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Houston, Texas 77251-1700

February 28, 2000

Mr. William Grimley
Emissions Measurement Center
Interstate 40 and Page Road
4930 Old Page Road
Room Number E-108
Durham, North Carolina 27709
Attn: Electric Utility Steam Generating Unit Mercury Test Program

**Re: Submittal of Mercury ICR Performance Test Report
Limestone Electric Generating Station**

Dear Mr. Grimley:

As required by the mercury information collection request (ICR) authorized by Section 114 of the Clean Air Act, as amended, Reliant Energy, Incorporated (Reliant Energy) has conducted flue gas mercury speciation measurements at the Reliant Energy Limestone Electric Generating Station.

All testing was performed in accordance with the approved mercury ICR site-specific test plan and Quality Assurance Project Plan (QAPP). Three copies of the performance test report, including one unbound copy, are enclosed with this transmittal letter.

If you have questions or require additional information, please contact Craig R. Eckberg at 713-945-7612.

Sincerely,

A handwritten signature in cursive script that reads "B.C. Carmine".

B.C. Carmine, P.E.
Manager, Air Resources Division
Environmental Department

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Enclosure(s)

Performance Test Report

**Mercury Speciation Measurements
at Reliant Energy
Houston Lighting and Power's
Limestone Electric Generating Station**

Prepared for:

**Reliant Energy Wholesale Group
12301 Kurland Drive
Houston, TX 77034**

Prepared by:

**Radian International
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January 2000

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1.0 Introduction

1.1 Summary of Test Program

The U.S. Environmental Protection Agency (EPA), Office of Air and Radiation (OAR) has implemented an information collection request (EPA ICR No. 1858.01) requiring electric utilities to submit data related to flue gas emissions of mercury. As part of the ICR, EPA/OAR selected Reliant Energy, Incorporated's (Reliant Energy) Limestone Electric Generating Station, located near Jewett, Texas, to participate in flue gas mercury emission testing. Radian International, LLC (Radian) was contracted by Reliant Energy to perform the required testing.

The Limestone Station Unit 1 boiler fires Texas Lignite and includes flue gas treatment by a cold-side electrostatic precipitator (ESP) and wet flue gas desulfurization (FGD) absorbers. Radian collected flue gas samples simultaneously from the inlet and outlet of the wet FGD Absorber "A" downstream of the Unit 1 boiler using the draft version (July 7, 1999) of the Ontario Hydro sampling method. Analysis of these samples provided mercury speciation data at both locations enabling calculation of mercury removal across the FGD absorber.

In addition to sampling the flue gas, representative lignite samples were collected during each sampling period and were analyzed for mercury content, chloride content, and ultimate/proximate parameters.

All required ICR sample collections occurred on November 16, 1999.

1.2 Test Program Organization

Key personnel associated with this program are listed in Figure 1-1. Mr. Craig Eckberg is the Program Director for Reliant Energy and is the primary point of contact between Reliant Energy and Radian. Dr. Eugene Youngerman is the Radian Project Director. Mr. John LaPierre was the leader of the Radian sampling team. Mr. David Maxwell coordinated the analytical measurements performed at Severn Trent Laboratories.

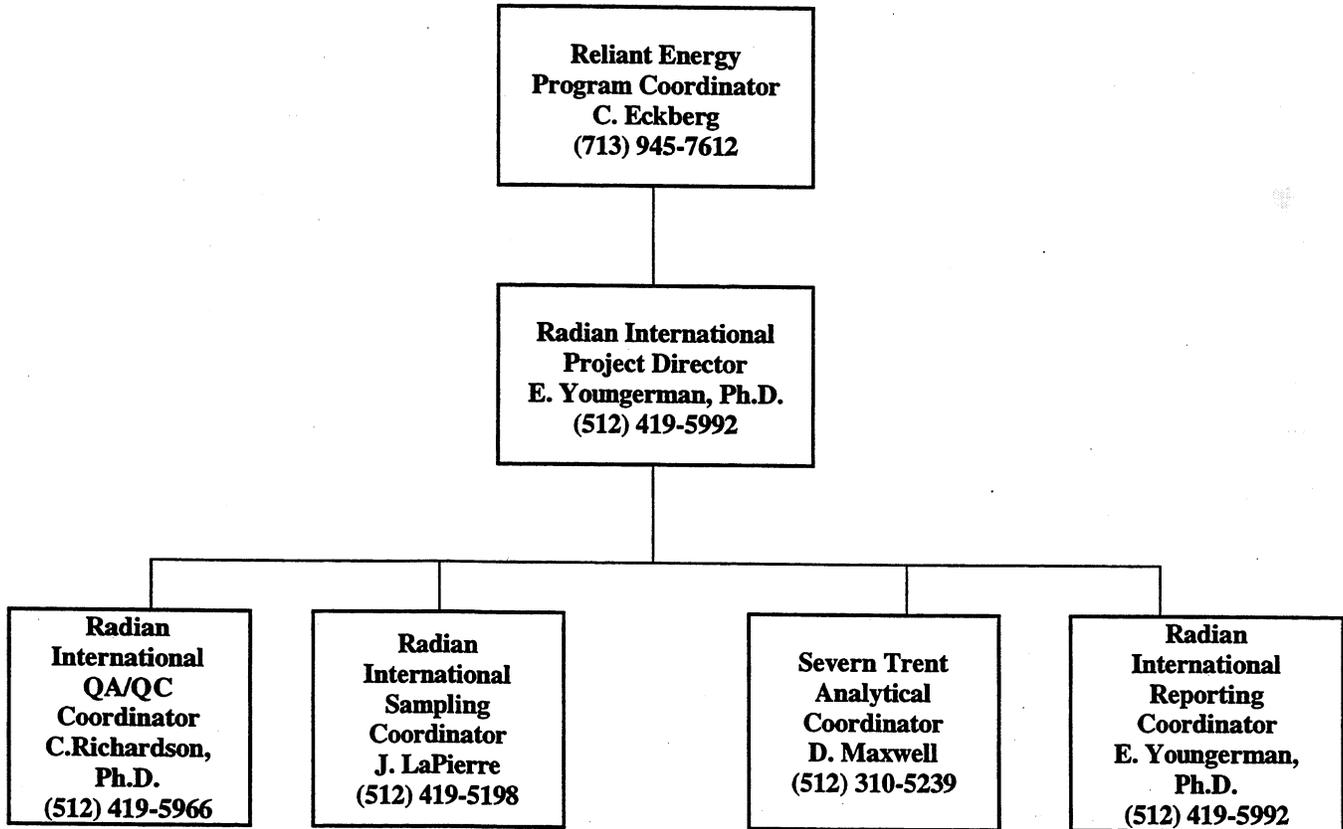


Figure 1-1. Project Organization

2.0 Facility Description

2.1 Process

Limestone Station's Unit 1 steam generator is a tangentially-fired, dual-chamber, balanced draft furnace manufactured by Combustion Engineering. It has a continuous gross generating capacity of 820 MW and a maximum heat input capacity of 7,863 mmBtu/hr while firing lignite. Boiler steam flow at maximum continuous rating is 5,520,000 lb/hr at sub-critical conditions of 2,615 psig and 1,005°F at the superheater outlet. Lignite is fired in the Unit 1 boiler by 80 burners arranged vertically in eight groups of ten burners. Lignite is supplied to the boiler by the lignite handling system and is deposited into ten silos, each feeding an individual pulverizer.

2.2 Control Devices

The flue gas pathway through Unit 1 is illustrated in Figure 2-1. Gas exiting the boiler passes through vertical-axis regenerative air preheaters before passing through a cold-side electrostatic precipitator (ESP) for particulate control. The ESP operates with no flue gas conditioning. As the flue gas leaves the ESP, it is divided into four streams that lead to induced-draft (ID) fans. From the ID fan outlets, the four streams enter ductwork feeding a flue gas desulfurization (FGD) system. The wet FGD system uses spray tower absorbers for flue gas contactors. The FGD reagent is ground limestone slurry containing dibasic acid. The system operates in an inhibited oxidation mode utilizing elemental sulfur addition. During normal operation there are four absorbers in use with a fifth absorber on standby. The flue gas leaving the absorbers is mixed with ID fan exit gas that is bypassed around the FGD system, and the resulting gas is exhausted through a single stack.

2.3 Flue Gas Sampling Locations

Samples of flue gas were collected simultaneously from the inlet and outlet ducts of FGD Absorber "A", downstream from the cold-side ESP leading from the Unit 1 Boiler. The inlet sampling ports were located on the top of the ductwork leading into the absorber module, approximately 13' downstream of the guillotine damper. A diagram of the inlet sampling location is shown in Figure 2-2. The inlet traverse points were arranged in a "5 x 5" grid pattern consisting of five equally-distributed points in each of five ports at the inlet location. This grid pattern assured representative sample collection along the cross-section of the duct.

