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Evaluation of Two Methods for the Measurement of Mercury Emissions in Exhaust Gases from a Municipal Waste Combustor

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EVALUATION OF TWO METHODS FOR THE MEASUREMENT OF MERCURY EMISSIONS IN EXHAUST GASES FROM A MUNICIPAL WASTE COMBUSTOR

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1.0 INTRODUCTION

1.1 BACKGROUND

Section 129 of the 1990 Clean Air Act Amendments requires the U.S. Environmental Protection Agency (EPA) to promulgate mercury (Hg) emission limits for municipal waste combustion (MWC) facilities. Section 129(c)(3) specifies that the test methods and procedures required as part of these regulations must be validated on solid waste incineration units. The two existing EPA test methods for sampling and analysis of Hg emissions are Method 101A "Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators" and Draft Method 29 for multiple metals (MM) "Determination of Metals Emissions from Stationary Sources." Both of these methods are modifications of EPA Method 5 for determining particulate emissions from stationary sources, but EPA has not field validated either method on an MWC.

Radian Corporation was contracted by the EPA's Air and Energy Engineering Research Laboratory (AEERL) to conduct tests on one of the two MWC units at the Ogden Martin Systems of Stanislaus, Inc. (OMSS) facility in Crows Landing, CA. The original objective of the tests was to determine the effect of activated carbon injection on Hg emissions.[1] The AEERL work assignment was modified before testing began to include work for the Emission Measurement Branch (EMB) of EPA's Office of Air Quality Planning and Standards. The primary objective of the EMB work was to assess the precision of Method 101A and the MM method

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[1] A separate EPA report discussing the carbon injection testing is available and is entitled "OMSS Field Test Report on Carbon Injection for Mercury Control."

for determining Hg emissions and the MM method for determining cadmium (Cd) and lead (Pb) emissions from MWC's. A secondary objective of the testing was to determine whether there is a difference in the average measured Hg concentrations between the two methods. This difference in average values between methods is referred to in this report as inter-method bias. Radian conducted field tests at OMSS from July 22 through August 10, 1991.

1.2 TEST DESIGN

1.2.1 Plant Description and Operation

The OMSS facility, which began operation in 1988, consists of two identical Martin GmbH mass burn waterwall (MB/WW) combustors, each of which is capable of combusting 400 tons per day (tpd) of municipal solid waste (MSW). Each unit is equipped with ammonia injection into the furnace, a spray dryer (SD), and a fabric filter (FF) to control emissions. The facility normally operates at full capacity 24 hours per day. All testing was conducted on Unit No. 2.

1.2.2 Test Matrix

All of the Method 101A and the MM method test data contained in this report were collected at the stack, downstream of all control devices. Two dual-train systems, each with side-by-side nozzles, were used to validate Method 101A and the MM method. The two dual-trains were operated through perpendicular ports, with inverse traversing, taking simultaneous samples during three runs at each of five plant operating conditions. Table 1-1 presents the test conditions for these validation tests. Each test run lasted approximately one hour. Test conditions were determined by the requirements of the AEERL control system evaluation effort and are not of specific importance to method validation, other than to provide a range of emission levels for sampling.

1.3 CONCLUSIONS

The following conclusions were reached based on the testing and analysis conducted on the OMSS MWC.

TABLE 1-1. TEST CONDITIONS MATRIX FOR OMSS EMISSISONS CONTROL FIELD TEST (1991)

CONDITION NUMBER	OPERATING PARAMETERS					
	THERMAL $deNO_x$	CARBON FEED RATE (lb/hr)	CARBON[a] (Raw Material)	FABRIC FILTER TEMPERATURE[b]	CARBON INJECTION LOCATION[c]	LIME FEED RATE[d]
4	Normal	Off	--	Normal	--	Normal
5	Off	Off	--	Normal	--	Normal
6	Normal	12.1	Coal	Normal	S.D. Inlet	Normal
8	Normal	6.1	Coal	Normal	S.D. Inlet	Normal
9	Normal	2.8	Lignite	Normal	S.D. Inlet	Normal

[a] Lignite Raw Material = DARCO FGD, Surface Area = 600 m^2/g.
Coal Raw Material = DARCO PC100, Surface Area = 950 m^2/g.
[b] Fabric filter outlet temperatures averaged 275-292°F during individual runs.
[c] S.D. Inlet = Spray Dryer Inlet.
[d] Lime feed rate based on outlet SO_2 levels, which averaged 3-11 ppmv at 7% O_2 during individual runs (equal to 89-96% SO_2 reduction).

1.3.1 Method Precision for Mercury

At measured Hg concentrations above approximately 200 micrograms per dry standard cubic meter (μg/dscm), the relative standard deviation (RSD) of Method 101A was 15.1 percent and the RSD of the MM method was 9.8 percent. At measured concentrations less than 200 μg/dscm, the RSD of Method 101A was 40.7 percent, and the RSD of the MM method was 20.7 percent. Both methods were demonstrated to be sufficiently precise in the determination of Hg concentrations of MWC stack gas to meet the EPA criterion of 50 percent RSD in "Protocol for the Field Validation of Emission Concentrations from Stationary Sources," EPA 450/4-90-015, April 1991 (hereafter referred to as the "validation protocol"). The variance of the MM method was lower than for Method 101A, but this difference could have been due to random variation in measurements, rather than real differences.

1.3.2 Method Comparison

The validation protocol allows alternative methods to be evaluated against validated methods to determine inter-method bias. Although no decision on the validation status of either method for MWC's has been made at this time, an assessment of inter-method bias will yield useful comparison information.

