

CEA MERCURY PROGRAM – SAMPLING & ANALYSIS IMPLEMENTATION PLAN

SECTION 2

COAL & RESIDUE SAMPLING GUIDELINE

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SECTION 2 COAL & RESIDUE SAMPLING & ANALYSIS GUIDELINE

INTRODUCTION

The purpose of this document is to define in general terms a process, consistent with recognised industrial standards, for representative sampling of coal and fly ash for the purpose of performing mercury analyses within the limitations specific to each coal fired generating station.

Sampling Frequency and Duration

The basic program design is to collect and analyse 36 coal and 36 residue weekly composite samples per year, over a 2-year period. The weekly composite samples may be made up of one or more daily samples taken during the week or a composite of the daily composite samples taken during the week as deemed appropriate. The sampling program will be reviewed on a quarterly basis, and sampling frequencies changed if appropriate.

SECTION 2.1 COAL SAMPLING & ANALYSIS GUIDELINE

General

Samples should be collected from each generating station via either of the two methods described below. Wherever possible, ASTM standards for coal and ash sampling and analysis should be followed.

Since this coal will be analysed for mercury, special care should be taken throughout the procedures to ensure that mercury contamination does not occur.

Sample Collection

Method 1 – Automatic Sampler

Daily composite samples will be collected from generating stations that have automatic samplers based on ASTM D2234 (examples of typical automatic samplers are the Heath and Sherwood or Ramsey two stage samplers) normally located at the utility plant.

NOTE: All stations need to follow this standard carefully if they are looking for an actual representative sample for the study.

A sample will be collected continuously based on the ASTM standard. The daily composites (24-hour composites) will be combined into a single weekly composite for analysis. The mass of coal collected on a daily basis for analysis should be between 2 – 4 kilograms.

Method 2 – Manual Sampling

For those stations without automatic samplers, samples can be taken in one of two ways: 1. A minimum of three times a week using either a “stop-belt” sampler (samples are typically taken off one of the main belts into the station or as close as possible) or a “thief” sampler (a slotted pipe that captures coal as the coal drops off the plant belt) to provide a representative sample or 2. A minimum of three times a week from the coal feeders.

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NOTE: Representative stop belt and thief sampling can be a labour intensive and time-consuming job.

The daily samples will be combined into a single weekly composite for analysis as in Method 1 above. The amount of coal collected on a daily basis for analysis should be between 2 – 4 kilograms.

Sample Identification

Each sample will be properly labelled for tracking and reporting purposes. Each daily (composite) sample shall be provided with a sample ID that will indicate the station/boiler unit #, coal type and date.

A sample ID format is: Station unit-fuel-Date-Comments

Station – 2 or 3 characters to ID station

Unit – unit # = 2

Fuel – fuel type (bituminous coal = CB; sub-bituminous coal = CS etc.)

Date – year month day =020315

Comments = daily comp, weekly comp etc.

An example is: the Battle River Generating Station unit #5 burns sub-bituminous coal and the sample was a daily composite taken April 10, 2002 as follows:

“BR5-CS-020410-daily comp”

Sample Preparation

Method 1 – At Station

Sample preparation is done in the preparation lab at the station. During preparation the samples are air-dried and the air-dry moisture loss is calculated (ASTM D2013). At that point they are reduced to 60-mesh size (or less if required). Approximately 250 grams of sample are required for analysis.

Method 2 – At Approved Laboratory

For those stations that do not do sample preparation, the composite coal sample will be sent to an approved lab for preparation as described in Method 1 above. If using an external lab for any preparation it would be required to provide a carefully written procedure for what is expected from them.

Sample Analysis

The weekly composite coal sample will be split into two or three equal sub-samples. All the coal sub-samples will be sent either to the CANMET lab or one of the laboratories participating in the Laboratory Round Robin from the utilities. Each station may also ship a split of the sample to Dr. Fari Goodarzi of Geological Survey of Canada in Calgary for preservation. At the station's discretion, a split of the sample may also be retained at the station for future use.

