

12.3 Sampling Equipment. Prepare the particulate emission sampling equipment as defined by ASTM E2515-11 *Standard Test Method for Determination of Particulate Matter Emissions Collected in a Dilution Tunnel* (IBR, see §60.17). Upon request, four-inch filters may be used. Upon request, Teflon membrane filters or Teflon-coated glass fiber filters may be used.

12.4 Appliance Startup. The appliance shall be fired with wood fuel of any species, size and moisture content at the laboratories' discretion to bring it up to operating temperature. Operate the appliance until the water is heated to the upper operating control limit and has cycled at least two times. Then remove all unburned fuel, zero the scale and verify the scales accuracy using dead weights.

12.4.1 Pretest Burn Cycle. Reload appliance with oak wood and allow it to burn down to the specified coal bed weight. The pretest burn cycle fuel charge weight shall be within ± 10 percent of the test fuel charge weight. Piece size and length shall be selected such that charcoaling is achieved by the time the fuel charge has burned down to the required coal bed weight. Pieces with a maximum thickness of approximately 2 inches have been found to be suitable. Charcoaling is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run are to be done to achieve charcoaling while maintaining the desired heat output rate. During the pre-test burn cycle and at least one hour prior to starting the test run, adjust water flow to the heat exchanger to establish the target heat draw for the test. For the first test run the heat draw rate shall be equal to the manufacturer's rated heat output capacity.

12.4.1.1 Allowable Adjustments. Fuel addition or subtractions, and coal bed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coal bed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of charcoaling. Record all adjustments to and additions or subtractions of fuel, and any other changes to the appliance operations that occur during pretest ignition period. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coal bed raking is the only adjustment allowed during this period.

12.4.2 Coal Bed Weight. The appliance is to be loaded with the test fuel charge when the coal bed weight is between 10 percent and

20 percent of the test fuel charge weight. Coals may be raked as necessary to level the coal bed but may only be raked and stirred once between 15 to 20 minutes prior to the addition of the test fuel charge.

12.5 Test Runs. For all test runs, the return water temperature to the hydronic heater must be equal to or greater than 120 °F. Aquastat or other heater output control device settings that are adjustable shall be set using manufacturer specifications, either as factory set or in accordance with the owner's manual, and shall remain the same for all burn categories.

Complete a test run in each heat output rate category, as follows:

12.5.1 Test Run Start. Once the appliance is operating normally and the pretest coal bed weight has reached the target value per section 12.4.2, tare the scale and load the full test charge into the appliance. Time for loading shall not exceed 5 minutes. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Start all sampling systems.

12.5.1.1 Record all water temperatures, differential water temperatures and water flow rates at time intervals of one minute or less.

12.5.1.2 Record particulate emissions data per the requirements of ASTM E2515 (IBR, see §60.17).

12.5.1.3 Record data needed to determine overall efficiency (SLM) per the requirements of CSA B415.1-10 (IBR, see §60.17), clauses 6.2.1, 6.2.2, 6.3, 8.5.7, 10.4.3 (a), 10.4.3 (f), and 13.7.9.3

12.5.1.3.1 Measure and record the test room air temperature in accordance with the requirements of CSA B415.1-10 (IBR, see §60.17), clauses 6.2.1, 8.5.7 and 10.4.3 (g).

12.5.1.3.2 Measure and record the flue gas temperature in accordance with the requirements of CSA B415.1-10 (IBR, see §60.17), clauses 6.2.2, 8.5.7 and 10.4.3 (f).

12.5.1.3.3 Determine and record the carbon monoxide (CO) and carbon dioxide (CO₂) concentrations in the flue gas in accordance with CSA B415.1-10 (IBR, see §60.17), clauses 6.3, 8.5.7 and 10.4.3 (i) and (j).

12.5.1.3.4 Measure and record the test fuel weight per the requirements of CSA B415.1-10 (IBR, see §60.17), clauses 8.5.7 and 10.4.3 (h).

12.5.1.3.5 Record the test run time per the requirements of CSA B415.1-10 (IBR, see §60.17), clauses 10.4.3 (a).

12.5.1.4 Monitor the average heat output rate on the load side of the heat exchanger. If the heat output rate gets close to the upper or lower limit of the target range (± 5 percent) adjust the water flow through the heat exchanger to compensate. Make changes as infrequently as possible while maintaining the target heat output rate. The first test run shall be conducted at the Category IV heat output rate to validate that

the appliance is capable of producing the manufacturer's rated heat output capacity.

12.5.2 Test Fuel Charge Adjustment. It is acceptable to adjust the test fuel charge (*i.e.*, reposition) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (1 lb or 0.5 kg) weight change while the operating control is in the demand mode. The time used to make this adjustment shall be less than 60 seconds.

12.5.3 Test Run Completion. The test run is completed when the remaining weight of the test fuel charge is 0.0 lb (0.0 kg). End the test run when the scale has indicated a test fuel charge weight of 0.0 lb (0.0 kg) or less for 30 seconds.

12.5.3.1 At the end of the test run, stop the particulate sampling train and overall efficiency (SLM) measurements, and record the run time, and all final measurement values.

12.5.4 Heat Output Capacity Validation. The first test run must produce a heat output rate that is within 10 percent of the manufacturer's rated heat output capacity (Category IV) throughout the test run and an average heat output rate within 5 percent of the manufacturer's rated heat output capacity. If the appliance is not capable of producing a heat output within these limits, the manufacturer's rated heat output capacity is considered not validated and testing is to be terminated. In such cases, the tests may be restarted using a lower heat output capacity if requested by the manufacturer.

12.5.5 Additional Test Runs. Using the manufacturer's rated heat output capacity as a basis, conduct a test for additional heat output categories as specified in section 4.3. It is not required to run these tests in any particular order.

12.5.6 Alternative Heat Output Rate for Category I. If an appliance cannot be operated in the Category I heat output range due to stopped combustion, two test runs shall be conducted at heat output rates within Category II, provided that the completed test run burn rate is no greater than the burn rate expected in home use. If this rate cannot be achieved, the test is not valid.

When the alternative heat output rate is used, the weightings for the weighted averages indicated in Table 2 shall be the average of the Category I and II weightings and shall be applied to both Category II results. The two completed runs in Category II will be deemed to meet the requirement for runs completed in both Category I and Category II. Appliances that are not capable of operation within Category II (<25 percent of maximum) cannot be evaluated by this test method. The test report must include full documentation and discussion of the attempted runs, completed runs and calculations.

12.5.6.1 Stopped Fuel Combustion. Evidence that an appliance cannot be operated at a Category I heat output rate due to stopped fuel combustion shall include documentation of two or more attempts to operate the appliance in burn rate Category I and fuel combustion has stopped prior to complete consumption of the test fuel charge. Stopped fuel combustion is evidenced when an elapsed time of 60 minutes or more has occurred without a measurable (1 lb or 0.5 kg) weight change in the test fuel charge while the appliance operating control is in the demand mode. Report the evidence and the reasoning used to determine that a test in burn rate Category I cannot be achieved. For example, two unsuccessful attempts to operate at an output rate of 10 percent of the rated output capacity are not sufficient evidence that burn rate Category I cannot be achieved. Note that section 12.5.6 requires that the completed test run burn rate can be no greater than the burn rate expected in home use. If this rate cannot be achieved, the test is not valid.

12.5.7 Appliance Overheating. Appliances shall be capable of operating in all heat output categories without overheating to be rated by this test method. Appliance overheating occurs when the rate of heat withdrawal from the appliance is lower than the rate of heat production when the unit control is in the idle mode. This condition results in the water in the appliance continuing to increase in temperature well above the upper limit setting of the operating control. Evidence of overheating includes: 1 hour or more of appliance water temperature increase above the upper temperature set-point of the operating control, exceeding the temperature limit of a safety control device (independent from the operating control), boiling water in a non-pressurized system or activation of a pressure or temperature relief valve in a pressurized system.

12.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the heat output categories specified in section 4.3.1. If more than one test run is conducted at a specified heat output rate, the results from at least two-thirds of the test runs in that heat output rate category shall be used in calculating the weighted average emission rate (See section 14.1.14). The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate.

13.0 Calculation of Results

13.1 Nomenclature

E_T —Total particulate emissions for the full test run as determined per ASTM E2515-11 (IBR, see § 60.17) in grams

Environmental Protection Agency

Pt. 60, App. A-8, Meth. 28WHH

$E_{p/MJ}$ —Emissions rate in grams per megajoule of heat output
 $E_{lb/mmBtu}$ output—Emissions rate in pounds per million Btu of heat output
 $E_{p/kg}$ —Emissions factor in grams per kilogram of dry fuel burned
 $E_{p/hr}$ —Emissions factor in grams per hour
 HHV—Higher heating value of fuel = 8600 Btu/lb (19.990 MJ/kg)
 LHV—Lower heating value of fuel = 7988 Btu/lb (18.567 MJ/kg)
 ΔT —Temperature difference between water entering and exiting the heat exchanger
 Q_{out} —Total heat output in BTU's (megajoules)
 Q_{in} —Total heat input available in test fuel charge in BTU (megajoules)
 M —Mass flow rate of water in lb/min (kg/min)

V_i —Volume of water indicated by a totalizing flow meter at the i th reading in gallons (liters)
 V_r —Volumetric flow rate of water in heat exchange system in gallons per minute (liters/min)
 Θ —Total length of test run in hours
 t_i —Data sampling interval in minutes
 η_{del} —Delivered heating efficiency in percent
 F_i —Weighting factor for heat output category i (See Table 2)
 $T1$ —Temperature of water at the inlet on the supply side of the heat exchanger
 $T2$ —Temperature of the water at the outlet on the supply side of the heat exchanger
 $T3$ —Temperature of water at the inlet to the load side of the heat exchanger
 TI_{avg} —Average temperature of the appliance and water at start of the test

$$TI_{avg} = (T1 + T2)/2 \text{ at the start of the test, } ^\circ F \quad \text{Eq. 1}$$

TF_{avg} —Average temperature of the appliance and water at the end of the test

$$TF_{avg} = (T1 + T2)/2 \text{ at the end of the test, } ^\circ F \quad \text{Eq. 2}$$

MC—Fuel moisture content in percent dry basis
 MC_i —Average moisture content of individual 4 x 4 fuel pieces in percent dry basis
 MC_{sp} —Moisture content of spacers assumed to be 10 percent dry basis
 σ —Density of water in pounds per gallon
 C_p —Specific heat of water in Btu/lb, $^\circ F$
 C_{steel} —Specific heat of steel (0.1 Btu/lb, $^\circ F$)
 W_{fuel} —Fuel charge weight in pounds (kg)
 W_i —Weight of individual fuel 4 x 4 pieces in pounds (kg)

W_{sp} —Weight of all spacers used in a fuel load in pounds (kg)
 W_{app} —Weight of empty appliance in pounds
 W_{wa} —Weight of water in supply side of the system in pounds

13.2 After the test is completed, determine the particulate emissions E_p in accordance with ASTM E2515-11 (IBR, see § 60.17).

13.3 Determine Average Fuel Load Moisture Content

$$MC_{Ave} = [(\sum W_i \times MC_i) + (W_{sp} \times MC_{sp})] \div W_{fuel}, \% \quad \text{Eq. 3}$$

13.4 Determine heat input

$$Q_{in} = (W_{fuel} / (1 + (MC/100))) \times HHV, \text{ BTU} \quad \text{Eq. 4}$$

$$Q_{in LHV} = (W_{fuel} / (1 + (MC/100))) \times LHV, \text{ BTU} \quad \text{Eq. 5}$$

13.5 Determine Heat Output and Efficiency

13.5.1 Determine heat output as:

$Q_{out} = \sum$ [Heat output determined for each sampling time interval] + Change in heat stored in the appliance.

$$Q_{out} = \left[\sum (C_{pi} \cdot \Delta T_i \cdot \dot{M}_i \cdot t_i) \right] + (W_{app} \cdot C_{Steel} + C_{pa} W_{water}) \cdot (TF_{avg} - TI_{avg}), \text{ BTU Eq. 6}$$

NOTE: The subscript (i) indicates the parameter value for sampling time interval t_i . \dot{M}_i = Mass flow rate = gal/min \times density of water (lb/gal) = lb/min

$$\dot{M}_i = V_{fi} \cdot \sigma_i, \text{ lb/min Eq. 7}$$

$$\Sigma_i = (62.56 + (-.0003413 \times T3_i) + (-.00006225 \times T3_i^2)) 0.1337, \text{ lbs/gal Eq. 8}$$

$$C_p = 1.0014 + (-.000003485 \times T3_i) \text{ Btu/lb, } ^\circ\text{F Eq. 9}$$

$$C_{steel} = 0.1 \text{ Btu/lb, } ^\circ\text{F}$$

$$C_{pa} = 1.0014 + (-.000003485 \times (TI_{avg} + TF_{avg})/2), \text{ Btu/lb-}^\circ\text{F Eq. 10}$$

$$V_{fi} = (V_i - V_{i-1}) / (t_i - t_{i-1}), \text{ gal/min Eq. 11}$$

NOTE: V_i is the total water volume at the end of interval i and V_{i-1} is the total water volume at the beginning of the time interval. This calculation is necessary when a totalizing type water meter is used.

13.5.2 Determine heat output rate as:

$$\text{Heat Output Rate} = Q_{out} / \Theta, \text{ BTU/hr Eq. 12}$$

13.5.3 Determine emission rates and emission factors as:

$$E_{g/MJ} = E_T / (Q_{out} \times 0.001055), \text{ g/MJ Eq. 13}$$

$$E_{lb/MM \text{ BTU output}} = (E_T / 453.59) / (Q_{output} \times 10^{-6}), \text{ lb/mmBtu Out Eq. 14}$$

$$E_{g/kg} = E_T / (W_{fuel} / (1 + MC/100)), \text{ g/dry kg Eq. 15}$$

$$E_{g/hr} = E_T / \Theta, \text{ g/hr Eq. 16}$$

13.5.4 Determine delivered efficiency as:

$$\eta_{\text{del}} = (Q_{\text{out}}/Q_{\text{in}}) \times 100, \% \quad \text{Eq. 17}$$

$$\eta_{\text{del LHV}} = (Q_{\text{out}}/Q_{\text{in LHV}}) \times 100, \% \quad \text{Eq. 18}$$

13.5.5 Determine η_{SLM} —Overall Efficiency (SLM) using Stack Loss

For determination of the average overall thermal efficiency (η_{SLM}) for the test run, use the data collected over the full test run and the calculations in accordance with CSA B415.1-10 (IBR, see §60.17), clause 13.7 except for 13.7.2 (e), (f), (g), and (h), use the following average fuel properties for oak: percent C = 50.0, percent H = 6.6, percent O = 43.2, percent ash = 0.2 percent. The averaging period for determination of efficiency by the stack loss method allows averaging over 10 minute time periods for flue gas temperature, flue gas CO₂, and flue gas CO for the determination of the efficiency. However, under some cycling conditions the “on” period may be short relative to this 10 minute period. For this reason, during cycling operation the averaging period for these parameters may not be longer than the burner on period divided by 10. The averaging period need not be shorter than one minute. During the off period, under cycling operation, the averaging periods specified may be used. Where short averaging times are used, however, the averaging period for fuel consump-

tion may still be at 10 minutes. This average wood consumption rate shall be applied to all of the smaller time intervals included.

13.5.5.1 Whenever the CSA B415.1-10 (IBR, see §60.17) overall efficiency is found to be lower than the overall efficiency based on load side measurements, as determined by Eq. 16 of this method, section 14.1.7 of the test report must include a discussion of the reasons for this result.

13.6 Weighted Average Emissions and Efficiency

13.6.1 Determine the weighted average emission rate and delivered efficiency from the individual tests in the specified heat output categories. The weighting factors (F_i) are derived from an analysis of ASHRAE bin data which provides details of normal building heating requirements in terms of percent of design capacity and time in a particular capacity range—or “bin”—over the course of a heating season. The values used in this method represent an average of data from several cities located in the northern United States.

$$\text{Weighted average delivered efficiency: } \eta_{\text{avg}} = \sum \eta_i \times F_i, \% \quad \text{Eq. 19}$$

$$\text{Weighted average emissions: } E_{\text{avg}} = \sum E_i \times F_i, \% \quad \text{Eq. 20}$$

13.7 Average Heat Output ($Q_{\text{out-8hr}}$) and Efficiency ($\eta_{\text{avg-8hr}}$) for 8 hour burn time.

13.7.1 Units tested under this standard typically require infrequent fuelling, 8 to 12 hours intervals being typical. Rating unit's

based on an average output sustainable over an 8 hour duration will assist consumers in appropriately sizing units to match the theoretical heat demand of their application.