The MM method consistently yielded higher Hg concentration measurements than Method 101A. The difference in measured concentration averaged 39 μg/dscm and is statistically significant at the 80 percent confidence level specified in the validation protocol. The bias correction factor (CF) exceeds the ±10 percent criteria allowed by the validation protocol.

1.3.3 Method Precision for Cadmium and Lead

Levels of Cd and Pb measured by the MM method during this test program were near or below the detection limits in many cases. Measured concentrations of Cd were especially low. Statistical analysis using two alternative assumptions regarding nondetected sample concentrations indicate that the precision of the method is probably sufficient to meet the EPA protocol of 50 percent RSD. However, a significant uncertainty is associated

with any conclusions about the Cd and Pb measurements with the MM method because of their proximity to the detection limits.

1.4 REPORT ORGANIZATION

Section 2.0 of this report details test design, including a description of the methodologies used for interpretation of the test data, the facility tested, and the sampling and analysis methods used. Section 3.0 details the results of tests of Method 101A for Hg. Section 4.0 details the MM test results for Hg, Cd, and Pb. Section 5.0 is a comparison of the results of the two methods in determining Hg emissions. Section 6.0 provides a detailed review of the Method 101A and MM sampling and analytical procedures used during the testing. Section 7.0 covers quality assurance/quality control (QA/QC) procedures used to ensure test data quality. Supporting documentation for the sampling and analytical data are provided in the appendices.

2.0 TEST DESIGN

2.1 METHOD VALIDATION REQUIREMENTS

Both Method 101A and the MM method were evaluated for Hg measurement precision. The Hg concentrations measured by each method were also compared to see if there was a significant difference in their values. The precision of the MM method for measuring Cd and Pb concentrations was also evaluated. The validation protocol for quadruplet sampling trains was used as a source for specific statistical techniques. The calculations and equations used are presented in Sections 3.0, 4.0, and 5.0 of this report.

Method precision statistics include sampling, recovery, and analysis variations. The primary statistics used to evaluate method precision are the RSD and variance. The RSD is the calculated method standard deviation divided by the mean value of the test concentrations. The validation protocol specifies an upper limit of 50 percent for the RSD in method validation studies. The method variance and standard deviation were calculated as intermediate values in the determination of RSD for each sampling method. To eliminate the effect of process variation on method precision statistics, estimates of precision were based on the differences in concentrations measured by sampling train pairs within single runs.

In addition to statistical comparisons outlined in the validation protocol, the variances of the two Hg sampling methods were compared by using a one-tailed F test to determine whether the variance of the Method 101A measurements was significantly greater than for the MM method.

Finally, Hg concentrations determined by the MM method were compared to those determined by Method 101A by comparing the mean values using the t statistic at the 80 percent confidence level.

Assessment of method accuracy was beyond the scope of this project, as known concentrations of Hg were not measured in the field. However, laboratory analysis accuracy was assessed using matrix spikes and laboratory control samples. Results of these tests are covered in Section 7.0.

2.2 FACILITY DESCRIPTION

2.2.1 Overview

The Stanislaus County MWC is owned and operated by OMSS. The plant began operation in 1988 and is located in Crows Landing, CA. The facility consists of two identical Martin GmbH mass burn waterwall (MB/WW) combustors, each of which is capable of combusting 400 tpd of municipal solid waste (MSW). The MSW burned at this plant is received from the City of Modesto and from Stanislaus County. Steam produced by the two boilers is used to generate electricity which is sold to Pacific Gas & Electric Company. The facility normally operates at full capacity, 24 hours per day. A plot plan of the facility is shown in Figure 2-1.

The air pollution control on each combustor consists of an Exxon Thermal DeNO$_x$® system and a Fläkt SD/FF system. A general schematic of the system is shown in Figure 2-2. The Thermal DeNO$_x$® system injects NH_3 into the upper furnace to control NO_x emissions. Flue gas leaving the combustor and boiler is routed to the top of the SD through a 10 foot (ft) x 3.5 ft duct that contains two sharp turns. The primary duct section between the economizer and SD is vertical and is approximately 40 ft long. Just prior to entering the SD, the flue gas is equally distributed to three inlet dispersers. At the exit of each disperser, slaked lime slurry is injected through dual-fluid nozzles. The slurry feed rate is controlled according to the stack SO_2 concentration, and the

