



*Kevin C. Galbreath
Principal Investigator*

MEASUREMENT OF HALOGENS

Key Personnel: Kevin Galbreath (EERC), Edwin Olson (EERC)

Project Description

A two-task project was proposed to further the understanding of halogen (Cl and Br) and Hg interactions in coal combustion flue gas. In the first task, selected coal, fly ash, and Hg sorbent samples produced as a result of testing in other CATM projects will be analyzed for Hg, Cl, and Br. A statistical analysis of the Hg, Cl, and Br measurement results will be performed to determine whether Hg concentrations are more strongly correlated to Cl or Br. During the second task, the recommended method for measuring halogens such as Cl and Br in coal combustion flue gas, EPA Method 26A, will be modified to enable gas chromatography–mass spectrometry (GC–MS) of Cl and Br inorganic and organic speciation measurements. A modified EPA Method 26A will also be evaluated by replacing the impinger solutions with a solid adsorption system.

Goal

The overall goal of this ongoing project is to use existing methods and develop improved methods for evaluating the effects of Cl and Br on the conversion of Hg⁰ to inorganic and organic Hg compounds with coal combustion flue gas. Two specific objectives to accomplish this goal are:

- Perform Hg, Cl, and Br analyses on coal, fly ash, and Hg sorbent samples and statistically evaluate the results for interelemental correlations.
- Modify and simplify EPA Method 26A for determining the concentrations and speciation of Cl and Br in coal combustion flue gas.

Rationale

Gaseous bromine oxide radicals (BrO) have been linked to the atmospheric chemistry of Hg and may account for the increase in Hg deposition to polar regions during springtime (1). In support of such a link, Roos-Barraclough et al. (2) found that Hg and Br deposition rates correlated throughout a 14,000-yr preanthropogenic-long record of Hg and Br concentrations in peat from a bog in the Swiss Jura Mountains. Hg concentrations in peat during the industrial period exceeded the Hg–Br correlation range,

suggesting the deposition of anthropogenic Hg^{1+} , $2+$ species (2). Raofie and Ariya (3) identified the products of BrO-initiated Hg^0 oxidation reactions as HgBr, HgBrO/HgOBr, and HgO.

Positive correlations between halogen, Cl and Br, and Hg concentrations in coal combustion by-products have been reported on a limited basis (4, 5). The Br that exists in coal may be more effective in promoting Hg^0 oxidation and capture relative to Cl, which has generally been implicated in Hg transformations. In addition, some coals contain more Br relative to Cl (6). Several researchers have developed Hg emission control strategies based on the addition of various Cl and Br species to coals, sorbents, and flue gases (7–9). An environmental concern with adding Cl and Br is the potential formation of hazardous polychlorinated or -bromated dibenzo-*p*-dioxins (PC/BDDs) and -furans (PC/BDFs) and tetrachlorobenzo-*p*-dioxin (TCBD), although the presence of relatively high SO_2 concentrations in coal combustion flue gases may suppress their formation (10).

Analytical methods for analyzing Cl and Br in coal and coal combustion by-products are lacking. For example, a round-robin study determined that most of the analytical techniques available for determining Cl in coal were unreliable and irreproducible (11). These conclusions were based on the Cl measurement results of three commonly used techniques: bomb combustion ion-selective electrode (ASTM D4208) and Eschka ignition ion chromatography (IC) or bomb combustion potentiometric titration (ASTM D2631).

None of these methods could consistently produce quantitative results below 200 ppm Cl. In addition, the methods were unsuitable for ash analysis. Given that more than a third of U.S. coals have <200 ppm Cl, the need for an improved Cl measurement method was apparent.

A promising new Cl analysis technique, oxidative hydrolysis microcoulometry, was identified (12). This new method is a modification of existing ASTM D5808, "Test Method for Determination of Organic Chloride in Aromatic Hydrocarbons and Related Chemicals by Microcoulometry." The method was modified to analyze coal, and the instrument required to implement this method, a Mitsubishi Model TOX-100 total chlorine analyzer, was made commercially available by Cosa Instrument Corporation. The method was approved by ASTM as Method D6721 (13), and in 2001, the EERC purchased an instrument.

The method involves the direct combustion of coal to liberate Cl and other halogens (Br and I) that are then passed through a titration cell where they are automatically titrated by silver anions generated coulometrically. Halogen concentrations are calculated from the quantity of electricity required for the titration. An inherent problem, however, with this relatively new method is that most of the halogens present in the coal sample, including Br and I, are reported as Cl, and thus Cl concentrations may be biased too high.