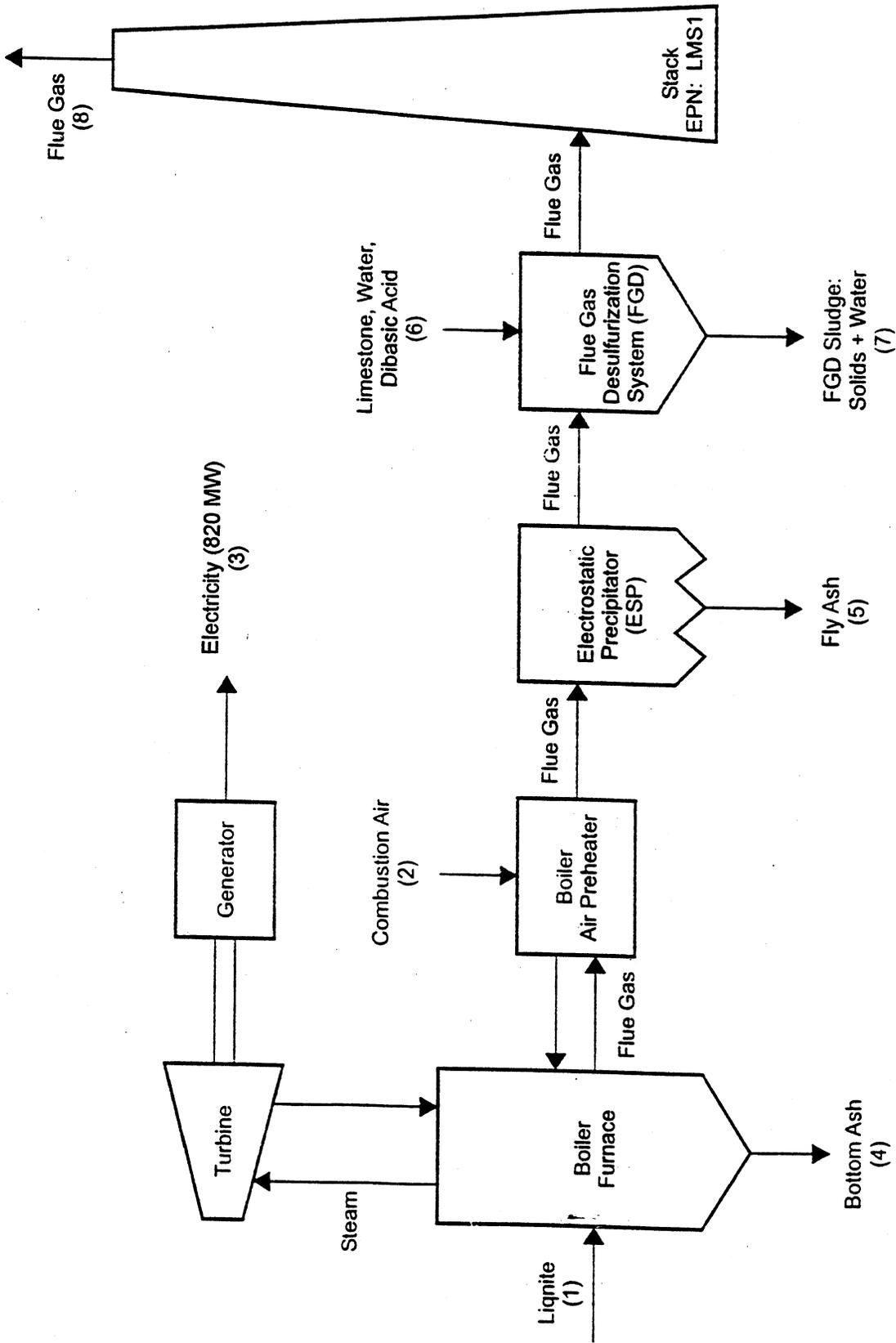


Figure 2-1. Limestone Station Unit 1 Process Flow Diagram

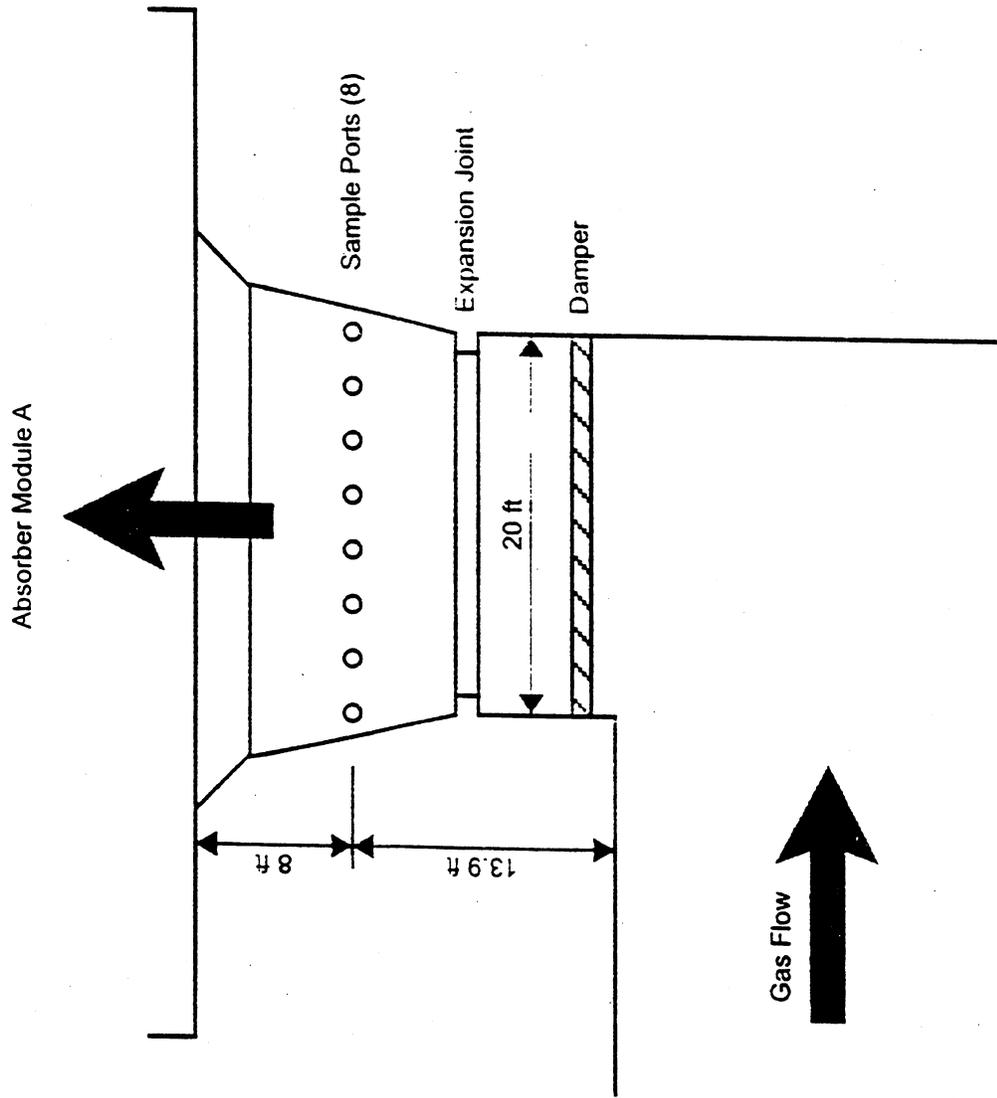


Figure 2-2. Limestone Unit 1 FGD Module A Inlet Duct - Top View

The outlet sampling port was located on the top of the ductwork leading from the absorber module outlet to the absorber bypass ducts. A single port was centrally located across the width of the duct, and was approximately 26' upstream of the bypass junction. The single port was pre-existing and to install additional ports across the entire width of the duct was cost-prohibitive if even technically feasible. The collection points were again arranged in five equally-distributed points along the depth of the outlet duct. Only five traverse points were used based on the observation that the velocity pressures and temperatures at each point were nearly identical across the entire traverse. A diagram of the outlet sampling location is presented in Figure 2-3.

2.4 Lignite Sampling Location

Samples of the lignite fuel fired in the Unit 1 Boiler were collected from the feed belt leading from the stock lignite silos to the pulverizers. Lignite was collected at a rate of approximately 60 pounds every 45 minutes to generate a composite over the duration of each flue gas sampling period. The collection device is manually operated and utilizes a retracting scoop that permits a full cross-sectional sample to be removed from the feed belt.

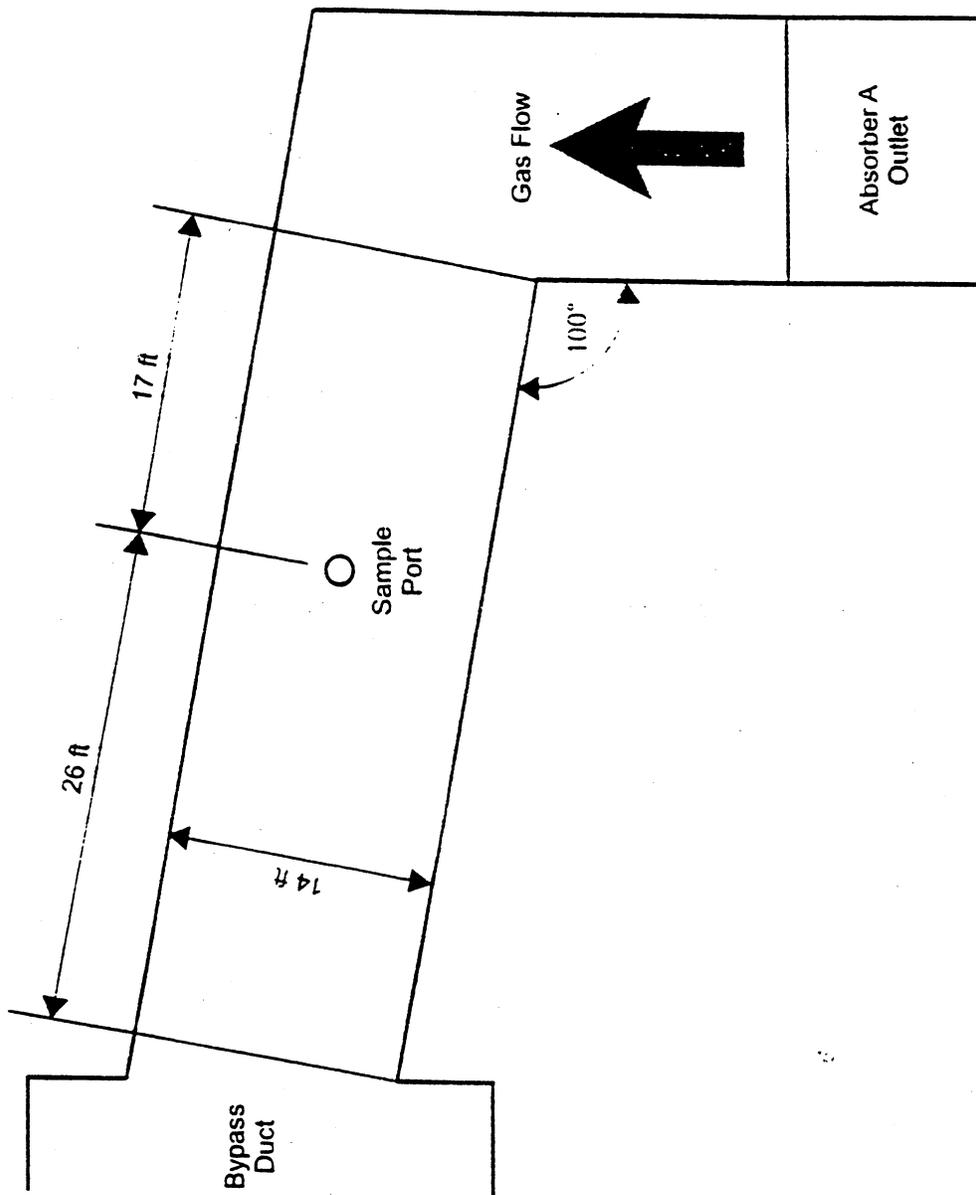


Figure 2-3. Limestone Unit 1 FGD Module A Outlet Duct - Top View

3.0 Test Program

3.1 Objectives

The main purpose of the sampling program was to measure speciated mercury in the flue gas entering and exiting one flue gas desulfurization (FGD) absorber module downstream of Limestone Station's Unit 1 boiler. However, the test program was designed to satisfy all EPA requirements associated with ICR No. 1858.01 and included:

- Simultaneous measurement of the concentrations of elemental and oxidized forms of mercury in the Unit 1 FGD system inlet and outlet flue gas using the draft Ontario Hydro sampling method (this included measurement of physical gas parameters such as temperature, and concentrations of moisture, oxygen, and carbon dioxide);
- Calculation of the FGD module efficiency at removing total mercury;
- Collection of representative lignite fuel samples during each gas sampling period for determination of
 - total sulfur, percent (dry basis),
 - heating value, Btu/lb (dry basis),
 - ash, percent (dry basis),
 - mercury, ppm (dry basis), and
 - chlorine, ppm (dry basis);
- Collection of process data for boiler load during each sample period.