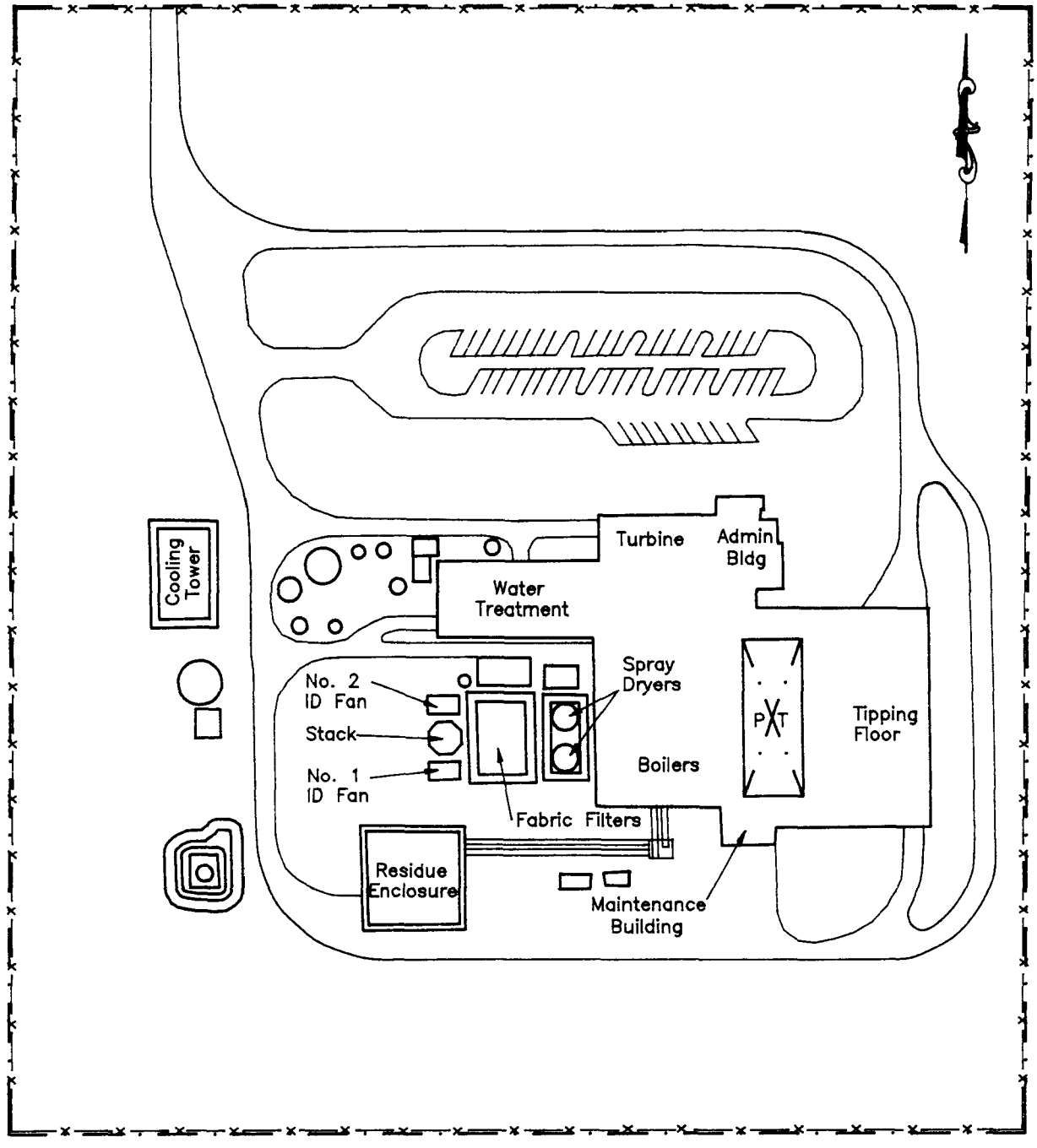

Figure 2-1. General Plot Plan
Ogden Martin Systems of Stanislaus, Inc. (1991)

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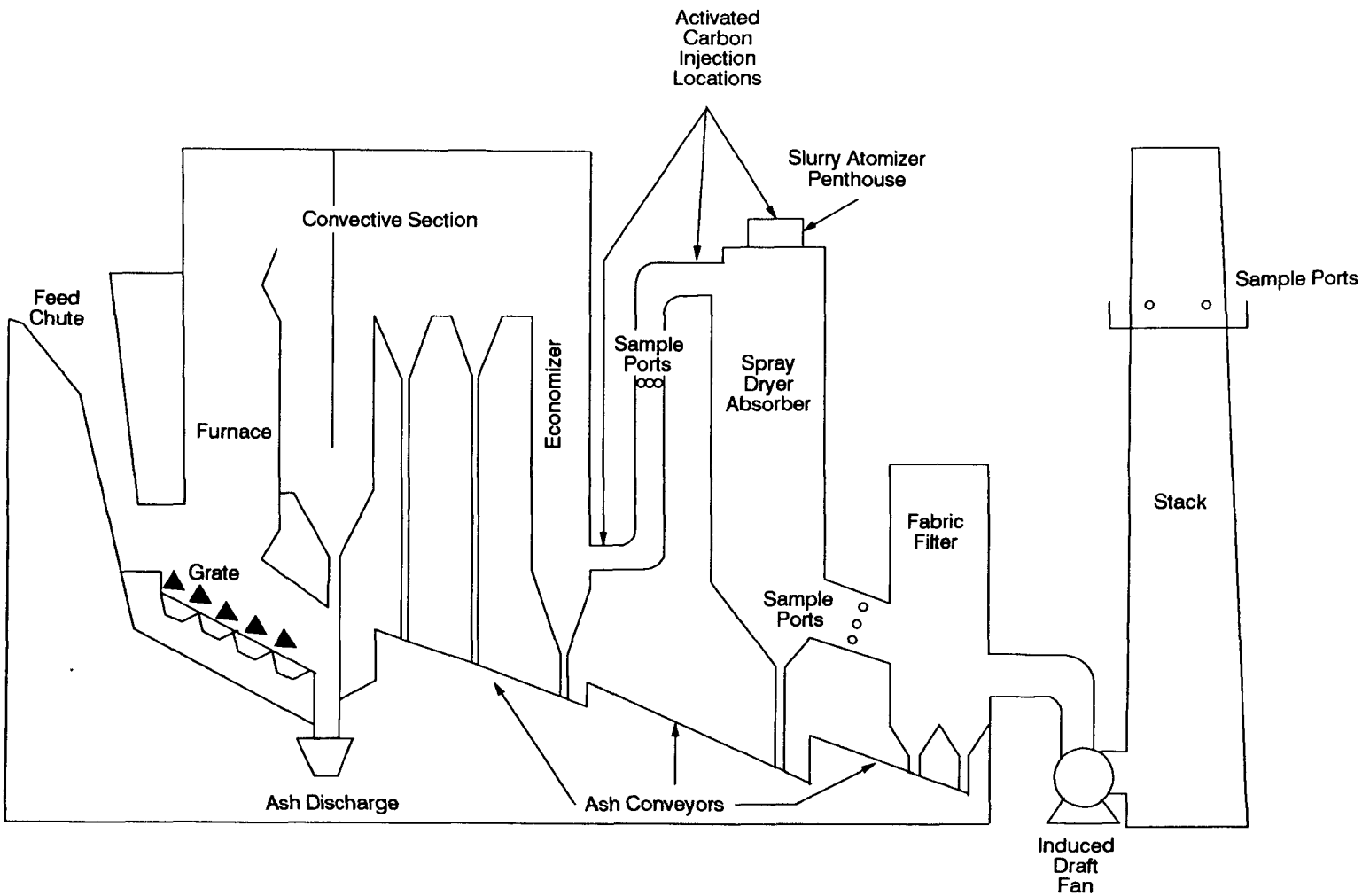

