio Lumex analyzer. The analysis done by FGS will be performed using EPA Method 1631. The sampling procedures and data acquisition will follow those outlined in Appendix K.

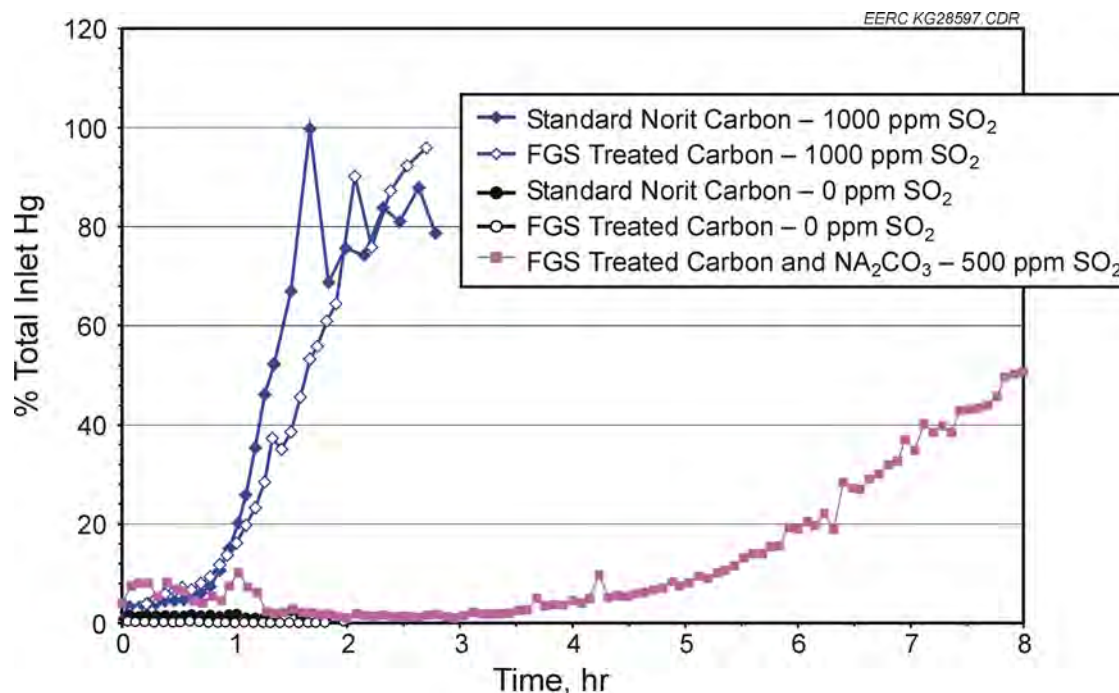


Figure 2. Mercury breakthrough of carbon sequestration.

Assessment and Validation

In addition to the QA/QC specific to this project, the EERC Analytical Research Laboratory (ARL) has established QA/QC procedures for all mercury samples that are done. This includes triplicate analysis and analyzing solution blanks and solution spikes. A copy of the ARL analytical QA/QC procedures is available upon request.

Status

The next activities planned for this project include preparation of modified carbon sorbent traps that will be used in a pilot-scale combustion test facility at the EERC. A separate CATM project will be conducting coal combustion tests in early 2007 using the EERC particulate test combustor burning an Illinois No. 6 bituminous coal. The PTC will be equipped with an electrostatic precipitator followed by a fabric filter baghouse. An Appendix K sampling system using the modified sorbent traps will be installed at the outlet of the FF. These traps will also be spiked with Hg prior to sampling. Flue gas will be sampled for the duration of the test burning the Illinois No. 6 coal, which will be approximately 72 hours. These samples will be analyzed and the results evaluated for the three main QA requirements outlined in the procedure: 1) triplicate trap agreement, 2) carryover to the second section, and 3) recovery of the spike.

When bench- and pilot-scale testing are complete, work will begin on developing a reliable spiking system.

Potential Applications and Benefits

The cost of installing CMMs is very high and, in the near term, it may be difficult for all utilities to purchase and install CMMs and meet the deadlines established by CAMR. Therefore, an alternative mercury method is essential. Assuming the success of this project, the technology will be transferred to others for use in large-scale facilities.

References

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Improving Laser Spectroscopic Techniques for Mercury Determination

Key Personnel: Blaise Mibeck (EERC), Kevin Galbreath (EERC)

Project Description

The focus of this project, continuing the development of a two-photon laser-induced mercury measurement technique, was prompted by recent advances in ultraviolet (UV) and near-UV laser diode technology and the need for more reliable mercury measurement techniques for applications in fossil fuel combustion systems. Initial work showed a two-photon excitation technique was possible at powers attainable with a UV lamp and violet diode laser. Initial investigations have tested two excitation schemes: parameters included laser excitation wavelengths and monitored emission wavelengths as well as control of quenching by choice of carrier gas (argon or nitrogen). Data from several experiments show how these parameters affect the detection limit of such a technique. Armed with this information, three areas of improvement have been identified: focus of the UV lamp, modulation of the laser, and improving the sensitivity of the measurement by lowering the pressure of the sample gas.

Goal

The goal is to improve the performance of a two-photon laser-induced fluorescence apparatus for measuring elemental mercury in flue gas.

Rationale

Mercury measurements in air or flue gas typically use the interaction with 253.67-nm light from a mercury lamp to induce fluorescence at the same excitation wavelength (1). This is problematic when NO_2 or SO_2 are present, as these compounds have broad absorptions in the UV. Techniques such as modulating the lamp wavelength and separating the mercury using gold amalgamation have been used with varying degrees of success (2). A laser spectroscopic technique for separating these interferences could be a valuable tool for conducting in situ transport and kinetics experiments.

To separate the mercury measurement from interferences, two successive transitions in mercury can be effected. The first transition is effected by a lamp filtered to emit 253.7-nm light and induce mercury to the first excited state. The second transition is caused by a laser that induces the mercury to fluorescence. A diode laser has been used to cause one of two secondary transitions. Compounds like NO_2 and SO_2 will not be mistaken for mercury in the measurement scheme because the two transitions will screen out the effects of these common interferences. Added to this is the benefit that the measurement takes place in the visible region of the spectrum (UV is more strongly scattered by air than visible light).

The two excitation schemes chosen for the initial study appear in Figure 1. Mercury behaves in the following way for each path:

Path A: At normal sample temperatures the majority of mercury atoms in a given sample will exist in the ground state; this is represented by the notation $\text{Hg}^0 \text{ } ^1\text{S}_0$. Upon interacting with a photon of wavelength 253.65 nm, the atom may absorb the photon and increase in energy to the $6\text{p}^3\text{P}_1$ state. In a gas comprising mostly a noble gas (like helium or argon), the $6\text{p}^3\text{P}_1$ state will eventually decay and a 253.65-nm photon will be spontaneously emitted. In Figure 1, Path A shows second

excitation occurring when a photon of wavelength 407.78 nm from the laser is absorbed by the $6p^3P_1$ mercury atom, raising it to the $7s^1S_0$ state. This new state is coupled with the $7s^3S_1$ state and, after a collision, will be quenched to this new state. After some time, this atom will decay to the $6p^3P_0$ state and, with this decay, will spontaneously emit a photon of wavelength 546.07 nm.

Path B: Mercury in the ground state, 1S_0 , is excited to the $6p^3P_1$ state where it is quenched to the $6p^3P_2$ state. This quenching is promoted by gases such as nitrogen and oxygen. From the $6p^3P_2$ state, the mercury atom can absorb a photon of wavelength 404.66 nm, rising in energy to the $7s^3S_1$ state where it will decay to the $6p^3P_0$ state while emitting a photon around 546.07 nm in wavelength.

Each path has advantages and disadvantages that dictate how each could be used. For instance, Path A is limited to use in argon or helium carrier gases because the absence of quenching would populate the $6p^3P_2$ state, preventing the second absorption needed for the measurement (3). Path B similarly requires this quenching, limiting its effectiveness when quenching gases like oxygen and nitrogen are present. In each case, fluorescence at 546.07 nm occurs. It is also possible for mercury in the $7s^3S_1$ state to decay to the $6p^3P_1$ state, emitting a 435.84-nm photon.