13.7.2 Calculations:

$$Q_{\text{out-8hr}} = X1 + \{ (8 - Y1) \times [(X2 - X1) / (Y2 - Y1)] \}, \% \quad \text{Eq. 21}$$

$$\eta_{\text{avg-8hr}} = \eta_{\text{del1}} + \{ (8 - Y1) \times [(\eta_{\text{del2}} - \eta_{\text{del1}}) / (Y2 - Y1)] \}, \% \quad \text{Eq. 22}$$

Where:

Y1 = Test duration just above 8 hrs
Y2 = Test duration just below 8 hrs
X1 = Actual load for duration Y1
X2 = Actual load for duration Y2

η_{del1} = Average delivered efficiency for duration Y1
 η_{del2} = Average delivered efficiency for duration Y2

13.7.2.1 Determine the test durations and actual load for each category as recorded in Table 1A.

13.7.2.2 Determine the data point that has the nearest duration greater than 8 hrs.

X1 = Actual load,

Y1 = Test duration, and

η_{del1} = Average delivered efficiency for this data point

13.7.2.3 Determine the data point that has the nearest duration less than 8 hours.

X2 = Actual load,

Y2 = Test duration, and

η_{del2} = Average delivered efficiency for this data point

13.7.2.4 Example:

CATEGORY ACTUAL LOAD DURATION

[Category Actual Load Duration η_{del}]

	(Btu/Hr)	(Hr)	(%)
1	15,000	10.2	70.0
2	26,000	8.4	75.5

**CATEGORY ACTUAL LOAD DURATION—
Continued**

[Category Actual Load Duration η_{del}]

	(Btu/Hr)	(Hr)	(%)
3	50,000	6.4	80.1
4	100,000	4.7	80.9

Category 2 duration is just above 8 hours, therefore: X1 = 26,000 Btu/hr, η_{del1} = 75.5% and Y1 = 8.4 hrs

Category 3 duration is just below 8 hours, therefore: X2 = 50,000 Btu/hr, η_{del2} = 80.1% and Y2 = 6.4 hrs

$$Q_{out-8hr} = 26,000 + \{(8-8.4) \times [(50,000-26,000)/(6.4-8.4)]\} = 30,800 \text{ BTU/hr}$$

$$\eta_{avg-8hr} = 75.5 + \{(8-8.4) \times [(80.1-75.5)/(6.4-8.4)]\} = 76.4\%$$

13.8 Carbon Monoxide Emissions

For each minute of the test period, the carbon monoxide emission rate shall be calculated as:

$$CO_{g/min} = Q_{std} \cdot CO_s \cdot 3.30 \times 10^{-5} \tag{Eq. 23}$$

Total CO emissions for each of the three test periods (CO₋₁, CO₋₂, CO₋₃) shall be calculated as the sum of the emission rates for each of the 1 minute intervals.

Total CO emission for the test run, CO_T, shall be calculated as the sum of CO₋₁, CO₋₂, and CO₋₃.

14.0 Report

14.1.1 The report shall include the following.

14.1.2 Name and location of the laboratory conducting the test.

14.1.3 A description of the appliance tested and its condition, date of receipt and dates of tests.

14.1.4 A statement that the test results apply only to the specific appliance tested.

14.1.5 A statement that the test report shall not be reproduced except in full, without the written approval of the laboratory.

14.1.6 A description of the test procedures and test equipment including a schematic or other drawing showing the location of all required test equipment. Also, a description of test fuel sourcing, handling and storage practices shall be included.

14.1.7 Details of deviations from, additions to or exclusions from the test method, and their data quality implications on the test results (if any), as well as information on specific test conditions, such as environmental conditions.

14.1.8 A list of participants and observers present for the tests.

14.1.9 Data and drawings indicating the fire box size and location of the fuel gate.

14.1.10 Drawings and calculations used to determine firebox volume.

14.1.11 Information for each test run fuel charge including piece size, moisture content, and weight.

14.1.12 All required data for each test run shall be provided in spreadsheet format. Formulae used for all calculations shall be accessible for review.

14.1.13 Test run duration for each test.

14.1.14 Calculated results for delivered efficiency at each burn rate and the weighted average emissions reported as total emissions in grams, pounds per mm Btu of delivered heat, grams per MJ of delivered heat, grams per kilogram of dry fuel and grams per hour. Results shall be reported for each heat output category and the weighted average.

14.1.15 Tables 1A, 1B, 1C and Table 2 must be used for presentation of results in test reports.

14.1.16 A statement of the estimated uncertainty of measurement of the emissions and efficiency test results.

14.1.17 Raw data, calibration records, and other relevant documentation shall be retained by the laboratory for a minimum of 7 years.

15.0 Precision and Bias

15.1 Precision—It is not possible to specify the precision of the procedure in Method 28WHH because the appliance operation and

Environmental Protection Agency

Pt. 60, App. A-8, Meth. 28WHH

fueling protocols and the appliances themselves produce variable amounts of emissions and cannot be used to determine reproducibility or repeatability of this measurement method.

15.2 Bias—No definitive information can be presented on the bias of the procedure in Method 28WHH for measuring solid fuel

burning hydronic heater emissions because no material having an accepted reference value is available.

16.0 Keywords

16.1 Solid fuel, hydronic heating appliances, wood-burning hydronic heaters.

Table 1A. Data Summary Part A

Category	Run No	Load % Capacity	Target Load BTU/hr	Actual Load BTU/hr	Act Load % of max	Θ	W_{fuel}	MC_{ave}	Q_{in}	Q_{out}
						Test Duration hrs	Wood Wt lb	Wood Moisture % DB	Heat Input BTU	Heat Output BTU
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1B. Data Summary Part B

Category	Run No	Load % Capacity	T2 Min	E_T	E	E	$E_{g/hr}$	$E_{g/kg}$	η_{del}	η_{SLM}
			Min Return Water Temp. °F	Total PM Emissions g	PM Output Based lb _{MMBTU} Out	PM Output Based g/MJ	PM Rate g/hr	PM Factor g/kg	Delivered Efficiency %	Stack Loss Efficiency %
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

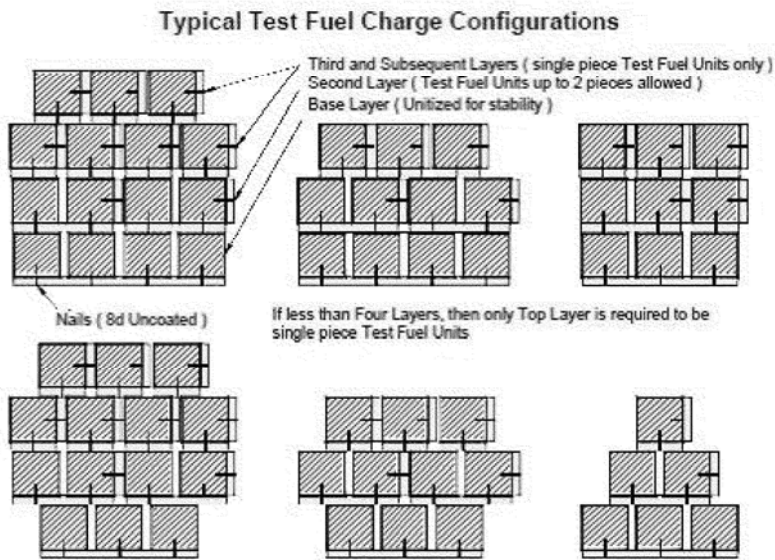
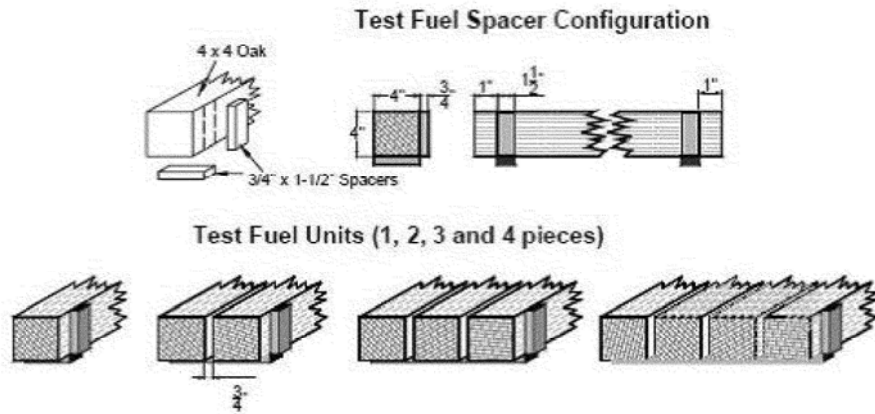
Table 1C: Hangtag Information (optional)

MANUFACTURER:		
MODEL NUMBER:		
MAXIMUM OUTPUT RATING:	Q_{max}	BTU/HR
ANNUAL EFFICIENCY RATING:	N_{avg}	(Using higher heating value)
PARTICLE EMISSIONS:	E_{avg}	GRAMS/HR (average)
		LBS/MILLION BTU OUTPUT
CARBON MONOXIDE:	CO _g /MIN	GRAMS/MINUTE

Table 2. Annual Weighting

Category	Weighting Factor (F_i)	$\eta_{del,i} \times F_i$	$E_{g/MJ,i} \times F_i$	$E_{g/kg,i} \times F_i$	$E_{lb/mmBtu Out,i} \times F_i$	$E_{g/hr,i} \times F_i$
I	0.437					
II	0.238					
III	0.275					
IV	0.050					
Totals	1.000					

Figure 1. Typical Test Fuel Piece



TEST METHOD 28WHH FOR CERTIFICATION OF
CORD WOOD-FIRED HYDRONIC HEATING AP-
PLIANCES WITH PARTIAL THERMAL STORAGE:
MEASUREMENT OF PARTICULATE MATTER
(PM) AND CARBON MONOXIDE (CO) EMIS-
SIONS AND HEATING EFFICIENCY OF WOOD-
FIRED HYDRONIC HEATING APPLIANCES WITH
PARTIAL THERMAL STORAGE

1.0 Scope and Application

1.1 This test method applies to wood-fired hydronic heating appliances with heat storage external to the appliance. The units typically transfer heat through circulation of a liquid heat exchange media such as water or a water-antifreeze mixture. Throughout this document, the term "water" will be used to denote any of the heat transfer liquids approved for use by the manufacturer.

1.2 The test method measures PM and CO emissions and delivered heating efficiency at specified heat output rates referenced against the appliance's rated heating capacity as specified by the manufacturer and verified under this test method.

1.3 PM emissions are measured by the dilution tunnel method as specified in the EPA Method 28WHH and the standards referenced therein with the exceptions noted in section 12.5.9. Delivered efficiency is measured by determining the fuel energy input and appliance output. Heat output is determined through measurement of the flow rate and temperature change of water circulated through a heat exchanger external to the appliance and the increase in energy of the external storage. Heat input is determined from the mass of dry wood fuel and its higher heating value (HHV). Delivered efficiency does not attempt to account for pipeline loss.

1.4 Products covered by this test method include both pressurized and non-pressurized hydronic heating appliances intended to be fired with wood and for which the manufacturer specifies for indoor or outdoor installation. The system, which includes the heating appliance and external storage, is commonly connected to a heat exchanger by insulated pipes and normally includes a pump to circulate heated liquid. These systems are used to heat structures such as homes, barns and greenhouses. They also provide heat for domestic hot water, spas and swimming pools.

1.5 Distinguishing features of products covered by this standard include:

1.5.1 The manufacturer specifies the application for either indoor or outdoor installation.

1.5.2 A firebox with an access door for hand loading of fuel.

1.5.3 Typically an aquastat mounted as part of the appliance that controls combustion air supply to maintain the liquid in the appliance within a predetermined temperature range provided sufficient fuel is avail-

able in the firebox. The appliance may be equipped with other devices to control combustion.

1.5.4 A chimney or vent that exhausts combustion products from the appliance.

1.5.5 A liquid storage system, typically water, which is not large enough to accept all of the heat produced when a full load of wood is burned and the storage system starts a burn cycle at 125 °F.

1.5.6 The heating appliances require external thermal storage and these units will only be installed as part of a system which includes thermal storage. The manufacturer specifies the minimum amount of thermal storage required. However, the storage system shall be large enough to ensure that the boiler (heater) does not cycle, slumber, or go into an off-mode when operated in a Category III load condition (See section 4.3).

1.6 The values stated are to be regarded as the standard whether in I-P or SI units. The values given in parentheses are for information only.

2.0 Summary of Method and References

2.1 PM and CO emissions are measured from a wood-fired hydronic heating appliance burning a prepared test fuel charge in a test facility maintained at a set of prescribed conditions. Procedures for determining heat output rates, PM and CO emissions, and efficiency and for reducing data are provided.

2.2 Referenced Documents

2.2.1 EPA Standards

2.2.1.1 Method 28 Certification and Auditing of Wood Heaters

2.2.1.2 Method 28WHH Measurement of Particulate Emissions and Heating Efficiency of Wood-Fired Hydronic Heating Appliances and the Standards Referenced therein.

2.2.2 Other Standards

2.2.2.1 CSA-B415.1-10 *Performance Testing of Solid-Fuel-Burning Heating Appliances*

3.0 Terminology

3.1 Definitions

3.1.1 Hydronic Heating—A heating system in which a heat source supplies energy to a liquid heat exchange media such as water that is circulated to a heating load and returned to the heat source through pipes.

3.1.2 Aquastat—A control device that opens or closes a circuit to control the rate of fuel consumption in response to the temperature of the heating media in the heating appliance.

3.1.3 Delivered Efficiency—The percentage of heat available in a test fuel charge that is delivered to a simulated heating load or the storage system as specified in this test method.

3.1.4 Emission Factor—The emission of a pollutant expressed in mass per unit of energy (typically) output from the boiler/heater.

3.1.5 Emission Index—The emission of a pollutant expressed in mass per unit mass of fuel used.

3.1.6 Emission Rate—The emission of a pollutant expressed in mass per unit time.

3.1.7 Manufacturer's Rated Heat Output Capacity—The value in Btu/hr (MJ/hr) that the manufacturer specifies that a particular model of hydronic heating appliance is capable of supplying at its design capacity as verified by testing, in accordance with section 12.5.4.

3.1.8 Heat Output Rate—The average rate of energy output from the appliance during a specific test period in Btu/hr (MJ/hr).

3.1.9 Firebox—The chamber in the appliance in which the test fuel charge is placed and combusted.

3.1.10 NIST—National Institute of Standards and Technology.

3.1.11 Test Fuel Charge—The collection of test fuel placed in the appliance at the start of the emission test run.

3.1.12 Test Run—An individual emission test which encompasses the time required to consume the mass of the test fuel charge. The time of the test run also considers the time for the energy to be drawn from the thermal storage.

3.1.13 Test Run Under "Cold-to-Cold" Condition—Under this test condition the test fuel is added into an empty chamber along with kindling and ignition materials (paper). The boiler/heater at the start of this test is typically 125° to 130 °F.

3.1.14 Test Run Under "Hot-to-Hot" Condition—Under this test condition the test fuel is added onto a still-burning bed of charcoals produced in a pre-burn period. The boiler/heater water is near its operating control limit at the start of the test.

3.1.15 Overall Efficiency, also known as Stack Loss Efficiency—The efficiency for each test run as determined using the CSA B415.1-10 (IBR, see §60.17) stack loss method (SLM).

3.1.16 Phases of a Burn Cycle—The "startup phase" is defined as the period from the start of the test until 15 percent of the test fuel charge is consumed. The "steady-state phase" is defined as the period from the end of the startup phase to a point at which 80 percent of the test fuel charge is consumed. The "end phase" is defined as the time from the end of the steady-state period to the end of the test.

3.1.17 Thermopile—A device consisting of a number of thermocouples connected in series, used for measuring differential temperature.

3.1.18 Slumber Mode—This is a mode in which the temperature of the water in the boiler/heater has exceeded the operating con-

trol limit and the control has changed the boiler/heater fan speed, dampers, and/or other operating parameters to minimize the heat output of the boiler/heater.

4.0 Summary of Test Method

4.1 Dilution Tunnel. Emissions are determined using the "dilution tunnel" method specified in EPA Method 28WHH and the standards referenced therein. The flow rate in the dilution tunnel is maintained at a constant level throughout the test cycle and accurately measured. Samples of the dilution tunnel flow stream are extracted at a constant flow rate and drawn through high efficiency filters. The filters are dried and weighed before and after the test to determine the emissions collected and this value is multiplied by the ratio of tunnel flow to filter flow to determine the total particulate emissions produced in the test cycle.

4.2 Efficiency. The efficiency test procedure takes advantage of the fact that this type of system delivers heat through circulation of the heated liquid (water) from the system to a remote heat exchanger (e.g. baseboard radiators in a room) and back to the system. Measurements of the cooling water temperature difference as it enters and exits the test system heat exchanger along with the measured flow rate allow for an accurate determination of the useful heat output of the appliance. Also included in the heat output is the change in the energy content in the storage system during a test run. Energy input to the appliance during the test run is determined by weight of the test fuel charge, adjusted for moisture content, multiplied by the higher heating value. Additional measurements of the appliance weight and temperature at the beginning and end of a test cycle are used to correct for heat stored in the appliance. Overall efficiency (SLM) is determined using the CSA B415.1-10 (IBR, see §60.17) stack loss method for data quality assurance purposes.

4.3 Operation. Four test categories are defined for use in this method. These are:

4.3.1 Category I: A heat output of 15 percent or less of manufacturer's rated heat output capacity.

4.3.2 Category II: A heat output of 16 percent to 24 percent of manufacturer's rated heat output capacity.

4.3.3 Category III: A heat output of 25 percent to 50 percent of manufacturer's rated heat output capacity.

4.3.4 Category IV: Manufacturer's Rated Heat Output Capacity. These heat output categories refer to the output from the system by way of the load heat exchanger installed for the test. The output from just the boiler/heater part of the system may be higher for all or part of a test, as part of this boiler/heater output goes to storage.

For the Category III and IV runs, appliance operation is conducted on a hot-to-hot test

cycle meaning that the appliance is brought to operating temperature and a coal bed is established prior to the addition of the test fuel charge and measurements are made for each test fuel charge cycle. The measurements are made under constant heat draw conditions within pre-determined ranges. No attempt is made to modulate the heat demand to simulate an indoor thermostat cycling on and off in response to changes in the indoor environment.