Figure 2-2. Process flow diagram for the Stanislaus County MWC.

dilution water flow is controlled according to the SD outlet temperature. A flue gas residence time in the SD of roughly 15 seconds is provided to dry the slurry and to neutralize acid gases. Following the SD, the flue gas enters the pulse-jet FF at a design flow rate of 94,000 cubic feet per minute (cfm) at 285°F (2,700 m^3/min at 140°C). The FF has six compartments of Teflon®-coated fiberglass bags (1,596 bags total) and a net air-to-cloth ratio of 3.2 cfm/ft^2. The cleaning cycle of the bags is approximately 2 minutes per compartment, equal to 12 minutes for the entire FF.

2.2.2 Sampling Locations

All flue gas samples were taken from the stack of Unit 2. Flue gas exits the FF on the east side of the unit and is directed into an induced draft (ID) fan located at the base of the stack. The in-house continuous emissions monitoring system (CEMS) stack probes are located on the downstream side of the ID fan in the stack breeching. The gas then enters the stack flue and is emitted into the atmosphere approximately 140 feet above ground level. The stack sampling platform is located approximately halfway up the stack as shown in Figure 2-3.

The flues for Units 1 and 2 are located in the same stack shell. Each flue has an inside diameter of 5 ft 3 inches. The two ports used for sampling were 6-inch flanged pipe ports with coplanar axes, perpendicular to each other and to the flue axis. The nipple length of the ports is approximately 20 inches.

The two ports meet the EPA Method 1 criterion of being perpendicular and of being eight duct diameters downstream and two duct diameters upstream from the closest flow disturbances. A total of 12 sample points was used. The stack sampling location was accessed from the ground by a ladder located on the outside wall of the stack.

2.3 SAMPLING MATRIX

Mercury emissions testing by Method 101A and the MM method was performed during Conditions 4, 5, 6, 8, and 9 of