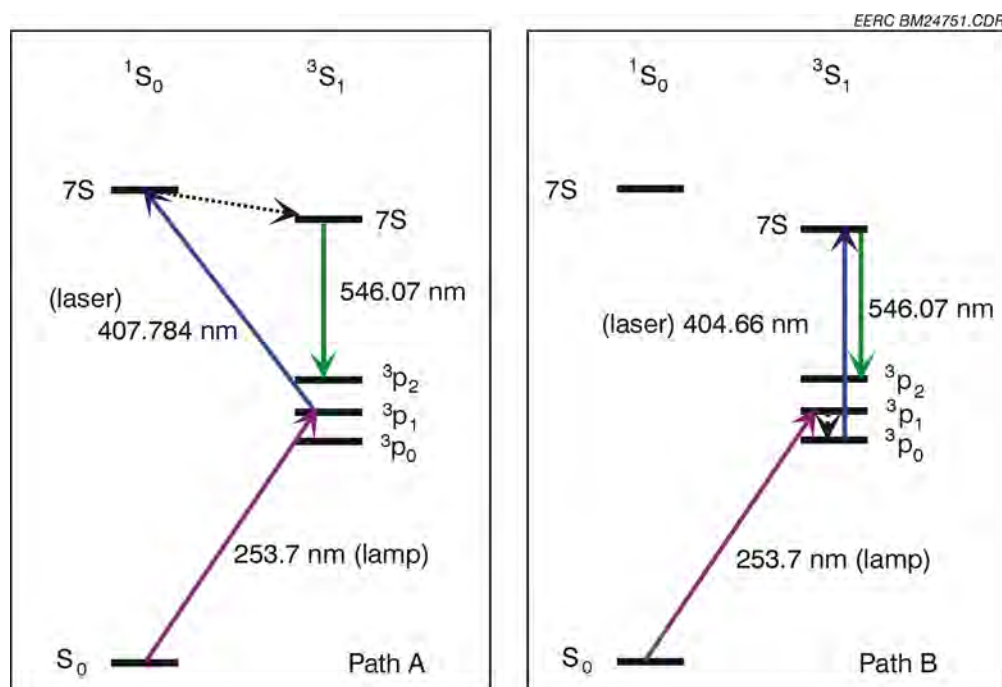


Figure 1. Schematic representation of electronic states important to this study.

Because Path B works in air, it became the focus of the current study. It is a long-term goal of this project to reduce the amount of separation and preconditioning involved in mercury measurement. Path A necessitates removing the mercury from the sample gas and transferring to an argon or helium carrier. Path B, on the other hand, can be coupled with an in situ method for converting mercury compounds to elemental mercury.

Approach

The experimental apparatus assembled for the initial study consists of two light sources: a high-powered mercury electrodeless discharge lamp (EDL) and a gallium nitride diode laser (Figure 2). The light from the lamp was passed through a lens and interference filter so that a spot of 253.7-nm radiation could be passed through the sample cell, a quartz flow-through cuvette. The laser (tuned to either 404.665 nm or 407.784 nm) propagated counter to the lamp light. Fluorescence leaving a side window of the cuvette enters a monochromator coupled to an inline photomultiplier tube (PMT). The monochromator allows the filtering of scattered lamp and laser light while passing through, at a high efficiency, the fluorescence signal of interest. The signal from the PMT is amplified and recorded with a data acquisition system that includes input from the wavelength meter used to monitor the laser diode wavelength during experiments.

The laser is tuned and monitored before experiments are performed. During experiments, data are collected from the wavelength meter. Example data from the wavelength meter appear in Figure 3.

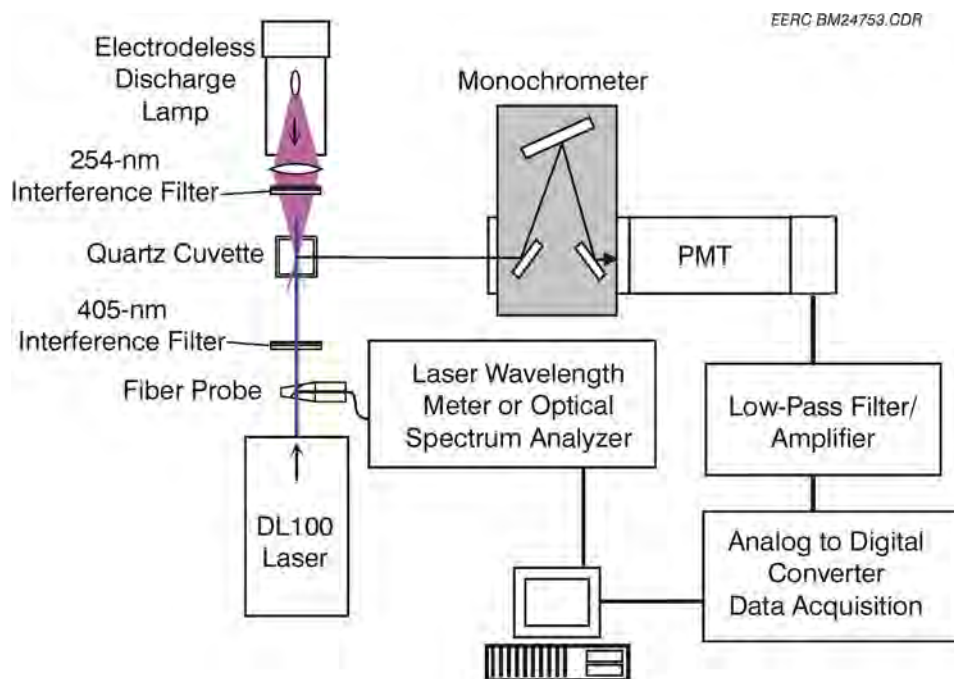


Figure 2. Original experimental apparatus used to study two-photon laser-induced fluorescence in mercury.

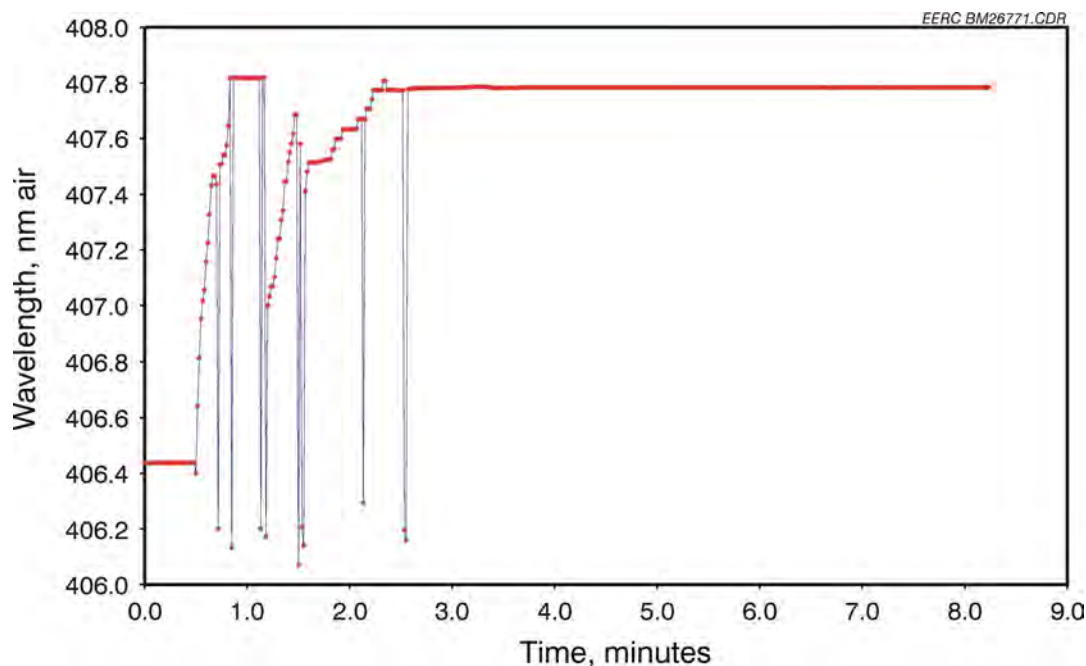


Figure 3. Example data from laser wavelength monitor during a tuning procedure.