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Method 1 – CANMET or a Participating Laboratory

These samples will be analysed for ash (ASTM D3174), sulphur (ASTM D4239C), total moisture (ASTM D3302 or ASTM D3173) and higher heat value analysis (ASTM D5865 or ISO 1928), mercury (EPA Method 7473 or ASTM D6414), and chlorine (ASTM D4208-88). This will ensure more consistent analysis across the board as well as credibility of the project. Other standard methods may be acceptable if the utility can defend the method.

Referenced materials or recognised standards will periodically be sent to the labs (including the CANMET lab that will initially be used for analysis) as part of the QA/QC of the program of the Laboratory Round Robin.

If after three months of analyses, the chlorine values are less than 100 ppm further analyses will not be required.

Method 2 - At Station

The stations coal analytical laboratory can be used for ash (ASTM D3174), sulphur (ASTM D4239C), total moisture (ASTM D3302) and higher heat value analysis (ASTM D5865).

Note: Tests for moisture and sulphur are not restricted to those listed above but may be done using any standard analytical method and service provider the utility chooses.

Sample Shipment to CANMET or a Participating Laboratory

Samples sent out to CANMET or one of the participating laboratories (in the Laboratory Round Robin) would leave the site at the 60 mesh size (or less), in appropriately labelled containers, with the air dry moisture loss recorded on the sample vial for later calculation of total moisture. Samples will be sent by courier to the laboratory.

Note: It is assumed that utilities will assemble four weeks worth of samples before sending them for analysis to CANMET or other participating laboratory. This is at the discretion of the utilities.

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SECTION 2.2 FLY ASH SAMPLING & ANALYSIS GUIDELINE

Sample Collection

Method 1 – At the Fly Ash Silo(s)

Samples from the waste and/or sales fly ash (sample size would be based on the approximate split between waste and sales ash where both are sampled) would be collected once or twice weekly from the fly ash silo. A reasonable option is to collect the fly ash in the station prior to conveyance of the fly ash to the ash lagoon (prior to the addition of water for sluicing) for those situations where it is more practicable. If more than one weekly sample is collected, it would be combined with the other weekly sample into one weekly composite sample.

Method 2 - At the ESP (Baghouse) Hoppers

Fly ash samples will be taken from one row in the first field of the hoppers under the Electrostatic Precipitator or baghouse weekly. Collection of a mid-week sample seems appropriate. Fly ash may be collected from all fields, at the discretion of the utility, for a short period to determine if there is significant capture of mercury in the later fields to warrant continuation of this method.

NOTE: This is not the most practical method of sampling flyash and will be extremely labour intensive. It may also require sampling points be installed at the hoppers. It is also not expected to render any better sample collection than Method 1.

Sample Identification

Each sample will be properly labelled for tracking and reporting purposes. Each sample shall be provided with a sample ID that will indicate the station/boiler unit #, ash type and date.

A sample format is: Station unit-fuel-Date-Comments

Station – 2 or 3 characters to ID station

Unit – unit # = 2

Ash type – fly ash = FA

Date – year month day =020315

Comments = daily comp, weekly comp etc.

An example is: the Battle River Generating Station unit #5 and the sample was a daily composite fly ash sample taken April 10, 2002 as follows:
“BR5-FA-020410-daily comp”

Sample Analysis

The weekly composite fly ash sample will be split into two or three equal sub-samples. All the fly ash sub-samples will be sent either to the CANMET lab or one of the laboratories participating in the Laboratory Round Robin from the utilities. Each station can also ship a split of the fly ash sub-sample to Dr. Fari Goodarzi of Geological Survey of Canada in Calgary for preservation. At the station's discretion, a split of the sample may also be retained at the station for future use.