For the Category I and II runs, the unit is tested with a "cold start." At the manufacturer's option, the Category II and III runs may be waived and it may be assumed that the particulate emission values and efficiency values determined in the startup, steady-state, and end phases of Category I are applicable in Categories II and III for the purpose of determining the annual averages in lb/mmBtu and g/MJ (See section 13). For the annual average in g/hr, the length of time for stored heat to be drawn from thermal storage shall be determined for the test load requirements of the respective category.

All test operations and measurements shall be conducted by personnel of the laboratory responsible for the submission of the test report.

5.0 Significance and Use

5.1 The measurement of particulate matter emission and CO rates is an important test method widely used in the practice of air pollution control.

5.1.1 These measurements, when approved by state or federal agencies, are often required for the purpose of determining compliance with regulations and statutes.

5.1.2 The measurements made before and after design modifications are necessary to demonstrate the effectiveness of design changes in reducing emissions and make this standard an important tool in manufacturers' research and development programs.

5.2 Measurement of heating efficiency provides a uniform basis for comparison of product performance that is useful to the consumer. It is also required to relate emissions produced to the useful heat production.

5.3 This is a laboratory method and is not intended to be fully representative of all actual field use. It is recognized that users of hand-fired, wood-burning equipment have a great deal of influence over the performance of any wood-burning appliance. Some compromises in realism have been made in the interest of providing a reliable and repeatable test method.

6.0 Test Equipment

6.1 Scale. A platform scale capable of weighing the boiler/heater under test and associated parts and accessories when completely filled with water to an accuracy of

+1.0 pound (± 0.5 kg) and a readout resolution of ± 0.2 pound (± 0.1 kg).

6.2 Heat Exchanger. A water-to-water heat exchanger capable of dissipating the expected heat output from the system under test.

6.3 Water Temperature Difference Measurement. A Type-T 'special limits' thermopile with a minimum of 5 pairs of junctions shall be used to measure the temperature difference in water entering and leaving the heat exchanger. The temperature difference measurement uncertainty of this type of thermopile is equal to or less than ± 0.50 °F (± 0.25 °C). Other temperature measurement methods may be used if the temperature difference measurement uncertainty is equal to or less than ± 0.50 °F (± 0.25 °C). This measurement uncertainty shall include the temperature sensor, sensor well arrangement, piping arrangements, lead wire, and measurement/recording system. The response time of the temperature measurement system shall be less than half of the time interval at which temperature measurements are recorded.

6.4 Water Flow Meter. A water flow meter shall be installed in the inlet to the load side of the heat exchanger. The flow meter shall have an accuracy of ± 1 percent of measured flow.

6.4.1 Optional—Appliance Side Water Flow Meter. A water flow meter with an accuracy of ± 1 percent of the flow rate is recommended to monitor supply side water flow rate.

6.5 Optional Recirculation Pump. Circulating pump used during test to prevent stratification in the boiler/heater, of liquid being heated.

6.6 Water Temperature Measurement. Thermocouples or other temperature sensors to measure the water temperature at the inlet and outlet of the load side of the heat exchanger must meet the calibration requirements specified in 10.1 of this method.

6.7 Lab Scale. For measuring the moisture content of wood slices as part of the overall wood moisture determination. Accuracy of ± 0.01 pounds.

6.8 Flue Gas Temperature Measurement. Must meet the requirements of CSA B415.1-10 (IBR, see §60.17), clause 6.2.2.

6.9 Test Room Temperature Measurement. Must meet the requirements of CSA B415.1-10 (IBR, see §60.17), clause 6.2.1.

6.10 Flue Gas Composition Measurement. Must meet the requirements of CSA B415.1-10 (IBR, see §60.17), clauses 6.3.1 through 6.3.3.

6.11 Dilution Tunnel CO Measurement. In parallel with the flue gas composition measurements, the CO concentration in the dilution tunnel shall also be measured and reported at time intervals not to exceed one minute. This analyzer shall meet the zero and span drift requirements of CSA B415.1-10 (IBR, see §60.17). In addition the measurement repeatability shall be better than ± 15

Environmental Protection Agency

Pt. 60, App. A-8, Meth. 28WHH-PTS

ppm over the range of CO levels observed in the dilution tunnel.

7.0 Safety

7.1 These tests involve combustion of wood fuel and substantial release of heat and products of combustion. The heating system also produces large quantities of very hot water and the potential for steam production and system pressurization. Appropriate precautions must be taken to protect personnel from burn hazards and respiration of products of combustion.

8.0 Sampling, Test Specimens and Test Appliances

8.1 Test specimens shall be supplied as complete appliances, as described in marketing materials, including all controls and accessories necessary for installation in the test facility. A full set of specifications, installation and operating instructions, and design and assembly drawings shall be provided when the product is to be placed under certification of a third-party agency. The manufacturer's written installation and operating instructions are to be used as a guide in the set-up and testing of the appliance and shall be part of the test record.

8.2 The size, connection arrangement, and control arrangement for the thermal storage shall be as specified in the manufacturer's documentation. It is not necessary to use the specific storage system that the boiler/heater will be marketed with. However, the capacity of the system used in the test cannot be greater than that specified as the minimum allowable for the boiler/heater.

8.3 All system control settings shall be the as-shipped, default settings. These default settings shall be the same as those communicated in a document to the installer or end user. These control settings and the documentation of the control settings as to be provided to the installer or end user shall be part of the test record.

8.4 Where the manufacturer defines several alternatives for the connection and loading arrangement, one shall be defined in the appliance documentation as the default or standard installation. It is expected that this will be the configuration for use with a simple baseboard heating system. This is the configuration to be followed for these tests. The manufacturer's documentation shall define the other arrangements as optional or alternative arrangements.

9.0 Preparation of Test Equipment

9.1 The appliance is to be placed on a scale capable of weighing the appliance fully loaded with a resolution of ± 0.2 lb (0.1 kg).

9.2 The appliance shall be fitted with the type of chimney recommended or provided by the manufacturer and extending to 15 ± 0.5 feet (4.6 ± 0.15 m) from the upper surface of

the scale. If no flue or chimney system is recommended or provided by the manufacturer, connect the appliance to a flue of a diameter equal to the flue outlet of the appliance. The flue section from the appliance flue collar to 8 ± 0.5 feet above the scale shall be single wall stove pipe and the remainder of the flue shall be double wall insulated class A chimney.

9.3 Optional Equipment Use

9.3.1 A recirculation pump may be installed between connections at the top and bottom of the appliance to minimize thermal stratification if specified by the manufacturer. The pump shall not be installed in such a way as to change or affect the flow rate between the appliance and the heat exchanger.

9.3.2 If the manufacturer specifies that a thermal control valve or other device be installed and set to control the return water temperature to a specific set point, the valve or other device shall be installed and set per the manufacturer's written instructions.

9.4 Prior to filling the boiler/heater with water, weigh and record the appliance mass.

9.5 Heat Exchanger

9.5.1 Plumb the unit to a water-to-water heat exchanger with sufficient capacity to draw off heat at the maximum rate anticipated. Route hoses and electrical cables and instrument wires in a manner that does not influence the weighing accuracy of the scale as indicated by placing dead weights on the platform and verifying the scale's accuracy.

9.5.2 Locate thermocouples to measure the water temperature at the inlet and outlet of the load side of the heat exchanger.

9.5.3 Install a thermopile (or equivalent instrumentation) meeting the requirements of section 6.3 to measure the water temperature difference between the inlet and outlet of the load side of the heat exchanger.

9.5.4 Install a calibrated water flow meter in the heat exchanger load side supply line. The water flow meter is to be installed on the cooling water inlet side of the heat exchanger so that it will operate at the temperature at which it is calibrated.

9.5.5 Place the heat exchanger in a box with 2 in. (50 mm) of expanded polystyrene (EPS) foam insulation surrounding it to minimize heat losses from the heat exchanger.

9.5.6 The reported efficiency and heat output rate shall be based on measurements made on the load side of the heat exchanger.

9.5.7 Temperature instrumentation per section 6.6 shall be installed in the appliance outlet and return lines. The average of the outlet and return water temperature on the supply side of the system shall be considered the average appliance temperature for calculation of heat storage in the appliance (TE_{avg} and TL_{avg}). Installation of a water flow meter in the supply side of the system is optional.

9.6 Storage Tank. The storage tank shall include a destratification pump as illustrated in Figure 1. The pump will draw from the bottom of the tank and return to the top as illustrated. Temperature sensors (TS1 and TS2 in Figure 1) shall be included to measure the temperature in the recirculation loop. The valve plan in Figure 1 allows the tank recirculation loop to operate and the boiler/heater-to-heat exchanger loop to operate at the same time but in isolation. This would typically be done before the start of a test or following completion of a test to determine the end of test average tank temperature. The nominal flow rate in the storage tank recirculation loop can be estimated based on pump manufacturers' performance curves and any significant restriction in the recirculation loop.

9.7 Fill the system with water. Determine the total weight of the water in the appliance when the water is circulating. Verify that the scale indicates a stable weight under operating conditions. Make sure air is purged properly.

10.0 Calibration and Standardization

10.1 Water Temperature Sensors. Temperature measuring equipment shall be calibrated before initial use and at least semi-annually thereafter. Calibrations shall be in compliance with National Institute of Standards and Technology (NIST) Monograph 175, Standard Limits of Error.

10.2 Heat Exchanger Load Side Water Flow Meter.

10.2.1 The heat exchanger load side water flow meter shall be calibrated within the flow range used for the test run using NIST-traceable methods. Verify the calibration of the water flow meter before and after each test run and at least once during each test run by comparing the water flow rate indicated by the flow meter to the mass of water collected from the outlet of the heat exchanger over a timed interval. Volume of the collected water shall be determined based on the water density calculated from section 13, Eq. 12, using the water temperature measured at the flow meter. The uncertainty in the verification procedure used shall be 1 percent or less. The water flow rate determined by the collection and weighing method shall be within 1 percent of the flow rate indicated by the water flow meter.

10.3 Scales. The scales used to weigh the appliance and test fuel charge shall be calibrated using NIST-traceable methods at least once every 6 months.

10.4 Flue Gas Analyzers—In accordance with CSA B415.1-10 (IBR, see §60.17), clause 6.8.

11.0 Conditioning

11.1 Prior to testing, an appliance is to be operated for a minimum of 50 hours using a

medium heat draw rate. The conditioning may be at the manufacturer's facility prior to the certification test. If the conditioning is at the certification test laboratory, the pre-burn for the first test can be included as part of the conditioning requirement. If conditioning is included in pre-burn, then the appliance shall be aged with fuel meeting the specifications outlined in section 12.2 with a moisture content between 19 and 25 percent on a dry basis. Operate the appliance at a medium heat output rate (Category II or III) for at least 10 hours for non-catalytic appliances and 50 hours for catalytic appliances. Record and report hourly flue gas exit temperature data and the hours of operation. The aging procedure shall be conducted and documented by a testing laboratory.

12.0 Procedure

12.1 Appliance Installation. Assemble the appliance and parts in conformance with the manufacturer's written installation instructions. Clean the flue with an appropriately sized, wire chimney brush before each certification test series.

12.2 Fuel. Test fuel charge fuel shall be red (*Quercus ruba L.*) or white (*Quercus Alba*) oak 19 to 25 percent moisture content on a dry basis. Piece length shall be 80 percent of the firebox depth rounded down to the nearest 1 inch (25mm) increment. For example, if the firebox depth is 46 inches (1168mm) the piece length would be 36 inches (46 inches \times 0.8 = 36.8 inches, rounded down to 36 inches). Pieces are to be placed in the firebox parallel to the longest firebox dimension. For fireboxes with sloped surfaces that create a non-uniform firebox length, the piece length shall be adjusted for each layer based on 80 percent of the length at the level where the layer is placed. The test fuel shall be cord wood with cross section dimensions and weight limits as defined in CSA B415.1-10 (IBR, see §60.17), section 8.3, Table 4. The use of dimensional lumber is not allowed.

12.2.1 Select three pieces of cord wood from the same batch of wood as the test fuel and the same weight as the average weight of the pieces in the test load ± 1.0 lb. From each of these three pieces, cut three slices. Each slice shall be $\frac{1}{2}$ inch to $\frac{3}{4}$ inch thick. One slice shall be cut across the center of the length of the piece. The other two slices shall be cut half way between the center and the end. Immediately measure the mass of each piece in pounds. Dry each slice in an oven at 220 °F for 24 hours or until no further weight change occurs. The slices shall be arranged in the oven so as to provide separation between faces. Remove from the oven and measure the mass of each piece again as soon as practical, in pounds.

The moisture content of each slice, on a dry basis, shall be calculated as:

$$MC_{slice} = 100 \cdot \frac{(W_{SliceWet} - W_{SliceDry})}{W_{SliceDry}}$$

Where:

$W_{SliceWet}$ = weight of the slice before drying in pounds

$W_{SliceDry}$ = weight of the slice after drying in pounds

MC_{slice} = moisture content of the slice in % dry basis

The average moisture content of the entire test load (MC) shall be determined using Eq. 6. Each individual slice shall have a moisture content in the range of 18 percent to 28 percent on a dry basis. The average moisture content for the test fuel load shall be in the range of 19 percent to 25 percent. Moisture shall not be added to previously dried fuel pieces except by storage under high humidity conditions and temperature up to 100 °F. Fuel moisture measurement shall begin within 4 hours of using the fuel batch for a test. Use of a pin-type meter to estimate the moisture content prior to a test is recommended.

12.2.2 Firebox Volume. Determine the firebox volume in cubic feet. Firebox volume shall include all areas accessible through the fuel loading door where firewood could reasonably be placed up to the horizontal plane defined by the top of the loading door. A drawing of the firebox showing front, side and plan views or an isometric view with interior dimensions shall be provided by the manufacturer and verified by the laboratory. Calculations for firebox volume from computer aided design (CAD) software programs are acceptable and shall be included in the test report if used. If the firebox volume is calculated by the laboratory the firebox drawings and calculations shall be included in the test report.

12.2.3 Test Fuel charge. Test fuel charges shall be determined by multiplying the firebox volume by 10 pounds (4.54 kg) per ft³ (28L), or a higher load density as recommended by the manufacturer's printed operating instructions, of wood (as used wet weight). Select the number of pieces of cord wood that most nearly match this target weight. However, the test fuel charge cannot be less than the target of 10 pounds (4.54 kg) per ft³ (28L).

12.3 Sampling Equipment. Prepare the particulate emission sampling equipment as defined by EPA Method 28WHH and the standards referenced therein.

12.4 Appliance Startup. The appliance shall be fired with wood fuel of any species, size and moisture content, at the laboratory's discretion, to bring it up to operating temperature. Operate the appliance until the

water is heated to the upper operating control limit and has cycled at least two times. Then remove all unburned fuel, zero the scale and verify the scales accuracy using dead weights.

12.4.1 Startup Procedure for Category III and IV Test Runs, "Hot-to-Hot."

12.4.1.1 Pretest t Burn Cycle. Following appliance startup (section 12.4), reload appliance with oak cord wood and allow it to burn down to the specified coal bed weight. The pre-test burn cycle fuel charge weight shall be within ±10 percent of the test fuel charge weight. Piece size and length shall be selected such that charcoaling is achieved by the time the fuel charge has burned down to the required coal bed weight. Pieces with a maximum thickness of approximately 2 inches have been found to be suitable. Charcoaling is a general condition of the test fuel bed evidenced by an absence of large pieces of burning wood in the coal bed and the remaining fuel pieces being brittle enough to be broken into smaller charcoal pieces with a metal poker. Manipulations to the fuel bed prior to the start of the test run are to be done to achieve charcoaling while maintaining the desired heat output rate. During the pre-test burn cycle and at least one hour prior to starting the test run, adjust water flow to the heat exchanger to establish the target heat draw for the test. For the first test run the heat draw rate shall be equal to the manufacturer's rated heat output capacity.

12.4.1.2 Allowable Adjustments. Fuel addition or subtractions, and coal bed raking shall be kept to a minimum but are allowed up to 15 minutes prior to the start of the test run. For the purposes of this method, coal bed raking is the use of a metal tool (poker) to stir coals, break burning fuel into smaller pieces, dislodge fuel pieces from positions of poor combustion, and check for the condition of charcoaling. Record all adjustments to and additions or subtractions of fuel, and any other changes to the appliance operations that occur during pretest ignition period. During the 15-minute period prior to the start of the test run, the wood heater loading door shall not be open more than a total of 1 minute. Coal bed raking is the only adjustment allowed during this period.

12.4.1.3 Coal Bed Weight. The appliance is to be loaded with the test fuel charge when the coal bed weight is between 10 percent and 20 percent of the test fuel charge weight. Coals may be raked as necessary to level the coal bed but may only be raked and stirred

once between 15 to 20 minutes prior to the addition of the test fuel charge.

12.4.1.4 Storage. The Category III and IV test runs may be done either with or without the thermal storage. If thermal storage is used, the initial temperature of the storage must be 125 °F or greater at the start of the test. The storage may be heated during the pre-test burn cycle or it may be heated by external means. If thermal storage is used, prior to the start of the test run, the storage tank destratification pump, shown in Figure 1, shall be operated until the total volume pumped exceeds 1.5 times the tank volume and the difference between the temperature at the top and bottom of the storage tank (TS₁ and TS₂) is less than 1 °F. These two temperatures shall then be recorded to determine the starting average tank temperature. The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6). If the Category III and IV runs are done with storage, it is recognized that during the last hour of the pre-burn cycle the storage tank must be mixed to achieve a uniform starting temperature and cannot receive heat from the boiler/heater during this time. During this time period, the boiler/heater might cycle or go into a steady reduced output mode. (Note—this would happen, for example, in a Category IV run if the actual maximum output of the boiler/heater exceed the manufacturer's rated output.) A second storage tank may be used temporarily to enable the boiler/heater to operate during this last hour of the pre-burn period as it will during the test period. The temperature of this second storage tank is not used in the calculations but the return water to the boiler/heater (after mixing device if used) must be 125 °F or greater.