A Nippon Instruments Corporation DM-6B mercury analyzer was used to monitor the mercury concentration in the sample stream (Figure 4). Calibration of this instrument was performed using the procedures described in the manual. After data are collected, the signal from the experimental apparatus and mercury analyzer are associated with each other using the time stamps in the data files. Excel is used to plot the PMT signal with respect to mercury concentration. Table 1 lists the tests performed with the apparatus during the initial study.

Data collected with these experimental conditions are displayed in Figures 3 and 6. The detection limit, in $\mu\text{g}/\text{m}^3$, is computed using the slope, m , and intercept, b , of the regression and the average standard deviation, σ_{ave} in the formula:

$$DL = \frac{3 \times \sigma_{ave} - b}{m}$$

Table 1. Summary of Experiments Conducted in the Initial Study

Test	Carrier Gas	Excitation Wavelength, nm	Fluorescence Wavelength, nm	Detection Limit, $\mu\text{g}/\text{m}^3$
1	Argon	404.66	546.01	>1000
2 ^a	Nitrogen	404.66	546.01	116
3 ^b	Argon	407.78	546.01	226
4	Nitrogen	407.78	546.01	>1000
5 ^c	Argon	253.67	253.67	2.6
6	Nitrogen	253.67	253.67	32.5

^a See Figures 5 and 6.

^b See Figures 7 and 8.

^c See Figure 9.

Progress

The current apparatus is illustrated in Figure 10. So far, improvements to the system include simultaneous monitoring of 546-nm and 253.7-nm radiation from the sample cell; chopping the laser at 30 Hz, focus and wavelength selection of the lamp are improved.

The lamp is now focused and the 253.7-nm wavelength selected via a concave monochromator grating. In the initial study, an interference filter and lens were used. Because of the difficulty in designing UV inference filters, the most efficient filters available allow only 12% of the light to be transmitted, the rest being absorbed by the filter medium or rejected. This presents the problem of how to properly populate the 3P_0 level by exciting the mercury to the 3P_1 level. While this filter-lens arrangement was bright enough to allow the initial proof of concept, developing an improvement became a priority.

To solve this problem, the lens and filter were replaced by a monochromator of the Seya-Namioka type. The grating was chosen for its high efficiency, around 250 nm. The grating produces a real image of the lamp light that is the same dimensions as the mercury-containing ampoule in the lamp, a spherical volume of approximately 0.5 cm^3 . This image is projected inside the sample cell. To prevent O_3 from forming in the vicinity of the lamp, an enclosure around the lamp and grating are continually purged with nitrogen.

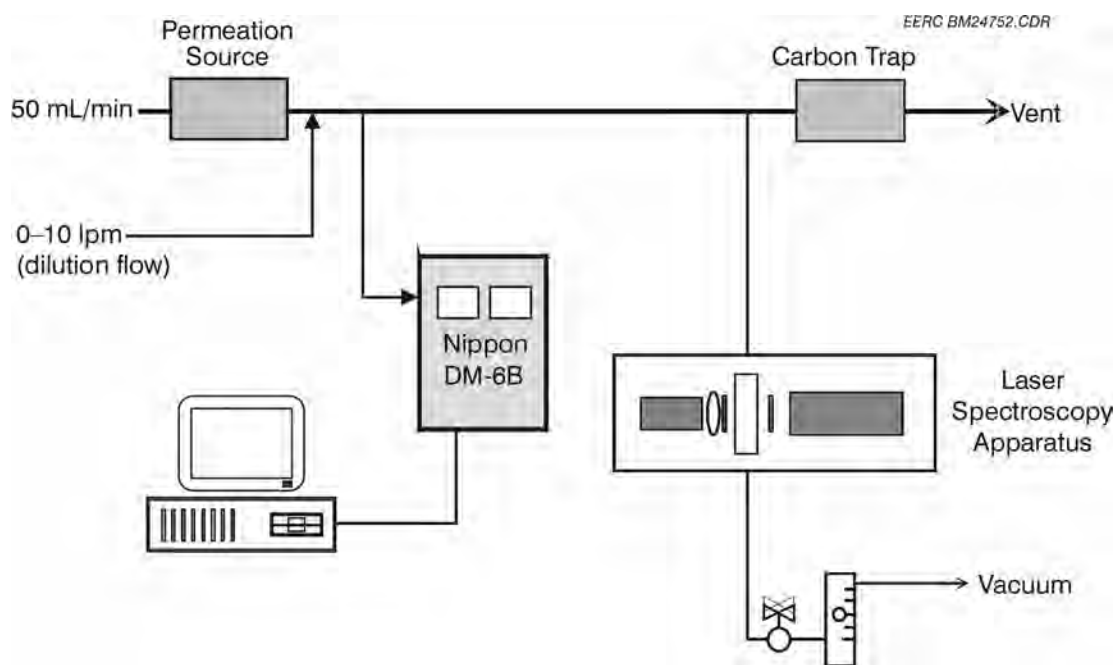


Figure 4. Experimental apparatus for testing the laser spectroscopy apparatus.

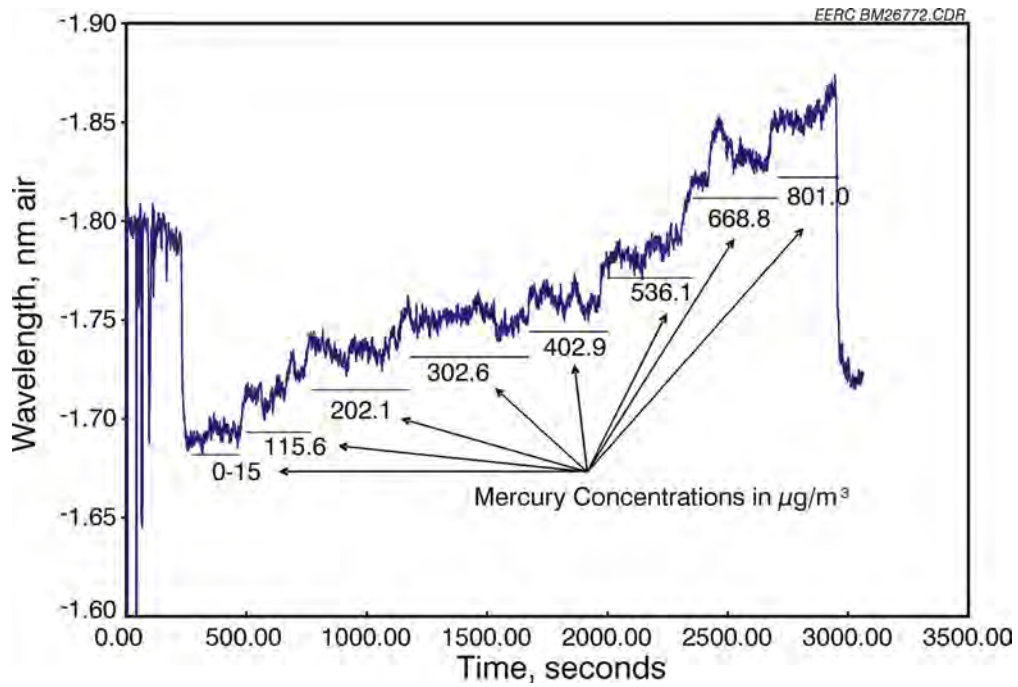


Figure 5. PMT signal versus time for experiment Test 2: Path B in nitrogen gas.

