

CCME Project 257-2003

Phase 1 Commissioning Sample Report

1 Use of this Report

The reader is cautioned the evaluations in this report serve only as indicators of laboratory performance. Laboratory competence can only be established and monitored through a properly conducted quality assurance program, which should be verified by an independent audit of the laboratory operations consistent with the requirements of ISO 17025.

2 Organization of the Report

Part 3 describes the approach used in the CCME study. Part 4 is a commissioning report summary. Part 5 evaluates ash results reported by each laboratory. Part 6 is an assessment of laboratory performance with respect to mercury analysis. Part 7 consists of laboratory briefs. Part 8 describes the calculations and basis for assessment. Part 9 provides a table of results reported by the laboratories. Part 10 provides method briefs summarizing the known advantages and limitations of methods for the analysis of mercury.

3 Approach

CCME project 257-2003 is a performance-based study using Certified Reference Materials (CRMs) and Reference Materials (RMs) of known concentration.

Quality Associates International® distributed a Reference Material (RM) coal sample of known composition to permit participating laboratories the opportunity to commission their test protocols in advance of receiving further Certified Reference Material (CRM) and Reference Material (RM) samples.

All RMs used in the CCME study are traceable to CRMs.

The commissioning sample designated as ES-1 was prepared in accordance with ASTM D 2013, *Standard Method of Preparation of Coal Samples for Analysis*. The sample, which consisted of approximately 25 kilograms of coal was ground to pass 60 mesh (250µm) and subdivided into bottles on a rotary carousel splitter.

Based on comparisons of measurements made on ash, sulfur and Btu, sample ES-1 was shown to be equivalent in homogeneity to at least one certified reference material (CRM) coal available from the National Institute of Standards and Technology (NIST) in the USA.

Sample ES-1 was used in Electric Power Research Institute (EPRI) study 100287 and the American Society for Testing and Material (ASTM) inter-laboratory study (ILS) conducted from 1999 through 2000. Those studies served as a basis for comparing and validating methods for the determination of mercury in coal and coal derived residues. At the completion of these studies ASTM confirmed the following test methods as suitable for the determination of mercury in coal;

ASTM D 3684 Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method

ASTM D 6414 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption

ASTM D 6722 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis

In the EPRI study and the ASTM ILS, ES-1 was run at the same time by the same group of laboratories for the same test parameters as and concurrent with the following Certified Reference Material (CRM) Coals, NIST SRM 2692b, NIST SRM 1632c and SABS SARM 20. Where certified values were available no significant bias was found for the CRM samples NIST SRM 2692b, NIST SRM 1632c or SABS SARM 20 when analyzed by the same methods as ES-1.

The RM values and Limits for ES-1 appear in the table below.

ES-1 High Volatile A Bituminous PA USA					
Parameter	RM Value	RM Limits	Number of Values	Number of Methods	Notes
Ash wt% dry basis	8.00	0.04	26	4	Reference
Sulphur wt% dry basis	2.13	0.02	26	3	Reference
Chlorine µg/g dry basis	1133	29	7	2	Reference
Mercury ng/g dry basis	114	4	34	3	Reference

CCME laboratory values were compared with the RM ash and mercury values.

In addition laboratory limits for mercury were compared with benchmark limits calculated from the RM limits of ES-1, as well as method limits determined in a method validation Interlaboratory Study (ILS). In instances where a laboratory reported the use of a method that is not supported by data from a method validation Interlaboratory Study (ILS), the Horwitz function as cited in the GeoPT™ *Proficiency Testing Protocol of Operation* was employed to estimate the method limits. The Horwitz function is an empirical function that applies over a wide range of concentrations, test materials, analytes and physical principles underlying an analytical procedure.

4 Commissioning Report Summary

Results

All 14 laboratories enlisted in CCME study 257-2003 reported results for the commissioning sample ES-1.

The performance results obtained for sample ES-1 in this commissioning study are remarkably similar to those reported in the EPRI and ASTM studies.

Six (6) CCME laboratories employed *ASTM D 6722 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis*. All 6 CCME laboratories produced results of acceptable accuracy and precision. The CCME laboratories performed at least as well as the laboratories that took part in the EPRI and ASTM studies.

Two (2) laboratories employed *ASTM D 6414 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption*. One of the two laboratories produced results of acceptable accuracy and precision. That laboratory also performed as well as the laboratories that took part in the EPRI and ASTM studies.

Six (6) laboratories did not use any of the three ASTM methods. Of those 6, one employing *instrumental neutron activation analysis (INAA)* produced results with acceptable accuracy and precision, another using a method *based on EPA 245.5* produced results with acceptable accuracy and precision, one applying *a microwave digestion* procedure produced results with acceptable accuracy and precision, another reporting results using *an acid digestion procedure with an ICP-MS finish* produced results with acceptable accuracy and precision, and one employing an “in-house” method produced results with acceptable accuracy and precision.

Completion of Phase 1

The laboratory briefs contain where appropriate recommendations for modifications to procedures that a laboratory may wish to implement prior to initiating tests of the CRM and RM samples that shall constitute the final stage of testing in Phase 1. In the final stage of Phase 1, each laboratory shall receive the same 7 CRM/RM coals and the same 3 CRM/RM samples (>80 % ash content) for analysis. Results from these 10 mandatory samples are intended to provide a more comprehensive assessment of laboratory performance over the normally expected range of thermal coal and coal residue quality.

After reporting results for these 10 samples each laboratory shall be given the opportunity to analyze up to 13 optional samples. These samples can be used to confirm the results obtained for the 10 mandatory samples and/or verify the capability of a laboratory at the extremes of coal quality.

5 Evaluation of Laboratory Determination of Ash Content

Participants were instructed to carry out a single determination of the ash content of ES-1. This was taken as a precautionary step to ensure the sample was of acceptable quality and that no inadvertent sample interchange had occurred. The accuracy of the ash result from each laboratory was compared with the ES-1 RM ash value. Ash values outside acceptable limits were investigated in an attempt to determine the cause.

Table 1 presents the evaluation of laboratory determination of ash content.