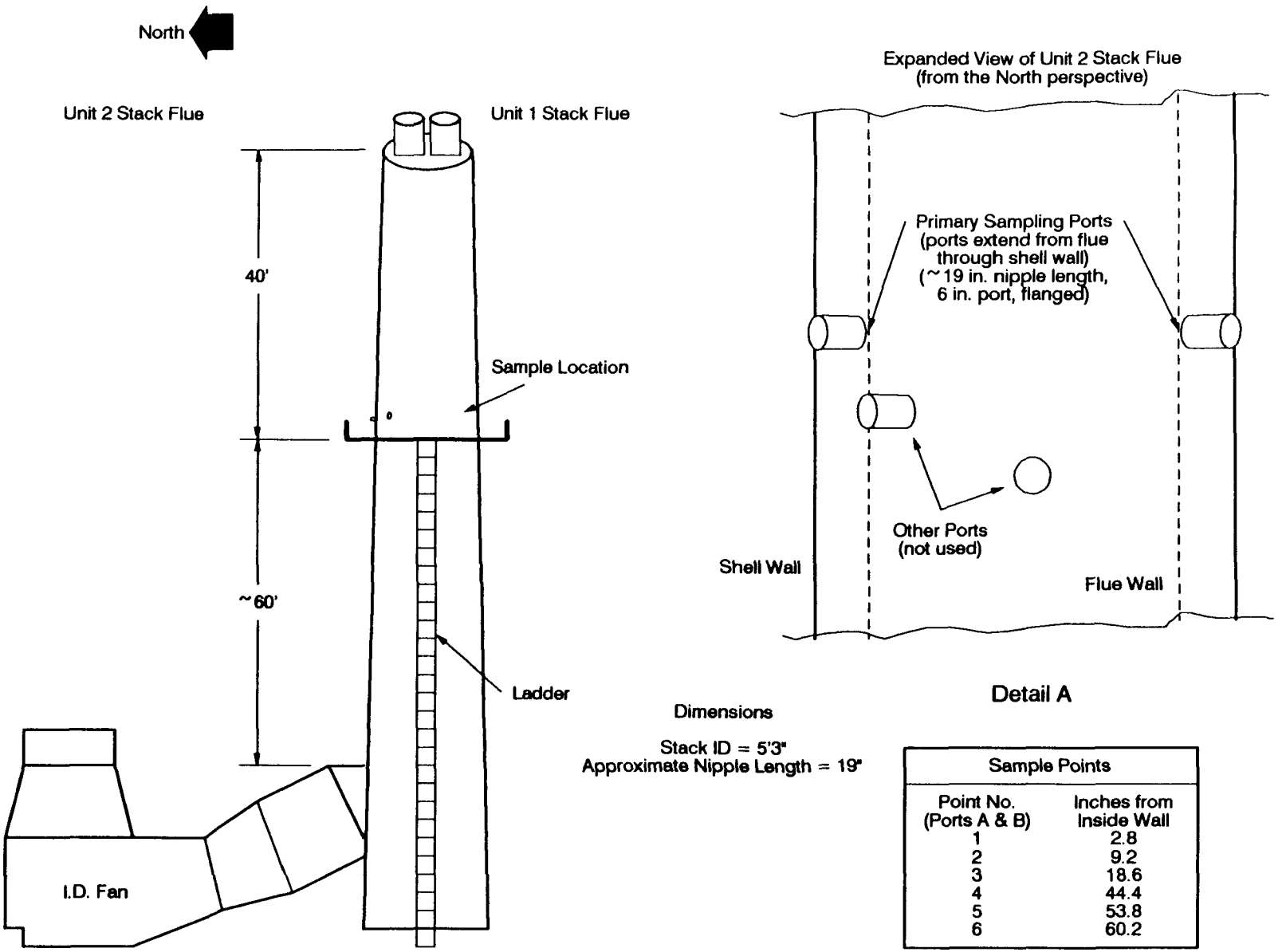

Figure 2-3. Stack Gas Sampling Ports
Ogden Martin Systems of Stanislaus, Inc. (1991)

the overall OMSS test program. Operating parameters for each test condition are shown in Table 1-1. Conditions 4 and 5 were baseline tests run with no carbon injection for control of Hg emissions. Conditions 6, 8, and 9 were run with carbon injection at the spray dryer inlet. The carbon feed rate and carbon type were varied between Conditions 6, 8, and 9. Condition 5 was conducted with the Thermal $DeNO_x$® system out of operation; the system was operating during Conditions 4, 6, 8, and 9. As a result of these process changes, a broad range of Hg levels was expected at the stack.

Three sampling runs were made for each operating condition. In each sampling run, two samples were collected using dual Method 101A trains, and two samples were simultaneously collected from the adjacent sampling port using dual MM method sampling trains.

2.4 DESCRIPTION OF METHOD 101A

2.4.1 Background

Method 101A was developed specifically for determination of particulate and gaseous Hg emissions from sewage sludge incinerators. The method is similar to EPA Method 101, which was developed for chlor-alkali plants. Method 101A has been used to measure Hg emissions from other incineration sources, including MWC's, although its use on MWC's has not been validated by the EPA.

2.4.2 Sampling System

Method 101A for Hg emissions testing is found in 40 CFR Part 61, Appendix B. The method calls for isokinetic extraction of flue gas through a sampling train similar to the standard EPA Method 5 train. The Method 101A sampling train is shown in Figure 2-4. Although Method 101A states that the use of a sampling train filter is optional, filters were included in all of the sampling trains used during the OMSS test. After passing through the filter, the sample stream is bubbled through three impingers containing acidified potassium permanganate ($KMnO_4$) solution.