12.4.2 Startup Procedure for Category I and II Test Runs, "Cold-to-Cold."

12.4.2.1 Initial Temperatures. This test shall be started with both the boiler/heater and the storage at a minimum temperature of 125 °F. The boiler/heater maximum temperature at the start of this test shall be 135 °F. The boiler/heater and storage may be heated through a pre-burn or it may be heated by external means.

12.4.2.2 Firebox Condition at Test Start. Prior to the start of this test remove all ash and charcoal from the combustion chamber(s). The loading of the test fuel and kindling should follow the manufacturer's recommendations, subject to the following constraints: Up to 10 percent kindling and paper may be used which is in addition to the fuel load. Further, up to 10 percent of the fuel load (*i.e.*, included in the 10 lb/ft³) may be smaller than the main fuel. This startup fuel shall still be larger than 2 inches.

12.4.2.3 Storage. The Category I and II test runs shall be done with thermal storage. The initial temperature of the storage must be 125 °F or greater at the start of the test.

The storage may be heated during the pre-test burn cycle or it may be heated by external means. Prior to the start of the test run, the storage tank destratification pump, shown in Figure 1, shall be operated until the total volume pumped exceeds 1.5 times the tank volume and the difference between the temperature at the top and bottom of the storage tank (TS₁ and TS₂) is less than 1 °F. These two temperatures shall then be recorded to determine the starting average tank temperature. The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6).

12.5 Test Runs. For all test runs, the return water temperature to the hydronic heater must be equal to or greater than 120 °F (this is lower than the initial tank temperature to allow for any pipeline losses). Where the storage system is used, flow of water from the boiler/heater shall be divided between the storage tank and the heat exchanger such that the temperature change of the circulating water across the heat exchanger shall be 30 ± 5 °F, averaged over the entire test run. This is typically adjusted using the system valves.

Complete a test run in each heat output rate category, as follows:

12.5.1 Test Run Start. For Category III and IV runs: Once the appliance is operating normally and the pretest coal bed weight has reached the target value per section 12.4.1, tare the scale and load the full test charge into the appliance. Time for loading shall not exceed 5 minutes. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Start all sampling systems.

For Category I and II runs: Once the appliance has reached the starting temperature, tare the scale and load the full test charge, including kindling into the appliance. The actual weight of the test fuel charge shall be measured and recorded within 30 minutes prior to loading. Light the fire following the manufacturer's written normal startup procedure. Start all sampling systems.

12.5.1.1 Record all water temperatures, differential water temperatures and water flow rates at time intervals of one minute or less.

12.5.1.2 Record particulate emissions data per the requirements of EPA Method 28WHH and the standards referenced therein.

12.5.1.3 Record data needed to determine overall efficiency (SLM) per the requirements of CSA B415.1-10 (IBR, see §60.17) clauses 6.2.1, 6.2.2, 6.3, 8.5.7, 10.4.3(a), 10.4.3(f), and 13.7.9.3

12.5.1.3.1 Measure and record the test room air temperature in accordance with the requirements of CSA B415.1-10 (IBR, see §60.17), clauses 6.2.1, 8.5.7 and 10.4.3(g).

12.5.1.3.2 Measure and record the flue gas temperature in accordance with the requirements of CSA B415.1-10 (IBR, see §60.17), clauses 6.2.2, 8.5.7 and 10.4.3(f).

12.5.1.3.3 Determine and record the carbon monoxide (CO) and carbon dioxide (CO₂) concentrations in the flue gas in accordance with CSA B415.1-10 (IBR, see §60.17), clauses 6.3, 8.5.7 and 10.4.3(i) and (j).

12.5.1.3.4 Measure and record the test fuel weight per the requirements of CSA B415.1-10 (IBR, see §60.17), clauses 8.5.7 and 10.4.3(h).

12.5.1.3.5 Record the test run time per the requirements of CSA B415.1-10 (IBR, see §60.17), clause 10.4.3(a).

12.5.1.3.6 Record and document all settings and adjustments, if any, made to the boiler/heater as recommended/required by manufacturer's instruction manual for different combustion conditions or heat loads. These may include temperature setpoints, under and over-fire air adjustment, or other adjustments that could be made by an operator to optimize or alter combustion. All such settings shall be included in the report for each test run.

12.5.1.4 Monitor the average heat output rate on the load side of the heat exchanger based on water temperatures and flow. If the heat output rate over a 10 minute averaging period gets close to the upper or lower limit of the target range (± 5 percent), adjust the water flow through the heat exchanger to compensate. Make changes as infrequently as possible while maintaining the target heat output rate. The first test run shall be conducted at the Category IV heat output rate to validate that the appliance is capable of producing the manufacturer's rated heat output capacity.

12.5.2 Test Fuel Charge Adjustment. It is acceptable to adjust the test fuel charge (*i.e.*, reposition) once during a test run if more than 60 percent of the initial test fuel charge weight has been consumed and more than 10 minutes have elapsed without a measurable (1 lb or 0.5 kg) weight change while the operating control is in the demand mode. The time used to make this adjustment shall be less than 60 seconds.

12.5.3 Test Run Completion. For the Category III and IV, "hot-to-hot" test runs, the test run is completed when the remaining weight of the test fuel charge is 0.0 lb (0.0 kg). ($W_{Fuel\text{Remaining}} = W_{fuel}$) End the test run when the scale has indicated a test fuel charge weight of 0.0 lb (0.0 kg) or less for 30 seconds.

For the Category I and II "cold-to-cold" test runs, the test run is completed; and the end of a test is defined at the first occurrence of any one of the following:

(a) The remaining weight of the test fuel charge is less than 1 percent of the total test fuel weight ($W_{Fuel\text{Remaining}} > 0.99 \cdot W_{fuel}$);

(b) The automatic control system on the boiler/heater switches to an off mode. In this case, the boiler/heater fan (if used) is typi-

cally stopped and all air flow dampers are closed by the control system. Note that this off mode cannot be an "overheat" or emergency shutdown which typically requires a manual reset; or

(c) If the boiler/heater does not have an automatic off mode: After 90 percent of the fuel load has been consumed and the scale has indicated a rate of change of the test fuel charge of less than 1.0 lb/hr for a period of 10 minutes or longer. Note—this is not considered "stopped fuel combustion." See section 12.5.6.1.

12.5.3.1 At the end of the test run, stop the particulate sampling train and overall efficiency (SLM) measurements, and record the run time, and all final measurement values.

12.5.3.2 At the end of the test run, continue to operate the storage tank destratification pump until the total volume pumped exceeds 1.5 times the tank volume. The maximum average of the top and bottom temperatures measured after this time may be taken as the average tank temperature at the end of the tests (TFSavg, See section 13.1). The total volume pumped may be based on the nominal flow rate of the destratification pump (See section 9.6).

12.5.3.3 For the Category I and II test runs, there is a need to determine the energy content of the unburned fuel remaining in the chamber if the remaining mass in the chamber is greater than 1 percent of the test fuel weight. Following the completion of the test, as soon as safely practical, this remaining fuel is removed from the chamber, separated from the remaining ash and weighed. This separation could be implemented with a slotted "scoop" or similar tool. A ¼ inch opening size in the separation tool shall be used to separate the ash and charcoal. This separated char is assigned a heating value of 12,500 Btu/lb.

12.5.4 Heat Output Capacity Validation. The first test run must produce a heat output rate that is within 10 percent of the manufacturer's rated heat output capacity (Category IV) throughout the test run and an average heat output rate within 5 percent of the manufacturer's rated heat output capacity. If the appliance is not capable of producing a heat output within these limits, the manufacturer's rated heat output capacity is considered not validated and testing is to be terminated. In such cases, the tests may be restarted using a lower heat output capacity if requested by the manufacturer. Alternatively, during the Category IV run, if the rated output cannot be maintained for a 15 minute interval, the manufacturer may elect to reduce the rated output to match the test and complete the Category IV run on this basis. The target outputs for Categories I, II, and III shall then be recalculated based on this change in rated output capacity.

12.5.5 Additional Test Runs. Using the manufacturer's rated heat output capacity

as a basis, conduct a test for additional heat output categories as specified in section 4.3. It is not required to run these tests in any particular order.

12.5.6 Alternative Heat Output Rate for Category I. If an appliance cannot be operated in the Category I heat output range due to stopped combustion, two test runs shall be conducted at heat output rates within Category II. When this is the case, the weightings for the weighted averages indicated in section 14.1.15 shall be the average of the Category I and II weightings and shall be applied to both Category II results. Appliances that are not capable of operation within Category II (<25 percent of maximum) cannot be evaluated by this test method.

12.5.6.1 Stopped Fuel Combustion. Evidence that an appliance cannot be operated at a Category I heat output rate due to stopped fuel combustion shall include documentation of two or more attempts to operate the appliance in heat output rate Category I and fuel combustion has stopped prior to complete consumption of the test fuel charge. Stopped fuel combustion is evidenced when an elapsed time of 60 minutes or more has occurred without a measurable (1 lb or 0.5 kg) weight change in the test fuel charge while the appliance operating control is in the demand mode. Report the evidence and the reasoning used to determine that a test in heat output rate Category I cannot be achieved. For example, two unsuccessful attempts to operate at an output rate of 10 percent of the rated output capacity are not sufficient evidence that heat output rate Category I cannot be achieved.

12.5.7 Appliance Overheating. Appliances with their associated thermal storage shall be capable of operating in all heat output categories without overheating to be rated by this test method. Appliance overheating occurs when the rate of heat withdrawal from the appliance is lower than the rate of heat production when the unit control is in the idle mode. This condition results in the water in the appliance continuing to increase in temperature well above the upper limit setting of the operating control. Evidence of overheating includes: 1 hour or more of appliance water temperature increase above the upper temperature set-point of the operating control, exceeding the temperature limit of a safety control device (independent from the operating control—typically requires manual reset), boiling water in a non-pressurized system or activation of a pressure or temperature relief valve in a pressurized system.

12.5.8 Option to Eliminate Tests in Category II and III. Following successful completion of a test run in Category I, the manufacturer may eliminate the Category II and III tests. For the purpose of calculating the annual averages for particulates and efficiency, the values obtained in the Category I

run shall be assumed to apply also to Category II and Category III. It is envisioned that this option would be applicable to systems which have sufficient thermal storage such that the fuel load in the Category I test can be completely consumed without the system reaching its upper operating temperature limit. In this case, the boiler/heater would likely be operating at maximum thermal output during the entire test and this output rate may be higher than the manufacturer's rated heat output capacity. The Category II and III runs would then be the same as the Category I run. It may be assumed that the particulate emission values and efficiency values determined in the startup, steady-state, and end phases of Category I are applicable in Categories II and III, for the purpose of determining the annual averages in lb/mmBtu and g/MJ (See section 13). For the annual average in g/hr, the length of time for stored heat to be drawn from thermal storage shall be determined for the test load requirements of the respective category.

12.5.9 Modification to Measurement Procedure in EPA Method 28WHH to Determine Emissions Separately During the Startup, Steady-State and End Phases. With one of the two particulate sampling trains used, filter changes shall be made at the end of the startup phase and the steady-state phase (See section 3.0). This shall be done to determine the particulate emission rate and particulate emission index for the startup, steady-state, and end phases individually. For this one train, the particulates measured during each of these three phases shall be added together to also determine the particulate emissions for the whole run.

12.5.10 Modification to Measurement Procedure in EPA Method 28WHH and the Standards Referenced therein on Averaging Period for Determination of Efficiency by the Stack Loss Method. The methods currently defined in Method 28WHH allow averaging over 10-minute time periods for flue gas temperature, flue gas CO₂, and flue gas CO for the determination of the efficiency with the stack loss method. However, under some cycling conditions the "on" period may be short relative to this 10-minute period. For this reason, during cycling operation the averaging period for these parameters may not be longer than the burner on period divided by 10. The averaging period need not be shorter than one minute. During the off period, under cycling operation, averaging periods as specified in EPA Method 28WHH and the standards referenced therein, may be used. Where short averaging times are used, however, the averaging period for fuel consumption may still be at 10 minutes. This average wood consumption rate shall be applied to all of the smaller time intervals included.

12.6 Additional Test Runs. The testing laboratory may conduct more than one test run in each of the heat output categories specified in section 4.3. If more than one test run is conducted at a specified heat output rate, the results from at least two-thirds of the test runs in that heat output rate category shall be used in calculating the weighted average emission rate. The measurement data and results of all test runs shall be reported regardless of which values are used in calculating the weighted average emission rate.

13.0 Calculation of Results

13.1 Nomenclature

- CO₁—Carbon monoxide measured in the dilution tunnel at arbitrary time in ppm dry basis.
- CO_{g/min}—Carbon monoxide emission rate in g/min.
- CO_T—Total carbon monoxide emission for the full test run in grams.
- CO₁—Startup period carbon monoxide emissions in grams.
- CO₂—Steady-state period carbon monoxide emission in grams.
- CO₃—End period carbon monoxide emission in grams.
- E_T—Total particulate emissions for the full test run as determined per EPA Method 28WHH and the standards referenced therein in grams.
- E₁—Startup period particulate emissions in grams.
- E₂—Steady-state period particulate emissions in grams.
- E₃—End period particulate emissions in grams.
- E_{1-g/kg}—Startup period particulate emission index in grams per kg fuel.
- E_{2-g/kg}—Steady-state period particulate emission index in grams per kg fuel.
- E_{3-g/kg}—End period particulate emission index in grams per kg fuel.
- E_{1-g/hr}—Startup period particulate emission rate in grams per hour.
- E_{2-g/hr}—Steady-state period particulate emission rate in grams per hour.
- E_{3-g/hr}—End period particulate emission rate in grams per hour.
- E_{g/MJ}—Emission rate in grams per MJ of heat output.
- E_{lb/mmBtu output}—Emissions rate in pounds per million Btu of heat output.
- E_{g/kg}—Emissions factor in grams per kilogram of dry fuel burned.
- E_{g/hr}—Emission factor in grams per hour.

- HHV—Higher heating value of fuel = 8600 Btu/lb (19.990 MJ/kg).
- LHV—Lower heating value of fuel = 7988 Btu/lb (18.567 MJ/kg).
- ΔT—Temperature difference between cooling water entering and exiting the heat exchanger.
- Q_{out}—Total heat output in Btu (MJ).
- Q_{in}—Total heat input available in test fuel charge in Btu's (MJ).
- Q_{std}—Volumetric flow rate in dilution tunnel in dscfm.
- M—Mass flow rate of water in lb/min (kg/min).
- V_i—Volume of water indicated by a totalizing flow meter at the i_{th} reading in gallons (liters).
- V_T—Volumetric flow rate of water in heat exchange system in gallons per minute (liters/min).
- Θ—Total length of burn period in hours (Θ₁ + Θ₂ + Θ₃).
- Θ₁—Length of time of the startup period in hours.
- Θ₂—Length of time of the steady-state period in hours.
- Θ₃—Length of time of the end period in hours.
- Θ₄—Length of time for stored heat to be used following a burn period in hours.
- t_i—Data sampling interval in minutes.
- η_{del}—Delivered heating efficiency in percent.
- F_i—Weighting factor for heat output category i. (See Table 2.)
- T₁—Temperature of water at the inlet on the supply side of the heat exchanger, °F.
- T₂—Temperature of the water at the outlet on the supply side of the heat exchanger, °F.
- T₃—Temperature of cooling water at the inlet to the load side of the heat exchanger, °F.
- T₄—Temperature of cooling water at the outlet of the load side of the heat exchanger, °F.
- T₅—Temperature of the hot water supply as it leaves the boiler/heater, °F.
- T₆—Temperature of return water as it enters the boiler/heater, °F.
- T₇—Temperature in the boiler/heater optional destratification loop at the top of the boiler/heater, °F.
- T₈—Temperature in the boiler/heater optional destratification loop at the bottom of the boiler/heater, °F.
- TI_{avg}—Average temperature of the appliance and water at start of the test.

$$TI_{avg} = (T5 + T6)/2 \text{ at the start of the test, } ^\circ F.$$

Eq. 1

TF_{avg}—Average temperature of the appliance and water at the end of the test.

$$TF_{avg} = (T5 + T6)/2 \text{ at the end of the test, } ^\circ\text{F.}$$

Eq. 2

TIS₁—Temperature at the inlet to the storage system at the start of the test.
 TIS₂—Temperature at the outlet from the storage system at the start of the test.
 TFS₁—Temperature at the inlet to the storage system at the end of the test.

TFS₂—Temperature at the outlet from the storage system at the end of the test.
 TIS_{avg}—Average temperature of the storage system at the start of the test.

$$TIS_{avg} = (TIS_1 + TIS_2)/2 \text{ at the end of the test.}$$

Eq. 3

TFS_{avg}—Average temperature of the storage system at the end of the test.

$$TFS_{avg} = (TFS_1 + TFS_2)/2.$$

Eq. 4

MC—Fuel moisture content in percent dry basis.

σ —Density of water in pounds per gallon.

$\sigma_{initial}$ —Density of water in the boiler/heater system at the start of the test in pounds per gallons.

$\sigma_{boiler/heater}$ —Density of water in the boiler/heater system at an arbitrary time during the test in pounds per gallon.

C_p —Specific heat of water in Btu/lb, $^\circ\text{F}$.

C_{steel} —Specific heat of steel (0.1 Btu/lb, $^\circ\text{F}$).

$V_{boiler/heater}$ —total volume of water in the boiler/heater system on the weight scale in gallons.