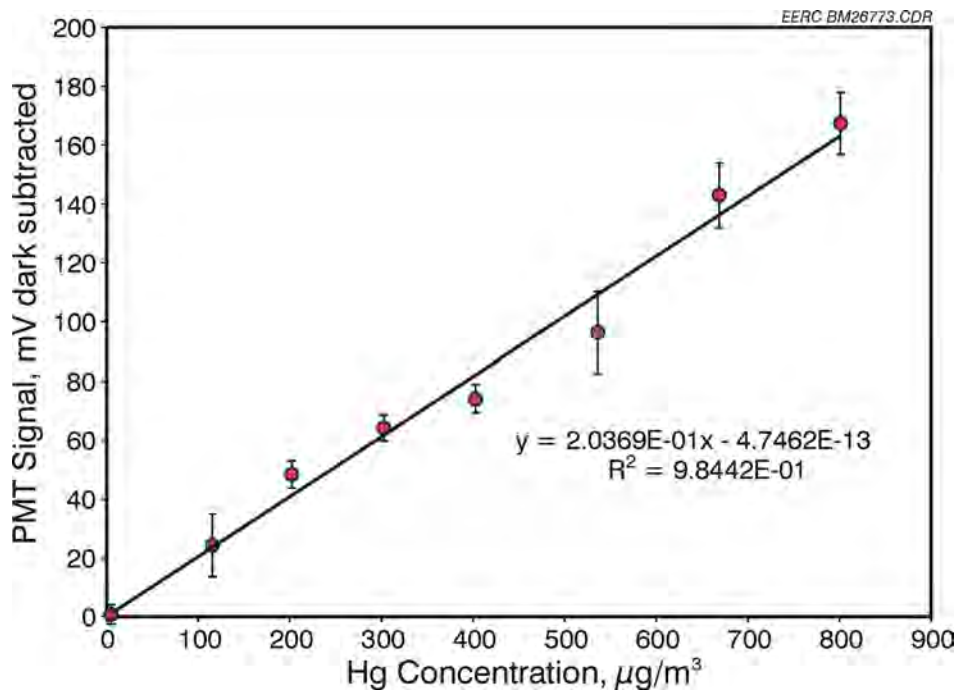


Figure 6. Laser-induced fluorescence (LIF) signal versus Hg concentration using 404.66 nm excitation and a nitrogen carrier (Test 2). The detection limit for mercury in this experiment is 116 $\mu\text{g}/\text{m}^3$.

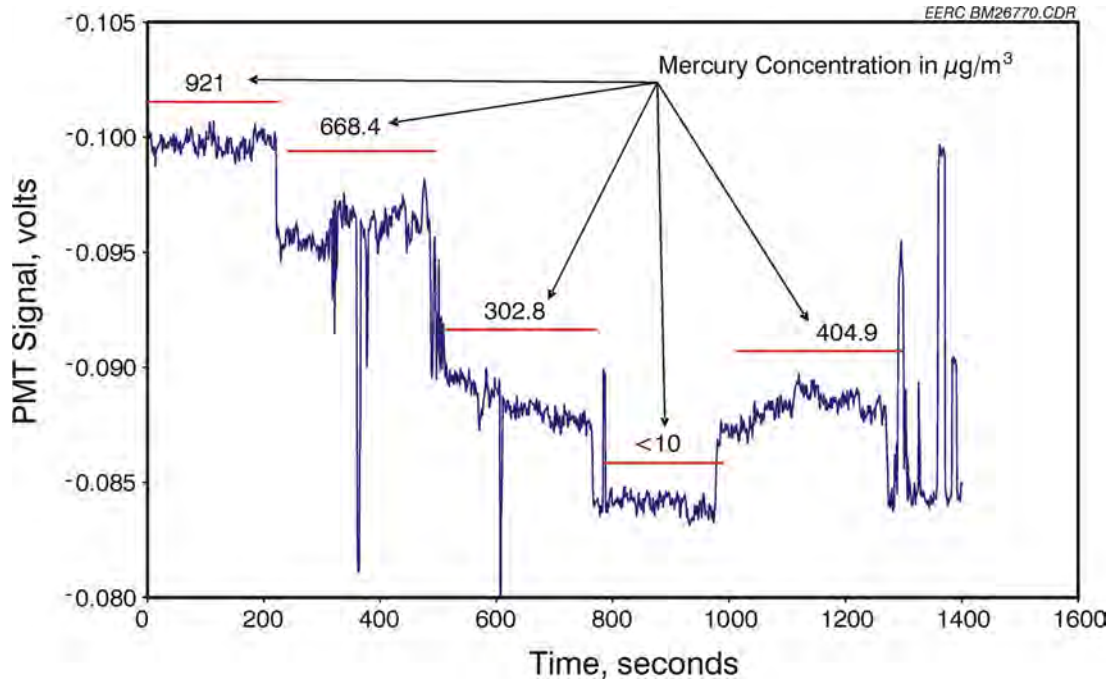


Figure 7. PMT signal versus time for experiment Test 3: Path A in argon gas.

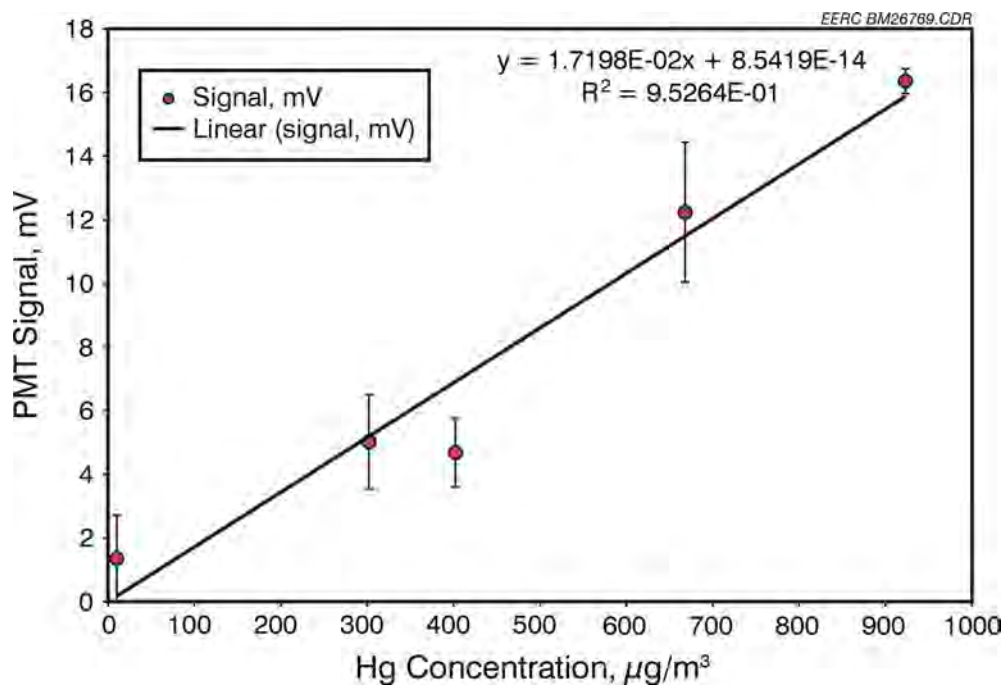


Figure 8. LIF versus Hg concentration using 407.78 nm excitation and an argon carrier gas. The detection limit calculated from this experiment is 226 µg/m³.