The results are sorted from lowest to highest ash value with the ES-1 RM values and limits included in the table as a point of reference.

The normal expectation is that the reported ash values should fall within benchmark ash limits calculated from the RM limits and the limits of the reference method for the determination of ash content of ES-1. The reference method for ash is *ASTM D 3174 Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal*.

Ash values that fell **within the ES-1 lower and upper RM limits are considered highly accurate and are in green**. Ash values that fell **within the lower and upper benchmark ash limits are considered acceptable and are in blue**. Ash values that fell **outside the lower and upper benchmark ash limits are considered suspect and are in red**.

The assessment column identifies laboratory accuracy that is not suspect with a blue **Accuracy OK**. Suspect laboratory accuracy is identified with a red **Accuracy Suspect**. Laboratories that reported corrected results are identified. Details of corrective action taken by the laboratory are provided in Part 7, the laboratory briefs.

Of the 14 laboratories taking part in the commissioning test, 13 reported ash results. Laboratory AF, which employs instrumental neutron activation (INAA) did not report an ash result. This laboratory has independent means of verifying sample homogeneity. Of the remaining 13 laboratories 5 reported results within the RM limits, and 7 reported results within the benchmark ash limits.

Laboratory G, F and AE reported results with suspect accuracy. These laboratories were contacted to ascertain the potential cause of the suspect value. It was evident these laboratories were not following conditions of temperature, time and/or calibration consistent with the requirements of ASTM. Laboratory G and F took corrective action to comply with the ASTM conditions of test. Laboratory AE needs additional time to make the necessary modifications

The corrected value reported by laboratory G is in perfect agreement with the RM value for ES-1. The corrected value reported by Laboratory F is the within the benchmark ash limits.

Table 1 Evaluation of Laboratory Determination of Ash Content							
ID	Assessment	Operator	Instrument	Benchmark ASTM Method	Laboratory Value	Lower Ash Limit	Upper Ash Limit
CCME-G	Accuracy Suspect	O-1	I-1	D 3174	7.62	7.76	8.24
CCME-W	Accuracy OK	O-1	I-1	D 3174	7.76	7.76	8.24
CCME-F Corrected	Accuracy OK	O-3	I-3	D 3174	7.80	7.76	8.24
CCME-W	Accuracy OK	O-2	I-2	D 3174	7.83	7.76	8.24
CCME-B	Accuracy OK	O-1	I-1	D 3174	7.84	7.76	8.24
CCME-AC	Accuracy OK	O-1	I-1	D 3174	7.87	7.76	8.24
CCME-AI	Accuracy OK	O-1	I-1	D 3174	7.94	7.76	8.24
CCME-L	Accuracy OK	O-1	I-1	D 3174	7.96	7.76	8.24
CCME-U	Accuracy OK	O-1	I-1	D 3174	7.97	7.76	8.24
CCME-G Corrected	Accuracy OK	O-1	I-1	D 3174	8.00	7.76	8.24
ES-1	RM	RM	RM	RM	8.00	7.96	8.04
CCME-D	Accuracy OK	O-1	I-1	D 3174	8.01	7.76	8.24
CCME-K	Accuracy OK	O-1	I-1	D 3174	8.04	7.76	8.24
CCME-AH	Accuracy OK	O-1	I-1	D 3174	8.06	7.76	8.24
CCME-Q	Accuracy OK	O-1	I-1	D 3174	8.07	7.76	8.24
CCME-F	Accuracy Suspect	O-1	I-1	D 3174	55.12	7.76	8.24
CCME-F	Accuracy Suspect	O-1	I-2	D 3174	56.45	7.76	8.24
CCME-AE	Accuracy Suspect	O-1	I-1	D 3174	79.82	7.76	8.24

6 Evaluation of Laboratory Determination of Mercury (Hg)

The assessment of the laboratory determination of mercury is presented in **tables 2 through 4**.

Laboratory accuracy and limits are assessed.

Laboratory Value Green and Laboratory Limits Blue

This condition suggests the laboratory is performing the test with a high degree of accuracy and with a degree of precision commensurate with that obtained in the method validation ILS or that predicted by the Horwitz function.

Laboratory Value Blue and Laboratory Limits Blue

This condition suggests the laboratory is performing the test with a degree of accuracy and precision commensurate with that obtained in the method validation ILS or that predicted by the Horwitz function.

Laboratory Value Red and Laboratory Limits Blue

This condition suggests the laboratory is performing the test with a degree precision commensurate with that obtained in the method validation ILS or that predicted by the Horwitz function. However, there is a definite indication a laboratory bias exists.

Laboratory Value Green and Laboratory Limits Red

Laboratory Value Blue and Laboratory Limits Red

Laboratory Value Red and Laboratory Limits Red

All of these conditions suggest a lack of control with respect to factors that can affect the precision of the final result. In all cases agreement or lack of agreement of the laboratory value with the final result may be entirely coincidental.

The assessment column of each table identifies laboratory accuracy and limits that are not suspect with a blue **Accuracy OK Precision OK**. If laboratory accuracy or precision or both are suspect the assessment appears in red **with the suspect component(s) identified**.

Table 2 Comparison of Determination of Mercury (Hg) by the CCME laboratories

Table 2 compares the performance of the 14 CCME laboratories for the commissioning sample ES-1. Laboratory F reported 3 operator instrument combinations. Laboratory AE reported two instrument operator combinations for 1 method and 1 for another. Laboratory W reported two instrument operator combinations. The laboratory results are sorted from lowest to highest mercury value. The anticipated ES-1 RM values and limits are also included in Table 2.

From table 2 it is evident the 6 laboratories that employed *ASTM D 6722 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis* consistently produced results of acceptable quality.

Laboratory L which employs *ASTM D 6414 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption* also produced results of acceptable quality as did laboratory F which uses an ‘in-house’ acid digestion procedure, laboratory Q which applies a *microwave digestion technique*, laboratory AC which employs *EPA 245.5*, laboratory AF which uses an *instrumental neutron activation analysis (INAA)* and laboratory AI which employs an *acid digestion followed by an ICP-MS finish*.