W_{fuel} —Fuel charge weight, as-fired or “wet”, in pounds (kg).

W_{fuel-1} —Fuel consumed during the startup period in pounds (kg).

W_{fuel-2} —Fuel consumed during the steady state period in pounds (kg).

W_{fuel-3} —Fuel consumed during the end period in pounds (kg).

$W_{FuelBurned}$ —Weight of fuel that has been burned from the start of the test to an arbitrary time, including the needed correction for the change in density and weight of the water in the boiler/heater system on the scale in pounds (kg).

$W_{RemainingFuel}$ —Weight of unburned fuel separated from the ash at the end of a test. Useful only for Category I and Category II tests.

W_{app} —Weight of empty appliance in pounds (kg).

W_{wat} —Weight of water in supply side of the system in pounds (kg).

$W_{ScaleInitial}$ —Weight reading on the scale at the start of the test, just after the test load has been added in pounds (kg).

W_{Scale} —Reading of the weight scale at an arbitrary time during the test run in pounds (kg).

$W_{StorageTank}$ —Weight of the storage tank empty in pounds (kg).

$W_{WaterStorage}$ —Weight of the water in the storage tank at TIS_{avg} in pounds (kg).

13.2 After the test is completed, determine the particulate emissions E_p in accordance with EPA Method 28WHH and the standards referenced therein.

13.3 Determination of the weight of fuel that has been burned at an arbitrary time.

For the purpose of tracking the consumption of the test fuel load during a test run the following may be used to calculate the weight of fuel that burned since the start of the test:

$$W_{FuelBurned} = (W_{ScaleInitial} - W_{Scale}) + V_{Boiler/heater} \cdot (\sigma_{Initial} - \sigma_{boiler/heater}) \quad \text{Eq. 5}$$

Water density, σ , is calculated using Equation 12.

13.4 Determine Average Fuel Load Moisture Content.

$$MC = \frac{\sum W_{SliceWet_i} - MC_{Slice_i}}{\sum W_{SliceWet_i}} \quad \text{Eq. 6}$$

13.5 Determine Heat Input.

$$Q_{in} = (W_{fuel}/(1+(MC/100))) \times HHV, \text{ Btu (MJ)}. \quad \text{Eq. 7}$$

$$Q_{inLHV} = (W_{fuel}/(1+(MC/100))) \times LHV, \text{ Btu (MJ)}. \quad \text{Eq. 8}$$

13.5.1 Correction to Q_{in} for the Category I and II tests, where there is greater than 1 percent of the test fuel charge in the chamber at the end of the test period.

$$Q_{InCorrected} = Q_{in} - W_{Remaining} \cdot 12,500 \text{ Btu} \quad \text{Eq. 9}$$

13.6 Determine Heat Output, Efficiency, and Emissions.

13.6.1 Determine heat output as:

$Q_{out} = \Sigma$ [Heat output determined for each sampling time interval] + Change in heat stored in the appliance + Change in heat in storage tank.

$$Q_{out} = \Sigma [C_{pi} \cdot \Delta T_i \cdot M_i \cdot t_i] + (W_{app} \cdot C_{steel} + W_{water} \cdot C_{pa}) \cdot (TF_{avg} - TI_{avg}) + (W_{StorageTank} \cdot C_{steel} + W_{WaterStorage} \cdot C_{pa}) \cdot (TFS_{avg} - TIS_{avg}) \text{ Btu (MJ)} \quad \text{Eq. 10}$$

NOTE: The subscript (i) indicates the parameter value for sampling time interval $t_i \cdot M_i$ = Mass flow rate = gal/min \times density of water (lb/gal) = lb/min.

$$M_i = V_{fi} \cdot \sigma_i, \text{ lb/min}. \quad \text{Eq. 11}$$

$$\sigma_i = (62.56 + (-.0003413 \times T_{3i}) + (-.00006225 \times T_{3i}^2)) 0.1337, \text{ lb/gal}. \quad \text{Eq. 12}$$

$$C_p = 1.0014 + (-.000003485 \times T_{3i}) \text{ Btu/lb, } ^\circ\text{F}. \quad \text{Eq. 13}$$

$$C_{steel} = 0.1 \text{ Btu/lb, } ^\circ\text{F}.$$

$$C_{pa} = 1.0014 + (-.000003485 \times (TI_{avg} + TF_{avg})/2), \text{ Btu/lb, } ^\circ\text{F}. \quad \text{Eq. 14}$$

$$V_{fi} = (V_i - V_{i-1}) / (t_i - t_{i-1}), \text{ gal/min}. \quad \text{Eq. 15}$$

NOTE: V_i is the total water volume at the end of interval i and V_{i-1} is the total water volume at the beginning of the time interval.

This calculation is necessary when a totalizing type water meter is used.

13.6.2 Determine Heat Output Rate Over Burn Period ($\Theta_1 + \Theta_2 + \Theta_3$) as:

$$\text{Heat Output Rate} = Q_{\text{out}}/\Theta, \text{ Btu/hr (MJ/hr).} \quad \text{Eq. 16}$$

13.6.3 Determine Emission Rates and Emission Factors as:

$$E_{\text{g/MJ}} = E_T/(Q_{\text{out}} \times 0.001055), \text{ g/MJ.} \quad \text{Eq. 17}$$

$$E_{\text{lb/MM Btu output}} = (E_T/453.59)/(Q_{\text{out}} \times 10^{-6}), \text{ lb/mmBtu out.} \quad \text{Eq. 18}$$

$$E_{\text{g/kg}} = E_T/(W_{\text{fuel}}/(1+MC/100)), \text{ g/dry kg.} \quad \text{Eq. 19}$$

$$E_{\text{g/hr}} = E_T/(\Theta_1 + \Theta_2 + \Theta_3 + \Theta_4), \text{ g/hr.} \quad \text{Eq. 20}$$

$$\Theta_4 = (W_{\text{StorageTank}} \cdot C_{\text{steel}} + W_{\text{WaterStorage}} \cdot C_{\text{pa}}) \cdot (TFS_{\text{avg}} - TIS_{\text{avg}})/(Q_{\text{out}}/\Theta) \quad \text{Eq. 21}$$

If thermal storage is not used in a Category III or IV run, then $\Theta_4 = 0$.

$$E_{1-\text{g/kg}} = E_1/(W_{\text{fuel}-1}/(1 + MC/100)), \text{ g/dry kg.}$$

$$E_{2-\text{g/kg}} = E_2/(W_{\text{fuel}-2}/(1 + MC/100)), \text{ g/dry kg.}$$

$$E_{3-\text{g/kg}} = E_3/(W_{\text{fuel}-3}/(1 + MC/100)), \text{ g/dry kg.}$$

$$E_{1-\text{g/hr}} = E_1/\Theta_1, \text{ g/hr.}$$

$$E_{2-\text{g/hr}} = E_2/\Theta_2, \text{ g/hr.}$$

$$E_{3-\text{g/hr}} = E_3/\Theta_3, \text{ g/hr.}$$

13.6.4 Determine delivered efficiency as:

$$\eta_{\text{del}} = (Q_{\text{out}}/Q_{\text{InCorrected}}) \times 100, \% \quad \text{Eq. 22}$$

$$\eta_{\text{del LHV}} = (Q_{\text{out}}/Q_{\text{in LHV}}) \times 100, \% \quad \text{Eq. 23}$$

13.6.5 Determine η_{SLM} —Overall Efficiency, also known as Stack Loss Efficiency, using stack loss method (SLM).

For determination of the average overall thermal efficiency (η_{SLM}) for the test run, use the data collected over the full test run and the calculations in accordance with CSA B415.1-10 (IBR, see §60.17), clause 13.7 except for 13.7.2(e), (f), (g), and (h), use the following average fuel properties for oak: %C = 50.0, %H = 6.6, %O = 43.2, %Ash = 0.2.

13.6.5.1 Whenever the CSA B415.1-10 (IBR, see §60.17) overall efficiency is found to be lower than the overall efficiency based on load side measurements, as determined by Eq. 22 of this method, section 14.1.7 of the test report must include a discussion of the reasons for this result. For a test where the CSA B415.1-10 overall efficiency SLM is less than 2 percentage points lower than the

overall efficiency based on load side measurements, the efficiency based on load side measurements shall be considered invalid. [Note on the rationale for the 2 percentage points limit. The SLM method does not include boiler/heater jacket losses and, for this reason, should provide an efficiency which is actually higher than the efficiency based on the energy input and output measurements or "delivered efficiency." A delivered efficiency that is higher than the efficiency based on the SLM could be considered suspect. A delivered efficiency greater than 2 percentage points higher than the efficiency based on the SLM, then, clearly indicates a measurement error.]

13.6.6 Carbon Monoxide Emissions

For each minute of the test period, the carbon monoxide emission rate shall be calculated as:

$$CO_{\text{g/min}} = Q_{\text{Std}} \cdot CO_3 \cdot 3.30 \times 10^{-5} \quad \text{Eq. 24}$$

Total CO emissions for each of the three test periods (CO_{-1} , CO_{-2} , CO_{-3}) shall be calculated as the sum of the emission rates for

each of the 1-minute intervals. Total CO emission for the test run, CO_T , shall be calculated as the sum of CO_{-1} , CO_{-2} , and CO_{-3} .

13.7 Weighted Average Emissions and Efficiency.

13.7.1 Determine the weighted average emission rate and delivered efficiency from the individual tests in the specified heat output categories. The weighting factors (F_i) are derived from an analysis of ASHRAE bin data which provides details of normal build-

ing heating requirements in terms of percent of design capacity and time in a particular capacity range—or "bin"—over the course of a heating season. The values used in this method represent an average of data from several cities located in the northern United States.

$$\text{Weighted average delivered efficiency: } \eta_{\text{avg}} = \sum \eta_i \times F_i, \% \quad \text{Eq. 25}$$

$$\text{Weighted average emissions: } E_{\text{avg}} = \sum E_i \times F_i, \% \quad \text{Eq. 26}$$

If, as discussed in section 12.5.8, the option to eliminate tests in Category II and III is elected, the values of efficiency and particulate emission rate as measured in Category I, shall be assigned also to Category II and III for the purpose of determining the annual averages.

14.0 Report

14.1.1 The report shall include the following:

14.1.2 Name and location of the laboratory conducting the test.

14.1.3 A description of the appliance tested and its condition, date of receipt and dates of tests.

14.1.4 A description of the minimum amount of external thermal storage that is required for use with this system. This shall be specified both in terms of volume in gallons and stored energy content in Btu with a storage temperature ranging from 125 °F to the manufacturer's specified setpoint temperature.

14.1.5 A statement that the test results apply only to the specific appliance tested.

14.1.6 A statement that the test report shall not be reproduced except in full, without the written approval of the laboratory.

14.1.7 A description of the test procedures and test equipment including a schematic or other drawing showing the location of all required test equipment. Also, a description of test fuel sourcing, handling and storage practices shall be included.

14.1.8 Details of deviations from, additions to or exclusions from the test method, and their data quality implications on the test results (if any), as well as information on specific test conditions, such as environmental conditions.

14.1.9 A list of participants and their roles and observers present for the tests.

14.1.10 Data and drawings indicating the fire box size and location of the fuel charge.

14.1.11 Drawings and calculations used to determine firebox volume.

14.1.12 Information for each test run fuel charge including piece size, moisture content and weight.

14.1.13 All required data and applicable blanks for each test run shall be provided in spreadsheet format both in the printed report and in a computer file such that the data can be easily analyzed and calculations easily verified. Formulas used for all calculations shall be accessible for review.

14.1.14 For each test run, $\Theta_1, \Theta_2, \Theta_3$, the total CO and particulate emission for each of these three periods, and Θ_4 .

14.1.15 Calculated results for delivered efficiency at each heat output rate and the weighted average emissions reported as total emissions in grams, pounds per mm Btu of delivered heat, grams per MJ of delivered heat, grams per kilogram of dry fuel and grams per hour. Results shall be reported for each heat output category and the weighted average.

14.1.16 Tables 1A, 1B, 1C, 1D, 1E and Table 2 must be used for presentation of results in test reports.

14.1.17 A statement of the estimated uncertainty of measurement of the emissions and efficiency test results.

14.1.18 A plot of CO emission rate in grams/minute vs. time, based on 1 minute averages, for the entire test period, for each run.

14.1.19 A plot of estimated boiler/heater energy release rate in Btu/hr based on 10 minute averages, for the entire test period, for each run. This will be calculated from the fuel used, the wood heating value and moisture content, and the SLM efficiency during each 10 minute period.

14.1.20 Raw data, calibration records, and other relevant documentation shall be retained by the laboratory for a minimum of 7 years.

15.0 Precision and Bias

15.1 Precision—It is not possible to specify the precision of the procedure in this test method because the appliance operation and

Pt. 60, App. A-8, Meth. 28WHH-PTS

40 CFR Ch. I (7-1-17 Edition)

fueling protocols and the appliances themselves produce variable amounts of emissions and cannot be used to determine reproducibility or repeatability of this test method.

15.2 *Bias*—No definitive information can be presented on the bias of the procedure in this test method for measuring solid fuel burning hydronic heater emissions because

no material having an accepted reference value is available.

16.0 Keywords

16.1 Solid fuel, hydronic heating appliances, wood-burning hydronic heaters, partial thermal storage.

Table IA. Data Summary Part A

						Θ	W_{fuel}	MC_{ave}	Q_{in}	Q_{out}
Category	Run No	Load % Capacity	Target Load	Actual Load	Actual Load	Test Duration	Wood Weight as-fired	Wood Moisture	Heat Input	Heat Output
		Btu/hr	Btu/hr	Btu/hr	% of max	hrs	lb	%DB	Btu	Btu
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1B. Data Summary Part B

			T2 Min	E_T	E	E	$E_{g/hr}$	$E_{g/kg}$	η_{del}	H_{SLM}
Category	Run No	Load % Capacity	Min Return Water Temp.	Total PM Emissions	PM Output Based	PM Output Based	PM Rate	PM Factor	Delivered Efficiency	Stack Loss Efficiency
			$^{\circ}F$	g	lb/mm Btu Out	g/MJ	g/hr	g/kg	%	%
I		< 15% of max								
II		16-24% of max								
III		25-50% of max								
IV		Max capacity								

Table 1C. Data Summary Part C

			Θ_1	Θ_2	Θ_3	CO ₁	CO ₂	CO ₃	CO _T
Category	Run No	Load % Capacity	Startup Time.	Steady State Time	End Time	Startup CO emission	Steady State CO emission	End CO emission	Total CO emission
			min	min	min	g	g	g	g
I		< 15% of max							
II		16-24% of max							
III		25-50% of max							
IV		Max capacity							

Table 1D. Data Summary Part D

			E ₁	E ₂	E ₃	E _{1,g/kg}	E _{2,g/kg}	E _{3,g/kg}
Category	Run No	Load % Capacity	Startup PM	Steady State PM	End PM	Startup PM emission index	Steady State PM emission index	End PM emission index
			g	g	g	g/kg fuel	g/kg fuel	g/kg fuel
I		< 15% of max						
II		16-24% of max						
III		25-50% of max						
IV		Max capacity						

Table 1E: Label Summary Information

MANUFACTURER:			
MODEL NUMBER:			
ANNUAL EFFICIENCY RATING:	η_{avg}		(Using higher heating value)
PARTICLE EMISSIONS:	E_{avg}		grams/hr (Average)
			lbs/mmBtu/hr Output

Table 2. Annual Weighting

Category	Weighting Factor (F_i)	$\eta_{del,i} \times F_i$	$E_{g/MJ,i} \times F_i$	$E_{g/kg,i} \times F_i$	$E_{lb/mmBtu Out,i} \times F_i$	$E_{g/hr,i} \times F_i$
I	0.437					
II	0.238					
III	0.275					
IV	0.050					
Totals	1.000					

Figure 1. Schematic of Equipment Test Setup

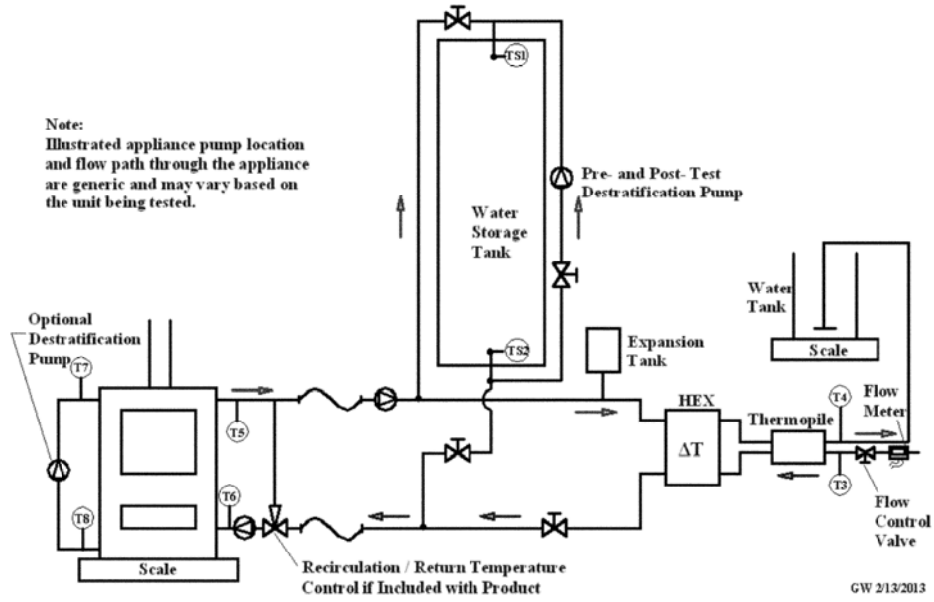
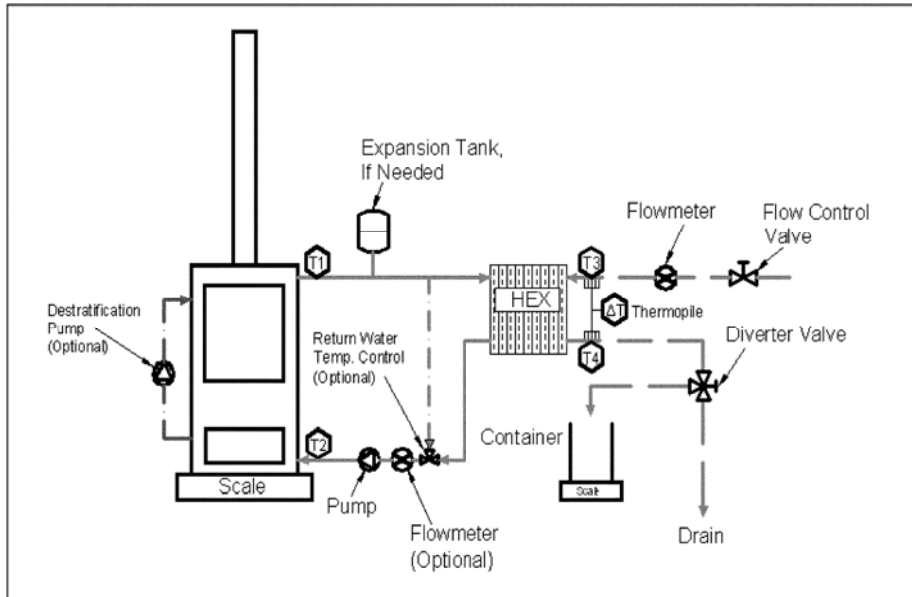


Figure 2. Schematic of Test Equipment Set-up



Note: Illustrated appliance pump location and flow path through the appliance.