A summary of the sampling and analytical activities is presented in Table 3-1. All samples were collected on November 16, 1999.

3.2 Results

3.2.1 Speciated Mercury in Flue Gas (Ontario Hydro Method)

Gas samples for determination of speciated mercury were collected simultaneously from the inlet and outlet of the FGD absorber using the draft (July 7, 1999) version of the Ontario Hydro (OH) sampling method. In conjunction with each OH sample, EPA Methods 2-5 were performed to yield gas flow rates, molecular weights, moisture content, and particulate loading.

Table 3-1. Limestone Station Sampling/Analytical Matrix

Sampling Location	No. of Runs	Sample/Type	Sampling Method	Sample Run Time (min)	Analytical Method
FGD Outlet	3	Speciated Mercury	Ontario Hydro (July '99 Draft)	125	M7470 Digestion CVAA Analysis
	3 ^a	Filtered Particulate Matter (non-condensable)	Method 5 in Combination with Ontario Hydro	125 ^b	Gravimetric
	3 ^a	Flue Gas Flow Rate	EPA Method 2	Concurrent with Ontario Hydro	NA
	3 ^a	O ₂ , CO ₂ (Fyrite®)	EPA Method 3	Concurrent with Ontario Hydro	NA
	3 ^a	Flue Gas Moisture	EPA Method 4	Concurrent with Ontario Hydro ^b	Gravimetric
FGD Inlet	3	Speciated Mercury	Ontario Hydro (July '99 Draft)	125	M7470 Digestion CVAA Analysis
	3 ^a	Filtered Particulate Matter (non-condensable)	Method 5 in Combination with Ontario Hydro	125 ^b	Gravimetric
	3 ^a	Flue Gas Flow Rate	EPA Method 2	Concurrent with Ontario Hydro	NA
	3 ^a	O ₂ , CO ₂ (Fyrite®)	EPA Method 3	Concurrent with Ontario Hydro	NA
	3 ^a	Flue Gas Moisture	EPA Method 4	Concurrent with Ontario Hydro ^b	Gravimetric
Boiler Lignite Feed	3	Lignite Fuel	Grab	Concurrent with Ontario Hydro	Digestion by ASTM D4208 Chloride by Method 300
					Digestion by ASTM 3684 Mercury by CVAA

^aSample obtained during Ontario Hydro sampling train.

^bSample time based upon that required for Ontario Hydro samples.

Three pairs of samples were collected in succession. A summary of the field data associated with the three Ontario Hydro samples collected at the FGD Inlet location is presented in Table 3-2. The field data associated with the FGD Outlet samples is presented in Table 3-3. Copies of the field data sheets are located in Appendix A.

The analytical results for the various fractions of each Ontario Hydro sampling train are presented in Table 3-4. Copies of the laboratory reports are in Appendix B. Mercury collected in the potassium chloride (KCl) impingers is considered to be in an oxidized state (Hg^{2+} or Hg_2^{2+}) in the gas stream prior to collection. Mercury found in the acidified peroxide ($\text{HNO}_3/\text{H}_2\text{O}_2$) and acidified permanganate ($\text{H}_2\text{SO}_4/\text{KMnO}_4$) impingers is considered to exist in an elemental state (Hg^0) in the gas stream. An approximation of the percent oxidation of the gas phase mercury is presented in Table 3-5. The oxidation state of the particle-bound mercury found in the filter/probe rinse fractions cannot be easily resolved. Therefore, while those contributions were used to determine total mercury concentrations in the gas samples, they were not included in the percent oxidation calculations.

Mass flow rates of mercury entering and exiting the FGD absorber are presented in Table 3-6. The gas flow rate as measured at the absorber inlet location was used to calculate mass flow rates for both the inlet and outlet locations. As previously discussed in Section 2.3, the inlet sampling location allowed for the use of a "5x5" traverse point grid. This resulted in a reliable measurement of gas flow at that point in the FGD system. Because the outlet duct was only accessible through a single port, and that port was relatively close to a large bend in the ductwork, the measured gas flow rate at the outlet was insufficient to produce a reliable determination of mercury mass flow at the outlet location. The outlet flow rate is considered to be biased-low and was not included in the mass emission rate determination.

The mercury control efficiency of the FGD absorber was determined for each sample collection period, and the results are presented in Table 3-7.

The percent of gas flow through the bypass duct surrounding FGD Module A was determined using the known gas temperatures at the FGD inlet, outlet, and stack locations. A summary of the bypass flow percentages is shown in Table 3-8, and an example calculation is presented in Appendix F. These bypass percentages were used to determine the mercury concentration in the flue gas at the bypass junction (point in the ductwork where the gas exiting

Table 3-2. Ontario Hydro Field Data (Inlet)

Date: Start/Finish Time: Operator:	Run 1	Run 2	Run 3	Average
	11/16/99 0800 - 1039 MLD	11/16/99 1130 - 1413 MLD	11/16/99 1513 - 1751 MLD	
Initial Leak Rate (ft ³ @ "Hg)	0.001 @ 15	0.010 @ 16	0.002 @ 15	-
Final Leak Rate (ft ³ @ "Hg)	0.002 @ 6	0.002 @ 7	0.002 @ 9	-
Duct Dimensions	20' x 22'	20' x 22'	20' x 22'	-
Equivalent Stack Diameter (ft)	23.7	23.7	23.7	-
Pitot Tube Correction Factor (Cp)	0.84	0.84	0.84	-
Dry Gas Meter Calibration (Yd)	1.006	1.006	1.006	-
Nozzle Diameter (in)	0.244	0.244	0.244	-
Barometric Pressure ("Hg)	29.7	29.7	29.7	29.7
Static Pressure ("H ₂ O)	4.5	4.5	4.5	4.5
Meter Volume (acf)	68.213	70.656	65.765	68.211
Meter Volume (m ³)	1.932	2.001	1.862	1.932
Average Square Root of Delta P	0.679	0.677	0.676	0.677
Average Delta H ("H ₂ O)	1.16	1.14	1.05	1.12
Average Stack Temperature (°F)	313	323	332	323
Average Dry Gas Meter Temperature (°F)	84	102	102	96
Test Duration (min)	125.0	125.0	125.0	125.0
Condensed Water (g)	214.1	222.2	205.3	213.9
% CO ₂	14.0	14.0	14.0	14.0
% O ₂	6.5	6.5	6.5	6.5
% N ₂	79.5	79.5	79.5	79.5
Meter Volume (dscf)	66.297	66.419	61.674	64.797
Meter Volume (Nm ³)	1.877	1.881	1.746	1.835
Flue Gas Moisture - Measured (%)	13.2	13.6	13.6	13.5
Gas Molecular Weight, Wet (g/mole)	28.8	28.8	28.8	28.8
Absolute Stack Pressure ("Hg)	30.0	30.0	30.0	30.0
Absolute Stack Temperature (R)	773	783	792	783
Gas Velocity (ft/sec)	46.1	46.2	46.4	46.3
Gas Velocity (m/sec)	14.0	14.1	14.1	14.1
Gas Flow Rate (acfm)	1.22E+06	1.22E+06	1.23E+06	1.22E+06
Gas Flow Rate (dscfm)	7.24E+05	7.13E+05	7.09E+05	7.15E+05
Gas Flow Rate (actual m ³ /min)	3.45E+04	3.46E+04	3.47E+04	3.46E+04
Gas Flow Rate (Nm ³ /min)	2.05E+04	2.02E+04	2.01E+04	2.02E+04
Isokinetic Sampling Rate (%)	99.3	101.0	94.4	98.2

Table 3-3. Ontario Hydro Field Data (Outlet)

	Run 1	Run 2	Run 3	Average
	11/16/99 0818 - 1023 AO	11/16/99 1138 - 1401 AO	11/16/99 1500 - 1728 AO	
Initial Leak Rate (ft ³ @ "Hg)	0.005 @ 10	0.005 @ 15	0.005 @ 15	--
Final Leak Rate (ft ³ @ "Hg)	0.002 @ 6	0.000 @ 5	0.000 @ 7	--
Duct Dimensions	14' x 14'	14' x 14'	14' x 14'	--
Equivalent Stack Diameter (ft)	15.8	15.8	15.8	--
Pitot Tube Correction Factor (Cp)	0.84	0.84	0.84	--
Dry Gas Meter Calibration (Yd)	0.979	0.979	0.979	--
Nozzle Diameter (in)	0.198	0.198	0.215	--
Barometric Pressure ("Hg)	29.7	29.7	29.7	29.7
Static Pressure ("H ₂ O)	1.6	1.6	1.6	1.6
Meter Volume (acf)	71.713	72.780	84.208	76.234
Meter Volume (m ³)	2.031	2.061	2.385	2.159
Average Square Root of Delta P	0.992	1.012	0.957	0.987
Average Delta H ("H ₂ O)	1.14	1.21	1.52	1.29
Average Stack Temperature (°F)	139	141	138	139
Average Dry Gas Meter Temperature (°F)	80	89	97	88
Test Duration (min)	125.0	125.0	125.0	125.0
Condensed Water (g)	328.1	350.1	392.5	356.9
% CO ₂	12.0	12.0	12.0	12.0
% O ₂	8.0	8.0	8.0	8.0
% N ₂	80.0	80.0	80.0	80.0
Meter Volume (dscf)	68.368	68.257	77.578	71.401
Meter Volume (m ³)	1.936	1.933	2.197	2.022
Flue Gas Moisture - Saturation (%)	19.1	20.2	18.7	19.3
Flue Gas Moisture - Measured (%)	18.5	19.5	19.3	19.1
Flue Gas Moisture for Calculations (%)	18.5	19.5	18.7	18.9
Gas Molecular Weight, Wet (g/mole)	28.0	27.9	28.0	27.9
Absolute Stack Pressure ("Hg)	29.8	29.8	29.8	29.8
Absolute Stack Temperature (R)	599	601	598	599
Average Gas Velocity (ft/sec)	60.3	61.8	58.2	60.1
Average Gas Velocity (m/sec)	18.4	18.8	17.7	18.3
Average Flow Rate (acfm)	7.09E+05	7.27E+05	6.84E+05	7.07E+05
Average Flow Rate (dscfm)	5.08E+05	5.12E+05	4.90E+05	5.03E+05
Average Flow Rate (actual m ³ /min)	2.01E+04	2.06E+04	1.94E+04	2.00E+04
Average Flow Rate (Nm ³ /min)	1.44E+04	1.45E+04	1.39E+04	1.43E+04
Isokinetic Sampling Rate (%)	98.7	97.7	98.6	98.3