The recommended method for measuring halogens such as Cl and Br in coal combustion flue gas is EPA Method 26A. The Method 26A sampling train consists of four impingers: the first two contain 0.1 N H_2SO_4 and the last two, 0.1 N NaOH. The first two acidic impinger solutions are expected to trap HCl while enabling Cl_2 to pass through where it is finally trapped in the third and fourth basic impinger solutions. Testing at the EERC, partially supported by CATM, indicated that the relatively high concentrations of SO_2 in coal combustion flue gas interfered with the selectivity of the 0.1 N H_2SO_4 to capture only HCl, resulting in a high HCl bias and low Cl_2 bias (14, 15). The 0.1 N NaOH, however, was robust in capturing Cl_2 even in the presence of relatively high SO_2 concentrations. A limitation of EPA Method 26A and potential source of bias that the fly ash and unburned carbon collected on the filter upstream from the impingers are not analyzed for halogens. Fly ash and unburned carbon particles collected on the filter may adsorb halogens. Interactions between unburned carbon particles and halogen species are important parameters in PC/BDD, TCBD, and PC/BDF formation, and they are likely to negatively bias EPA Method 26A Cl measurements.

Approach

Task 1 – Determination of Coal, Fly Ash, and Sorbent Cl and Br Concentrations

Selected coal, fly ash, and Hg sorbent samples produced as a result of testing in other EERC and CATM projects will be analyzed for Hg, Cl, and Br. Coal, fly ash, and sorbent Hg contents will be determined using cold-vapor atomic absorption spectroscopy according to EPA Method 245.1 and EPA SW-846 Method 7470. The EERC will analyze coal, fly ash, and Hg sorbent samples for Cl and Br at relatively high (>100 ppm) concentrations using a leaching sample preparation (water extraction) combined with IC. However, at lower concentrations, an alternative method is required. Instrumental neutron activation analysis (INAA) is a very sensitive technique for measuring halogen concentrations. The estimated detection limit for Cl and Br using decay gamma rays in a reactor neutron flux of 1×10^{13} n cm⁻² s⁻¹ is 100–1000 picograms (16). Selected samples containing relatively low (<100 ppm) Cl and Br concentrations will be analyzed using INAA at the University of Missouri Research Reactor Center in Columbia, Missouri. A statistical analysis of the Hg, Cl, and Br measurement results will be performed to determine whether Hg concentrations in coal, ash, and sorbents are more strongly correlated to Cl or Br, or both.

Task 2 – Modification of EPA Method 26A for Determining Cl and Br Concentrations and Speciation in Coal Combustion Flue Gas

The coal combustion flue gases produced as a result of pilot-scale testing for the other EERC and CATM projects will be sampled using EPA Method 26A and a modified Method 26A. The impinger solutions will be modified to include a reactive olefin, such as styrene and cyclohexane, to selectively sample HBr, Br₂, and HCl. The EERC through past research has reacted HBr, Br₂, and HCl with styrene and identified the reaction products using GC as bromoethylbenzene, dibromoethylbenzene, and chloroethylbenzene, respectively. HF and Cl₂ are expected to produce unique styrene reaction products also. Cyclohexene reacts to form similarly unique products and, in addition, is expected to react differently with Cl radicals as compared to Cl₂. Sample filters and impinger solutions will be extracted with hexane–dichloromethane. Any unburned carbon particles in the filter that may contain halogens will be digested and analyzed separately. In addition, a separate sampling device may have to be used to capture gaseous organohalogen. The applicability of using glassy carbons for sampling gaseous organohalogen compounds will be evaluated. A carbon trap will be inserted into the EPA Method 26A sampling train. The filter and solution extracts, digestion solutions, and carbon trap samples will be analyzed using GC–MS and 13C standards (commercially available).

As an alternative to the impinger solutions used in EPA Method 26A, a silver membrane filter may be used to capture gaseous halogens followed by separation and quantification using IC. This is the approach used in the method recommended for ambient air measurements of Cl and Br, National Institute for Occupational Safety and Health Method 6011. The method involves the use of a prefilter for capturing particulate halogens followed by a silver membrane for capturing gaseous halogens. The EERC will evaluate whether this silver membrane filter approach could be used to measure the Cl and Br concentrations in coal combustion flue gases. A solid Br and Cl sampling system would be simpler to operate and reduce the number and amount of chemicals required. For Br and Cl speciation measurements, an olefin-coated resin filter will be evaluated for determining HCl, Cl₂, HBr, and Br₂ as an alternative solid approach to that proposed herein.

Experimental Apparatus

Analytical Research Laboratory

The EERC Analytical Research Laboratory 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 following equipment is available for this ongoing project:

- 4200-ft², fully equipped, exceedingly clean laboratory with seven fume hoods
- CETAC M6000A cold-vapor atomic absorption spectrometer mercury analyzer
- Mitsubishi TOX100 chlorine analyzer with oxidative hydrolysis microcoulometry
- 2020i ion chromatograph with UV–VIS, conductivity, and electrochemical detection
- CEM MDS 2100 microwave with temperature and pressure control

Particulate Research Laboratory

The Particulate Research Laboratory (PRL) specializes in flue gas sampling on bench-, pilot-, and full-scale systems including boilers and power generation facilities. PRL staff have intensive training in emission testing and sampling. PRL staff maintain and certify calibration of equipment used for EPA-approved sampling methods. The following equipment is available for this ongoing project:

- Leeman PS200 automated mercury analyzer
- Sierra Misco 7200 stack-sampling control boxes
- Anderson auto five stack-sampling control boxes
- Baldwin Environmental, Inc., 31-C-200 auto stack-sampling control boxes (two)
- Semtech mercury analyzers (two)
- EPM mercury analyzer
- PSA Sir Galahad mercury analyzer (atomic fluorescence)
- Ritter wet-test gas meters (two)
- Gilibrator gas flow calibrator
- Bios gas flow calibrator

Gas Chromatography–Mass Spectroscopy Laboratory

The GC–MS Laboratory has several Hewlett-Packard 5890 capillary gas chromatographs equipped with both on-column and split/splitless injection ports and a variety of detectors (flame ionization, electron capture, and atomic emission).