METHOD 29—DETERMINATION OF METALS EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 5 and Method 12.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Lead (Pb)	7439-92-1
Manganese (Mn)	7439-96-5
Mercury (Hg)	7439-97-6
Nickel (Ni)	7440-02-0
Phosphorus (P)	7723-14-0

Analyte	CAS No.
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Thallium (Tl)	7440-28-0
Zinc (Zn)	7440-66-6

1.2 Applicability. This method is applicable to the determination of metals emissions from stationary sources. This method may be used to determine particulate emissions in addition to the metals emissions if the prescribed procedures and precautions are followed.

1.2.1 Hg emissions can be measured, alternatively, using EPA Method 101A of Appendix B, 40 CFR Part 61. Method 101-A measures only Hg but it can be of special interest to sources which need to measure both Hg and Mn emissions.

2.0 Summary of Method

2.1 Principle. A stack sample is withdrawn isokinetically from the source, particulate emissions are collected in the probe and on a heated filter, and gaseous emissions are then collected in an aqueous acidic solution of hydrogen peroxide (analyzed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analyzed only for Hg). The recovered samples are digested, and appropriate fractions are analyzed for Hg by cold vapor atomic absorption spectroscopy.

(CVAAS) and for Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, P, Se, Ag, Tl, and Zn by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of Sb, As, Cd, Co, Pb, Se, and Tl if these elements require greater analytical sensitivity than can be obtained by ICAP. If one so chooses, AAS may be used for analysis of all listed metals if the resulting in-stack method detection limits meet the goal of the testing program. Similarly, inductively coupled plasma-mass spectroscopy (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl and Zn.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Iron (Fe) can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Aluminum (Al) can be a spectral interference during the analysis of As and Pb by ICAP. Generally, these interferences can be reduced by diluting the analytical sample, but such dilution raises the in-stack detection limits. Background and overlap corrections may be used to adjust for spectral interferences. Refer to Method 6010 of Reference 2 in section 16.0 or the other analytical methods used for details on potential interferences to this method. For all GFAAS analyses, use matrix modifiers to limit interferences, and matrix match all standards.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Nitric Acid (HNO₃). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.2 Sulfuric Acid (H₂SO₄). Rapidly destructive to body tissue. Will cause third de-

gree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m³ for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.3 Hydrochloric Acid (HCl). Highly corrosive liquid with toxic vapors. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.4 Hydrofluoric Acid (HF). Highly corrosive to eyes, skin, nose, throat, and lungs. Reaction to exposure may be delayed by 24 hours or more. Provide ventilation to limit exposure.

5.2.5 Hydrogen Peroxide (H₂O₂). Irritating to eyes, skin, nose, and lungs. 30% H₂O₂ is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.6 Potassium Permanganate (KMnO₄). Caustic, strong oxidizer. Avoid bodily contact with.

5.2.7 Potassium Persulfate. Strong oxidizer. Avoid bodily contact with. Keep containers well closed and in a cool place.

5.3 Reaction Pressure. Due to the potential reaction of the potassium permanganate with the acid, there could be pressure build-up in the acidic KMnO₄ absorbing solution storage bottle. Therefore these bottles shall not be fully filled and shall be vented to relieve excess pressure and prevent explosion potentials. Venting is required, but not in a manner that will allow contamination of the solution. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

6.0 Equipment and Supplies

6.1 Sampling. A schematic of the sampling train is shown in Figure 29-1. It has general similarities to the Method 5 train.

6.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, sections 6.1.1.1 and 6.1.1.2, except that glass nozzles are required unless alternate tips are constructed of materials that are free from contamination and will not interfere with the sample. If a probe tip other than glass is used, no correction to the sample test results to compensate for the nozzle's effect on the sample is allowed. Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended instead of metal fittings to prevent contamination. If one chooses to do so, a single glass piece consisting of a combined probe tip and probe liner may be used.

6.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, sections 6.1 and 6.2, respectively.

6.1.3 Filter Holder. Glass, same as Method 5, section 6.1.1.5, except use a Teflon filter support or other non-metallic, non-contaminating support in place of the glass frit.

6.1.4 Filter Heating System. Same as Method 5, section 6.1.1.6.

6.1.5 Condenser. Use the following system for condensing and collecting gaseous metals and determining the moisture content of the stack gas. The condensing system shall consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Use the first impinger as a moisture trap. The second impinger (which is the first $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger) shall be identical to the first impinger in Method 5. The third impinger (which is the second $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger) shall be a Greenburg Smith impinger with the standard tip as described for the second impinger in Method 5, section 6.1.1.8. The fourth (empty) impinger and the fifth and sixth (both acidified KMnO_4) impingers are the same as the first impinger in Method 5. Place a temperature sensor capable of measuring to within 1 °C (2 °F) at the outlet of the last impinger. If no Hg analysis is planned, then the fourth, fifth, and sixth impingers are not used.

6.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, sections 6.1.1.9, 6.1.2, and 6.1.3, respectively.

6.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

6.2 Sample Recovery. Same as Method 5, sections 6.2.1 through 6.2.8 (Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

6.2.1 Non-metallic Probe-Liner and Probe-Nozzle Brushes or Swabs. Use non-metallic probe-liner and probe-nozzle brushes or swabs for quantitative recovery of materials collected in the front-half of the sampling train.

6.2.2 Sample Storage Containers. Use glass bottles (see section 8.1 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml. for storage of acidified KMnO_4 -containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

6.2.3 Graduated Cylinder. Glass or equivalent.

6.2.4 Funnel. Glass or equivalent.

6.2.5 Labels. For identifying samples.

6.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

6.3 Sample Preparation and Analysis.

6.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample dilutions.

6.3.2 Graduated Cylinders. For preparation of reagents.

6.3.3 Parr Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent). For sample digestion.

6.3.4 Beakers and Watch Glasses. 250-ml beakers, with watch glass covers, for sample digestion.

6.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

6.3.6 Filter Funnels. For holding filter paper.

6.3.7 Disposable Pasteur Pipets and Bulbs.

6.3.8 Volumetric Pipets.

6.3.9 Analytical Balance. Accurate to within 0.1 mg.

6.3.10 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures, respectively.

6.3.11 Hot Plates.

6.3.12 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

6.3.12.1 Graphite Furnace Attachment. With Sb, As, Cd, Co, Pb, Se, and Tl hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as Reference 2 in section 16.0. Methods 7041 (Sb), 7060 (As), 7131 (Cd), 7201 (Co), 7421 (Pb), 7740 (Se), and 7841 (Tl).

6.3.12.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL, an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp shall be capable of raising the temperature at the quartz cell by 10 °C above ambient, so that no condensation forms on the wall of the quartz cell. Same as Method 7470 in Reference 2 in section 16.0. See note 2: section 11.1.3 for other acceptable approaches for analysis of Hg in which analytical detection limits of 0.002 ng/ml were obtained.

6.3.13 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010 in Reference 2 in section 16.0.

6.3.14 Inductively Coupled Plasma-Mass Spectrometer.

Same as EPA Method 6020 in Reference 2 in section 16.0.

7.0 Reagents and Standards

7.1 Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are

available. Otherwise, use the best available grade.

7.2 Sampling Reagents.

7.2.1 Sample Filters. Without organic binders. The filters shall contain less than 1.3 µg/in.² of each of the metals to be measured. Analytical results provided by filter manufacturers stating metals content of the filters are acceptable. However, if no such results are available, analyze filter blanks for each target metal prior to emission testing. Quartz fiber filters meeting these requirements are recommended. However, if glass fiber filters become available which meet these requirements, they may be used. Filter efficiencies and unreactiveness to sulfur dioxide (SO₂) or sulfur trioxide (SO₃) shall be as described in section 7.1.1 of Method 5.

7.2.2 Water. To conform to ASTM Specification D1193-77 or 91, Type II (incorporated by reference—see §60.17). If necessary, analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

7.2.3 HNO₃, Concentrated. Baker Intra-analyzed or equivalent.

7.2.4 HCl, Concentrated. Baker Intra-analyzed or equivalent.

7.2.5 H₂O₂, 30 Percent (V/V).

7.2.6 KMnO₄.

7.2.7 H₂SO₄, Concentrated.

7.2.8 Silica Gel and Crushed Ice. Same as Method 5, sections 7.1.2 and 7.1.4, respectively.

7.3 Pretest Preparation of Sampling Reagents.

7.3.1 HNO₃/H₂O₂ Absorbing Solution, 5 Percent HNO₃/10 Percent H₂O₂. Add carefully with stirring 50 ml of concentrated HNO₃ to a 1000-ml volumetric flask containing approximately 500 ml of water, and then add carefully with stirring 333 ml of 30 percent H₂O₂. Dilute to volume with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.3.2 Acidic KMnO₄ Absorbing Solution, 4 Percent KMnO₄ (W/V), 10 Percent H₂SO₄ (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H₂SO₄ into approximately 800 ml of water, and add water with stirring to make a volume of 1 liter; this solution is 10 percent H₂SO₄ (V/V). Dissolve, with stirring, 40 g of KMnO₄ into 10 percent H₂SO₄ (V/V) and add 10 percent H₂SO₄ (V/V) with stirring to make a volume of 1 liter. Prepare and store in glass bottles to prevent degradation. This reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper.

7.3.3 HNO₃, 0.1 N. Add with stirring 6.3 ml of concentrated HNO₃ (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. This

reagent shall contain less than 2 ng/ml of each target metal.

7.3.4 HCl, 8 N. Carefully add with stirring 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of Hg.

7.4 Glassware Cleaning Reagents.

7.4.1 HNO₃, Concentrated. Fisher ACS grade or equivalent.

7.4.2 Water. To conform to ASTM Specifications D1193, Type II.

7.4.3 HNO₃, 10 Percent (V/V). Add with stirring 500 ml of concentrated HNO₃ to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5 Sample Digestion and Analysis Reagents. The metals standards, except Hg, may also be made from solid chemicals as described in Reference 3 in section 16.0. Refer to References 1, 2, or 5 in section 16.0 for additional information on Hg standards. The 1000 µg/ml Hg stock solution standard may be made according to section 7.2.7 of Method 101A.

7.5.1 HCl, Concentrated.

7.5.2 HF, Concentrated.

7.5.3 HNO₃, Concentrated. Baker Intra-analyzed or equivalent.

7.5.4 HNO₃, 50 Percent (V/V). Add with stirring 125 ml of concentrated HNO₃ to 100 ml of water. Dilute to 250 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.5 HNO₃, 5 Percent (V/V). Add with stirring 50 ml of concentrated HNO₃ to 800 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

7.5.6 Water. To conform to ASTM Specifications D1193, Type II.

7.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See Reference 2 in section 16.0 for preparation.

7.5.8 Stannous Chloride. See Reference 2 in section 16.0 for preparation.

7.5.9 KMnO₄, 5 Percent (W/V). See Reference 2 in section 16.0 for preparation.

7.5.10 H₂SO₄, Concentrated.

7.5.11 Potassium Persulfate, 5 Percent (W/V). See Reference 2 in section 16.0 for preparation.

7.5.12 Nickel Nitrate, Ni(NO₃)₂·6H₂O.

7.5.13 Lanthanum Oxide, La₂O₃.

7.5.14 Hg Standard (AAS Grade), 1000 µg/ml.

7.5.15 Pb Standard (AAS Grade), 1000 µg/ml.

7.5.16 As Standard (AAS Grade), 1000 µg/ml.

7.5.17 Cd Standard (AAS Grade), 1000 µg/ml.

7.5.18 Cr Standard (AAS Grade), 1000 µg/ml.

7.5.19 Sb Standard (AAS Grade), 1000 µg/ml.

7.5.20 Ba Standard (AAS Grade), 1000 µg/ml.

7.5.21 Be Standard (AAS Grade), 1000 µg/ml.

7.5.22 Co Standard (AAS Grade), 1000 µg/ml.

7.5.23 Cu Standard (AAS Grade), 1000 µg/ml.

- 7.5.24 Mn Standard (AAS Grade), 1000 µg/ml.
- 7.5.25 Ni Standard (AAS Grade), 1000 µg/ml.
- 7.5.26 P Standard (AAS Grade), 1000 µg/ml.
- 7.5.27 Se Standard (AAS Grade), 1000 µg/ml.
- 7.5.28 Ag Standard (AAS Grade), 1000 µg/ml.
- 7.5.29 Tl Standard (AAS Grade), 1000 µg/ml.
- 7.5.30 Zn Standard (AAS Grade), 1000 µg/ml.
- 7.5.31 Al Standard (AAS Grade), 1000 µg/ml.
- 7.5.32 Fe Standard (AAS Grade), 1000 µg/ml.
- 7.5.33 Hg Standards and Quality Control Samples. Prepare fresh weekly a 10 µg/ml intermediate Hg standard by adding 5 ml of 1000 µg/ml Hg stock solution prepared according to Method 101A to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO₃ and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working Hg standard solution fresh daily; add 5 ml of the 10 µg/ml intermediate standard to a 250-ml volumetric flask, and dilute to 250 ml with 5 ml of 4 percent KMnO₄, 5 ml of 15 percent HNO₃, and then water. Mix well. Use at least five separate aliquots of the working Hg standard solution and a blank to prepare the standard curve. These aliquots and blank shall contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until in the calibration range.
- 7.5.34 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn.
II	Ba, Co, Cu, Fe.
III	Al, Cr, Ni.
IV	Ag, P, Sb, Tl.

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/ml solutions with 5 percent HNO₃. A minimum of one standard and a blank can be used to form each calibration curve. However, prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the mid-range of the calibration curve. Suggested standard levels are 25 µg/ml for Al, Cr and Pb, 15 µg/ml for Fe, and 10 µg/ml for the remaining elements. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks. For ICP-MS, follow Method 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

7.5.35 GFAAS Standards. Sb, As, Cd, Co, Pb, Se, and Tl. Prepare a 10 µg/ml standard by adding 1 ml of 1000 µg/ml standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent HNO₃. For GFAAS, matrix match the standards. Prepare a 100 ng/ml standard by adding 1 ml of the 10 µg/ml standard to a 100-ml volumetric flask, and dilute to 100 ml with the appropriate matrix solution. Prepare other standards by diluting the 100 ng/ml standards. Use at least five standards to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until it is in the range of the samples. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

7.5.36 Matrix Modifiers.

7.5.36.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of Ni(NO₃)₂·6H₂O or other nickel compound suitable for preparation of this matrix modifier in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

7.5.36.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

7.5.36.3 Lanthanum. Carefully dissolve 0.5864 g of La₂O₃ in 10 ml of concentrated HNO₃, and dilute the solution by adding it with stirring to approximately 50 ml of water. Dilute to 100 ml with water, and mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

7.5.37 Whatman 40 and 541 Filter Papers (or equivalent). For filtration of digested samples.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Sampling. The complexity of this method is such that, to obtain reliable results, both testers and analysts must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment and procedures; analytical calculations; reporting; and the specific procedural descriptions throughout this method.

8.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, section 8.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. First, rinse all sampling train glassware with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water, followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4

hours, rinse three times with water, rinse a final time with acetone, and allow to air dry. Cover all glassware openings where contamination can occur until the sampling train is assembled for sampling.

8.1.2 Preliminary Determinations. Same as Method 5, section 8.1.2.

8.1.3 Preparation of Sampling Train.

8.1.3.1 Set up the sampling train as shown in Figure 29-1. Follow the same general procedures given in Method 5, section 8.3, except place 100 ml of the $\text{HNO}_3/\text{H}_2\text{O}_2$ solution (Section 7.3.1 of this method) in each of the second and third impingers as shown in Figure 29-1. Place 100 ml of the acidic KMnO_4 absorbing solution (Section 7.3.2 of this method) in each of the fifth and sixth impingers as shown in Figure 29-1, and transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to final train assembly.