Table 3-4. Ontario Hydro Analytical Results

Run No.	PNR/Filter (µg)	KCl Impingers (µg)	HNO ₃ /H ₂ O ₂ Impingers (µg)	KMnO ₄ Impingers (µg)	Total Mass Found (µg)	Sample Gas Volume (Nm ³)	Conc. (µg/Nm ³)
FGD Inlet							
1	0.0218	35.6	0.940	19.3	55.8	1.877	29.7
2	0.0198	37.2	1.26	18.6	57.1	1.881	30.3
3	0.0309	39.6	1.46	18.4	59.4	1.746	34.0
Field Blank	<0.003	1.73	0.0880	0.116	1.93	-	-
FGD Outlet							
1	0.0526	3.75	0.225	22.1	26.1	1.936	13.5
2	0.459	4.44	0.646	22.0	27.5	1.933	14.3
3	0.205	2.03	0.357	26.9	29.5	2.197	13.4
Field Blank	0.0153	0.0245	0.0551	0.0447	0.140	-	-

Table 3-5. Percent Oxidation of Mercury in Flue Gas

Run No.	Concentration of Oxidized Mercury ^a (µg/Nm ³)	Concentration of Elemental Mercury ^b (µg/Nm ³)	Percent Oxidation (%)
FGD Inlet			
1	18.9	10.8	63.7
2	19.8	10.6	65.2
3	22.7	11.3	66.7
FGD Outlet			
1	1.93	11.5	14.4
2	2.30	11.7	16.4
3	0.923	12.4	6.92

^a Includes mercury collected only in KCl impingers.

^b Includes mercury collected only in HNO₃ and KMnO₄ impingers.

Table 3-6. Mercury Mass Flow Rates

Run No.	Concentration (µg/Nm ³)	Gas Flow Rate (Nm ³ /min)	Mass Emission Rate (kg/hr)
FGD Inlet			
1	29.7	2.05E+04	0.0366
2	30.3	2.02E+04	0.0368
3	34.0	2.01E+04	0.0410
FGD Outlet			
1	13.5	2.05E+04	0.0166
2	14.3	2.02E+04	0.0173
3	13.4	2.01E+04	0.0162

Table 3-7. Mercury Control Efficiency of FGD Module A

Run No.	Input Rate (kg/hr)	Output Rate (kg/hr)	Control Efficiency (%)
1	0.0366	0.0166	54.6
2	0.0368	0.0173	53.0
3	0.0410	0.0162	60.5

Table 3-8. Summary of Bypass Flow Percentages

Run No.	Average FGD Outlet Temp. (°F)	Average FGD Inlet Temp. (°F)	Average Stack Temp. (°F)	Percent of Gas Through Bypass (%)
1	139	313	146	4.44
2	141	323	148	3.82
3	138	332	153	7.97

the FGD module recombines with the bypassed flow prior to entering the stack). Mass flow rates of mercury through the stack were then calculated by multiplying the bypass junction gas concentrations times the gas flow rate through the stack. A summary of the bypass gas mercury concentrations and mass flow rates of mercury through the stack are shown in Table 3-9.

3.2.2 Particulate Loading in Flue Gas

Measurements of non-condensable particulate loading were made concurrently with each Ontario Hydro sampling train. While the Ontario Hydro sampling method includes recovery of the filter and a nitric acid rinse of the probe assembly for mercury speciation, the method allows for an additional acetone rinse of the probe assembly and the use of pre-weighed filters for determination of "filterable particulate". This is the procedure described in EPA Method 5. The non-condensable particulate loading from each sampling period is shown in Table 3-10.

3.2.3 Ultimate/Proximate Analysis of Lignite

Three discreet grab samples of lignite were collected at regular intervals during each of the Ontario Hydro sampling periods. The grab samples from each period were ground and riffled according to ASTM standards, then delivered to the laboratory for analysis of ultimate/proximate parameters as well as mercury content and chlorine content. The results for the three sampling periods are presented in Tables 3-11, 3-12, and 3-13.

Table 3-9. Summary of Mercury Concentrations and Mass Flow Rates in Stack

Run No.	Concentration Before Mixing at Bypass ($\mu\text{g}/\text{Nm}^3$)	Percent of Gas Stream at Bypass (%)	Concentration Contribution ($\mu\text{g}/\text{Nm}^3$)	Concentration After Mixing at Bypass ($\mu\text{g}/\text{Nm}^3$)	Gas Flow Rate Through Stack (dscfh)	Mass Emission Rate (kg/hr)
FGD Inlet				14.2 14.9 15.1	1.36E+08 1.35E+08 1.38E+08	0.0546 0.0568 0.0588
1	29.7	4.44	1.32			
2	30.3	3.82	1.16			
3	34.0	7.97	2.71			
FGD Outlet						
1	13.5	95.6	12.9			
2	14.3	96.2	13.7			
3	13.4	92.0	12.4			

Table 3-10. Particulate Loading in Flue Gas

Run No.	Mass Gain			Gas Sample Volume (Nm^3)	Non-Condensable Particulate Conc. ($\text{grains}/\text{Nm}^3$)
	Filter (g)	Probe Rinse (g)	Total (g)		
FGD Inlet					
1	0.0257	0.0000	0.0257	1.877	0.211
2	0.0216	0.0011	0.0227	1.881	0.186
3	0.0688	0.0070	0.0758	1.746	0.670
FGD Outlet					
1	0.0112	0.0137	0.0249	1.936	0.198
2	0.0081	0.0021	0.0102	1.933	0.0814
3	0.0217	0.0067	0.0284	2.197	0.200

Table 3.11 Lignite Analyses from Sample Period One ^a

	Sample No. 1	Sample No. 2	Sample No. 3	Average
Ultimate Analysis				
Moisture (%)	31.74	32.00	31.13	31.62
Carbon (%)	61.03	60.94	59.88	60.62
Hydrogen (%)	4.52	4.57	4.52	4.54
Nitrogen (%)	1.13	1.12	1.08	1.11
Sulfur (%)	1.22	1.28	1.60	1.37
Ash (%)	18.11	18.41	20.33	18.95
Oxygen (% by Difference)	13.99	13.68	12.59	13.42
Proximate Analysis				
Heat Content (Btu/lb)	10,479	10,450	10,336	10,422
Sulfur Content (lb SO ₂ /MMBtu)	2.32	2.45	3.09	2.62
Chlorine (ppm)	<100	<100	<100	<100
Mercury (ppm)	0.102	0.122	0.140	0.121

^a Results reported on a “dry basis”, excluding Moisture (%).

Table 3.12 Lignite Analyses from Sample Period Two ^a

	Sample No. 1	Sample No. 2	Sample No. 3	Average
Ultimate Analysis				
Moisture (%)	31.80	31.46	32.11	31.79
Carbon (%)	61.97	61.68	62.32	61.99
Hydrogen (%)	4.68	4.59	4.60	4.62
Nitrogen (%)	1.13	1.12	1.11	1.12
Sulfur (%)	1.51	1.57	1.48	1.52
Ash (%)	17.67	18.03	16.63	17.44
Oxygen (% by Difference)	13.04	13.01	13.86	13.30
Proximate Analysis				
Heat Content (Btu/lb)	10,654	10,650	10,796	10,700
Sulfur Content (lb SO ₂ /MMBtu)	2.84	2.96	2.73	2.84
Chlorine (ppm)	<100	<100	<100	<100
Mercury (ppm)	0.0979	0.290	0.125	0.171

^a Results reported on a “dry basis”, excluding Moisture (%).

Table 3.13 Lignite Analyses from Sample Period Three ^a

	Sample No. 1	Sample No. 2	Sample No. 3	Average
Ultimate Analysis				
Moisture (%)	31.49	31.67	31.81	31.66
Carbon (%)	61.50	61.64	60.95	61.36
Hydrogen (%)	4.60	4.55	4.49	4.55
Nitrogen (%)	1.12	1.13	1.11	1.12
Sulfur (%)	1.61	1.47	1.53	1.54
Ash (%)	18.34	18.39	18.72	18.48
Oxygen (% by Difference)	12.83	12.82	13.20	12.95
Proximate Analysis				
Heat Content (Btu/lb)	10,625	10,579	10,517	10,574
Sulfur Content (lb SO ₂ /MMBtu)	3.02	2.77	2.90	2.90
Chlorine (ppm)	<100	<100	<100	<100
Mercury (ppm)	0.168	0.0865	0.119	0.125

^a Results reported on a “dry basis”, excluding Moisture (%).

3.2.4 Process Operating Data

Operating parameters for the Unit 1 Boiler were recorded by the on-site distributed control system (DCS) in use at Limestone Station. These included:

- Unit load (MW);
- Lignite feed rate (tons/hr);
- Steam production rate (klb/hr);
- Steam temperature (°F);
- Stack gas flow rate (SCFH); and
- SO₂ removal across the FGD module.

A summary of these data are presented in Table 3-14, and the raw DCS data are included in Appendix C.