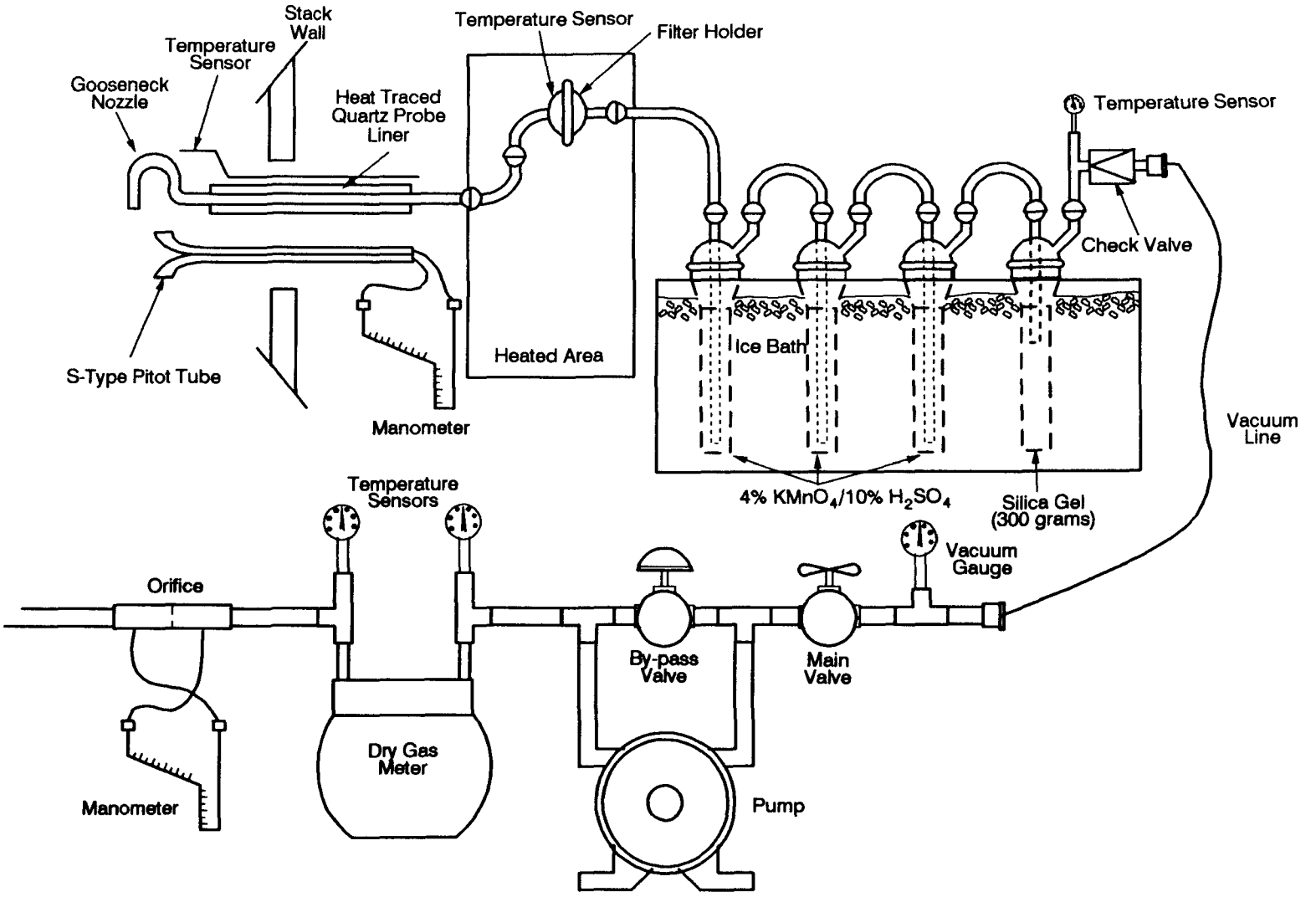

Figure 2-4. EPA Method 101A Sampling Train

In the Method 101A tests conducted at OMSS, the sample train was recovered in two fractions: the probe rinse/impinger catch and the filter. The Method 101A recovery scheme is shown in Figure 2-5. Following sample recovery, the rinse/impinger catch and filter fractions were stored in separate containers and shipped back to Radian's Perimeter Park (PPK) laboratory for analysis.

The analytical preparation procedures are shown in Figure 2-6. They consisted of filtering the rinse/impinger and filter solutions, combining the filtrates, and analyzing an aliquot by Cold Vapor Atomic Absorption Spectroscopy (CVAAS). Studies recently conducted by the EPA show that after a certain sample storage time, the laboratory filtering procedures may remove a portion of the collected Hg contained in a manganese dioxide (MnO_2) precipitate. For this test program, the analytical filters were redigested, the digestion solution was filtered, and the filtrate was analyzed for Hg by CVAAS. A graphical output of the CVAAS results is provided for each analysis.

The approximate analytical and corresponding flue gas detection limits for Hg using Method 101A are summarized in Table 2-1. A detailed discussion of Method 101A sampling and analytical procedures is presented in Section 6.1. A full description of the method is provided in Appendix A of this test report.

2.5 MULTIPLE METALS SAMPLING

2.5.1 Background

The MM method, also known as Draft Method 29, was developed by the EPA to support regulation of toxic metals emissions from incineration processes. The method was designed to measure emissions of the following 16 toxic metals: Hg, Cd, Pb, zinc (Zn), phosphorus (P), chromium (Cr), copper (Co), nickel (Ni), manganese (Mn), selenium (Se), arsenic (As), beryllium (Be), thallium (Tl), silver (Ag), antimony (Sb), and barium (Ba). The method has undergone

