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MEASUREMENT OF HALOGENS

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Project Description

A two-task project has been completed 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 were analyzed for Hg, Cl, and Br. A statistical analysis of the Hg, Cl, and Br measurement results were performed to determine whether Hg concentrations were 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 was 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 within coal combustion flue gas. Two specific objectives to accomplish this goal were the following:

- Perform Hg, Cl, and Br analyses on coal and fly ash 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 Hg¹⁺, ²⁺ species (2). Raofie and Ariya (3) identified the products of BrO-initiated Hg⁰ 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 Hg⁰ 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 SO₂ 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 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 and implemented this method.

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 H₂SO₄ and the last two, 0.1 N NaOH. The first two acidic impinger solutions are expected to trap HCl while enabling Cl₂ 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 SO₂ in coal combustion flue gas interfered with the selectivity of the 0.1 N H₂SO₄ to capture only HCl, resulting in a high HCl bias and low Cl₂ bias (14, 15). The 0.1 N NaOH, however, was robust in capturing Cl₂, even in the presence of relatively high SO₂ 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 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 Br, Cl, and Hg in Coal and Fly Ash Samples

Selected coal and fly ash samples produced as a result of testing in other EERC and CATM projects were analyzed for Hg, Cl, and Br. Coal samples were prepared for analysis by air drying and grinding to -60 mesh (250 μm). Moisture was determined on a separate portion of the prepared sample according to ASTM Method D3173, and all results were reported on a dry basis. Mercury in the coal and fly ash samples was determined using heated acid extraction followed by cold-vapor atomic absorption spectroscopy according to ASTM Method D6414. The fly ash samples were analyzed for Cl and Br using a leaching sample preparation (water extraction) combined with IC.

The coals were analyzed for Cl and Br using instrumental neutron activation analysis (INAA) because preliminary information suggested that most of the coals contained very low levels of the halogens which could not be detected by other methods. The INAA was conducted at the University of Missouri Research Reactor (MURR) Center in Columbia, Missouri (16). For this method, approximately 50 mg of coal was weighed into a 1/4-dram polyethylene irradiation vial. The Cl measurements involved an irradiation of 60 seconds followed by a decay of 25 minutes and real time counted for 15 minutes. For the Br analysis the samples were irradiated for 60 seconds and then allowed to decay for 24 to 36 hours before being live-time-counted for 3600 seconds. Standard reference materials were included in the INAA. In addition to the standards, six empty 1/4-dram polyethylene irradiation vials were irradiated and counted under the same conditions as the samples and standards to correct for the Cl and Br blank in the irradiation vials. Five comparator Br/Cl standards were prepared by pipetting a known mass of Br and Cl from a commercially available mixed halogen standard into a 1/4-dram polyethylene irradiation vial to achieve 10 μg Cl and 1 μg Br.

After all of the samples were analyzed by the methods described above, a statistical analysis of the Hg, Cl, and Br measurement results for both the coal and fly ash samples was performed to determine whether Hg concentrations in coal and ash were 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 are sampled using a modified Method 26A. For analysis of halogen species (Cl_2 , Br_2 , HCl, HBr) in a gas stream, we have explored methods that utilize impinger solutions modified to include a reactive olefin, such as styrene and cyclohexane, to selectively sample HBr, Br_2 , and HCl and Cl_2 by reaction with the olefin to produce reaction products that are identified and quantitated as separated peaks using GC and GC-MS. The reaction of these four halogen components with styrene-trapping reagent produces specifically 1,2-dichloroethylbenzene, 1,2-dibromoethylbenzene, 1-chloroethylbenzene, and 1-bromoethylbenzene, respectively, which give widely separated peaks in the capillary gas chromatogram. Cyclohexene reacts to form similarly unique products and, in addition, is expected to react differently with Cl radicals as compared to Cl_2 . Sample filters and impinger solutions were extracted with hexane-dichloromethane.

*Progress***Determination of Br, Cl, and Hg in Coal and Fly Ash Samples**

Twenty-one coals, 14 fly ash samples, and four standard reference materials were selected for Task 1 and analyzed for Br, Cl, and Hg. The coals that were selected included lignite, subbituminous, and bituminous ranks and represented several different geographic locations throughout the United States and Canada (Table 1). The fly ash samples were collected from a variety of pollution control devices (PCDs) such as electrostatic precipitator (ESPs), fabric filter (FFs), and spray dryer adsorber-FFs (SDA-FFs). 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, mercury concentration, and halogen concentrations were considered in the selection process of the coals to obtain a final suite of samples with varying characteristics. One of the selection criteria for the fly ash samples was to select samples with a low carbon content (<1%), because carbon will absorb Hg, causing a bias in the results. Therefore, the ashes selected for this project were those that were generated when carbon injection or other technologies for Hg capture were not being tested. Analysis results of the coal and fly ash samples are presented in Tables 1 and 2.