Table 3-14. Summary of Process Data

	Parameter	Minimum	Average	Maximum
Sample Period 1	Load (MW)	766.60	785.21	808.60
	Lignite Feed Rate (tons/hr)	493.96	536.39	565.72
	Steam Production (klb/hr)	5258.71	5405.68	5620.55
	Steam Temperature (°F)	1000.47	1000.94	1002.26
	Stack Gas Flow Rate (SCFH)	1.29E+08	1.36E+08	1.40E+08
	SO ₂ Removal (%)	78.1	79.0	80.1
Sample Period 2	Load (MW)	769.19	800.28	812.43
	Lignite Feed Rate (tons/hr)	511.65	543.41	559.66
	Steam Production (klb/hr)	5263.38	5541.92	5630.66
	Steam Temperature (°F)	1001.40	1003.50	1004.85
	Stack Gas Flow Rate (SCFH)	1.28E+08	1.35E+08	1.38E+08
	SO ₂ Removal (%)	78.3	79.2	80.0
Sample Period 3	Load (MW)	788.33	803.67	811.7
	Lignite Feed Rate (tons/hr)	531.15	556.20	584.07
	Steam Production (klb/hr)	5469.25	5556.60	5596.40
	Steam Temperature (°F)	997.63	999.53	1001.98
	Stack Gas Flow Rate (SCFH)	1.34E+08	1.38E+08	1.41E+08
	SO ₂ Removal (%)	80.5	83.0	86.7

4.0 Sampling and Analytical Procedures

4.1 Test Methods

The test methods used to collect and analyze the flue gas samples included EPA Methods 1-4 as described in 40 CFR, Part 60, Appendix A, and the draft version (July 7, 1999) of the Ontario Hydro Method published under jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres. A copy of the Ontario Hydro Method is provided in Appendix D.

Samples of the lignite fuel were collected and analyzed following procedures described in the Annual Book of ASTM Methods.

4.1.1 EPA Method 1 – Sample and Velocity Traverses for Stationary Sources

Method 1 was followed as outlined in 40 CFR, Part 60, Appendix A to identify the quantity and locations of the traverse points at the flue gas desulfurization (FGD) inlet sampling location. Based on the physical dimensions of the ductwork and the port locations, the resultant traverse grid consisted of 25 sampling points arranged in a “5 x 5” pattern (five points in each of the five ports). This is the maximum number of points suggested by Method 1 for a rectangular duct.

The traverse point locations at the FGD outlet location were determined by dividing the duct into five equivalent areas and locating a traverse point at the centroid of each of the five areas as described in Method 1. Preliminary observations revealed that the velocity pressures and temperatures were nearly identical across the duct, negating the need for additional points along the traverse.

4.1.2 EPA Method 2 - Determination of Stack Gas Velocity and Volumetric Flow Rate (Type-S Pitot Tube)

Flow rate measurements were made concurrently with collection of the Ontario Hydro samples. A Type-S pitot tube was used in accordance with Method 2 as outlined in 40 CFR, Part 60, Appendix A.

4.1.3 EPA Method 3 – Gas Analysis for the Determination of Dry Molecular Weight

Oxygen and carbon dioxide concentrations in the flue gas were measured using Fyrite® combustion gas analyzers as referenced in Section 2.3 of 40 CFR, Part 60, Appendix A,

Method 3. Nitrogen was calculated by difference, as outlined in the method. Single-point grab samples were collected from a tube mounted adjacent to the sampling nozzle of the Ontario Hydro sampling train.

4.1.4 EPA Method 4 – Determination of Moisture Content in Stack Gases

The moisture content of the flue gases was determined concurrently with collection of the Ontario Hydro samples. Following the procedures referenced in 40 CFR, Part 60, Appendix A, Method 4, the impingers of each Ontario Hydro sampling train were weighed prior to and immediately following each sampling run.

4.1.5 Ontario Hydro Method – Determination of Elemental, Oxidized, Particle-Bound, and Total Mercury Emissions from Coal-Fired Stationary Sources

The draft (July 7, 1999) Ontario Hydro Method was used to collect simultaneous mercury speciation samples at the FGD absorber inlet and outlet locations. A copy of the draft procedure is provided in Appendix D.

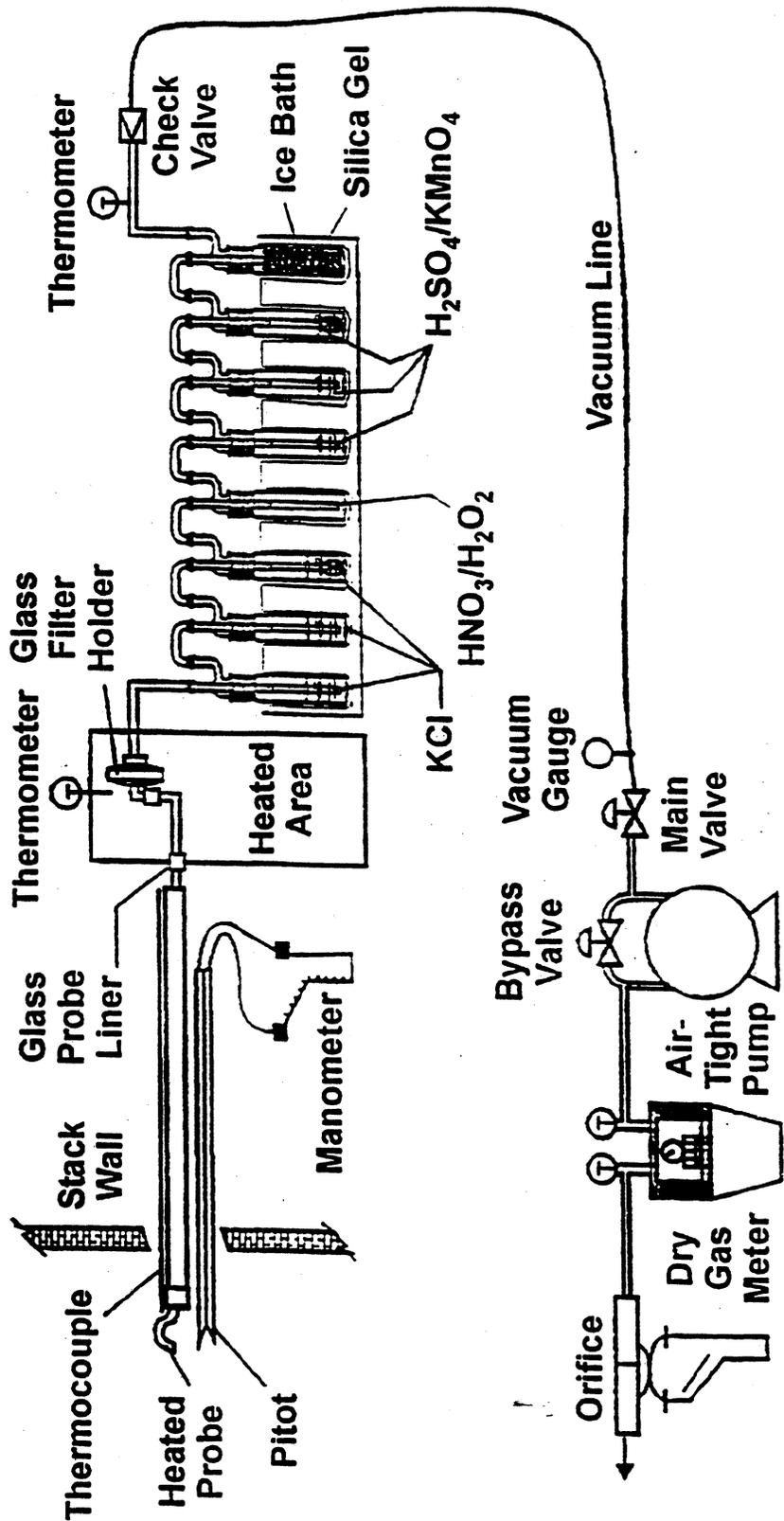
A schematic of the draft Ontario Hydro sampling train is shown in Figure 4-1. The Ontario Hydro sampling train was constructed in a manner identical to the metals sampling train described in EPA Method 29 (40 CFR, Part 60, Appendix A) with the following modifications:

- Impingers 1-3 contained 1.0N KCl;
- The fourth impinger contained a 5% HNO₃/10% H₂O₂ solution; and
- Impingers 5-8 contained a 4% KMnO₄/10% H₂SO₄ solution.

The sample recovery schemes used for the front and back portions of the sampling train are shown in Figures 4-2 and 4-3, respectively. During the recovery process, sufficient KMnO₄ solution was added to each KCl impinger to maintain a purple color. Rinses of hydroxylamine solution were used on the KCl and KMnO₄/H₂SO₄ impingers only if needed; this was indicated by the presence of residue on the impinger glass surfaces.

The analytical scheme for the Ontario Hydro samples is depicted in Figure 4-4. Sample aliquots of the impinger contents were digested using a modified version of EPA Method 7470. The digested samples were analyzed for mercury by cold vapor atomic absorption (CVAA) spectroscopy. Particulate-bound mercury collected in the probe rinse and on the filter was determined as indicated in Figure 4-4. The entire contents of the filter and probe rinse were