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Method 1 – CANMET or a Participating Laboratory

The fly ash will be analysed for mercury, unburned carbon (loss of ignition) and moisture (ASTM C 311), chlorine and sulphur (ASTM D5016-98).

NOTE: If the analysis shows a very small, almost negligible amount of any of the parameters after a reasonable number of samples have been analysed, then that parameter can be eliminated at the discretion of the utility.

Referenced materials or recognised standards will periodically be sent to the labs (including the CANMET lab that will be initially used for analysis) as part of the QA/QC of the program of the Laboratory Round Robin.

Method 2 – At Station

The fly ash will be analysed at the station analytical lab for unburned carbon, chlorine, sulphur (ASTM D5016-98) and moisture (ASTM C 311).

NOTE: If the analysis shows a very small, almost negligible amount of any of the parameters after a reasonable number of samples have been analysed, then that parameter can be eliminated at the discretion of the utility. If after three months of analyses the values for unburned carbon are less than 0.5 %, and the values for chlorine are less than 100 ppm, further analyses will not be required.

Sample Shipment to CANMET or a Participating Laboratory

Samples sent out to CANMET or one of the participating laboratories (in the Laboratory Round Robin) would leave the site in appropriately labelled containers. Samples will be sent by courier to the laboratory.

Note: It is assumed that utilities will assemble four weeks worth of samples before sending them for analysis to CANMET or other participating laboratory. This is at the discretion of the utilities.

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SECTION 2.3 BOTTOM ASH SAMPLING & ANALYSIS GUIDELINE

Sample Collection

Three weekly samples of bottom ash will be obtained during the beginning of the coal and ash sampling program (one per week). If during that time, the samples show that the mercury content in the bottom ash is less than 5% of the total mercury input in the coal, the requirement for bottom ash sampling may be eliminated.

Sample Identification

Each sample will be properly labelled for tracking and reporting purposes. Each sample shall be provided with a sample ID that will indicate the station/boiler unit #, ash type and date.

A sample format is: Station unit-fuel-Date-Comments

Station – 2 or 3 characters to ID station
Unit – unit # = 2
Ash type – bottom ash = BA
Date – year month day =020315
Comments = grab, daily comp, weekly comp etc.

An example is: the Battle River Generating Station unit #5 bottom ash and the sample was a grab sample taken April 10, 2002 as follows:
“BR5-BA-020410-grab”

Sample Analysis

The weekly bottom ash sample will be split into two or three equal sub-samples. All the bottom ash sub-samples will be sent either to the CANMET lab or one of the laboratories participating in the Laboratory Round Robin from the utilities and will be analysed for mercury. Each station may also ship a split of the bottom ash sub-sample to Dr. Fari Goodarzi of Geological Survey of Canada in Calgary for preservation. At the station's discretion, a split of the sample may also be retained at the station for future use.

Sample Shipment to CANMET or a Participating Laboratory

Samples sent out to CANMET or one of the participating laboratories (in the Laboratory Round Robin) would leave the site in appropriately labelled containers. Samples will be sent by courier to the laboratory.

Note: It is assumed that utilities will assemble a minimum of three bottom ash samples before sending them for analysis to CANMET or other participating laboratory. This is at the discretion of the utilities.

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REPORTING

Reporting of results will be as per each utility's agreement with their respective provincial governments as outlined in Section 4.

QUALIFICATIONS

Utilities will be expected to follow the guidelines/requirements set out for sample gathering and preparation in the appropriate ASTM or EPA standard. Deviation from or modifications to those standards must be approved by their respective jurisdictions. Participating laboratories (including CANMET) must undergo laboratory verification and be approved by the appropriate jurisdiction for use.