Laboratory AE produced suspect accuracy results for the one *EPA 245.5* instrument operator combination and suspect precision results for the other. This is a strong indication that the *EPA 245.5* method as conducted in laboratory AE is likely to produce results with inconsistent and erratic recovery. Laboratory AE produced suspect precision results for the NIOSH 6009 method. NIOSH procedure 6009 as applied in laboratory AE appears to be susceptible to erratic recovery of mercury from coal. The acceptable accuracy for the NIOSH method can be at best viewed as coincidental. Laboratory AH which uses *ASTM D 6414 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption* produced results with suspect accuracy albeit with acceptable precision. This could indicate either a problem with incomplete extraction of mercury or alternatively with instrument calibration.

Table 2 Comparison of Determination of Mercury (Hg) by the CCME laboratories.									
ID	Assessment	Operator	Instrument	Benchmark Hg Method	Laboratory Hg Method	Laboratory Value	±	Laboratory Limits	Benchmark Limits
CCME-AE	Accuracy Suspect Precision OK	O-1	I-1	Horwitz	EPA245.5	64	±	27	27
CCME-AH	Accuracy Suspect Precision OK	O-1	I-1	D 6414	D 6414	73	±	15	18
CCME-F	Accuracy OK Precision OK	O-3	I-3	Horwitz	Acid Digestion CVAA	94	±	26	27
CCME-AC	Accuracy OK Precision OK	O-1	I-1	Horwitz	EPA245.5	94	±	27	27
CCME-AE	Precision Suspect Accuracy OK	O-1	I-3	Horwitz	EPA245.5	96	±	44	27
CCME-F	Accuracy OK Precision OK	O-1	I-2	Horwitz	Acid Digestion CVAA	101	±	26	27
CCME-AF	Accuracy OK Precision OK	O-1	I-1	Horwitz	INAA	103	±	26	27
CCME-Q	Accuracy OK Precision OK	O-1	I-1	Horwitz	Microwave CVAAS	109	±	27	27
CCME-K	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	109	±	13	14
CCME-AE	Precision Suspect Accuracy OK	O-1	I-2	Horwitz	NIOSH 6009	110	±	29	27
CCME-B	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	112	±	14	14
CCME-G	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	113	±	13	14
CCME-U	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	113	±	13	14
CCME-D	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	114	±	13	14
ES-1	RM	RM	RM	RM	RM	114	±		4
CCME-F	Accuracy OK Precision OK	O-1	I-1	Horwitz	Acid Digestion CVAA	116	±	26	27
CCME-W	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	118	±	14	14
CCME-W	Accuracy OK Precision OK	O-2	I-2	D 6722	D 6722	119	±	13	14
CCME-L	Accuracy OK Precision OK	O-1	I-1	D 6414	D 6414	119	±	15	18
CCME-AI	Accuracy OK Precision OK	O-1	I-1	Horwitz	Acid Digestion ICP-MS	120	±	26	27

Table 3 Comparison of Determination of Mercury (Hg) by ASTM D 6722 CCME laboratories vs. ASTM laboratories

Table 3 compares the accuracy and limits of the CCME laboratories that reported mercury results using *ASTM D 6722 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis* with the accuracy and limits of the laboratories that took part in the ASTM validation study for D 6722. It is evident that the CCME laboratories performed at least as well as the ASTM laboratories. In fact combining the CCME and ASTM data sets would yield single and multiple laboratory uncertainty indistinguishable from that obtained in the original ASTM study for sample ES-1. This is a strong endorsement of the ruggedness of the method.

Table 3 Comparison of Determination of Mercury (Hg) by ASTM D 6722 CCME laboratories vs. ASTM laboratories									
ID	Assessment	Operator	Instrument	Benchmark Hg Method	Laboratory Hg Method	Laboratory Value	±	Laboratory Limits	Benchmark Limits
ASTM-14	Accuracy OK Precision OK	O-1	O-1	D 6722	D 6722	105	±	13	14
CCME-K	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	109	±	13	14
ASTM-22	Accuracy OK Precision OK	O-1	O-1	D 6722	D 6722	111	±	14	14
CCME-B	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	112	±	14	14
ASTM-43	Accuracy OK Precision OK	O-1	O-1	D 6722	D 6722	112	±	13	14
CCME-G	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	113	±	13	14
CCME-U	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	113	±	13	14
ASTM-44	Accuracy OK Precision OK	O-1	O-1	D 6722	D 6722	113	±	14	14
CCME-D	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	114	±	13	14
ES-1	RM	RM	RM	RM	RM	114	±		4
ASTM-28	Accuracy OK Precision OK	O-1	O-1	D 6722	D 6722	117	±	13	14
CCME-W	Accuracy OK Precision OK	O-1	I-1	D 6722	D 6722	118	±	14	14
CCME-W	Accuracy OK Precision OK	O-2	I-2	D 6722	D 6722	119	±	13	14
ASTM-45	Accuracy OK Precision OK	O-1	O-1	D 6722	D 6722	120	±	13	14
ASTM-25	Accuracy OK Precision OK	O-1	O-1	D 6722	D 6722	125	±	14	14

Table 4 Comparison of Determination of Mercury (Hg) by ASTM D 6414 CCME laboratories vs. ASTM laboratories

Table 4 compares the accuracy and limits of the CCME laboratories that reported mercury results using *ASTM D 6414 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption* with the accuracy and limits of the laboratories that took part in the ASTM validation study for D 6414. It is worthwhile noting that one of the ASTM laboratories produced results with suspect precision in the ASTM study and one of the CCME laboratories produced results of suspect accuracy. Although ASTM D 6414 is relatively simple to apply, the original ASTM study demonstrated that the digestion step must be closely monitored and controlled to ensure complete and uniform recovery of mercury.