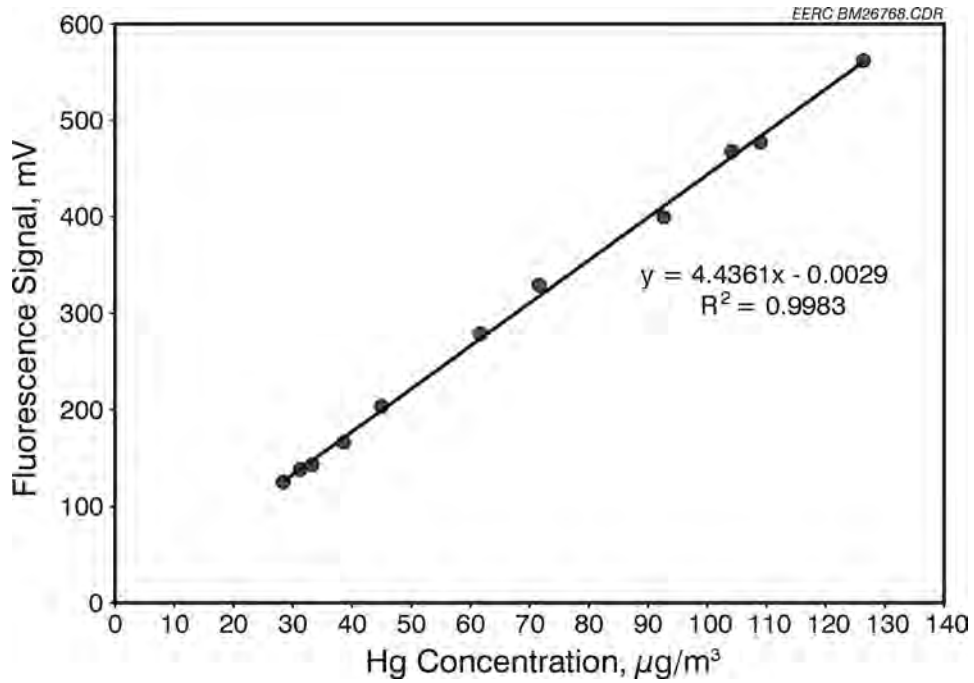


Figure 9. Fluorescence signal versus mercury concentration using 253.67 nm excitation (Test 5).
 Detection limit calculated to be 2.6 µg/m³.

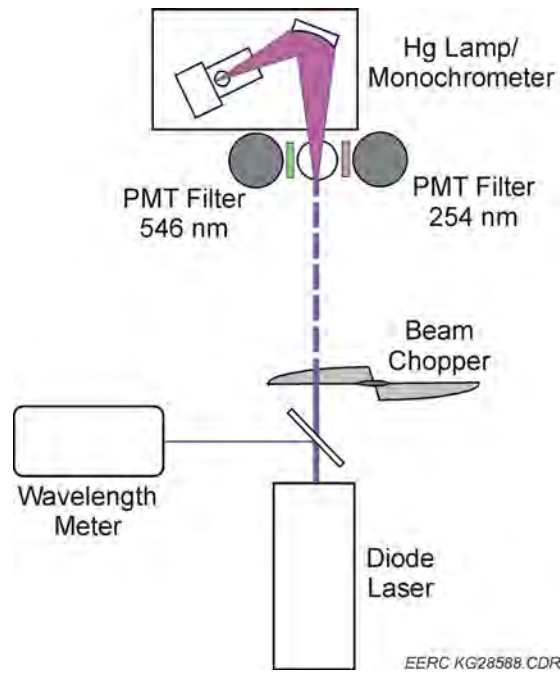


Figure 10. Layout of optical components for current project.

Detectors used in these experiments are side-on PMTs; one is filtered to detect light from the 546-nm fluorescence and the other filtered to detect 253.7-nm fluorescence (5). These are positioned on opposite sides detecting fluorescence orthogonal to the directions of the laser and lamp (Figure 11). Each are powered using a separate high-voltage power supply. The signal of each, consisting of the photocurrent generated by the PMT, is connected across a 50- Ω resistor so that the corresponding change in voltage can be amplified and recorded. These signals are recorded either using an analog-to-digital converter (for recording the average peak-to-peak voltage) or a digital storage oscilloscope which allows the wave form itself to be recorded.

To assist in signal detection, an optical chopper is being used to periodically interrupt the laser beam. When the laser is blocked, fluorescence at 546 nm stops and fluorescence at 253.7 nm resumes. Because both signals can be observed during an experiment, the detection limit using two-photon LIF can be compared directly to traditional 253.7-nm fluorescence.

Preliminary data used mercury vapor in a closed container at room temperature. Data of the 546-nm fluorescence oscilloscope wave form are displayed in Figure 12. The feature recorded when the laser is interacting with the mercury is of particular note. During the time that the lamp is blocked, the 3P_0 level becomes populated. At the moment the laser interacts with the mercury atoms in this state, the number of atoms in this state quickly drops as they become excited and then fluoresce down to the 3P_2 level. Atoms in this state eventually decay to the 3P_1 and 3P_0 level after collisional quench with nitrogen oxygen molecules. At higher laser intensities, this quenching process is much slower than the absorption/fluorescence process. This is manifested in the wave forms collected by the intensity increasing rapidly, dropping off, and then slowly climbing.

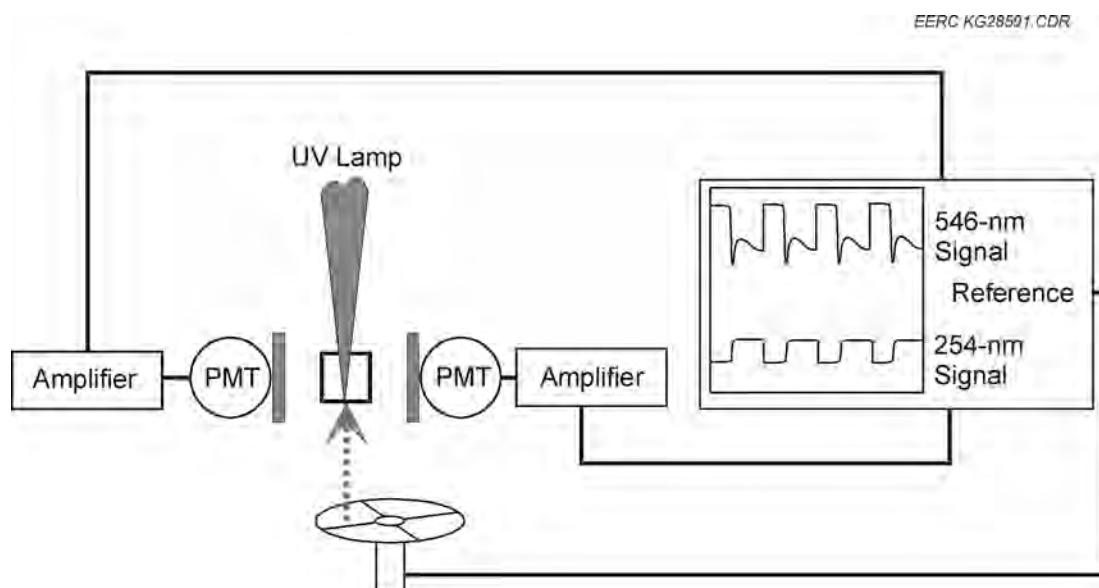


Figure 11. Signals measured using current experimental apparatus.

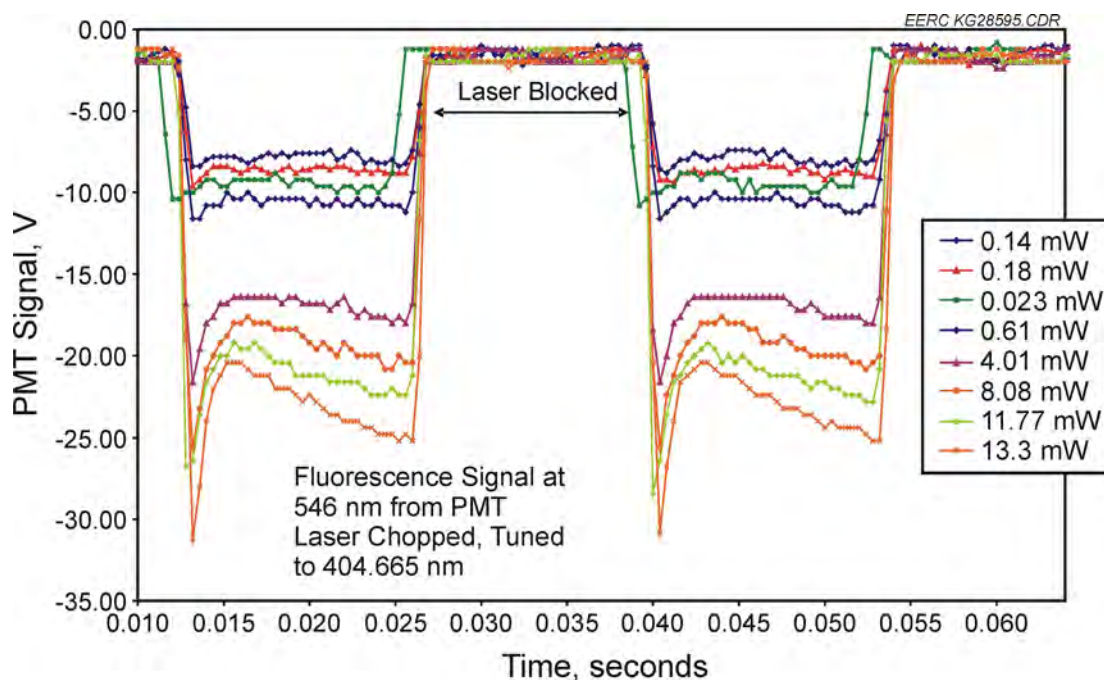


Figure 12. Fluorescence signal from 546-nm PMT. The fluorescence increases with negative voltage.