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EERC KG 13642.CDR

Figure 4-1. Draft Ontario Hydro Sampling Train

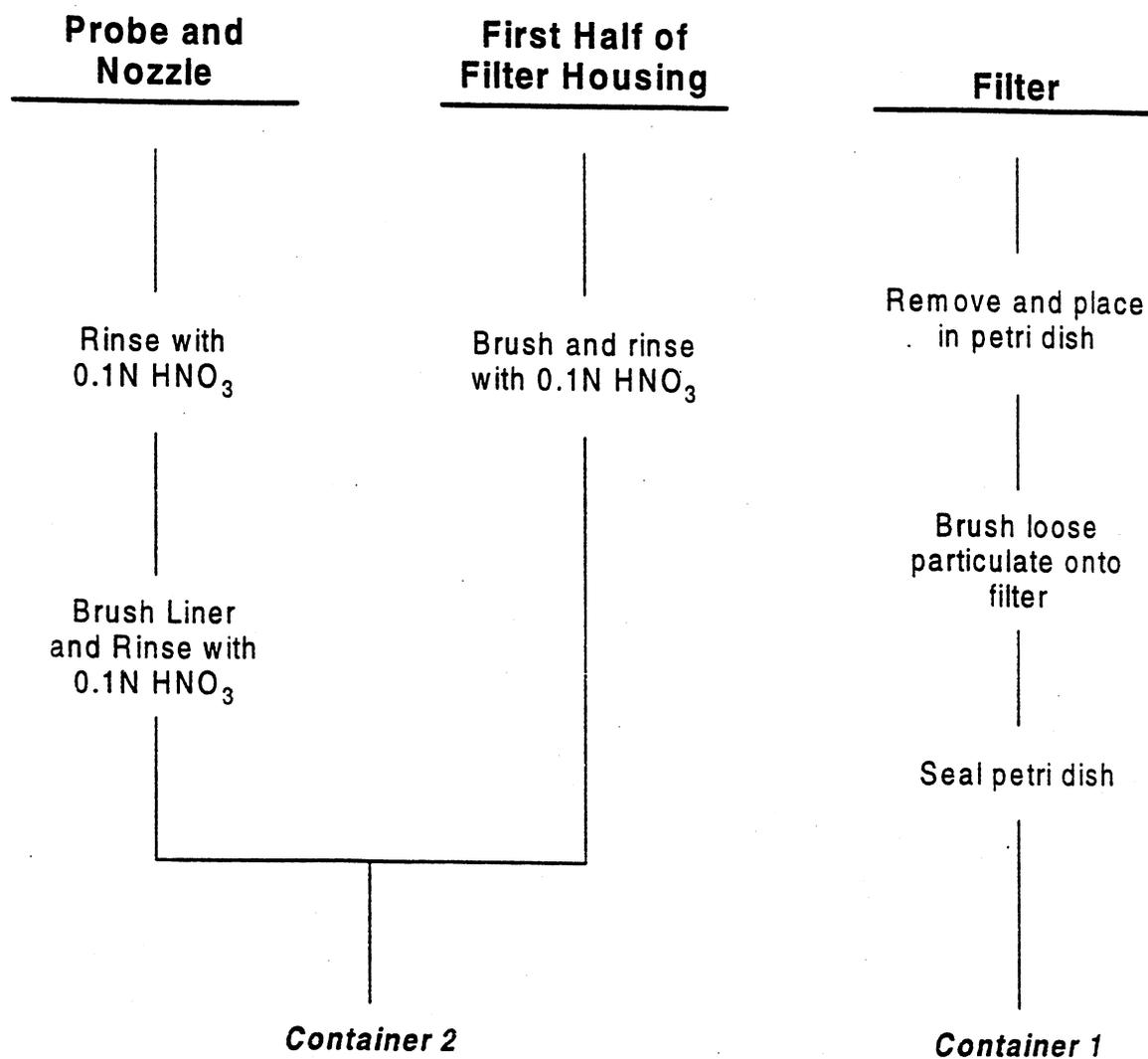
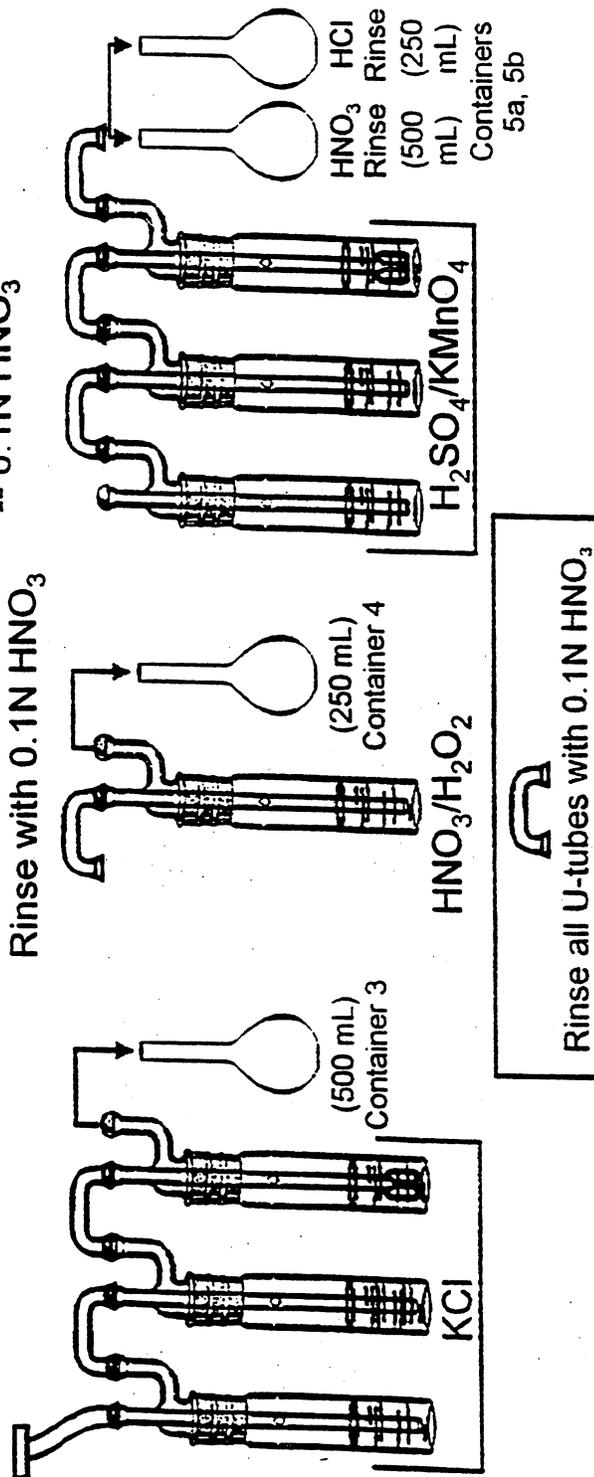


Figure 4-2. Recovery Scheme of Front Portion of Ontario Hydro Sample Train

DRAFT

1. Rinse filter holder and connector with 0.1N HNO₃.
2. Add H₂SO₄/KMnO₄ to each impinger bottle until purple color remains.
3. Rinse with 0.1N HNO₃.
4. Rinse with 8N HCl if brown residue remains.
5. Final rinse with 0.1N HNO₃.

Rinse bottles sparingly with
 -- 0.1N HNO₃
 -- 8N HCl
 -- 0.1N HNO₃



EERC KG 13178b. CDR

Figure 4-3. Recovery Scheme of Back Portion of Ontario Hydro Sample Train (Impingers)

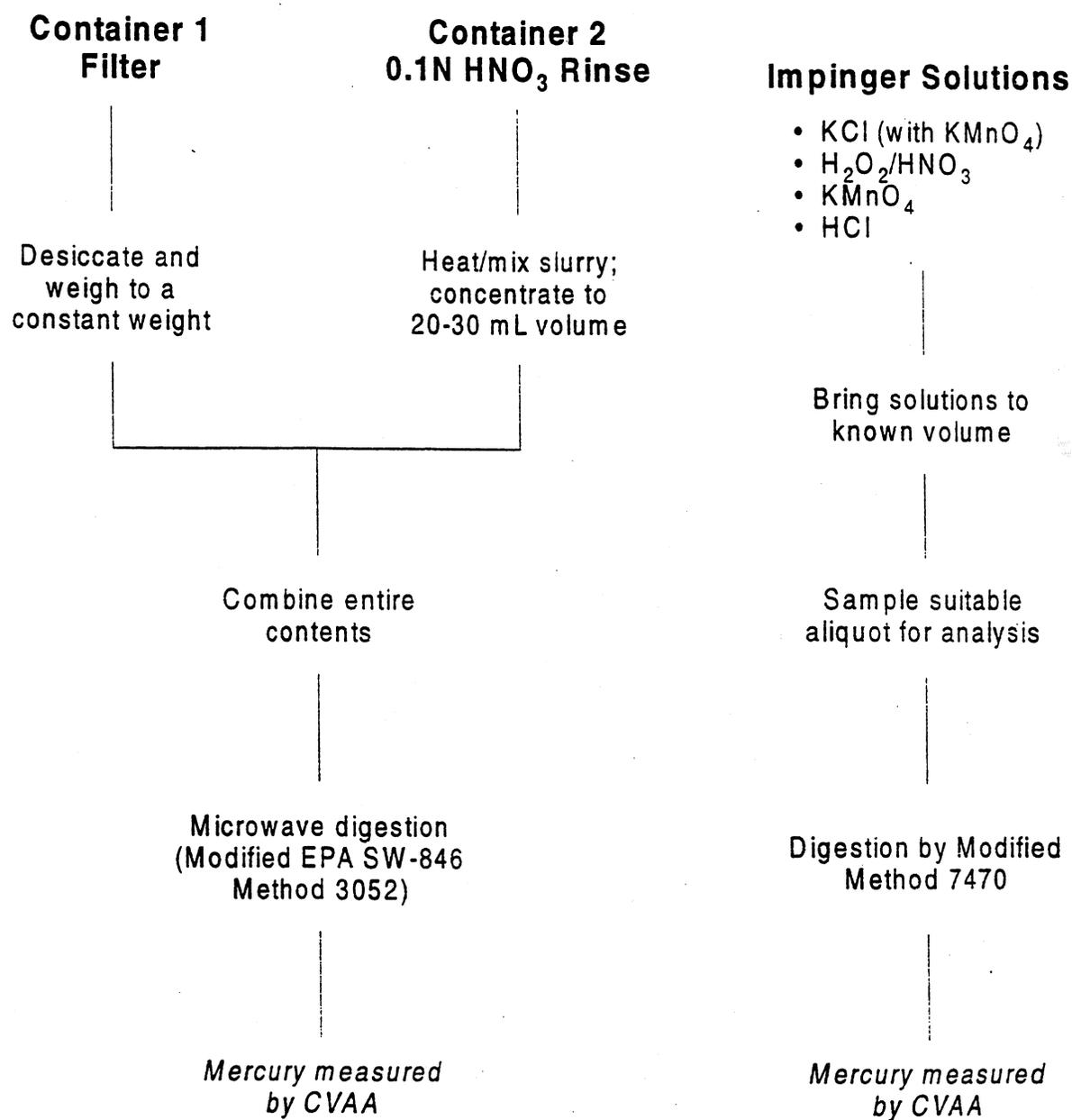


Figure 4-4. Analytical Scheme for Ontario Hydro Samples

added together, digested using a microwave method (EPA Method 3052) and analyzed by CVAA for mercury. This provided a value for total particulate-bound mercury in the Ontario Hydro samples.

4.1.6 Collection and Analysis of Lignite Samples

Lignite samples were obtained concurrently with the Ontario Hydro samples as outlined in Section 3.1. The analytical scheme for these samples is illustrated in Figure 4-5. All analyses were carried out as defined in the respective test methods referenced in Table 3-1 with the following exceptions:

- A modification was made to the procedure for measuring coal chloride in order to decrease the analytical detection limit. This included the use of an ion chromatographic determination of chloride (EPA Method 300) as opposed to using an ion selective electrode as indicated in ASTM D4208.
- Prior to lignite mercury analyses using ASTM Method D3684, the samples were digested with nitric and sulfuric acids. This is consistent with the alternative digestion procedure listed in the method.

4.2 Process Test Methods

4.2.1 Procedures for Process Stream and Control Equipment Data

Unit 1 boiler operational data was collected from the plant Distributed Control System (DCS). During the gas sampling test periods, data was collected from the DCS for the following parameters:

- Unit load (MW);
- Lignite feed rate (tons/hr);
- Steam production rate (klb/hr);
- Steam temperature (°F);
- Stack gas flow rate (SCFH); and
- SO₂ removal across the FGD module.

The SO₂ data was obtained from on-site continuous emission monitors (CEMs) installed at the facility.