Table 4 Comparison of Determination of Mercury (Hg) by ASTM D 6414 CCME laboratories vs. ASTM laboratories									
ID	Assessment	Operator	Instrument	Benchmark Hg Method	Laboratory Hg Method	Laboratory Value	±	Laboratory Limits	Benchmark Limits
CCME-AH	Accuracy Suspect Precision OK	O-1	I-1	D 6414	D 6414	73	±	15	18
ASTM-19	Accuracy OK Precision OK	O-1	O-1	D 6414	D 6414	106	±	17	18
ASTM-11	Accuracy OK Precision OK	O-1	O-1	D 6414	D 6414	111	±	16	18
ASTM-7	Accuracy OK Precision OK	O-1	O-1	D 6414	D 6414	111	±	16	18
ASTM-22	Accuracy OK Precision OK	O-1	O-1	D 6414	D 6414	114	±	15	18
ES-1	RM	RM	RM	RM	RM	114	±		4
ASTM-29	Accuracy OK Precision OK	O-1	O-1	D 6414	D 6414	115	±	18	18
ASTM-15	Precision Suspect Accuracy OK	O-1	O-1	D 6414	D 6414	115	±	19	18
CCME-L	Accuracy OK Precision OK	O-1	I-1	D 6414	D 6414	119	±	15	18
ASTM-26	Accuracy OK Precision OK	O-1	O-1	D 6414	D 6414	122	±	16	18
ASTM-8	Accuracy OK Precision OK	O-1	O-1	D 6414	D 6414	129	±	16	18

7 Laboratory Briefs

The laboratory briefs not only provide individual narrative assessments of laboratory performance but also make recommendations for modifications to procedures that a laboratory may wish to implement prior to initiating tests of the CRM and RM samples that shall constitute the final stage of testing in Phase 1.

Laboratory B

The mercury method employed to assess the performance of Laboratory B is ASTM D 6722.

Laboratory B produced mercury results with a high degree of accuracy and a level of precision commensurate with that obtained in the method validation study for ASTM D 6722.

The ash result reported by laboratory B is within the benchmark ash limits.

Laboratory B confirmed that the coal was dried in a cabinet using ambient air heated to 107 C. The ambient air was not pre-dried. The ASTM standard for determination of residual moisture not only specifies the air be heated to a temperature of 105 C to 110 C but also that air be dried to a moisture content of 1.9 mg/L or less. If the air is not dried then the determined moisture value can be biased low. This in turn leads to dry mercury and dry ash values that are biased low. This trend is noted for both the dry mercury and dry ash values reported by laboratory B although both are certainly within acceptable limits.

It is recommended that laboratory B comply with the *Dry Air* requirement specified in *ASTM D 3173 Standard Test Method for Moisture in the Analysis Sample of Coal and Coke* to avoid introducing a moisture bias into dry basis calculations.

Laboratory D

The mercury method employed to assess the performance of laboratory D is ASTM D 6722.

Laboratory D produced mercury results with a high degree of accuracy and a level of precision commensurate with that obtained in the method validation study for ASTM D 6722.

The ash result reported by laboratory D is within the RM limits for ES-1.

It would appear that laboratory D is complying with the requirements of ASTM standards for the determination of mercury, moisture and ash in coal.

Laboratory F

Laboratory F employs an “in-house” modification of EPA 245.5. The laboratory F modification employs an acid digestion in an open Erlenmeyer flask at approximately 50 C to 60 C. Since the laboratory F method has not been validated for analysis of coal in a controlled Interlaboratory Study (ILS), the Horwitz was employed to assess the performance of laboratory F.

Laboratory F reported results for three different operator instrument combinations.

The O-1, I-1 combination produced results with a high degree of accuracy and precision within the limits predicted by the Horwitz function.

The combination O-1, I-2 and O-2 I-2 also produce results that are within the limits predicted by the Horwitz function.

However, although the O-1, I-2 and O-2 I-2 combinations yield laboratory limits similar to the O-1, I-1 combination there is a definite trend to lower recovery.

The trend to low recovery could be either a result of incomplete extraction of mercury from the sample or alternatively a result of a drift in instrument calibration. Assuming laboratory F calibrates their instrumentation prior to determining mercury for each test batch and verifies the calibration then the trend to low recovery appears to be a method related issue.

In EPRI study 1000287 the results on Certified Reference Material (CRM) coals for laboratories using the EPA method for mercury were consistently low. In the EPRI study, the EPA method recovery for NIST SRM 1632c and NIST SRM 2683b, which are similar in composition to sample ES-1, was low by 13ng/g and 9 ng/g respectively. Applying an average correction of 11 ng/g to the results reported for all the Lab F operator instrument combinations would yield the following results;

O-1 I-1	127 ng/g
O-1 I-2	112 ng/g
O-2 I-3	105 ng/g

The average of these three sets of results would be 115 ng/g, which is within the RM limits for ES-1.

EPA method 245.5 was originally developed for waste materials and sediments. Unlike coal, these materials do not normally contain significant quantities of refractory organic components. The mercury in coal can be dispersed throughout these refractory organic components in a non-uniform way. Extraction of mercury from these components without complete dissolution of the organic matter may not be complete. Studies conducted in Australia have also shown that unless coals are refluxed in a digestion apparatus for at least 24 hours mercury recovery by acid extraction can be low.

It is recommended that laboratory F modify their extraction procedure to comply with the conditions specified in ASTM D 6414 prior to proceeding with the completion of Phase 1.

The initial ash results reported by laboratory F were well outside the benchmark ash limits.

Laboratory F indicated they are igniting the coal at 550 C. The temperature specified by ASTM D 3174 for the determination of ash content of coal is 750 C. Ignition of coal at 550 C can result in unburned carbon remaining. Since the coal may ash on the surface the unburned carbon may not be noticed unless the sample is stirred after the ashing step. This precaution is recommended even for coals ignited at 750 C. In addition, ignition of coal at 550 C can also result in incomplete decomposition of alkaline carbonate compounds.

Laboratory F was requested to rerun the ash determination on the coal sample. Laboratory F reported a corrected ash value, which calculated to 7.80 wt % on a dry basis. This value is within the benchmark ash limits.

Laboratory G

The mercury method employed to assess the performance of Laboratory G is ASTM D 6722.