A statistical analysis of the coal results in Table 1 was performed to evaluate interelemental correlations. The correlation coefficients for all the coals and those for the three coal ranks represented are presented in Table 3. Overall, Hg did not significantly correlate to Cl or Br. Hg correlated the best to

Table 1. Coals Selected for Characterization

Sample ID	Coal Type	Source	Br, $\mu\text{g/g}$	Cl, $\mu\text{g/g}$	Hg, $\mu\text{g/g}$
L-1	Lignite	Oak Hill, TX	3.39	20.0	0.327
L-2	Lignite	Center, ND	<2.67	21.6	0.061
L-3	Lignite	Poplar River, CA	2.90	27.7	0.174
L-4	Lignite	Coteau, ND	<4.12	37.7	0.078
L-5	Lignite	Falkirk, ND	<5.81	26.8	0.104
L-6	Lignite	Red Hills, MS	3.79	49.5	0.213
S-1	Subbituminous	Carter, AL	4.67	19.5	0.109
S-2	Subbituminous	PRB ¹ , WY	<0.87	12.0	0.101
S-3	Subbituminous	PRB, MT	<5.58	14.8	0.072
S-4	Subbituminous	PRB, WY	<0.81	13.4	0.079
S-6	Subbituminous	PRB, WY	36.9	40.0	0.103
S-8	Subbituminous	Buckskin, WY	1.40	16.7	0.112
S-9	Subbituminous	Eagle Butte, WY	4.56	21.1	0.178
B-1	Bituminous	Oklahoma	34.7	2951	0.100
B-2	Bituminous	West Virginia	26.0	1465	0.093
B-3	Bituminous	Blacksville, PA	17.0	1023	0.106
B-4	Bituminous	West Virginia	6.36	494	0.128
B-6	Bituminous	West Elk, CO	<3.79	93.4	0.0375
B-7	Bituminous	Lee Ranch, NM, Nov '04	<0.83	11.8	0.052
B-8	Bituminous	Lee Ranch, NM, Oct '06	<5.42	21.0	0.068
B-9	Bituminous	Illinois No. 6, IL	4.30	109	0.065

¹ Powder River Basin.

Table 2. Fly Ash Samples Selected for Characterization

Sample ID	PCD	Br, $\mu\text{g/g}$	Cl, $\mu\text{g/g}$	Hg, $\mu\text{g/g}$
LA-1	FF	<2	3.6	0.568
LA-2	ESP	<3	7.5	0.311
LA-3	FF	3.8	133	<0.002
LA-4	ESP	<2	5.6	0.021
LA-5	FF	6.4	193	0.333
LA-6	FF	<3	3.4	0.114
SA-1	ESP	2.9	14.0	0.416
SA-2	ESP	13.0	37.4	0.041
SA-3	ESP	<2	3.0	0.076
SA-4	SDA-FF	6.1	102	0.302
SA-5	ESP	<2	7.1	0.134
BA-1	ESP	<2	4.5	0.118
BA-2	ESP	<2	6.2	0.140
BA-3	FF	<2	<2	0.118

Table 3. Coal Hg and Halogen (Cl and Br) Correlation Coefficients

	Hg-Cl	Hg-Br
All Coals	-0.08	-0.03
Lignite	-0.05	0.83
Subbituminous	0.76	0.71
Bituminous	0.52	0.57

Br in the limited lignite coal data set. Hg also correlated with Cl and Br in the subbituminous coals, but not as strongly as in the bituminous coals.

Correlation coefficients were also determined using the Hg, Br, and Cl values determined in the fly ash samples (Table 2). The calculated coefficients for the Hg-Br relationship was -0.08, and the coefficient for the Hg-Cl relationship was 0.07, resulting in no correlation of these constituents in the samples selected for this task.

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

The first step in the method development was the calibration of the GC analyzer for the four organohalogen analytes. The GC method used a 60-m, 0.25- μm DB5 phase for the chromatography. Concentrations of the organohalides in the range 1 to 100 ppm in a carbon tetrachloride solution were used. Carbon tetrachloride as the solvent for the analytes resulted in very sharp analyte peaks, and it is a very good solution to use in the presence of molecular chlorine and bromine, since it does not produce a lot of free-radical halogenation by-products that are typically encountered when using hydrocarbon solvents. Initially the flame ionization detector (FID) was used, rather than the more sensitive electron capture detector (ECD) or the GC-MS, which will be utilized in later work with lower concentrations. For the ECD system, a nonhalogenated solvent will be utilized, owing to the very small amounts of chlorinated solvent impurity peaks that can interfere. The GC-MS does not pose this restriction, and

carbon tetrachloride can be used. Low inlet temperatures (125°C) were used for injection of the analytes, since decomposition occurred in the inlet at higher temperatures, resulting in poor calibration curves.

Seven point calibration curves (amount ratio plotted versus area ratio) were obtained for each analyte, using 1-chloro-4-nitrobenzene as the internal standard. The trendlines were highly linear ($R^2 = 0.999$), although the slopes varied quite a lot between the four analytes, because of the different response factors for the organohalogen compounds. Styrene was also calibrated so that a mass balance can be performed and determination of all was consumed. The precision and accuracy in determining these analytes was high for the FID method.

Methods for trapping and reacting the halogen species (Cl_2 , Br_2 , HCl , HBr) with styrene were extensively investigated. These investigations focused on finding a solvent system that could accommodate the styrene reactant as well as the halogen species from the gas phase. These investigations achieved varying degrees of success as described below.