This process was examined more closely by adjusting the power of the laser diode between 0.14 mW and 13.3 mW (Figure 13 and Table 2). The depletion/repopulation effect becomes stronger at higher power. This is in agreement with the explanation above because at lower laser powers, the absorption would be less frequent and, therefore, the process of depopulating the 3P_0 level would approach the time needed to repopulate by collisional quenching.

Plotting the average peak-to-peak signal with respect to laser power shows that the laser, at higher operating powers, comes close to saturating the sample (Figure 14). Determining an optimum laser power is now possible, i.e., the power at which fluctuations in laser power do not lead to significant changes in output signal. For the duration of these tests, the laser will be operated above 8 mW. To the authors' knowledge this is the first investigation ever reported on the saturation and quenching dynamics of elemental mercury in a nitrogen matrix using a continuous-wave laser.

Table 2. Data from Saturation Curve

Power mW	Estimated Standard		Laser Current	Signal, av volts
	Deviation (ESD)			
0.14	0.01		29	6.4
0.18	0.01		34	7.4
0.23	0.01		40	7.2
0.61	0.01		44	8.8
4.04	0.04		50	15.6
8.08	0.01		54	17.2
11.77	0.12		58	19.2
13.30	0.01		64	20.4

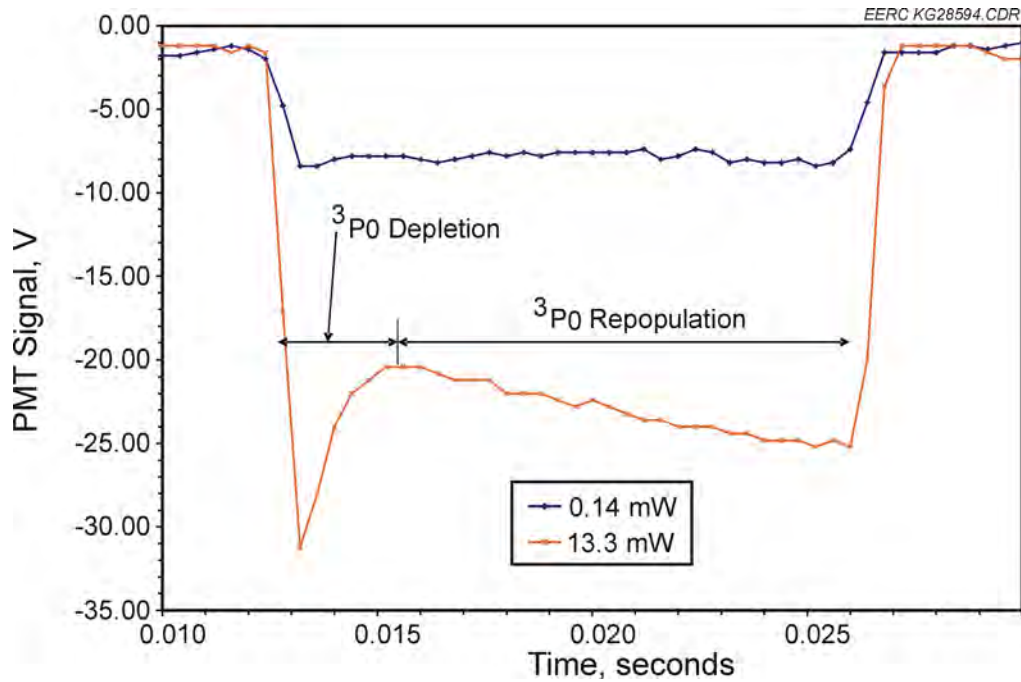


Figure 13. Plot showing fluorescence due to depletion and repopulation of the 3P0 level. Lowest intensity is observed about 5 ms after the laser begins draining the 3P0 level.

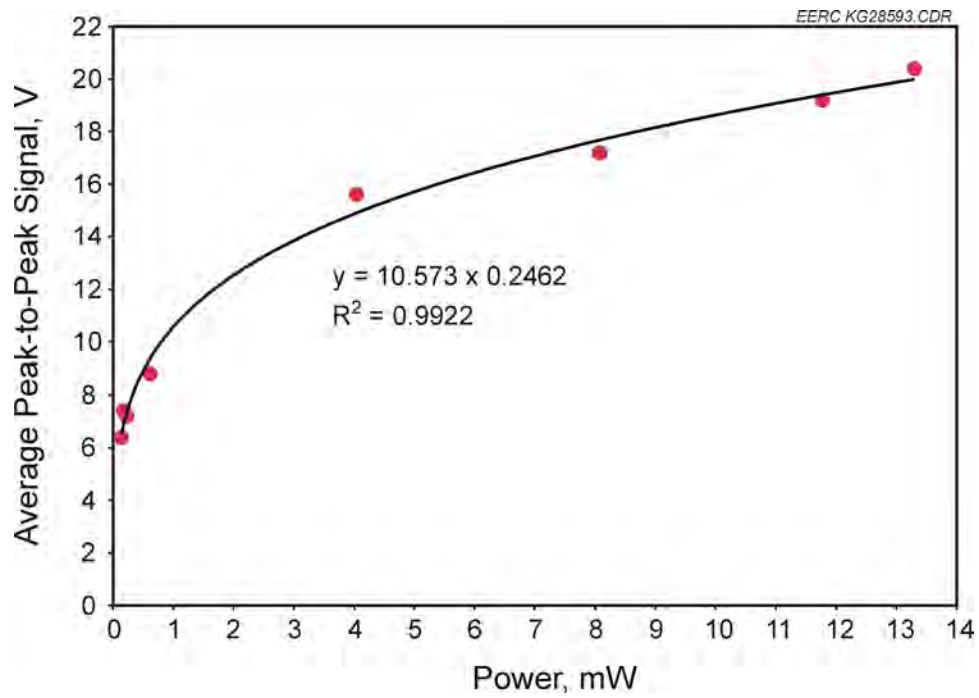


Figure 14. Saturation curve.

Quality Assurance/Quality Control (QA/QC)

QA/QC design for this project includes the following issues:

1. The precise measurement of laser wavelength to facilitate tuning required by the experiment.
2. Conditioning and acquisition of analog signals such as the signal from the PMT used to measure the strength of the fluorescence.
3. Relate the signal produced by the experiment to a mercury concentration by appropriately measuring said concentration.

The requirement for precision in laser wavelength measurement was determined to be 1 pm (picometer) or less. This determination took into account the spectral width of the laser and the spectral width of the atomic transition being effected by the laser, allowing for Doppler and pressure broadening. Because an absolute measurement of fluorescence intensity is not within the technical scope of this initial study, it was only necessary to condition the PMT signal by measuring and subtracting the dark background signal from the signal during data collection. This was accomplished using a light-tight shutter between the PMT and monochromator. Before data collection, equipment was allowed enough warm-up time to ensure stable operation during tests. During each test, a detection limit was obtained that ranged from between 2.6 and 226 $\mu\text{g}/\text{m}^3$. The detection limit of the Nippon DM-6B being used for this study is many times lower (0.1 $\mu\text{g}/\text{m}^3$). Calibration and maintenance of the mercury continuous emission monitor (CEM) were performed in accordance with the practices devised by the Nippon Instrument Corporation.

