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## MEASUREMENT OF HALOGENS

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### *Project Description*

A two-task project is under way to further improve the understanding of halogen (Cl and Br) and Hg interactions in coal combustion flue gas. In the first task, selected coal and fly ash samples produced as a result of testing in other EERC or CATM projects are being 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 the project is to use existing methods and develop improved methods for evaluating the effects of Cl and Br on the conversion of Hg<sup>0</sup> to inorganic and organic Hg compounds within 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-Barracough et al. (2) found that Hg and Br deposition rates correlated throughout a 14,000-yr

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preanthropogenic 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<sup>1+, 2+</sup> species (2). Raofie and Ariya (3) identified the products of BrO-initiated Hg<sup>0</sup> 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<sup>0</sup> 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<sub>2</sub> 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 (American Society for Testing and Materials) International 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<sub>2</sub>SO<sub>4</sub> and the last two, 0.1 N NaOH. The first two acidic impinger solutions are expected to trap HCl while enabling Cl<sub>2</sub> 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<sub>2</sub> in coal combustion flue gas interfered with the selectivity of the 0.1 N H<sub>2</sub>SO<sub>4</sub> to capture only HCl, resulting in a high HCl bias and low Cl<sub>2</sub> bias (14, 15). The 0.1 N NaOH, however, was robust in capturing Cl<sub>2</sub>, even in the presence of relatively high SO<sub>2</sub> concentrations. A limitation of EPA Method 26A and potential source of bias is 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

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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*

#### **Determination of Coal, Fly Ash, and Sorbent Cl and Br Concentrations**

Selected coal and fly ash samples produced as a result of testing in other EERC and CATM projects analyzed for Hg, Cl, and Br. Coal Hg contents were determined using cold-vapor atomic absorption spectroscopy according to EPA Method 245.1 and EPA SW-846 Method 7470. The EERC will analyze coal and fly ash 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  $1 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$  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 (MURR) 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 and ash are more strongly correlated to Cl or Br, or both.

#### **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, Br<sub>2</sub>, and HCl. The EERC, through past research, has reacted HBr, Br<sub>2</sub>, and HCl with styrene and identified the reaction products using GC as bromoethylbenzene, dibromoethylbenzene, and chloroethylbenzene, respectively. HF and Cl<sub>2</sub> are also expected to produce unique styrene reaction products. Cyclohexene reacts to form similarly unique products and, in addition, is expected to react differently with Cl radicals as compared to Cl<sub>2</sub>. 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, Cl<sub>2</sub>, HBr, and Br<sub>2</sub> as an alternative solid approach.

### ***Progress***

Several coal and fly ash samples have been prepared and are in the process of being analyzed for Br, Cl, and Hg. The coals that have been selected include lignite, subbituminous, and bituminous and represent several different geographic locations throughout the United States and Canada (Table 1). Because the majority of the samples selected for this task were obtained from past and current EERC projects, important sample information was also provided to help identify suitable candidates. Coal rank, ash content, ash chemistry, mercury concentration, and halogen concentrations were considered in the selection process to obtain a final suite of samples with varying characteristics. It is expected that samples with a wide range of Br, Cl, and Hg concentrations will aid in the final data analysis. The Cl and Hg values listed in Table 1 were provided with the samples when they were collected for this project and were used as a means of selecting samples with a range of concentrations. The preliminary values show that Cl ranges from <10 µg/g to 2500 µg/g and Hg ranges from 0.022 µg/g to 0.232 µg/g. With the exception of the standard reference materials, Br values were not available when the samples were selected. To meet the objectives of this task, Cl analysis will be repeated on these samples using either INAA or a combustion technique followed by IC, and Hg will be determined using ASTM Method D6414.

Coal samples are being prepared for analysis by air drying and grinding to -60 mesh (250 µm). Twelve of the 17 coals listed in Table 1 have been sent to MURR for INAA, and results are pending. Moisture is being determined on a separate portion of the prepared sample, and all results will be reported on a dry basis. Approximately ten fly ash samples have been selected for analysis.

### ***Quality Assurance/Quality Control***

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 quality assurance auditor will review all aspects of quality assurance/quality control 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 2. 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.

#### **Measurement/Data Acquisition**

The following measurement and data acquisition methods are being employed:

- Coal and fly ash contents are being determined using cold-vapor atomic absorption spectroscopy according to EPA Method 245.1 and EPA SW-846 Method 7470.
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**Table 1. Coals Selected for Characterization**

Sample ID	Coal Type	Mine Location	Chlorine, $\mu\text{g/g}$	Mercury, $\mu\text{g/g}$
SRM-1	Bituminous (NIST <sup>1</sup> 1632c)	PA	1139	0.094
SRM-2	Bituminous (SARM <sup>2</sup> 18)	South Africa	100	0.022
L-1	Lignite	TX	17	0.232
L-2	Lignite	ND	10	0.060
L-3	Lignite	Canada	10	0.150
S-1	Subbituminous	PRB <sup>3</sup>	50	NA <sup>4</sup>
S-2	Subbituminous	PRB	NA	0.100
S-3	Subbituminous	MT	NA	0.065
S-4	Subbituminous	WY	8.0	0.098
S-6	Subbituminous	PRB	55	0.107
S-7	Subbituminous	PRB	182	0.135
B-1	Bituminous	OK	2500	NA
B-2	Bituminous	WV	1300	NA
B-3	Bituminous	PA	961	0.072
B-4	Bituminous	WV	500	0.120
B-6	Bituminous	CO	100	0.033
B-7	Bituminous	NM	100	0.040

<sup>1</sup> National Institute of Standards and Technology.

<sup>2</sup> South African Reference Materials.

<sup>3</sup> Powder River Basin.

<sup>4</sup> Not available.

- Coal and fly ash samples are being analyzed for Cl and Br at relatively high (>100 ppm) concentrations using water extraction combined with IC.
- Coal and fly ash samples are being analyzed for Cl and Br at relatively low (<100 ppm) concentrations using INAA at MURR.
- 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.

**Table 2. Quality Assurance Objectives**

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

<sup>1</sup> Relative percent difference.

### Assessment and Validation

The QC activities described in Table 3 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 2 are being flagged with a precautionary statement regarding the validity of the results in question.

#### Status

About one-half of the samples listed in Table 1 have been analyzed using INAA. The remaining samples will be analyzed in about a month from now.

#### 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 which is crucial for developing and improving mercury control technologies.

**Table 3. 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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