Laboratory G produced mercury results with a high degree of accuracy and a level of precision commensurate with that obtained in the method validation study for ASTM D 6722.

The initial ash result reported by laboratory G was outside the benchmark ash limits.

Laboratory G was contacted to determine whether this was sample related or a method related problem. Laboratory G indicated they were using a TGA calibrated with fly ash to run at 950 C. The temperature specified by ASTM D 3174 for the determination of ash content of coal is 750 C. Fly ash samples normally have ash contents in excess of 90 %. This is well in excess of the amount of ash normally expected in coal and could lead to significant interpolation errors when applying the fly ash calibration to coal. Laboratory G recalibrated their instrument at 750 C using coals of ash composition in the range of 7 wt % to 15 wt %.

The corrected dry basis result of 8.00 % for ES-1 run under this calibration is in perfect agreement with the ES-1 RM value.

This situation underlines the fact that methods of test such as determination of moisture and ash, which are empirical, are definitely affected by conditions of test.

Laboratory K

The mercury method employed to assess the performance of laboratory K is ASTM D 6722.

Laboratory K produced mercury results with a degree of accuracy and a level of precision commensurate with that obtained in the method validation study for ASTM D 6722.

The ash result reported by laboratory K is within the RM limits for ES-1.

It would appear that laboratory K is complying with the requirements of ASTM standards for the determination of mercury, moisture and ash in coal.

Laboratory L

The mercury method employed to assess the performance of laboratory L is ASTM D 6414.

Laboratory L produced mercury results with a degree of accuracy and a level of precision commensurate with that obtained in the method validation study for ASTM D 6414.

The ash result reported by laboratory L is within the RM limits for ES-1.

Laboratory L also reported results for sulfur and calorific value. Laboratory L requested an evaluation for these two parameters. The ES-1 RM value and limit for sulfur is 2.13 ± 0.02 wt % dry basis. Assuming Laboratory L employed ASTM D 4239 for Sulfur the benchmark limits for the ES-1 are 1.98 wt % dry basis to 2.28 wt % sulfur dry basis. Laboratory L reported a value that calculated as 2.06 wt % sulfur dry basis.

It would appear that laboratory L is complying with the requirements of ASTM standards for the determination of mercury, moisture, ash and sulfur in coal.

The laboratory L results for calorific value was not assessed as there are no assigned ES-1 RM values and limits for calorific value. This is because coal calorific value is known to degrade with time.

Laboratory Q

Laboratory Q employs a microwave digestion followed by a CVAA finish. Since this procedure has not been validated for analysis of coal in a controlled Interlaboratory Study (ILS), the Horwitz function was employed to assess the performance of laboratory Q.

Laboratory Q produced mercury results with a degree of accuracy and a level of precision commensurate with that estimated from the Horwitz function.

The ash result reported by laboratory Q is within the benchmark ash limits.

Laboratory Q confirmed that the coal was dried in a cabinet using heated ambient air. The ambient air was not pre-dried. The ASTM standard for determination of residual moisture specifies the air be heated to a temperature of 105 C to 110 C and that air be dried to moisture content of 1.9 mg/L or less. If the air is not dried then the determined moisture value can be biased low. This in turn, leads to dry mercury and dry ash values that are biased low. This trend is noted for the dry mercury reported by laboratory Q although the value is certainly within acceptable limits.

It is recommended that laboratory Q comply with the *Dry Air* requirement specified in *ASTM D 3173 Standard Test Method for Moisture in the Analysis Sample of Coal and Coke* to avoid introducing a moisture bias into dry basis calculations.

Laboratory U

The mercury method employed to assess the performance of laboratory U is ASTM D 6722.

Laboratory U produced mercury results with a high degree of accuracy and a level of precision commensurate with that obtained in the method validation study for ASTM D 6722.

The ash result reported by laboratory U is within the RM limits for ES-1.

It would appear that laboratory U is complying with the requirements of ASTM standards for the determination of mercury, moisture and ash in coal.

Laboratory W

The mercury method employed to assess the performance of laboratory W is ASTM D 6722.

Laboratory W reported mercury results for two operator instrument combinations

One combination produced mercury results with a high degree of accuracy and a level of precision commensurate with that obtained in the method validation study for ASTM D 6722.

The other combination produced with a degree of accuracy and a level of precision commensurate with that obtained in the method validation study for ASTM D 6722.

Both operator instrument combinations for ash reported by laboratory W were within the benchmark ash limits.

It would appear that laboratory W is complying with the requirements of ASTM standards for the determination of mercury, moisture and ash in coal.

Laboratory AC

Laboratory AC employs EPA 245.5. Since EPA 245.5 has not been validated for analysis of coal in a controlled Interlaboratory Study (ILS), the Horwitz function was employed to assess the performance of laboratory AC.

Laboratory AC produced mercury results with a degree of accuracy and a level of precision commensurate with that estimated from the Horwitz function.

The ash result reported by laboratory AC is within the benchmark ash limits.

Laboratory AC confirmed that the coal was dried in a cabinet using heated ambient air. The ambient air was not pre-dried. The ASTM standard for determination of residual moisture not only specifies the air be heated to a temperature of 105 C to 110 C but also that air be dried to a moisture content of 1.9 mg/L or less. If the air is not dried then the determined moisture value can be biased low. This in turn, leads to dry mercury and dry ash values that are biased low. This trend is noted for both the dry mercury and dry ash values reported by laboratory AC although both are within acceptable limits.

In EPRI study 1000287 the results on Certified Reference Material (CRM) coals for laboratories using the EPA method for mercury were consistently low. In the EPRI study, the EPA method recovery for NIST SRM 1632c and NIST SRM 2683b, which are similar in composition to sample ES-1, was low by 13ng/g and 9 ng/g respectively. Applying an average correction of 11 ng/g to the result of 94 ng/g reported for laboratory AC would yield 105 ng/g, which is in much closer agreement with the ES-1 RM value of 114 ng/g.