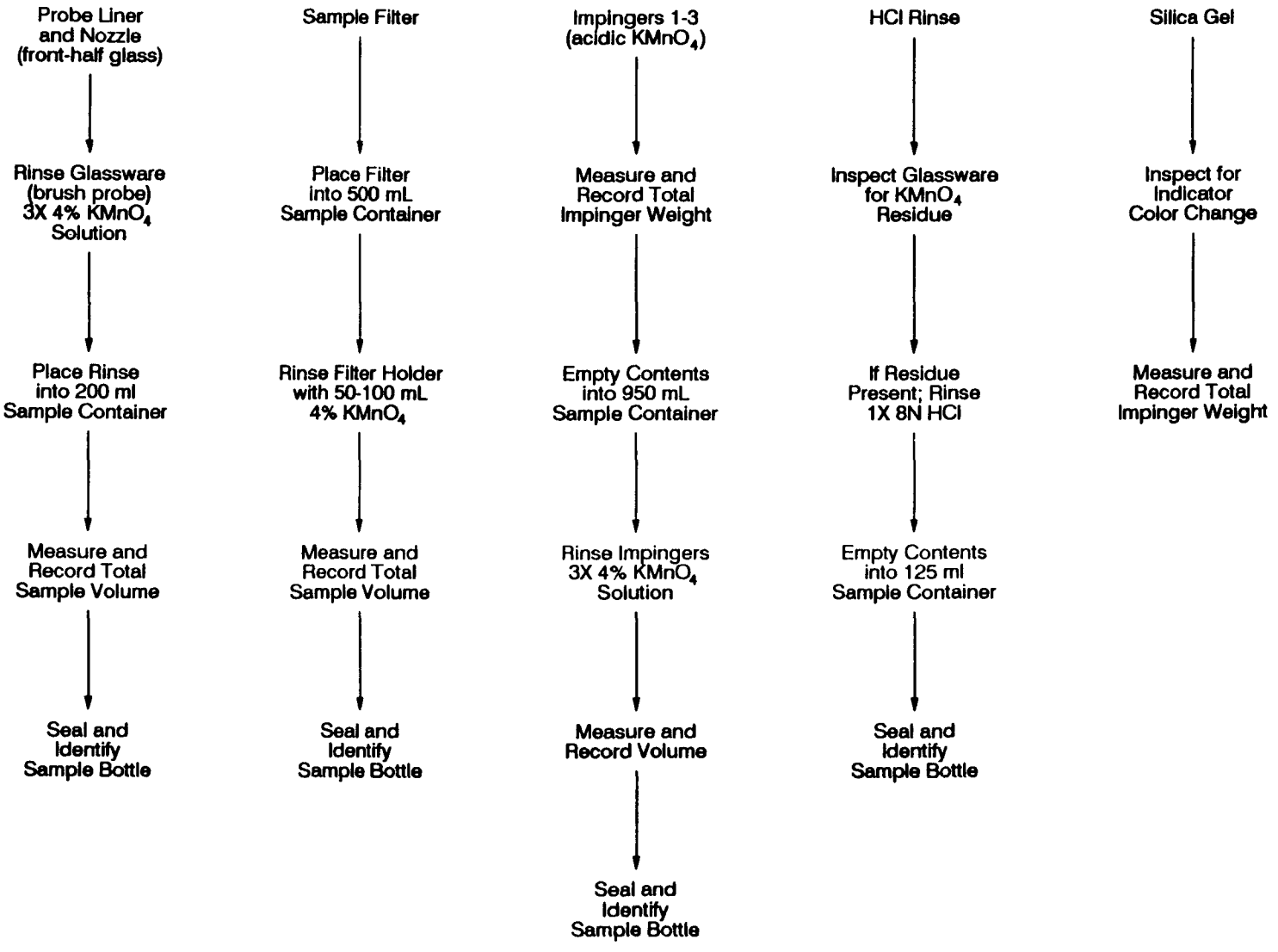

Figure 2-5. Method 101A sample recovery scheme.

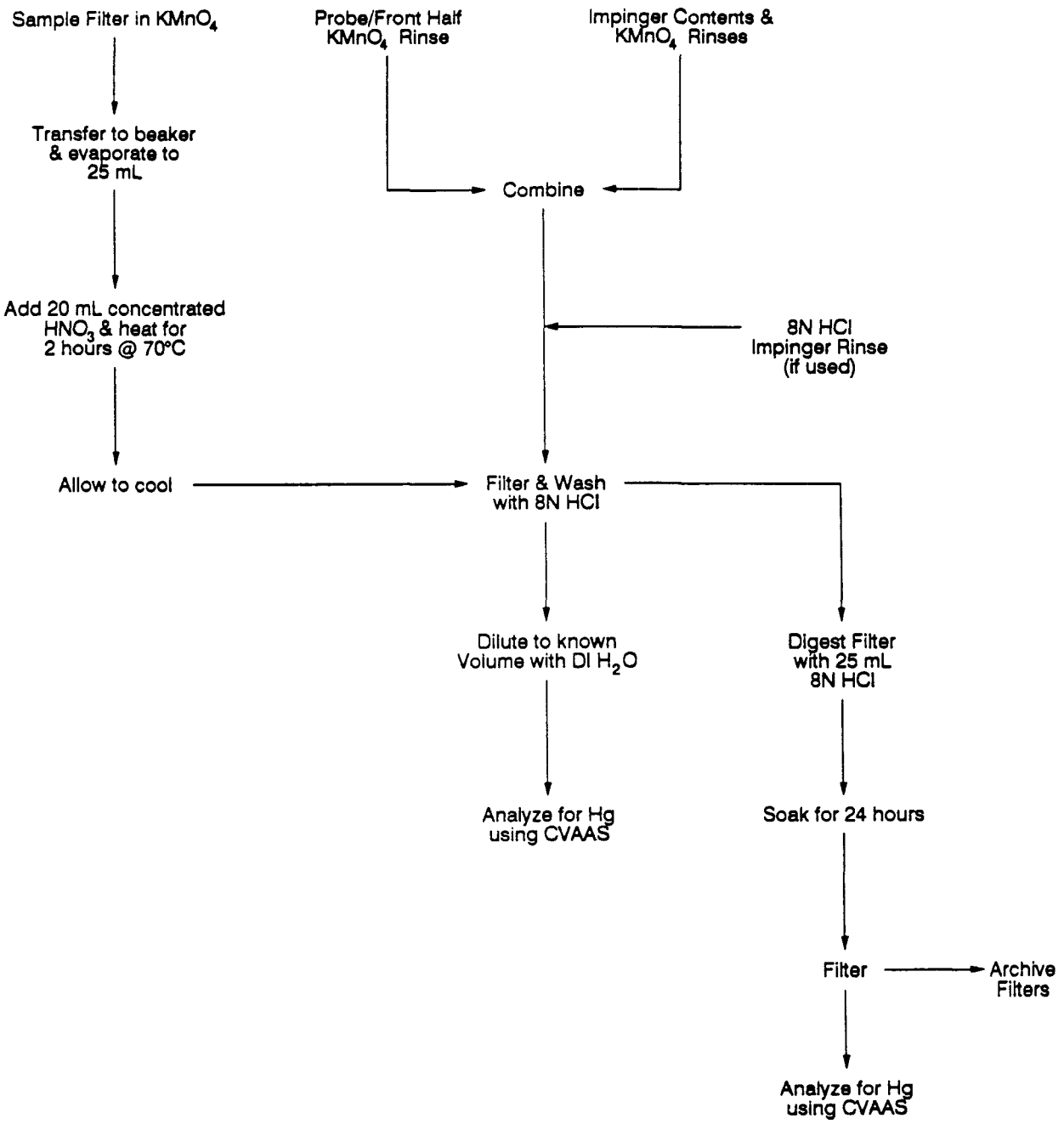

Figure 2-6. Method 101A sample preparation and analysis scheme.

TABLE 2-1. SAMPLING TIMES, MINIMUM SAMPLING VOLUMES, AND DETECTION LIMITS

Sampling Train	Sampling Time (hours)	Minimum Sample Volume (dscf)	Analyte	Detection Limit	
				Flue Gas	Analytical
101A	1[a]	30	Hg	25 μg/dscm	0.25 μg/ml
MM	1	30	Cd	0.6 μg/dscm	0.006 μg/ml
			Pb	0.2 μg/dscm	0.002 μg/ml
			Hg	25 μg/dscm	0.25 μg/ml

[a] An average sampling rate of 0.5 ft^3/min was used to calculate sampling time.

extensive laboratory testing and field evaluation, including field use at MWC's.

The OMSS test samples were analyzed for As, Cd, Cr, Pb, Hg, and Ni. Results for Cd, Pb, and Hg are presented in this report.