Status

This research project is active. One issue exists with the signal from the 254-nm PMT. It is believed that the signal is being overpowered by fluorescence in the larger volume illuminated by the lamp. The problem and potential solution are illustrated below. When this has been solved, the sample cell will be modified in order to analyze mercury at a slightly lower pressure than is currently possible. Lowering the pressure is suspected to increase the signal by increasing the lifetime of the $^3\text{P}_0$ state. This hypothesis is based on observations by Pool and others (4), and data from that work is displayed in Figure 16.

After this final apparatus and improvements are in place, a series of tests will be performed to determine the detection limit in air for mercury. A separate mercury analyzer will be used to compare the output of the laser apparatus with the measurement from the instrument. A permeation tube source of elemental mercury will be used to vary the concentration flowing through the sample cuvette. This work is currently taking place and should be completed before June 2007.

Potential Users/Technology Transfer

Instrumentation developed in this area could impact research requiring small, low-power measurement techniques for high-speed mercury determination.

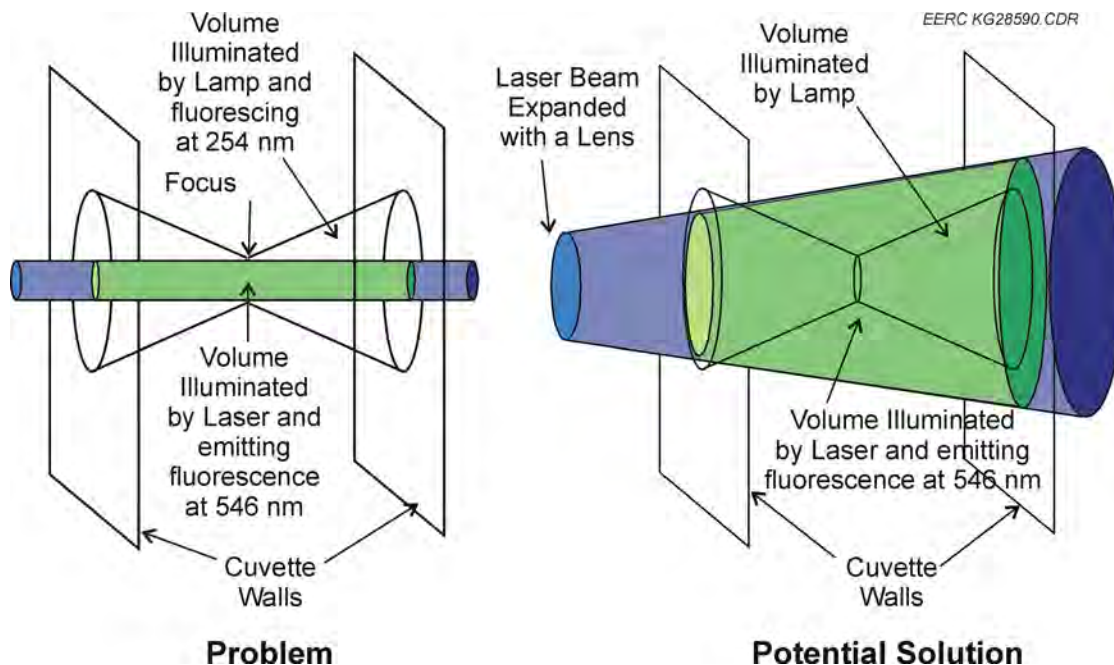


Figure 15. Illustration of problems related to nonoverlapping volumes of lamp and laser beams.

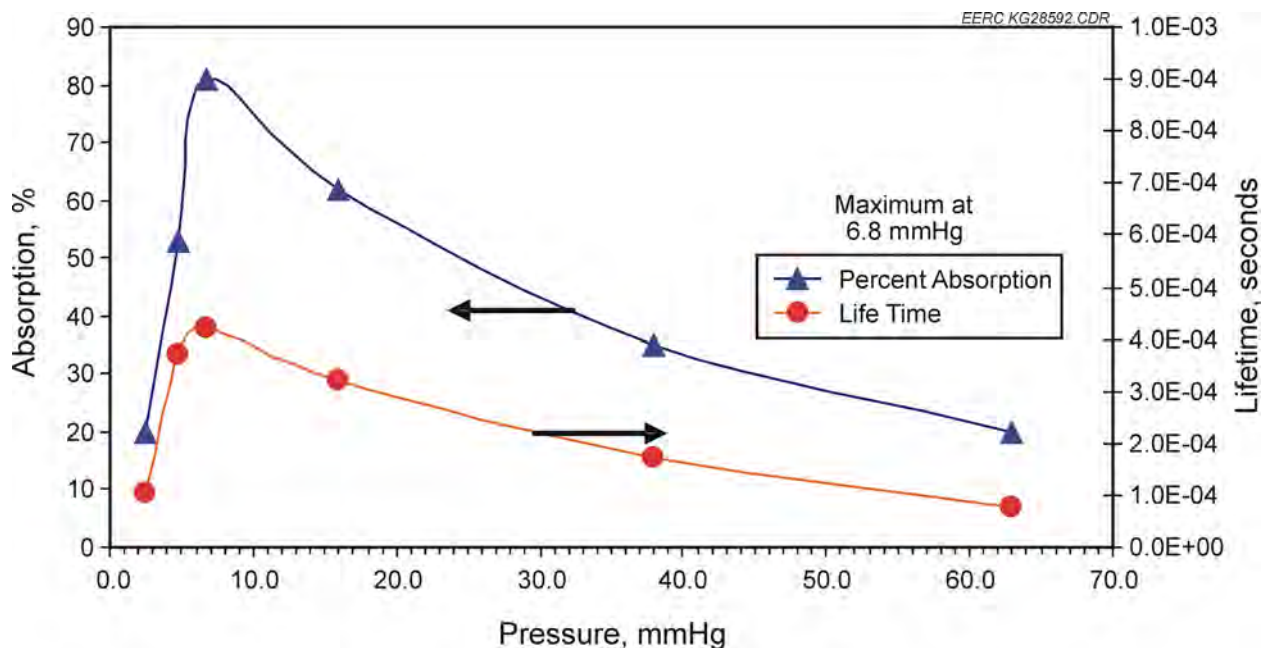


Figure 16. Data showing increased absorption with lower pressure of quenching gas (4).

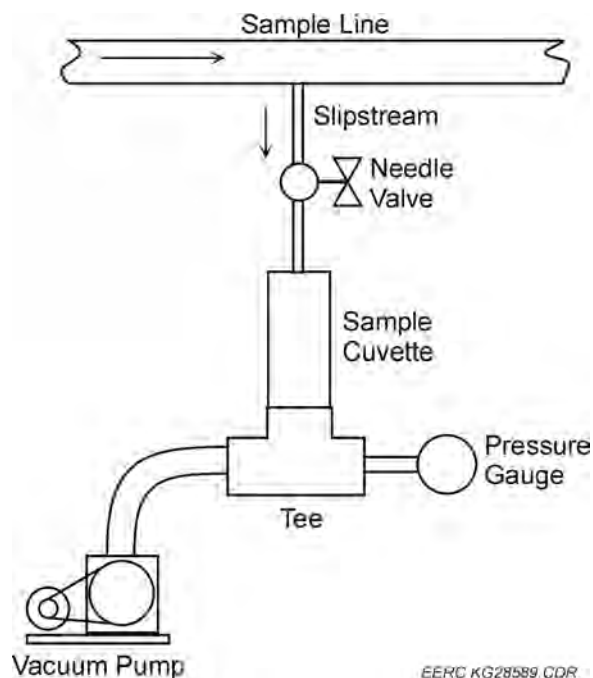


Figure 17. Modification of sample cuvette to allow low-pressure sampling.