Examination of the individual results reported by laboratory AC revealed a result, which was markedly lower than the other three results. Recalculation of the laboratory AC average value upon eliminating the low result yielded average dry basis mercury value of 98 ng/g. Applying the 11 ng/g correction would yield 109 ng/g which is even in closer agreement with ES-1 RM value. It is possible to estimate that the amount of moisture reported by lab AC is biased low. This can be done by determining the adjustment required to bring the dry ash value within the ES-1 reference ash limits. When the adjustment is made the dry basis mercury value for laboratory AC calculates to 99 ng/g. Applying the 11 ng/g correction would yield 110 ng/g, which agrees with ES-1 RM value within the ES-1 RM limits.

Prior to proceeding with the completion of Phase 1, it is recommended that laboratory AC modify their extraction procedure to comply with the conditions specified in ASTM D 6414 and also with the *Dry Air* requirement specified in *ASTM D 3173 Standard Test Method for Moisture in the Analysis Sample of Coal and Coke* to avoid introducing a low moisture bias into dry basis calculations.

Laboratory AE

Laboratory AE employs two procedures EPA 245.5 and NIOSH 6009 for the determination of mercury. Since EPA 245.5 and NIOSH 6009 have not been validated for analysis of coal in a controlled Interlaboratory Study (ILS), the Horwitz function was employed to assess the performance of laboratory AE.

In the case of EPA 245.5 laboratory AE reported results for two operator instrument combinations. In one case the accuracy of the results is suspect and in another the precision is suspect. This is a strong indication that the application of EPA 245.5 to coal in laboratory AE would likely generate unreliable results.

In the case of NIOSH 6009 laboratory AE reported one set of results with suspect precision.

Erratic precision can be an indication of erratic mercury recovery. Laboratory AE indicated the NIOSH procedure consisted of allowing the sample to soak in acid mix at ambient temperature without continuous stirring. The validation study for *ASTM D 6414 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption* coupled with studies conducted in Australia have demonstrated that coal must be digested under reflux conditions at temperatures of 95 C or greater to optimize complete and consistent acid extraction of mercury.

Laboratory AE reported an ash value with suspect accuracy.

Laboratory AE indicated they are igniting the coal at 460 C. The temperature specified by ASTM D 3174 for the determination of ash content of coal is 750 C. Ignition of coal at 460 C can result in unburned carbon remaining. Since the coal may ash on the surface the unburned carbon may not be noticed unless the sample is stirred after the ashing step. This precaution is recommended even for coals ignited at 750 C. In addition, ignition of coal at 460 C can also result in incomplete decomposition of alkaline carbonate compounds.

It is recommended that laboratory AE modify their acid extraction procedure to comply with the conditions specified in ASTM D 6414 and modify their ashing procedure to comply with the requirements of *ASTM D 3174 Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal* prior to proceeding with the completion of Phase 1.

Laboratory AF

Laboratory AF employs instrumental neutron activation analysis (INAA) for the determination of mercury. Since INAA has not been validated for analysis of coal in a controlled Interlaboratory Study (ILS), the Horwitz function was employed to assess the performance of laboratory AF.

Laboratory AF produced mercury results with a degree of accuracy and a level of precision commensurate with that estimated from the Horwitz function.

It must be noted that the Horwitz function may not be a completely objective benchmark for INAA. The Horwitz function was developed employing ILS method validation data from studies primarily based on chemical methods. INAA is a non-destructive nuclear analysis technique. Laboratory AF took part in EPRI study 1000287. To confirm that the laboratory limits calculated for laboratory AF employing the Horwitz function are reasonable the laboratory AF mercury results from the EPRI study for CRM coals of composition similar to ES-1 were used to estimate the INAA multiple laboratory uncertainty. The result calculated from the EPRI study justified the use of the Horwitz function for laboratory AF.

Laboratory AF did not report an ash value. INAA is a technique that allows laboratory AF to conduct analysis of other parameters which can be used to ascertain the homogeneity of a sample.

Laboratory AH

The mercury method employed to assess the performance of laboratory AH is ASTM D 6414.

Laboratory AH produced mercury results suspect accuracy but a level of precision commensurate with that obtained in the method validation study for ASTM D 6414.

This could indicate either a problem with incomplete extraction of mercury or alternatively with instrument calibration.

Laboratory AH is directed to the method brief for ASTM D 6414 to ensure they are complying with the procedural steps required to ensure complete and uniform extraction of mercury from coal samples.

Laboratory AH reported an ash value that is within the benchmark ash limits for sample ES-1.

Laboratory AI

Laboratory AI employs an acid digestion followed by an ICP-MS finish. Since this procedure has not been validated for analysis of coal in a controlled Interlaboratory Study (ILS), the Horwitz function was employed to assess the performance of laboratory AI.

Laboratory AI produced mercury results with a degree of accuracy and a level of precision commensurate with that estimated from the Horwitz function.

The ash result reported by laboratory AI is within the benchmark ash limits.

8 Description of Calculations

Basis for evaluation of Laboratory Performance

Laboratories indicating the use a specific standard method or a method closely resembling a standard method were evaluated against the method validation data for that standard method.

In instances where a laboratory reported the use of a method that is not supported by data from a method validation Interlaboratory Study (ILS) the Horwitz function as cited in the GeoPT™ *Proficiency Testing Protocol of Operation* was employed to evaluate laboratory performance. The Horwitz function is an empirical equation that applies over a wide range of concentrations, test materials, analytes and physical principles underlying an analytical procedure.

The accuracy and precision of each laboratory were assessed for the commissioning sample ES-1.

Laboratory accuracy was assessed by comparing the average of the four (4) reported laboratory values with the ES-1 RM value.

Benchmark limits were calculated from the RM limits of ES-1, as well as method limits which are a combination of the single (within) laboratory and the multiple (among) laboratory uncertainty as determined in a method validation Interlaboratory Study (ILS) or the single (within) laboratory and the multiple (among) laboratory uncertainty calculated from the Horwitz function.

Laboratory limits were calculated from the RM limits of ES-1, the laboratory precision determined from the 4 results reported by the laboratory, and the multiple (among) laboratory uncertainty as determined in a method validation Interlaboratory Study (ILS) or the multiple (among) laboratory calculated from the Horwitz function.