GC with capillary columns is utilized to separate complex mixtures of volatile materials into their individual components. When a GC is interfaced to a flame ionization detector, one obtains data essentially proportional to the number of CH groups in the component (GC peak). This can then be related to the weight percentage of the component in the sample. An atomic emission detector interfaced to a GC allows for specific element detection. The halogen compounds will be analyzed using an electron capture detector that provides very sensitive and specific detection for halogen compounds.

The GC–MS Laboratory has three Hewlett-Packard GC–MS systems (5985B, 5988, and 5972). These instruments can operate in either the electron impact or chemical ionization mode. Additional interfaces for techniques such as supercritical fluid chromatography–MS, high-performance liquid chromatography–MS, and thermogravimetric analysis–MS are available in addition to the standard GC interface.

When GC is interfaced to a mass spectrometer (GC–MS), the identity of the eluting organic compounds can be determined. Electron impact ionization of organic molecules produces fragmentation patterns that can be used (within limitations) to identify individual compounds present in a GC peak. Many compounds do not produce a recognizable molecular ion under electron impact conditions. Altering the amount of energy used in the ionization process (e.g., chemical ionization methods) generally produces a detectable pseudomolecular ion that can be used to confirm the molecular weight of the compound.

Progress

Project Task 1 and 2 research will begin in early 2006.

Quality Assurance/Quality Control (QA/QC)

An EERC quality management system, authorized and supported by EERC managers, is in effect and governs all programs within the organization. Additionally, the CATM Program at the EERC has a Quality Management Plan (QMP) in effect that addresses trace metal emission research at the EERC (17). The QMP has been reviewed and accepted by EPA. The project is following the Quality Manual, the QMP, and all revisions. An independent QA auditor will review all aspects of QA/QC for this project.

Quality Objectives

Quality assurance objectives (QAOs) were established to support decisions concerning test validity and adequacy with respect to the project objectives. The QAOs are presented in Table 1. Measurement methods that produce results not conforming to these QAOs are being rejected. Nonconforming results are being flagged with a precautionary statement regarding the validity of the results in question.

Table 1. Quality Assurance Objectives

Parameters/Sample Type	Accuracy, recovery %	Precision, RPD ¹	Completeness, %
Hg	80–120	<20	>90
Cl and Br	80–120	<20	>90

¹ Relative percent difference.

Measurement/Data Acquisition

The following measurement and data acquisition methods will be employed once testing is under way:

- Coal, fly ash, and sorbent Hg contents are being determined using cold-vapor atomic absorption spectroscopy according to EPA Method 245.1 and EPA SW-846 Method 7470.
- Coal, fly ash, and Hg sorbent samples are being analyzed for Cl and Br at relatively high (>100 ppm) concentrations using water extraction combined with IC.
- Coal, fly ash, and Hg sorbent samples are being analyzed for Cl and Br at relatively low (<100 ppm) concentrations using INAA at the University of Missouri Research Reactor Center in Columbia.
- Coal combustion flue gas Cl and Br concentration and speciation measurements are being performed using a modified EPA Method 26A sampling train and procedures for separating, recovering, and analyzing the Cl and Br species.

The measurements are consistent with accuracy and precision of the methods and techniques.

Assessment and Validation

The QC activities described in Table 2 are being performed to assess and validate Cl and Br species measurement methods and results. Measurement results that do not conform to the QAOs in Table 1 are being flagged with a precautionary statement regarding the validity of the results in question.

Status

Samples appropriate for performing Task 1 activities have been identified. The chemical supplies required for Task 2 activities have been acquired. Project research will begin in early 2006.

Potential Applications and Benefits

The development of an analytical method that produces Cl and Br speciation results conforming to the QAOs in Table 1 will be very useful for furthering the scientific community's understanding of Hg transformations that is crucial for developing and improving mercury control technologies.

Table 2. Quality Control Activities

QC Activity	Performance Characteristic Measured
Replicate Samples Collected Sequentially	Total variability, including process or temporal, sampling, and analytical
Replicate Analyses	Analytical variability at the actual sample concentration
Laboratory Control Samples	Analyte recovery in the absence of actual sample matrix effects, used as an indicator of analytical control
Matrix Spiking	Analyte recovery in the sample matrix, indicating possible matrix interferences and other effects
Standard Reference Material	Analyte recovery in a matrix similar to the actual samples
Field Blank	Total sampling and analytical blank effects, including sampling equipment and reagents; sample handling, transport, and storage; and analytical reagents and equipment
Method Blank	Blank effects inherent in analytical method, including reagents and equipment

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