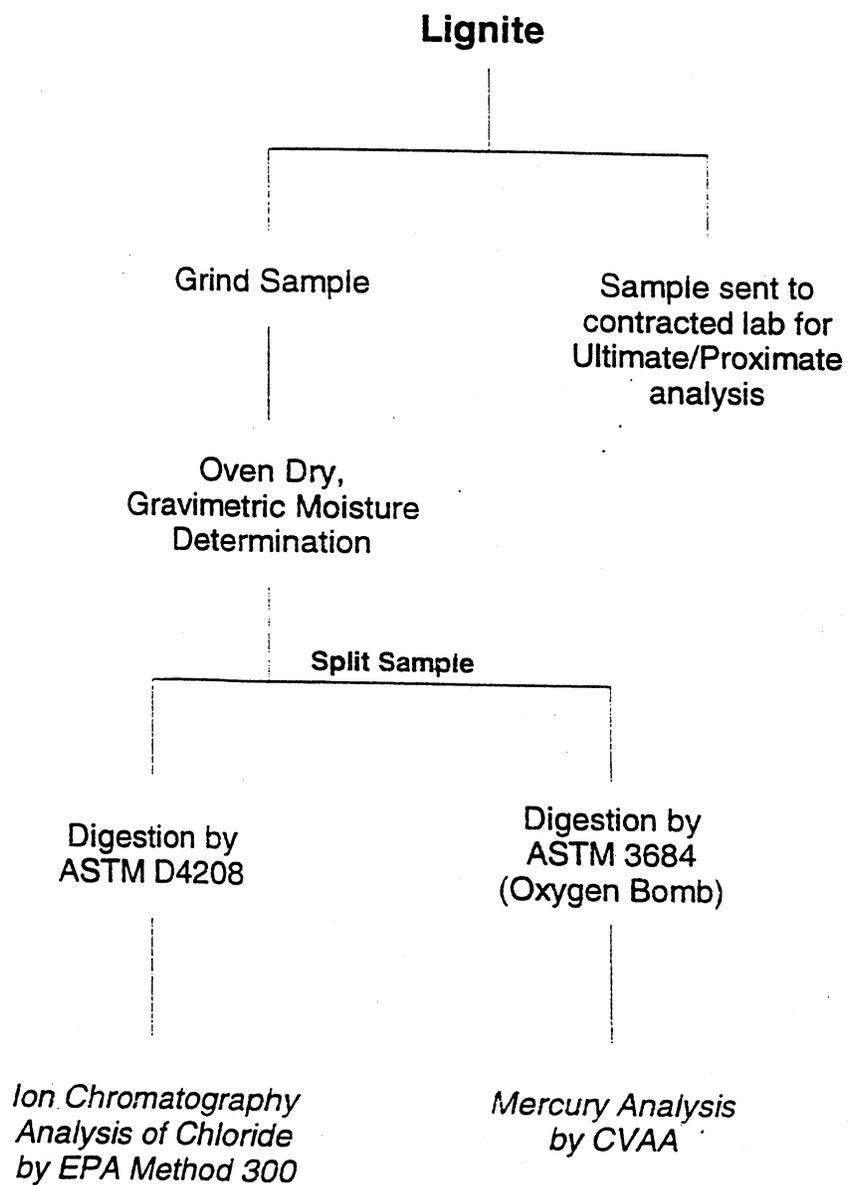


Figure 4-5. Analytical Scheme for Lignite Samples

5.0 Internal QA/QC Activities

As part of this mercury speciation test program, a comprehensive QA/QC protocol was designed and is documented in the *Quality Assurance Project Plan (QAPP) for Mercury Speciation Measurements at the Reliant Energy Houston Lighting and Power's Limestone Electric Generating Station (September, 1999)*. The QAPP details QA/QC activities for the sampling program and conforms to the requirements detailed in "Preparation Aid for HWERL's Category II Quality Assurance Project Plans," U.S. EPA, June 1987 (PA QAPjP-0007-GFS).

The QAPP delineates specific sampling and analytical procedures, calibration requirements, internal QC procedures, data reduction and validation procedures, and sample custody requirements for each sampling/analytical activity. It also addresses general QA/QC considerations such as:

- Data recording;
- Documentation procedures;
- Project organization and responsibilities;
- Preventative maintenance operations;
- Reporting requirements; and
- Corrective action mechanisms.

The QAPP also devotes considerable attention to internal QC procedures that will be used to ensure that the measurement data meet data quality requirements. These activities are summarized in the following sections. Detailed descriptions of the individual QC parameters may be found in the project QAPP.

The QA/QC data presented below confirm that the analytical results generated by this test program are of high quality and are sufficient to be used for the desired purpose.

5.1 Sample Collection

The QAPP prescribes QC procedures to be implemented during all sampling activities and specifies guidelines for:

- Equipment calibration;
- Sampling protocol; and
- Sample handling techniques.

The QA/QC guidelines associated with sampling equipment operation are listed below.

5.1.1 Equipment Calibration

The following equipment calibration methods were utilized during the test program to ensure the collection of accurate data.

Sampling Nozzle Calibration

All nozzles used for isokinetic sampling were calibrated according to the procedure outlined in Section 3.4.2 of EPA Document 600/4-77-027b. The nozzle calibrations were recorded on the field sampling data sheets presented in Appendix A.

Temperature Measuring Device Calibration

All thermocouple temperature sensors used for field sampling were calibrated at a single point against an NIST-traceable, mercury-in-glass thermometer. The thermocouple calibration data sheets are presented in Appendix E.

Dry Gas Meter Calibration

All of the dry gas meters used in the sampling program were subjected to both a semi-annual, "five-point" (five different critical orifices) calibration and a post-test, "three-point" calibration. The meter correction factors generated from the two calibrations must agree within $\pm 5\%$ for the meter to be used. The dry gas meter calibration data sheets are presented in Appendix E.

5.1.2 QA/QC Checks For Field Samples

Table 5-1 lists the quality assurance requirements associated with the gas and lignite samples obtained at Limestone Station. Ontario Hydro field blank samples were collected from both the FGD inlet and outlet locations. The objective of these samples is to account for "background" mercury associated with the sample collection area, sampling media, handling, and storage containers. The Ontario Hydro Method requires that the sample results must be considered "suspect" if the field blank concentrations are greater than or equal to 30% of the sample concentrations. The analytical results of the field blank samples are presented in Table 3-4, and are well below the 30% criteria.

Reagent blank samples were also collected for each batch of sampling media used in the test program. The reagent blank solutions are currently in storage and will only be analyzed if deemed necessary.

Table 5-1. Ontario Hydro QA Requirements

QA Requirement	Frequency	Action Taken
Field Blank	1 per sample location	Analyze all samples
Reagent Blanks	1 per reagent type	Hold all, selective analysis
Duplicate Analyses	100% of samples in duplicate, 10% of samples in triplicate	Analyze all samples, duplicate analyses must agree $\leq 10\%$ RPD
NIST 1633b Control Sample	1 per program	Run with "front-half" analyses (filter/probe rinse fractions)
SARM 20 Control Sample	1 per program	Run with analyses for coal in mercury

All mercury analyses performed on the Ontario Hydro samples were done in duplicate or triplicate as required by the method. The analytical results and RPD calculations are presented in Table 5-2. As can be seen, the reproducibility is good in all samples.

A standard ash sample (NIST 1633b, certified at 0.141 mg/kg) was digested and analyzed in the same batch as the Ontario Hydro "front-half" (filter/probe rinse) fractions. The duplicate analyses of the NIST standard resulted in an average concentration of 1.03 mg/kg, well above the certified value. A second aliquot of the same standard was again digested and analyzed in the same manner. The averaged result from the second aliquot was 0.268 mg/kg, again well above the certified value. The variability is believed to be a result of the analytical technique. The Ontario Hydro samples are analyzed using CVAA, and the coal standard is certified by NIST using ICP and ID-TIMS. The Ontario Hydro method does not include any accuracy or precision limits that must be met to qualify the data. And, while the variability of these analyses does indicate some difficulty in achieving accurate results for this particular standard, the "front-half" mercury concentrations contribute less than 0.5% (on average) of the total mercury found in the flue gas samples. In addition, the higher NIST recoveries indicate a positive bias (more conservative estimate) of the sample results for the "front-half" fractions. Thus, there is no impact on the determinations of gas-phase mercury concentration, mercury control efficiency, or mercury emission rates.

An aliquot of a coal standard (SARM 20, certified at 0.25 mg/kg mercury) was digested and analyzed in the same batch as the lignite samples. The results indicated a concentration of 0.139 mg/kg, which is below the certified value. However, while the mercury recovery in this particular coal standard was low (~56%), the measured mercury concentrations in the collected

lignite samples are typical of those historically seen in Texas Lignite. For this test program, there are no performance specifications associated with the analysis of this standard.

Table 5-2. Summary of Ontario Hydro RPD Calculations

	FGD Inlet			FGD Outlet					
	Run 1	Run 2	Run 3	Field Blank	Run 1	Run 2	Run 3	Field Blank	NIST 1633b
Filter/Probe Rinse									
1 st Result (µg)	0.0228	0.0189	0.0300	0.00283	0.0532	0.460	0.205	0.0140	0.144
2 nd Result (µg)	0.0208	0.0207	0.0318	0.00115	0.0520	0.457	0.204	0.0165	0.142
RPD (%)	8.8	9.4	5.8	84	2.2	0.61	0.46	16	1.2
KCl Impinger									
1 st Result (µg)	34.8	37.8	39.5	1.68	3.75	4.44	2.00	0.0258	-
2 nd Result (µg)	36.3	36.6	39.7	1.78	3.74	4.44	2.08	0.0231	-
RPD (%)	4.3	3.2	0.50	5.6	0.47	0.14	3.8	11	-
HNO₃H₂O₂ Impinger									
1 st Result (µg)	0.948	1.25	1.45	0.0817	0.236	0.637	0.359	0.0548	-
2 nd Result (µg)	0.931	1.26	1.47	0.0942	0.214	0.652	0.354	0.0554	-
RPD (%)	1.8	1.5	1.5	14	9.6	2.4	1.5	1.0	-
KMnO₄ Impinger									
1 st Result (µg)	19.3	18.7	18.4	0.115	22.2	21.5	26.9	0.0429	-
2 nd Result (µg)	19.4	18.5	18.3	0.117	22.0	22.5	26.9	0.0464	-
RPD (%)	0.23	1.1	0.67	1.3	0.71	4.6	0.063	8.0	-

5.2 Procedures for Analytical Quality Control

QA/QC protocols for sample analysis are derived from the referenced analytical methods and laboratory standard specifications. The procedures required for this test program are detailed in the project QAPP and included the areas of:

- Instrument calibration; and
- Accuracy and precision.