Laboratory limits were compared with benchmark limits.

Assessment of Laboratory Accuracy

A laboratory average that **agrees with the RM value within the RM limits is considered highly accurate and designated green**. A laboratory average that **agrees with the RM value within the benchmark limits is considered acceptable and designated blue**. A laboratory average that **does not agree with the RM value within the laboratory limits is considered suspect and is designated red**.

Assessment of Laboratory Precision

Laboratory limits less than or equal to the benchmark limits are considered acceptable and designated blue. Laboratory limits greater than the benchmark limits are considered suspect and designated red.

Calculation of Benchmark Limits

Benchmark limits are calculated according to ISO 5725-6 4.2.3. ISO 5725 employs the principles outlined in the ISO Guide for Uncertainty Measurement (GUM). The ISO GUM states the total uncertainty of a measurement is made up of the components of uncertainty that can impact the measurement result.

For a measurement on coal the 95% uncertainty can be expressed in the following way;

$$m\Gamma = 2\sqrt{m_{homogeneity}^2 + m_{stability}^2 + m_{bias}^2 + m_{precision}^2} \quad (1)$$

Where;

$\mu_{homogeneity}$	is the uncertainty contributed by the inhomogeneity of the coal
$\mu_{stability}$	is the uncertainty contributed by the stability of the coal
μ_{bias}	is the uncertainty contributed by bias of the measurement
$\mu_{precision}$	is the uncertainty contributed by the precision of the measurement

In the case of a CRM or RM μ_{bias} is assumed to be 0 and $\mu_{homogeneity}$, $\mu_{stability}$, $\mu_{precision}$ can all combined into $\mu_{reference}$.

So for a CRM or an RM the GUM equation becomes

$$m\Gamma = 2\sqrt{m_{reference}^2} \quad (2)$$

In the case of a method validation ILS, if the experimental design does not take them into account, $\mu_{homogeneity}$ and $\mu_{stability}$ are incorporated into μ_{bias} and $\mu_{precision}$.

For a method ILS the GUM equation becomes.

$$m\Gamma = 2\sqrt{m_{bias}^2 + m_{precision}^2} \quad (3)$$

For a method validation ILS μ_{bias} can be estimated from the multiple laboratory uncertainty μ_L while $\mu_{precision}$ can be estimated from the within laboratory uncertainty μ_r/n where n is the number of replicate measurements.

So for a method validation ILS the GUM equation becomes

$$m\bar{I} = 2\sqrt{\mathbf{m}_L^2 + \mathbf{m}_r^2 / n} \quad (4)$$

Equation 4 is equivalent to the preliminary equation stated in ISO 5725-6 4.2.3, which provides guidance for calculating benchmark limits. However, the benchmark limit determined from equation (4) could lead to rejection of an acceptable laboratory result because there is no allowance made for the uncertainty of the RM. As written equation 4 assumes the RM has 0 uncertainty.

In reality coal RM values have very real uncertainties associated with them.

In fact RMs with exactly the same level of a given parameter could have very different uncertainties.

According to the ISO GUM the equation for the benchmark limit incorporating the uncertainty of an RM would be;

$$m\bar{I} = 2\sqrt{\mathbf{m}_L^2 + \mathbf{m}_r^2 / n + \mathbf{m}_{reference}^2} \quad (5)$$

where;

$$\mathbf{m}_{reference} = \text{RM Limits}/2$$

From X1.2 ASTM E 691

$$\mathbf{m}_R^2 = \mathbf{m}_L^2 + \mathbf{m}_r^2 \quad (6)$$

Where;

μ_R is the reproducibility standard deviation of the method.

μ_r is the repeatability standard deviation of the method

And

$$\mathbf{m}_L = \sqrt{\mathbf{m}_R^2 - \mathbf{m}_r^2} \quad (7)$$

In the case where specific knowledge concerning the multiple laboratory uncertainty \mathbf{m}_L is not available the Horwitz function can be used to estimate \mathbf{m}_L ;

$$\mathbf{m}_{Lm} = (0.02c^{0.8495})/2 \quad (8)$$

Where both \mathbf{m}_{Lm} and c are both expressed as mass ratios (e.g. 1 ng/g = 10^{-9})

The within laboratory uncertainty μ_r for a “Horwitz” method is usually estimated by $\mathbf{m}_{Lm}/2$.

Using equations (5) through (8) benchmark limits can be calculated for Horwitz as well as ASTM methods D 3684, D 6414 and D 6722.

Calculation of Laboratory Limits

From equation (5) it is evident that for a given method, RM combination the value of $m_{reference}$ is fixed. In absence of specific knowledge of the laboratory component of bias the value of m_L is a fixed outcome of the method validation ILS or the Horwitz function. The only value that can change is the laboratory precision m and this can be estimated from replicate results reported by a laboratory.

By using this information the laboratory method limit can be calculated and compared directly with the benchmark limits.

9 Summary of Laboratory Results

Table 5 lists the moisture and ash results reported by the CCME laboratories.

Table 5 CCME Laboratory Moisture and Ash Values Commissioning Sample ES-1		
ID	Laboratory Residual Moisture wt %	Laboratory Ash wt % dry basis
CCME-AC	1.86	7.87
CCME-AE	2.66	79.82
CCME-AF	2.46	No Value Reported
CCME-AH	2.09	8.06
CCME-AI	2.24	7.94
CCME-B	2.38	7.84
CCME-D	2.95	8.01
CCME-F Corrected	2.20	7.80
CCME-F	2.20	56.45
CCME-F	2.20	55.12
CCME-G Corrected	2.92	8.00
CCME-G	2.92	7.62
CCME-K	2.58	8.04
CCME-L	1.36	7.96
CCME-Q	1.53	8.07
CCME-U	2.56	7.97
CCME-W	3.05	7.76
CCME-W	2.85	7.83

Table 6 lists the mercury results reported by the CCME laboratories.