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SECTION 2.4: SAMPLING & ANALYSIS: APPLICABLE METHODOLOGIES

SAMPLE COLLECTION

The following methods are recommended for collecting samples of coal based on the type of coal shipment and feed configuration:

- ASTM D6315 - Standard Practice for Manual Sampling of Coal from Tops of Barges
- ASTM D6610 - Standard Practice for Manual Sampling Coal from Surfaces of a Stockpile
- ASTM D4915 - Standard Guide for Manual Sampling of Coal from Tops of Railroad Cars
- ASTM D4916 - Standard Practice for Mechanical Auger Sampling
- ASTM D6609 - Standard Guide for Part-Stream Sampling of Coal
- ASTM D2234 - Standard Practice for Collection of a Gross Sample of Coal

In addition to the sampling methods, a few methods related to sampling procedures/protocols that could be used in conjunction with the standard sampling methods are listed here.

- ASTM D4702 - Standard Guide for Inspecting Crosscut, Sweep-Arm, and Auger Mechanical Coal Sampling Systems for Conformance with Current ASTM Standards
- ASTM D6518 - Standard Practice for Bias Testing a Mechanical Coal Sampling System
- ASTM D4182 - Standard Practice for Evaluation of Laboratories Using ASTM Procedures in the Sampling and Analysis of Coal and Coke

SAMPLE PREPARATION

Coal Samples:

- ASTM D2013 - Standard Practice of Preparing Coal Samples for Analysis

Solid Residue Samples:

- Standard practices for the sampling and preparation of residues have not been established. The recommended size reduction is 150-um (No. 100) U.S.A. standard sieve.

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ANALYSIS OF MERCURY

Coal:

For the analysis of mercury in coal, the following methods are recommended:

- ASTM D3684 - Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method
 - This method can achieve lower quantitative limit (LQL) of 60 ng/g (ppb) and hence is suitable for high mercury coals only. The method is unsuitable for ashes and other low-BTU materials.
- ASTM D6414 - Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapour Atomic Adsorption
 - This method can achieve a LQL of 30 ng/g (ppb). The method is suitable for ash and can be adopted for high-mercury samples by decreasing the weight of the sample.
- ASTM D6722 - Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis
 - This method can achieve a LQL of 20 ng/g (ppb) and is suitable for ash and other solid residues. **CAUTION:** In some cases, a coal sample can cause problems with uniform combustion depending on its composition, including moisture content. The sample might explode or spark in the combustion chamber.
- U.S. EPA Method 7473 - Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry
 - The instrument has a LQL at 20 ng/g. This technique can analyse replicate samples in a relatively short time with little or no contamination problems.

Solid Residues:

For the analysis of mercury in solid residues such as ashes, the following methods are recommended:

- ASTM D6414 - Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapour Atomic Adsorption
 - This method can achieve a LQL of 30 ng/g (ppb). The method is suitable for ash and can be adopted for high-mercury samples by decreasing the weight of the sample.
- ASTM D6722 - Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis
 - This method can achieve a LQL of 20 ng/g (ppb) and is suitable for ash and other solid residues. **CAUTION:** In some cases, a coal sample can cause problems with uniform combustion depending on its composition, including moisture content. The sample might explode or spark in the combustion chamber.
- U.S. EPA Method 7473 - Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry
 - The instrument has a LQL at 20 ng/g. This technique can analyse replicate samples in a relatively short time with little or no contamination problems.

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Other Residues:

For the analysis of mercury in liquid residues, the following methods are recommended:

- EPA 7471A (Acid Extraction CVAA)
- EPA 1631 (Acid Extraction CVAFS¹)
- Microwave Digestion CVAA.

ANALYSIS OF CHLORINE

Coal:

The following methods are available for the analysis of chlorine in coal.

- ASTM D4208 - Bomb Combustion Ion Selective Electrode (ISE)
- Pyrohydrolysis / Ion Chromatography
- ASTM D2361 - Standard Test Method for Chlorine in Coal
- ASTM D6721 - Standard Test Method for Determination of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry

Solid Residues:

- Pyrohydrolysis / Ion Chromatography
- Instrumental Neutron Activation