It would have been very convenient to use a carbon tetrachloride (or other inert solvent) impinger containing the styrene to collect and react the halogen species from a gas phase bubbling through the cold solution, followed by adding internal standard and directly injecting the solution into the GC for the analysis. This worked for the molecular halogens, because they are highly soluble in the carbon tetrachloride. Quantitative recovery of the dihalide derivatives gave accurate results for halogen concentrations.

However, the hydrogen chloride and hydrogen bromide did not dissolve and react with the styrene in the ice cold impinger solution. No organochlorine species were observed in the chromatogram when 50 ppm HCl in nitrogen was bubbled into the carbon tetrachloride impinger. Likewise, no products were observed for 50 ppm HCl in synthetic flue gas. Even very high concentrations of HCl in nitrogen gave no reaction.

Condensation of HCl from a flue gas stream involves simultaneous condensation of moisture. To simulate this eventuality, 0.1 N HCl solution in water was added to styrene dissolved in carbon tetrachloride and stirred. No reaction occurred, owing to the total insolubility of the ionized HCl in the organic solvent. It is probable that the desorption rate of HCl from the solvent is much higher than the reaction rate with the styrene substrate.

Several attempts were made to find a more compatible solvent for trapping and reacting the halogen acids. Using methanol as the trapping solvent, 1-chloroethylbenzene was produced; however, other by-product species were also formed. Since we need to see all the halogen end up in a single peak rather than many, this was unsatisfactory. Likewise, THF and pyridine were examined, but produced no useful product. Diglyme was also investigated as the solvent, but there was an interference of a solvent peak with the styrene derivatives. The derivatives were extracted out of the diglyme with carbon tetrachloride, but the interfering peaks were still present.

Several experiments were conducted whereby HCl was trapped out of a gas stream using a quaternary ammonium cation exchange resin or a solution (phase transfer catalysis). These trapped species did not directly react with styrene, however. Addition of sulfuric acid also did not liberate the HCl in a form that would react with styrene.

A trapping experiment for HCl with styrene in acetic acid solvent gave a high yield of 1-chloroethylbenzene. This solvent should be compatible with the flue gas moisture and other reactive gases. Unfortunately, it was difficult to concentrate this solution. Secondly, the reaction of molecular

chlorine with acetic acid can occur to produce HCl and chloroacetic acid, so the solvent would interfere with the determination of HCl.

Thus the analytical method investigated was useful for quantitative conversion of the bimolecular halogen species (Br_2 and Cl_2) to unique organohalogen derivatives that can be determined with high specificity and precision and at low detection limits using gas chromatographic methods. However, trapping and analysis of the hydrogen halides failed. Separate analyses of these two groups could be attempted.

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 quality assurance 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 4. Measurement methods that produced results not conforming to these QAOs were rejected or flagged with a precautionary statement regarding the validity of the results in question.

Table 4. 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 were employed:

- Mercury in the coal and fly ash samples was determined using cold-vapor atomic absorption spectroscopy according to ASTM Method D6414.
- Fly ash samples were analyzed for Cl and Br using water extraction combined with IC.
- Coal samples were analyzed for Cl and Br using INAA at MURR.
- Coal combustion flue gas Cl and Br concentration and speciation measurements were performed using a modified EPA Method 26A sampling train and procedures for separating, recovering, and analyzing the Cl and Br species.

Assessment and Validation

The QC activities described in Table 5 were performed to assess and validate Hg, Cl, and Br species measurement methods and results. Measurement results did not conform to the QAOs in Table 5 were flagged with a precautionary statement regarding the validity of the results in question.

Table 5. 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

Status

This project was completed.

More research is needed to develop the organic trapping approach for halogen gases. There are two potentially viable options using this approach, one is to use acetic acid as the solvent for styrene and extract the styrene derivatives out of the acetic acid into a very nonpolar solvent like carbon tetrachloride or pentane followed by GC-MS or ECD analysis of the derivatives or otherwise analyze the acetic acid solution directly without extraction using the chromatographic methods. This presupposes that the molecular halogens can be shown not to react with the acetic acid under cold conditions and react entirely with the more reactive styrene.

An alternative approach is to use a more reactive scavenger for the hydrogen halide (HX). The substrates to be investigated are epoxides, such as styrene oxide, and more reactive olefins, such as cyclopentadiene. The epoxides have an advantage for analyzing the hydrohalogens in that they are more polar scavengers and should decrease the desorption rate as well as increase the reaction rate with hydrohalogens. The products from the reaction of hydrohalogens with epoxides are halohydrins (haloalcohols), which can be analyzed by GC, but the peaks tail somewhat. On the other hand, the bimolecular halogens (Cl₂, Br₂) will be trapped and analyzed by the olefins conveniently. Thus it may be necessary to analyze the bimolecular halogens independently of the hydrohalogens.

Potential Applications and Benefits

The development of an analytical method that produces Cl and Br speciation results conforming to the QAOs in Table 4 will be very useful for furthering the scientific community's understanding of Hg transformations which is crucial for developing and improving mercury control technologies.

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