The method-derived and standard laboratory protocols for mercury analyses are presented in Table 5-3, Table 5-4, and Table 5-5. The tables include detection and reporting limits, accuracy and precision requirements, and a summary of calibration and QC requirements, respectively.

5.2.1 Calibration of Analytical Instrumentation

All laboratory mercury measurements were preceded by instrument calibrations. A detailed description of the calibration procedure is given in the CVAA method included in the project QAPP and includes:

- Six-point calibration curve with correlation ≥ 0.995 ;
- Pre-analysis calibration verification;
- Mid-analysis calibration verification every ten analyses; and
- End-analysis calibration verification.

A summary of the calibration QC parameters is presented in Table 5-6.

5.2.2 QA/QC for Analytical Determinations

Mercury analysis of the Ontario Hydro and lignite samples was carried out at Radian International's Fixed-Price Analytical Services (FPAS) laboratories. The analyses were carried out using CVAA spectroscopy as specified in the Ontario Hydro Method. The QA/QC specifications for Radian's CVAA analysis of mercury are listed in Table 5-5, and the results of the QC procedures are presented in Table 5-6.

A pair of laboratory control standards (LCS/LCSD) is used to show proper operation of the analytical instrument in the absence of the sample matrix. They consist of reagent water spiked with target analytes. An LCS/LCSD is included with each analytical batch. The results are presented in Table 5-6.

Table 5-3. Protocol Required Detection Limits and Reporting Limits

Analyte	Aqueous		Solid		Microwave ^b		TCLP	
	PRDL (mg/L)	Reporting Limit (mg/L)	PRDL (mg/kg) ^a	Reporting Limit (mg/kg) ^a	PRDL (mg/kg) ^b	Reporting Limit (mg/kg) ^b	PRDL (mg/L)	Reporting Limit (mg/L)
Mercury	0.00020	0.00020	0.020	0.020	0.20	0.20	0.0010	0.0010

^a Nominal value. Solid digestion assumes 0.5 g (dry weight) sample digested with a final volume of 50 mL.

^b Nominal value. Microwave digestion assumes a 0.1 g (dry weight) sample digested with a final volume of 100 mL.

Table 5-4. Accuracy and Precision Requirements

Analyte	LCS Tolerance (%) ^a		Matrix Spike Tolerance (%)		Analytical Spike Tolerance (%)
	Recovery	Precision (RPD)	Recovery ^b	Precision (RPD) ^c	Recovery
Mercury	70 - 130	<25	70-130	<25	70-130

^a LCS tolerances statistically derived from historical data from Radian's Laboratory.

^b Matrix spike accuracy tolerances are adopted from EPA Method 245.1 Matrix spike tolerances also used for media spikes and for analytical spikes when no sample is available for MS/MSD.

^c As adopted from USACE EM 200-1-1.

The use of matrix spikes (MS/MSD) and duplicate sample analyses represent the primary forms of QC samples in the analytical determinations. MS/MSD samples are prepared by spiking sample splits with known concentrations of target analytes prior to digestion and are included in every analytical batch if possible. Exceptions to this include the Ontario Hydro, "front-half" fractions where it would be extremely difficult to split the filters into representative samples. Matrix spike results provide a measure of the effectiveness of the method, in terms of analyte recovery (accuracy), in the actual sample matrices. Matrix spike duplicate results provide a measure of variability, much like field or analytical duplicate samples, but at a predictable concentration. The results of the MS/MSD quality control checks are presented in Table 5-6. As can be seen, the MS/MSD results from the KMnO₄ impinger were out of the acceptable range. This was due to the relatively high parent concentration (approximately one order of magnitude larger than the spike levels) preventing accurate quantitation of the much smaller spike amounts. As a result, an analytical spike was performed to confirm instrument operation.

Analytical spikes (AS/ASD) are usually only performed in the absence of valid matrix spike data. This would be the case for the "front-half" fractions of the Ontario Hydro samples,

or where there is no valid MS/MSD data. AS/ASDs are generated by spiking the digestate with a known concentration of target analytes. The results are presented in Table 5-6, and are shown to meet the requirements in Table 5-4.

Table 5-5. Summary of Calibration and QC Analyses

Calibration and QC Analyses	Description	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	A blank + 6-point calibration; for concentrations see Table 6	Daily before any other analysis	Correlation coefficient ≥ 0.995 ; calculated intercept = 0.000 ± 0.001 absorbance units	Identify and reanalyze outlying point(s); recalculate curve using repeated points
Demonstration of Capability (DOC - Initial)	Quadruplicate analysis of LCS; for concentration see Table 7	For each new instrument and each new analyst prior to analyzing samples	<ol style="list-style-type: none"> Accuracy: See Table 5-3 for limits Precision: See Table 5-3 for s limits 	<ol style="list-style-type: none"> Accuracy: <ol style="list-style-type: none"> Verify calibration with 2nd source standard and repeat DOC If still out, repeat multipoint calibration Precision: <ol style="list-style-type: none"> Repeat DOC If still out, identify and correct source of excess variability
Demonstration of Capability (DOC - on-going)	Control charts generated by instrument and by analyst	Semi-annually	25 of the last 30 points must be within statistical control. Control limits must be within LCS tolerances	<ol style="list-style-type: none"> Analyst technique will be evaluated Analyze DOC as described above
Initial Calibration Verification (ICV)	Primary source calibration standard with final digestate concentration at 0.010 mg/L	Daily before batch one is analyzed	90-110% of true value	Accuracy: <ol style="list-style-type: none"> Repeat calibration verification If still out, identify and correct problem, run calibration verification again; if still out, recalibrate
Initial Calibration Blank (ICB)	Deionized water with digestion reagents	After initial calibration verification	Within \pm PRDL	<ol style="list-style-type: none"> Reanalyze calibration blank If still out, recalibrate

Table 5-5. (Continued)

Calibration and QC Analyses	Description	Frequency	Acceptance Criteria	Corrective Action
Method Blank	Deionized water with digestion reagents and analyzed as a sample	Once for each preparative and analytical batch	Measured concentrations must be <PRDL	Blank Contamination: 1. Reanalyze method blank; 2. If method blank is still contaminated, identify and correct source of contamination, then reprepare samples with new method blank
LCS/LCSD	Deionized water with digestion reagents, spiked with second source standard, and analyzed with samples For standard concentration, see Table 7	One LCS/LCSD pair for each preparative and analytical batch	1. Accuracy: See Table 2 LCS tolerances (see Appendix A) 2. Precision: See Table 2 LCS tolerances (see Appendix A)	1. Accuracy: Reanalyze LCS/LCSD. If recovery is still out, stop, identify, and correct problem before proceeding. If digestion batch is to be reprepared, write Level 1 QCER. If samples can't be redigested, contact CSC and write Level 2 QCER 2. Precision: Reanalyze LCS/LCSD. If recovery is still out, stop, identify, and correct problem before proceeding.

Table 5-5. (Continued)

Calibration and QC Analyses	Description	Frequency	Acceptance Criteria	Corrective Action
MS/MSD	<p>Two aliquots of a native sample spiked with a standard solution.</p> <p>For concentration see Table 7</p>	<p>One MS/MSD pair for each preparative and analytical batch</p>	<p>1. Accuracy: See Table 2 MS tolerances (see Appendix A)</p> <p>2. Precision: See Table 2 MS tolerances (see Appendix A)</p>	<p>1. Accuracy:</p> <ul style="list-style-type: none"> a. If there is an assignable cause, and LCS/LCSD are within tolerance, flag data and contact CSC; write a Level 2 QCER b. If no assignable cause, run analytical spike c. If analytical spike fails, and LCS/LCSD results are within tolerance, flag MS/MSD results as matrix interference, write Level 2 QCER <p>2. Precision:</p> <ul style="list-style-type: none"> a. If there is an assignable cause, and LCS/LCSD are within tolerance, flag data and contact CSC; write Level 2 QCER b. If there is no assignable cause, analyze analytical spike
Continuing Calibration Verification (CCV)	<p>Primary source calibration standard with final digestate concentration at 0.010 mg/L</p>	<p>After 10th sample and at the end of each analytical batch</p>	<p>90-110% of true value</p>	<p>Accuracy:</p> <ul style="list-style-type: none"> 1. Repeat calibration verification 2. If still out, identify and correct problem, then reanalyze all samples analyzed since last passing calibration verification

Table 5-5. (Continued)

Calibration and QC Analyses	Description	Frequency	Acceptance Criteria	Corrective Action
Continuing Calibration Blank (CCB)	Deionized water with digestion reagents	Following each continuing calibration verification and at the end of each analytical batch	Within \pm PRDL	<ol style="list-style-type: none"> 1. Reanalyze calibration blank 2. If still out, correct the problem and reanalyze all samples since last passing calibration blank
Serial Dilution	A five-fold (1+4) dilution of a sample digestate prior to analysis	Once per analytical batch	Within 10% of the undiluted value if parent sample is $>5x$ PRDL	Perform analytical spike
Analytical Spike	Sample digestate spiked with a 0.020 mg/L calibration standard prior to analysis	<ol style="list-style-type: none"> 1. When serial dilution fails or if parent sample $<5x$ PRDL. 2. When MS/MSD fails without assignable cause. 	85% - 115% recovery	<ol style="list-style-type: none"> 1. Flag data 2. Contact CSC 3. Write Level 2 QCER

Table 5-6. Summary of Analytical Quality Control Parameters

QA/QC Parameter	Acceptable Range	Filter/ Probe Rinse	KCl Impinger	HNO ₃ /H ₂ O ₂ Impinger	KMnO ₄ Impinger
Initial Calibration	Correlation >0.995	1.000	1.000	1.000	1.000
Initial Calibration Verification	90-110%	100	100	97	97
LCS/LCSD	70-130% (RPD <25%)	107, 107 (0%)	99, 102 (3.0%)	101, 100 (1.0%)	98, 95 (3.1%)
MS/MSD	70-130% (RPD <25%)	NA ^a	88, 91 (3.4%)	100, 101 (1.0%)	218, 128 (52%)
Mid. Continuing Calibration	90-110%	101	103	98	103
End Continuing Calibration	90-110%	101	105	97	102
AS/ASD ^b	70-130% (RPD <25%)	108, 106 (1.9%)	NA	NA	121

^a The filter is digested in whole, therefore, it is not possible to split the sample to form an MS/MSD pair. Per Table 5-5, an AS/ASD pair is substituted.

^b Per Table 5-5, analytical spike(s) required if either the serial dilution check fails or if MS/MSD fails.