8.1.3.2 Based on the specific source sampling conditions, the use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml.

8.1.3.3 If Hg analysis will not be performed, the fourth, fifth, and sixth impingers as shown in Figure 29-1 are not required.

8.1.3.4 To insure leak-free sampling train connections and to prevent possible sample contamination problems, use Teflon tape or other non-contaminating material instead of silicone grease.

Precaution: Exercise extreme care to prevent contamination within the train. Prevent the acidic KMnO_4 from contacting any glassware that contains sample material to be analyzed for Mn. Prevent acidic H_2O_2 from mixing with the acidic KMnO_4 .

8.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, section 8.4.2 (Pretest Leak-Check), section 8.4.3 (Leak-Checks During the Sample Run), and section 8.4.4 (Post-Test Leak-Checks).

8.1.5 Sampling Train Operation. Follow the procedures given in Method 5, section 8.5. When sampling for Hg, use a procedure analogous to that described in section 8.1 of Method 101A, 40 CFR Part 61, Appendix B, if necessary to maintain the desired color in the last acidified permanganate impinger. For each run, record the data required on a data sheet such as the one shown in Figure 5-3 of Method 5.

8.1.6 Calculation of Percent Isokinetic. Same as Method 5, section 12.11.

8.2 Sample Recovery.

8.2.1 Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-con-

taminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling; a vacuum can form in the filter holder with the undesired result of drawing liquid from the impingers onto the filter.

8.2.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon[®] tape to close these openings.

8.2.3 Alternatively, the following procedure may be used to disassemble the train before the probe and filter holder/oven are completely cooled: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

8.2.4 Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. Take special precautions to assure that all the items necessary for recovery do not contaminate the samples. The sample is recovered and treated as follows (see schematic in Figures 29-2a and 29-2b):

8.2.5 Container No. 1 (Sample Filter). Carefully remove the filter from the filter holder and place it in its labeled petri dish container. To handle the filter, use either acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

8.2.6 Container No. 2 (Acetone Rinse). Perform this procedure only if a determination of particulate emissions is to be made. Quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with a total of 100 ml of acetone, while simultaneously taking great care to see that no dust on the outside of the probe or other surfaces gets in the sample. The use of exactly 100 ml

is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis.

8.2.6.1 Carefully remove the probe nozzle, and clean the inside surface by rinsing with acetone from a wash bottle while brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, then make a final rinse of the inside surface with acetone.

8.2.6.2 Brush and rinse the sample exposed inside parts of the probe fitting with acetone in a similar way until no visible particles remain. Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a non-metallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action three times through the probe. Hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

8.2.6.3 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination. Clean the inside of the front-half of the filter holder by rubbing the surfaces with a non-metallic brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid so that acetone will not leak out when shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Clearly label the container to identify its contents.

8.2.7 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination during the probe rinse. Rinse the probe nozzle and fitting, probe liner, and front-half of the filter holder thoroughly with a total of 100 ml of 0.1 N HNO₃, and place the wash into a sample storage container. Perform the rinses as applicable and generally as described in Method 12, section

8.7.1. Record the volume of the rinses. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container, and clearly label the contents. Finally, rinse the nozzle, probe liner, and front-half of the filter holder with water followed by acetone, and discard these rinses.

NOTE: The use of a total of exactly 100 ml is necessary for the subsequent blank correction procedures.

8.2.8 Container No. 4 (Impingers 1 through 3, Moisture Knockout Impinger, when used, HNO₃/H₂O₂ Impingers Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from impingers 1 through 3 in more than one container, if necessary. Measure the liquid in the first three impingers to within 0.5 ml using a graduated cylinder. Record the volume. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N HNO₃ using the procedure as applicable in Method 12, section 8.7.3.

NOTE: The use of exactly 100 ml of 0.1 N HNO₃ rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the final total volume. Mark the height of the fluid level, seal the container, and clearly label the contents.

8.2.9 Container Nos. 5A (0.1 N HNO₃), 5B (KMnO₄/H₂SO₄ absorbing solution), and 5C (8 N HCl rinse and dilution).

8.2.9.1 When sampling for Hg, pour all the liquid from the impinger (normally impinger No. 4) that immediately preceded the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Container No. 5A. Rinse the impinger with exactly 100 ml of 0.1 N HNO₃ and place this rinse in Container No. 5A.

8.2.9.2 Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this acidic KMnO₄ solution into Container No. 5B. Using a total of exactly 100 ml of fresh acidified KMnO₄ solution for all rinses (approximately 33 ml per rinse), rinse the two permanganate impingers and connecting glassware a minimum of three times. Pour the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers. Similarly, using 100 ml total of water, rinse the permanganate impingers and connecting

glass a minimum of three times, and pour the rinses into Container 5B, carefully assuring transfer of any loose precipitated material. Mark the height of the fluid level, and clearly label the contents. Read the *Precaution*: in section 7.3.2.

NOTE: Due to the potential reaction of KMnO_4 with acid, pressure buildup can occur in the sample storage bottles. Do not fill these bottles completely and take precautions to relieve excess pressure. A No. 70-72 hole drilled in the container cap and Teflon liner has been used successfully.

8.2.9.3 Wash the two permanganate impingers with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled No. 5C containing 200 ml of water. First, place 200 ml of water in the container. Then wash the impinger walls and stem with the 8 N HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing *both permanganate impingers combined*. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into the container with the 200 ml of water. Mark the height of the fluid level on the outside of the container in order to determine if leakage occurs during transport.

8.2.10 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal it. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that might adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

8.2.11 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a container labeled No. 7. Seal the container.

8.2.12 Container No. 8A (0.1 N HNO_3 Blank). At least once during each field test, place 300 ml of the 0.1 N HNO_3 solution used in the sample recovery process into a container labeled No. 8A. Seal the container.

8.2.13 Container No. 8B (Water Blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a container labeled No. 8B. Seal the container.

8.2.14 Container No. 9 (5 Percent $\text{HNO}_3/10$ Percent H_2O_2 Blank). At least once during each field test, place 200 ml of the 5 Percent $\text{HNO}_3/10$ Percent H_2O_2 solution used as the nitric acid impinger reagent into a container labeled No. 9. Seal the container.

8.2.15 Container No. 10 (Acidified KMnO_4 Blank). At least once during each field test, place 100 ml of the acidified KMnO_4 solution used as the impinger solution and in the sample recovery process into a container labeled No. 10. Prepare the container as described in section 8.2.9.2. Read the *Precaution*: in section 7.3.2 and read the note in section 8.2.9.2.

8.2.16 Container No. 11 (8 N HCl Blank). At least once during each field test, place 200 ml of water into a sample container labeled No. 11. Then carefully add with stirring 25 ml of 8 N HCl. Mix well and seal the container.

8.2.17 Container No. 12 (Sample Filter Blank). Once during each field test, place into a petri dish labeled No. 12 three unused blank filters from the same lot as the sampling filters. Seal the petri dish.

8.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 29-3.

8.3.1 Container No. 1 (Sample Filter).

8.3.1.1 If particulate emissions are being determined, first desiccate the filter and filter catch without added heat (do not heat the filters to speed the drying) and weigh to a constant weight as described in section 11.2.1 of Method 5.

8.3.1.2 Following this procedure, or initially, if particulate emissions are not being determined in addition to metals analysis, divide the filter with its filter catch into portions containing approximately 0.5 g each. Place the pieces in the analyst's choice of either individual microwave pressure relief vessels or Parr Bombs. Add 6 ml of concentrated HNO_3 and 4 ml of concentrated HF to each vessel. For microwave heating, microwave the samples for approximately 12 to 15 minutes total heating time as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). Microwave heating times are approximate and are dependent upon the number of samples being digested simultaneously. Sufficient heating is evidenced by sorbent reflux within the vessel. For conventional heating, heat the Parr Bombs at 140 °C (285 °F) for 6 hours. Then cool the samples to

room temperature, and combine with the acid digested probe rinse as required in section 8.3.3.

8.3.1.3 If the sampling train includes an optional glass cyclone in front of the filter, prepare and digest the cyclone catch by the procedures described in section 8.3.1.2 and then combine the digestate with the digested filter sample.

8.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically within 1 ml or gravimetrically within 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in section 11.2.1 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated HNO_3 . Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning section 8.3.3.

8.3.3 Container No. 3 (Probe Rinse). Verify that the pH of this sample is 2 or lower. If it is not, acidify the sample by careful addition with stirring of concentrated HNO_3 to pH 2. Use water to rinse the sample into a beaker, and cover the beaker with a ribbed watch glass. Reduce the sample volume to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr Bombs by quantitatively transferring the sample to the vessel or bomb, carefully adding the 6 ml of concentrated HNO_3 , 4 ml of concentrated HF, and then continuing to follow the procedures described in section 8.3.1.2. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in section 8.3.1.2. The resultant combined sample is referred to as "Sample Fraction 1". Filter the combined sample using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This diluted sample is "Analytical Fraction 1". Measure and record the volume of Analytical Fraction 1 to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as "Analytical Fraction 1B". Label the remaining 250-ml portion as "Analytical Fraction 1A". Analytical Fraction 1A is used for ICAP or AAS analysis for all desired metals except Hg. Analytical Fraction 1B is used for the determination of front-half Hg.

8.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sam-

ple to within 0.5 ml and label it "Sample Fraction 2". Remove a 75- to 100-ml aliquot for Hg analysis and label the aliquot "Analytical Fraction 2B". Label the remaining portion of Container No. 4 as "Sample Fraction 2A". Sample Fraction 2A defines the volume of Analytical Fraction 2A prior to digestion. All of Sample Fraction 2A is digested to produce "Analytical Fraction 2A". Analytical Fraction 2A defines the volume of Sample Fraction 2A after its digestion and the volume of Analytical Fraction 2A is normally 150 ml. Analytical Fraction 2A is analyzed for all metals except Hg. Verify that the pH of Sample Fraction 2A is 2 or lower. If necessary, use concentrated HNO_3 by careful addition and stirring to lower Sample Fraction 2A to pH 2. Use water to rinse Sample Fraction 2A into a beaker and then cover the beaker with a ribbed watchglass. Reduce Sample Fraction 2A to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in sections 8.3.4.1 or 8.3.4.2.

8.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent HNO_3 , and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent H_2O_2 and heat for 10 more minutes. Add 50 ml of hot water, and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

8.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent HNO_3 , and heat for 6 minutes total heating time in alternations of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in section 8.3.1. Allow the sample to cool. Add 10 ml of 3 percent H_2O_2 and heat for 2 more minutes. Add 50 ml of hot water, and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

NOTE: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

8.3.5 Container No. 5A (Impinger 4), Container Nos. 5B and 5C (Impingers 5 and 6). Keep the samples in Containers Nos. 5A, 5B, and 5C separate from each other. Measure and record the volume of 5A to within 0.5 ml. Label the contents of Container No. 5A to be

Analytical Fraction 3A. To remove any brown MnO_2 precipitate from the contents of Container No. 5B, filter its contents through Whatman 40 filter paper into a 500 ml volumetric flask and dilute to volume with water. Save the filter for digestion of the brown MnO_2 precipitate. Label the 500 ml filtrate from Container No. 5B to be Analytical Fraction 3B. Analyze Analytical Fraction 3B for Hg within 48 hours of the filtration step. Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriately sized vented container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2 , add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature. Filter the contents of Container No. 5C through a Whatman 40 filter into a 500-ml volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 5B through a Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-ml dilute HCl solution as Analytical Fraction 3C.

8.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

9.0 Quality Control

9.1 Field Reagent Blanks, if analyzed. Perform the digestion and analysis of the blanks in Container Nos. 7 through 12 that were produced in sections 8.2.11 through 8.2.17, respectively. For Hg field reagent blanks, use a 10 ml aliquot for digestion and analysis.

9.1.1 Digest and analyze one of the filters from Container No. 12 per section 8.3.1, 100 ml from Container No. 7 per section 8.3.2, and 100 ml from Container No. 8A per section 8.3.3. This step produces blanks for Analytical Fractions 1A and 1B.

9.1.2 Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and analyze the resultant volume per section 8.3.4. This step produces blanks for Analytical Fractions 2A and 2B.

9.1.3 Digest and analyze a 100-ml portion of Container No. 8A to produce a blank for Analytical Fraction 3A.

9.1.4 Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B to produce a blank for Analytical Fraction 3B. Filter the resultant 133 ml as described for Container No. 5B in section 8.3.5, except do not dilute the 133 ml. Analyze this blank for Hg within 48 hr of the filtration step, and use 400 ml as the blank volume when calculating the blank mass value. Use the actual volumes of the other analytical blanks when calculating their mass values.

9.1.5 Digest the filter that was used to remove any brown MnO_2 precipitate from the

blank for Analytical Fraction 3B by the same procedure as described in section 8.3.5 for the similar sample filter. Filter the digestate and the contents of Container No. 11 through Whatman 40 paper into a 500-ml volumetric flask, and dilute to volume with water. These steps produce a blank for Analytical Fraction 3C.

9.1.6 Analyze the blanks for Analytical Fraction Blanks 1A and 2A per section 11.1.1 and/or section 11.1.2. Analyze the blanks for Analytical Fractions 1B, 2B, 3A, 3B, and 3C per section 11.1.3. Analysis of the blank for Analytical Fraction 1A produces the front-half reagent blank correction values for the desired metals except for Hg; Analysis of the blank for Analytical Fraction 1B produces the front-half reagent blank correction value for Hg. Analysis of the blank for Analytical Fraction 2A produces the back-half reagent blank correction values for all of the desired metals except for Hg, while separate analyses of the blanks for Analytical Fractions 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for Hg.

9.2 Quality Control Samples. Analyze the following quality control samples.

9.2.1 ICAP and ICP-MS Analysis. Follow the respective quality control descriptions in section 8 of Methods 6010 and 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i). For the purposes of a source test that consists of three sample runs, modify those requirements to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (analyze by Method of Standard Additions unless within 25 percent), one quality control sample to check the accuracy of the calibration standards (required to be within 25 percent of calibration), and one duplicate analysis (required to be within 20 percent of average or repeat all analyses).

9.2.2 Direct Aspiration AAS and/or GFAAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Co, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. Analyze all samples in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample, or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the Method of Standard Additions. Analyze a quality control sample to check the accuracy of the calibration standards. If the results are not within 20 percent, repeat the calibration.

9.2.3 CVAAS Analysis for Hg. Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (if not within 15 percent, repeat calibration). Perform a matrix spike on one sample (if not within 25 percent,

analyze all samples by the Method of Standard Additions). Additional information on quality control can be obtained from Method 7470 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater Method 303F*.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 10.1); Pitot Tube (Section 10.2); Metering System (Section 10.3); Probe Heater (Section 10.4); Temperature Sensors (Section 10.5); Leak-Check of the Metering System (Section 8.4.1); and Barometer (Section 10.6).

10.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in section 7.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using those standards. Check the calibration once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, perform the complete calibration procedures. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

10.3 Atomic Absorption Spectrometer—Direct Aspiration AAS, GFAAS, and CVAAS analyses. Prepare the standards as outlined in section 7.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29-2 and in Method 7470 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater Method 303F* (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

10.4 Field Balance Calibration Check. Check the calibration of the balance used to weigh impingers with a weight that is at least 500g or within 50g of a loaded impinger. The weight must be ASTM E617-13 "Standard Specification for Laboratory Weights and Precision Mass Standards" (incorporated by reference—see 40 CFR 60.17) Class 6 (or better). Daily before use, the field balance must measure the weight within $\pm 0.5g$ of the certified mass. If the daily balance calibration check fails, perform corrective measures and repeat the check before using balance.

10.5 Analytical Balance Calibration. Perform a multipoint calibration (at least five

points spanning the operational range) of the analytical balance before the first use, and semiannually thereafter. The calibration of the analytical balance must be conducted using ASTM E617-13 "Standard Specification for Laboratory Weights and Precision Mass Standards" (incorporated by reference—see 40 CFR 60.17) Class 2 (or better) tolerance weights. Audit the balance each day it is used for gravimetric measurements by weighing at least one ASTM E617-13 Class 2 tolerance (or better) calibration weight that corresponds to 50 to 150 percent of the weight of one filter or between 1g and 5g. If the scale cannot reproduce the value of the calibration weight to within 0.5 mg of the certified mass, perform corrective measures, and conduct the multipoint calibration before use.

11.0 Analytical Procedure

11.1 Sample Analysis. For each sampling train sample run, seven individual analytical samples are generated; two for all desired metals except Hg, and five for Hg. A schematic identifying each sample container and the prescribed analytical preparation and analysis scheme is shown in Figure 29-3. The first two analytical samples, labeled Analytical Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Analytical Fraction 1A is for ICAP, ICP-MS or AAS analysis as described in sections 11.1.1 and 11.1.2, respectively. Analytical Fraction 1B is for front-half Hg analysis as described in section 11.1.3. The contents of the back-half of the train are used to prepare the third through seventh analytical samples. The third and fourth analytical samples, labeled Analytical Fractions 2A and 2B, contain the samples from the moisture removal impinger No. 1, if used, and HNO₃/H₂O₂ impingers Nos. 2 and 3. Analytical Fraction 2A is for ICAP, ICP-MS or AAS analysis for target metals, except Hg. Analytical Fraction 2B is for analysis for Hg. The fifth through seventh analytical samples, labeled Analytical Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty impinger No. 4 and the H₂SO₄/KMnO₄ Impingers Nos. 5 and 6. These analytical samples are for analysis for Hg as described in section 11.1.3. The total back-half Hg catch is determined from the sum of Analytical Fractions 2B, 3A, 3B, and 3C. Analytical Fractions 1A and 2A can be combined proportionally prior to analysis.