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Development of an As, Se, and Hg Sampling and Analytical Method for Reducing Flue Gas Environments

Key Personnel: Michael Swanson (EERC), Grant Dunham (EERC)

Project Description

This project is developing a sampling protocol for arsenic (as arsine gas), selenium (as hydrogen selenide), and mercury (as elemental mercury) including sample-conditioning solutions that will convert the desired species into a form suitable for continuous emission monitoring.

Goal

The overall goal of this task is to develop a sampling protocol for arsenic (as arsine gas), selenium (as hydrogen selenide), and mercury (as elemental mercury) including sample-conditioning solutions that will convert the desired species into a form suitable for continuous emission monitor (CEM) analysis. Specific objectives include the following:

- Develop a sampling protocol/conditioning system that will allow arsenic and selenium to be accurately measured with a CEM. Arsenic and selenium will be measured as arsine gas and hydrogen selenide gas under reducing conditions and compared to wet-chemistry EPA Method 29 sampling. A sample-conditioning protocol that ensures all of the arsenic and selenium is converted to hydrides will possibly need to be developed.
- A second objective will be to attempt to simplify a sample-conditioning protocol already demonstrated for measuring mercury in gases from a coal gasifier. The currently demonstrated Hg-sampling protocol utilizes a stannous chloride–sodium hydroxide mixture to precondition the fuel gas sample prior to flow through the Hg CEM. Since it has been shown that under a reducing/gasification condition the Hg is primarily in the elemental form, it might be possible to simplify the sample-conditioning system by eliminating the SnCl_2 and, possibly, even the NaOH solution.

Rationale

Arsenic and selenium can be continuously measured in a syngas environment. Arsenic and selenium are expected to be found in the hydride form (as arsine and hydrogen selenide gas) in a reducing flue gas environment. Analyzers are currently available for measuring arsine and hydrogen selenide and are being purchased as part of a separate project; however, whether these analyzers are capable of working successfully with a syngas mixture is not known. This test program will verify their operation against proven wet-chemistry techniques to determine what sampling protocol is necessary to obtain successful operation of these continuous analyzers.

Approach

Experimental Apparatus

This project will use a system that is being built under another EERC project. The laboratory-scale design was completed, and all of the laboratory-scale equipment has been ordered, the majority of which has been received. Installation of the equipment in the dual-hood area has been started. A diagram of the designed laboratory-scale test rig is shown in Figure 1. Mass flow controllers sized for 6 scfh of CO₂, 8 scfh of H₂, 10 scfh of CO, 1 scfh CH₄, and 12 scfh of N₂ will allow the test apparatus to blend bottled gases to simulate the desired gas composition for any of the major gasifiers, including entrained-flow slurry feed and dry feed gasifiers, and fluid-bed gasifiers, including transport reactor and GTI U-Gas systems. These flow rates were calculated as a function of desired space velocities and operating temperature and pressure. Operation at the maximum pressure of 1200 psig resulted in the need for the highest flow rates given a specific desired space velocity in the monolith. Impurities such as H₂S, COS, HCl, ArH₃, and H₂Se will be added to certain cylinders of bottled gas to get the appropriate concentrations in the simulated bottled gas mixture. All fittings downstream from the mercury injection point have been coated with Restek's Sulfinert[®] coating to reduce any chances for mercury absorption on the metal surfaces. Testing was conducted with a Hg permeation source to verify that reasonable vapor-phase mercury concentrations could be achieved while operating with a CO₂ gas stream instead of N₂ and at elevated pressures up to 500 psig.

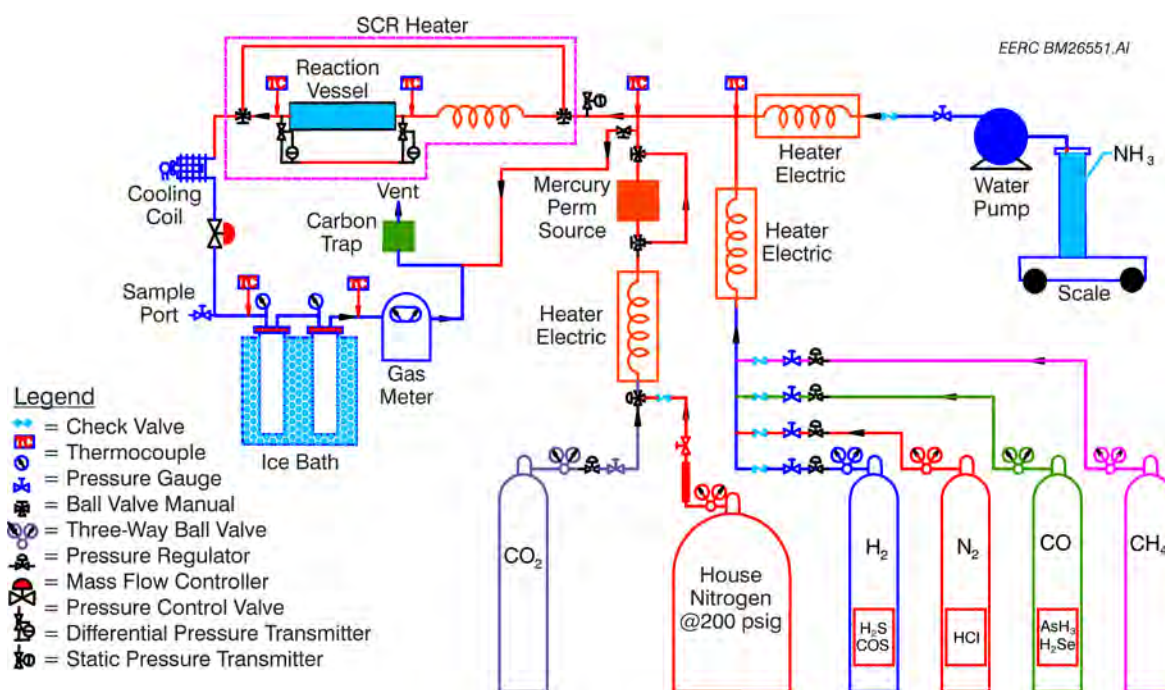


Figure 1. Diagram of the laboratory-scale test rig design.

Work Plan

A pressurized laboratory-scale test rig that is currently under construction for a separate project will be used to accomplish the project goal of developing a sampling protocol for arsenic (as arsine gas), selenium (as hydrogen selenide), and mercury (as elemental mercury) including sample-conditioning solutions that will convert the desired species into a form suitable for CEM analysis. This test rig has the capability to mix bottled gases to achieve a wide range of simulated syngas from a wide variety of gasifier types. These gases can be mixed (including impurities such as H₂S, COS, AsH₃, and H₂Se) and preheated to $\leq 700^{\circ}\text{F}$ while operating at pressures of ≤ 1200 psig. All exposed metal has been coated with a Sulfinert[®] coating to minimize the removal of trace metals on metal tubing. In a typical trace metal removal test, a sorbent is inserted in the coated tubing to test its ability to remove the Hg, Ar, or Se contaminant. However, for these proposed tests, no sorbent will be used. Instead, a gas mixture with known concentrations of the desired contaminants will be injected into the tubing to flow out the other side before being measured by both the continuous analyzer and by wet-chemistry EPA Method 29 analysis. If comparable results are not obtained, then the sampling protocol will be modified until consistent results from all three measurements are obtained.

Progress

A laboratory-scale test rig has been constructed, and the As, Se, and Hg analyzer has been purchased.

Quality Assurance/Quality Control

Quality Objective

The primary quality objective and measure of success is that the relative standard deviation for all As, Se, and Hg measurements will be $\leq 10\%$. If measurement results have a relative standard deviation of $>10\%$, then the data will be flagged and evaluated as to the source of the variability.

Measurement/Data Acquisition

The new instrumentation will be operated and calibrated according to the manufacturer's recommendations and specifications.

Assessment and Validation

Measurement results from the new CEM will be compared to those obtained using EPA Method 29. Acceptable results will be those that have a relative percent difference from the Method 29 results of $\leq 20\%$.

Status

This project is set to begin during the first quarter of 2007.