Table 6 CCME Laboratory Hg Values Commissioning Sample ES-1								
ID	Operator	Instrument	Hg Method	Laboratory Hg ng/g dry basis				
				Run 1	Run 2	Run 3	Run 4	Average
CCME-AC	O-1	I-1	EPA245.5	99	97	95	82	94
CCME-AE	O-1	I-1	EPA245.5	62	63	60	70	64
CCME-AE	O-1	I-3	EPA245.5	95	74	145	66	96
CCME-AE	O-1	I-2	NIOSH 6009	97	104	126	111	110
CCME-AF	O-1	I-1	INAA	104	98	101	108	103
CCME-AH	O-1	I-1	D 6414	71	71	74	73	73
CCME-AI	O-1	I-1	Acid Digestion ICP-MS	121	116	123	119	120
CCME-B	O-1	I-1	D 6722	105	108	116	116	112
CCME-D	O-1	I-1	D 6722	114	112	113	115	114
CCME-F	O-3	I-3	Acid Digestion CVAA	94	97	90	91	94
CCME-F	O-1	I-2	Acid Digestion CVAA	98	100	106	100	101
CCME-F	O-1	I-1	Acid Digestion CVAA	110	120	114	117	116
CCME-G	O-1	I-1	D 6722	116	111	115	107	113
CCME-K	O-1	I-1	D 6722	110	110	108	104	109
CCME-L	O-1	I-1	D 6414	120	119	115	120	119
CCME-Q	O-1	I-1	Microwave CVAAS	110	101	109	116	109
CCME-U	O-1	I-1	D 6722	113	115	111	113	113
CCME-W	O-1	I-1	D 6722	117	123	109	120	118
CCME-W	O-2	I-2	D 6722	119	124	114	117	119

10 Method Briefs

ASTM D 3684 Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method

ASTM D 3684 Bomb Combustion CVAA involves igniting approximately 1 g of coal inside a sealed stainless steel bomb in an oxygen atmosphere. The bomb solution is treated to unify all mercury species into the elemental state. A concentrated cloud of the ground state atoms is introduced into a light path. These ground state atoms are irradiated with light at a characteristic wavelength for mercury. The amount of light absorbed is proportional to the amount of mercury present.

Although the weight of coal can be lowered for high mercury coals, increasing the weight much beyond 1.3 g for low mercury coals tends to result in incomplete combustion of the coal. Consequently, the lower limit of the method is constrained by the maximum weight of coal that can be burned in the combustion bomb. Samples that do not burn well can be a real problem for the bomb combustion method, and thus the method is generally unsuitable for ashes and other low-Btu materials. Coal samples that do not burn well fall into two categories: high moisture or high ash coals, and at the other end of the spectrum, highly swelling coals that can be ejected from the sample crucible during the combustion process. Some practitioners resort to the use of combustion aids or mediators to deal with ashes and difficult to burn coals, but these substances can introduce significant opportunities for contamination. The large internal volume and surface of the oxygen bomb, as well as the number of contact surfaces and valves, increase the risk of contamination or loss of mercury. The use of non-corrosion resistant bombs and crucibles can result in mercury being trapped in the bomb components, resulting in either low or erratic recoveries.

The precision and accuracy of ASTM D 3684 has been validated for a range of 60 ng/g to 200 ng/g mercury in coal.

ASTM D 6414 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption

ASTM D 6414 involves extracting up to 2 g of coal in a sealed plastic container. The solution is treated to unify all mercury species into the elemental state. The principle of detection is the same as for D 3684. The method can be adapted for high mercury samples by decreasing the weight of sample. The method is also suitable for ash materials.

Recovery of mercury can be a problem if the digestion bottles are not properly sealed and checked and the sample is not periodically mixed during heating. If these precautions are not taken, mercury can be lost, the digestion environment may not be severe enough to extract all the mercury from the coal, or the coal may migrate up the sides of the digestion bottle away from the digestion mix.

The procedure uses inexpensive lab-ware and common chemicals. Contamination is not a problem if good laboratory practice is followed. The procedure is readily amenable to batching.

The precision and accuracy of ASTM D 6414 has been validated for a range of 30 ng/g to 600 ng/g mercury in coal and coal derived residues.

ASTM D 6722 Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis.

ASTM D 6722 involves igniting a quantity of coal in a combustion train and capturing the mercury in its elemental state on gold amalgam. The principle of detection is the same as for D 3684.

Because the weight of sample can be increased and successive aliquots can be ignited before releasing the mercury from the amalgam, the procedure is adequate for all U.S. thermal coals. The method is also suitable for ash materials. The method can be adapted for high mercury samples merely by decreasing the weight of sample.

Some samples can cause problems with uniform combustion depending on their moisture content or mineral composition. The physical properties of these samples may cause the sample to explode or “spark” in the combustion train, carrying material out of the combustion region before mercury is completely released. In this case the coal carried out of the combustion zone can act to absorb mercury from subsequent samples or result in unpredictable mercury spikes in the analysis of subsequent samples. It is essential that direct combustion instruments be kept clean.

Since the procedure involves very little handling of the sample and a limited number of reagents, loss of mercury and contamination should not be a serious problem if good laboratory practice is followed. Direct combustion systems can be constructed or purchased. Some manufactured systems are factory calibrated and can be difficult to re-calibrate. Analysis times are in the order of 10 minutes per sample.

The precision and accuracy of ASTM D 6722 has been validated for a range of 20 ng/g to 600 ng/g mercury in coal and coal derived residues.

EPA 245.5 Acid Extraction/wet oxidation CVAA

This method was originally developed and is approved for analysis of mercury in soils, sediments and sludge. Although very similar to ASTM D 6414 this method was shown to give consistently low results for mercury CRM coals in the EPRI study 1000287. It is speculated that the digestion may not be severe enough to extract all the mercury from coal when using EPA 245.5.

Although this method has been adapted for use on coal by many laboratories seeking to comply with environmental regulations for mercury analysis, there is no firm evidence that a controlled inter-laboratory study (ILS) has ever been conducted to validate this method for a wide range of coal quality.