11.1.1 ICAP and ICP-MS Analysis. Analyze Analytical Fractions 1A and 2A by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in section 9.2.1. Recommended wavelengths for analysis are as shown in Table 29-2. These wavelengths represent the best combination of specificity

and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICP-MS analysis by following Method 6020 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i).

NOTE: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

11.1.2 AAS by Direct Aspiration and/or GFAAS. If analysis of metals in Analytical Fractions 1A and 2A by using GFAAS or direct aspiration AAS is needed, use Table 29-3 to determine which techniques and procedures to apply for each target metal. Use Table 29-3, if necessary, to determine techniques for minimization of interferences. Calibrate the instrument according to section 10.3 and follow the quality control procedures specified in section 9.2.2.

11.1.3 CVAAS Hg analysis. Analyze Analytical Fractions 1B, 2B, 3A, 3B, and 3C separately for Hg using CVAAS following the method outlined in Method 7470 in EPA Publication SW-846 Third Edition (November 1986) including updates I, II, IIA, IIB and III, as incorporated by reference in §60.17(i), or in *Standard Methods for Water and Wastewater Analysis*, 15th Edition, Method 303F, or, optionally using note no. 2 at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see note no. 1 at end of this section). The total amount of Hg in the aliquot shall be less than 1 µg and within the range (zero to 1000 ng) of the calibration curve. Place the sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of Method 7470 or Method 303F. (See note no. 2 at the end of this section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was di-

gested), then dilute the original sample (or a portion of it) with 0.15 percent HNO₃ (1.5 ml concentrated HNO₃ per liter aqueous solution) so that when a 1- to 10-ml aliquot of the "0.15 HNO₃ percent dilution of the original sample" is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

NOTE No. 1: When Hg levels in the sample fractions are below the in-stack detection limit given in Table 29-1, select a 10 ml aliquot for digestion and analysis as described.

NOTE No. 2: Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIAS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in this section: (*The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.*); (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

- A = Analytical detection limit, µg/ml.
- B = Liquid volume of digested sample prior to aliquotting for analysis, ml.
- C = Stack sample gas volume, dsm³.
- C_{a1} = Concentration of metal in Analytical Fraction 1A as read from the standard curve, µg/ml.
- C_{a2} = Concentration of metal in Analytical Fraction 2A as read from the standard curve, (µg/ml).
- C_s = Concentration of a metal in the stack gas, mg/dscm.
- D = In-stack detection limit, µg/m³.
- F_d = Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (see section 8.3.4.)
- F_d = Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}). For example, if a 2 ml aliquot of Analytical Fraction 1A is diluted to 10 ml to place it in the calibration range, F_d = 5).
- Hg_{sh1} = Total mass of Hg collected in the back-half of the sampling train, µg.
- Hg_{sh2} = Total mass of Hg collected in Sample Fraction 2, µg.

$Hg_{bb3(A,B,C)}$ = Total mass of Hg collected separately in Fraction 3A, 3B, or 3C, μg .

Hg_{bbh} = Blank correction value for mass of Hg detected in back-half field reagent blanks, μg .

Hg_{fh} = Total mass of Hg collected in the front-half of the sampling train (Sample Fraction 1), μg .

Hg_{fhh} = Blank correction value for mass of Hg detected in front-half field reagent blank, μg .

Hg_f = Total mass of Hg collected in the sampling train, μg .

M_{bh} = Total mass of each metal (except Hg) collected in the back-half of the sampling train (Sample Fraction 2), μg .

M_{bbh} = Blank correction value for mass of metal detected in back-half field reagent blank, μg .

M_{fh} = Total mass of each metal (except Hg) collected in the front half of the sampling train (Sample Fraction 1), μg .

M_{fhh} = Blank correction value for mass of metal detected in front-half field reagent blank, μg .

M_i = Total mass of each metal (separately stated for each metal) collected in the sampling train, μg .

M_i = Total mass of that metal collected in the sampling train, μg ; (substitute Hg, for M_i for the H_g calculation).

Q_{bb2} = Quantity of Hg, μg , TOTAL in the ALIQUOT of Analytical Fraction 2B selected for digestion and analysis.

NOTE: For example, if a 10 ml aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to section 11.1.3 and its notes nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{bb2} .

$Q_{bb3(A,B,C)}$ = Quantity of Hg, μg , TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, or 3C selected for digestion and analysis (see notes in sections 12.7.1 and 12.7.2 describing the quantity "Q" and calculate similarly).

Q_{bh} = Quantity of Hg, μg , TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis.

NOTE: For example, if a 10 ml aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to section 11.1.3 and its notes nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{bh} .

V_a = Total volume of digested sample solution (Analytical Fraction 2A), ml (see section 8.3.4.1 or 8.3.4.2, as applicable).

V_{f1B} = Volume of aliquot of Analytical Fraction 1B analyzed, ml.

NOTE: For example, if a 1 ml aliquot of Analytical Fraction 1B was diluted to 50 ml with 0.15 percent HNO_3 as described in section 11.1.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml was

digested according to section 11.1.3 and analyzed, V_{f1B} would be 0.02 ml.

V_{f2B} = Volume of Analytical Fraction 2B analyzed, ml.

NOTE: For example, if 1 ml of Analytical Fraction 2B was diluted to 10 ml with 0.15 percent HNO_3 as described in section 11.1.3 to bring it into the proper analytical range, and then 5 ml of that 10 ml was analyzed, V_{f2B} would be 0.5 ml.

$V_{3(A,B,C)}$ = Volume, separately, of Analytical Fraction 3A, 3B, or 3C analyzed, ml (see previous notes in sections 12.7.1 and 12.7.2, describing the quantity "V" and calculate similarly).

$V_{m(std)}$ = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

$V_{soln,1}$ = Total volume of digested sample solution (Analytical Fraction 1), ml.

$V_{soln,1}$ = Total volume of Analytical Fraction 1, ml.

$V_{soln,2}$ = Total volume of Sample Fraction 2, ml.

$V_{soln,3(A,B,C)}$ = Total volume, separately, of Analytical Fraction 3A, 3B, or 3C, ml.

$K_4 = 10^{-3} \text{ mg}/\mu\text{g}$.

12.2 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in section 12.3 of Method 5.

12.3 Volume of Water Vapor and Moisture Content. Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_w of the stack gas. Use Equations 5-2 and 5-3 of Method 5.

12.4 Stack Gas Velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

12.5 In-Stack Detection Limits. Calculate the in-stack method detection limits shown in Table 29-4 using the conditions described in section 13.3.1 as follows:

$$A \times \frac{B}{C} = D \quad \text{Eq. 29-1}$$

12.6 Metals (Except Hg) in Source Sample.
12.6.1 Analytical Fraction 1A, Front-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Sample Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{al} F_d V_{soln,1} \quad \text{Eq. 29-2}$$

NOTE: If Analytical Fractions 1A and 2A are combined, use proportional aliquots. Then make appropriate changes in Equations 29-2 through 29-4 to reflect this approach.

12.6.2 Analytical Fraction 2A, Back-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation:

$$M_{bh} = C_{a2} F_a V_a \quad \text{Eq. 29-3}$$

12.6.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_{fh} - M_{fbb}) + (M_{bh} - M_{bbh}) \quad \text{Eq. 29-4}$$

NOTE: If the measured blank value for the front half (M_{fbb}) is in the range 0.0 to "A" μg (where "A" μg equals the value determined by multiplying 1.4 $\mu\text{g}/\text{in.}^2$ times the actual area in in.^2 of the sample filter), use M_{fbb} to correct the emission sample value (M_{fh}); if M_{fbb} exceeds "A" μg , use the greater of I or II:

I. "A" μg .

II. The lesser of (a) M_{fbb} , or (b) 5 percent of M_{fh} . If the measured blank value for the back-half (M_{bbh}) is in the range 0.0 to 1 μg , use M_{bbh} to correct the emission sample value (M_{bh}); if M_{bbh} exceeds 1 μg , use the greater of I or II:

I. 1 μg .

II. The lesser of (a) M_{bbh} , or (b) 5 percent of M_{bh} .

12.7 Hg in Source Sample.

12.7.1 Analytical Fraction 1B; Front-Half Hg. Calculate the amount of Hg collected in the front-half, Sample Fraction 1, of the sampling train by using Equation 29-5:

$$\text{Hg}_{fh} = \frac{Q_{fh}}{V_{f1B}} (V_{\text{soln},1}) \quad \text{Eq. 29-5}$$

12.7.2 Analytical Fractions 2B, 3A, 3B, and 3C; Back Half Hg.

12.7.2.1 Calculate the amount of Hg collected in Sample Fraction 2 by using Equation 29-6:

$$\text{Hg}_{bh2} = \frac{Q_{bh2}}{V_{f2B}} (V_{\text{soln},2}) \quad \text{Eq. 29-6}$$

12.7.2.2 Calculate each of the back-half Hg values for Analytical Fractions 3A, 3B, and 3C by using Equation 29-7:

$$\text{Hg}_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}} (V_{\text{soln},3(A,B,C)}) \quad \text{Eq. 29-7}$$

12.7.2.3 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 29-8:

$$\text{Hg}_{bh} = \text{Hg}_{bh2} + \text{Hg}_{bh3A} + \text{Hg}_{bh3B} + \text{Hg}_{bh3C} \quad \text{Eq. 29-8}$$

12.7.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 29-9:

$$\text{Hg}_t = (\text{Hg}_{fh} - \text{Hg}_{fbb}) + (\text{Hg}_{bh} - \text{Hg}_{bbh}) \quad \text{Eq. 29-9}$$

NOTE: If the total of the measured blank values ($\text{Hg}_{fbb} + \text{Hg}_{bbh}$) is in the range of 0.0 to 0.6 μg , then use the total to correct the sample value ($\text{Hg}_{fh} + \text{Hg}_{bh}$); if it exceeds 0.6 μg , use the greater of I. or II:

I. 0.6 μg .

II. The lesser of (a) ($\text{Hg}_{fbb} + \text{Hg}_{bbh}$), or (b) 5 percent of the sample value ($\text{Hg}_{fh} + \text{Hg}_{bh}$).

12.8 Individual Metal Concentrations in Stack Gas. Calculate the concentration of

each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 29-10:

$$C_s = \frac{K_4 M_t}{V_{m(\text{std})}} \quad \text{Eq. 29-10}$$

12.9 Isokinetic Variation and Acceptable Results. Same as Method 5, sections 12.11 and 12.12, respectively.

13.0 Method Performance

13.1 Range. For the analysis described and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per ml (ng/ml) to micrograms per ml ($\mu\text{g/ml}$) range in the final analytical solution can be analyzed using this method. Samples containing greater than approximately 50 $\mu\text{g/ml}$ As, Cr, or Pb should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 $\mu\text{g/ml}$ of Cd should be diluted to that level before analysis.

13.2 Analytical Detection Limits.

NOTE: See section 13.3 for the description of in-stack detection limits.

13.2.1 ICAP analytical detection limits for the sample solutions (based on *SW-846*, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Co (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). ICP-MS analytical detection limits (based on *SW-846*, Method 6020) are lower generally by a factor of ten or more. Be is lower by a factor of three. The actual sample analytical detection limits are sample dependent and may vary due to the sample matrix.

13.2.2 The analytical detection limits for analysis by direct aspiration AAS (based on *SW-846*, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Co (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml).

13.2.3 The detection limit for Hg by CVAAS (on the resultant volume of the digestion of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2 ng/ml, depending upon the type of CVAAS analytical instrument used. 13.2.4 The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Co (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

13.3 In-stack Detection Limits.

13.3.1 For test planning purposes in-stack detection limits can be developed by using

the following information: (1) The procedures described in this method, (2) the analytical detection limits described in section 13.2 and in *SW-846*, (3) the normal volumes of 300 ml (Analytical Fraction 1) for the front-half and 150 ml (Analytical Fraction 2A) for the back-half samples, and (4) a stack gas sample volume of 1.25 m^3 . The resultant in-stack method detection limits for the above set of conditions are presented in Table 29-1 and were calculated by using Eq. 29-1 shown in section 12.5.

13.3.2 To ensure optimum precision/resolution in the analyses, the target concentrations of metals in the analytical solutions should be at least ten times their respective analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, these concentrations can be as low as approximately three times the respective analytical detection limits without seriously impairing the precision of the analyses. On at least one sample run in the source test, and for each metal analyzed, perform either repetitive analyses, Method of Standard Additions, serial dilution, or matrix spike addition, etc., to document the quality of the data.

13.3.3 Actual in-stack method detection limits are based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be improved over those shown in Table 29-1 for a specific test by either increasing the sampled stack gas volume, reducing the total volume of the digested samples, improving the analytical detection limits, or any combination of the three. For extremely low levels of Hg only, the aliquot size selected for digestion and analysis can be increased to as much as 10 ml, thus improving the in-stack detection limit by a factor of ten compared to a 1 ml aliquot size.

13.3.3.1 A nominal one hour sampling run will collect a stack gas sampling volume of about 1.25 m^3 . If the sampling time is increased to four hours and 5 m^3 are collected, the in-stack method detection limits would be improved by a factor of four compared to the values shown in Table 29-1.

13.3.3.2 The in-stack detection limits assume that all of the sample is digested and the final liquid volumes for analysis are the normal values of 300 ml for Analytical Fraction 1, and 150 ml for Analytical Fraction 2A. If the volume of Analytical Fraction 1 is reduced from 300 to 30 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of ten. If the volume of Analytical Fraction 2A is reduced from 150 to 25 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of six. Matrix effect checks are necessary on sample analyses and typically are of much greater significance for samples that have been concentrated to

less than the normal original sample volume. Reduction of Analytical Fractions 1 and 2A to volumes of less than 30 and 25 ml, respectively, could interfere with the redissolving of the residue and could increase interference by other compounds to an intolerable level.

13.3.3.3 When both of the modifications described in sections 13.3.3.1 and 13.3.3.2 are used simultaneously on one sample, the resultant improvements are multiplicative. For example, an increase in stack gas volume by a factor of four and a reduction in the total liquid sample digested volume of both Analytical Fractions 1 and 2A by a factor of six would result in an improvement by a factor of twenty-four of the in-stack method detection limit.

13.4 Precision. The precision (relative standard deviation) for each metal detected in a method development test performed at a sewage sludge incinerator were found to be as follows:

Sb (12.7 percent), As (13.5 percent), Ba (20.6 percent), Cd (11.5 percent), Cr (11.2 percent), Cu (11.5 percent), Pb (11.6 percent), P (14.6 percent), Se (15.3 percent), Tl (12.3 percent), and Zn (11.8 percent). The precision for Ni was 7.7 percent for another test conducted at a source simulator. Be, Mn, and Ag were not detected in the tests. However, based on the analytical detection limits of the ICAP for these metals, their precisions could be similar to those for the other metals when detected at similar levels.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Alternative Analyzer. Samples may also be analyzed by cold vapor atomic fluorescence spectrometry.

16.2 [Reserved]

17.0 References

1. Method 303F in *Standard Methods for the Examination of Water Wastewater*, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street N.W., Washington, D.C. 20036.

2. EPA Methods 6010, 6020, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. SW-846, Third Edition, November 1986, with updates I, II, IIA, IIB and III. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, DC 20460.

3. EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

4. EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1991.

5. EPA Method 101A, Code of Federal Regulations, Title 40, Part 61, Appendix B, July 1, 1991.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 29-1—IN STACK METHOD DETECTION LIMITS (UG/M³) FOR THE FRONT-HALF, THE BACK HALF, AND THE TOTAL SAMPLING TRAIN USING ICAP, GFAAS, AND CVAAS

Metal	Front-half: probe and filter	Back-half: impingers 1-3	Back-half: impingers 4-6 ^a	Total train
Antimony	¹ 7.7 (0.7)	¹ 3.8 (0.4)	¹ 11.5 (1.1)
Arsenic	¹ 12.7 (0.3)	¹ 6.4 (0.1)	¹ 19.1 (0.4)
Barium	0.5	0.3	0.8
Beryllium	¹ 0.07 (0.05)	¹ 0.04 (0.03)	¹ 0.11 (0.08)
Cadmium	¹ 1.0 (0.02)	¹ 0.5 (0.01)	¹ 1.5 (0.03)
Chromium	¹ 1.7 (0.2)	¹ 0.8 (0.1)	12.5 (0.3)
Cobalt	¹ 1.7 (0.2)	¹ 0.8 (0.1)	¹ 2.5 (0.3)
Copper	1.4	0.7	2.1
Lead	¹ 10.1 (0.2)	15.0 (0.1)	¹ 15.1 (0.3)
Manganese	¹ 0.5 (0.2)	¹ 0.2 (0.1)	¹ 0.7 (0.3)
Mercury	² 0.06	² 0.3	² 0.2	² 0.56
Nickel	3.6	1.8	5.4
Phosphorus	18	9	27
Selenium	¹ 18 (0.5)	¹ 9 (0.3)	127 (0.8)
Silver	1.7	0.9 (0.7)	2.6
Thallium	¹ 9.6 (0.2)	¹ 4.8 (0.1)	¹ 14.4 (0.3)
Zinc	0.5	0.3	0.8

^a Mercury analysis only.
¹ Detection limit when analyzed by ICAP or GFAAS as shown in parentheses (see section 11.1.2).
² Detection limit when analyzed by CVAAS, estimated for Back-half and Total Train. See sections 13.2 and 11.1.3. Note: Actual method in-stack detection limits may vary from these values, as described in section 13.3.3.