2.5.2 Sampling System

The MM method uses the sampling train shown in Figure 2-7. The seven-impinger train consists of a quartz nozzle/probe liner followed by a heated filter assembly with a Pallflex Tissuequartz 2500QAS filter and Teflon® filter support, a series of impingers, the usual EPA Method 5 meterbox, and a vacuum pump. The sample is not exposed to any metal surfaces in this train. The contents of the sequential impingers are: two impingers with a 5 percent nitric acid (HNO_3)/10 percent hydrogen peroxide (H_2O_2) solution, two impingers with a 4 percent $KMnO_4$/10 percent sulfuric acid (H_2SO_4) solution, and one impinger containing silica gel. Empty knockout impingers are located both before and after the HNO_3/H_2O_2 impingers. The impingers are connected together with clean glass U-tube connectors. Sampling train components are recovered in five fractions as shown in Figure 2-8.

The laboratory preparation and analysis scheme for the MM method samples is shown in Figure 2-9. The sampling train filter was digested with hydrofluoric acid (HF) and HNO_3. The front half acetone rinse was dried, dissolved in HNO_3, and combined with the front half HNO_3 rinse. This solution was combined with the filter digestion solution and aliquots were analyzed for target metals by Inductively-Coupled Plasma (ICP) spectroscopy, for Pb by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS), and for Hg by CVAAS. The HNO_3/H_2O_2 impingers fraction was digested and aliquots were analyzed by GFAAS and CVAAS. Aliquots from the $KMnO_4$ impingers and the rinse of the two empty impingers were analyzed by CVAAS for Hg.

The approximate analytical and corresponding flue gas detection limits for Hg, Cd, and Pb for the MM method are

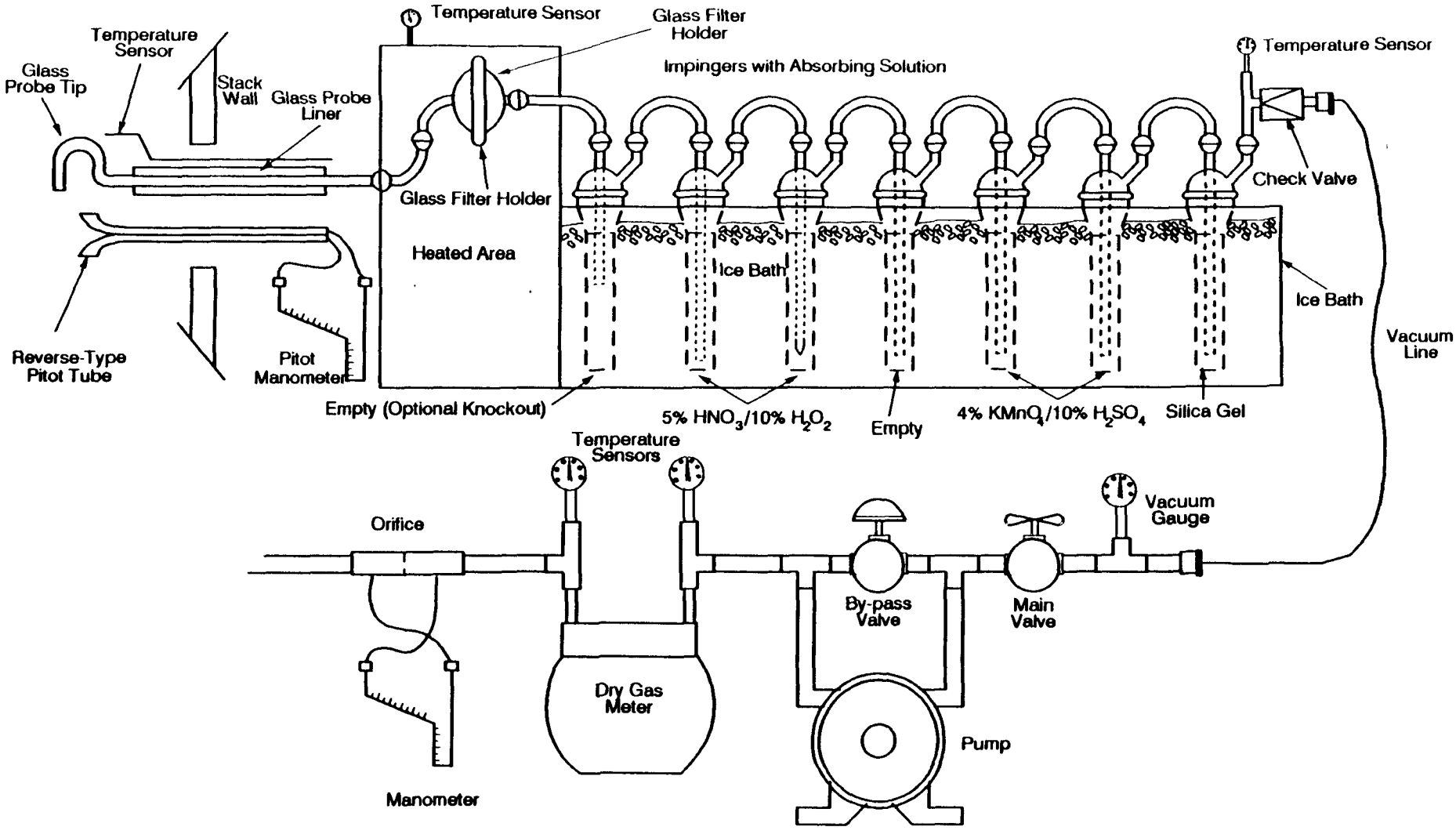

Figure 2-7. Schematic of Multiple Metals sampling train.

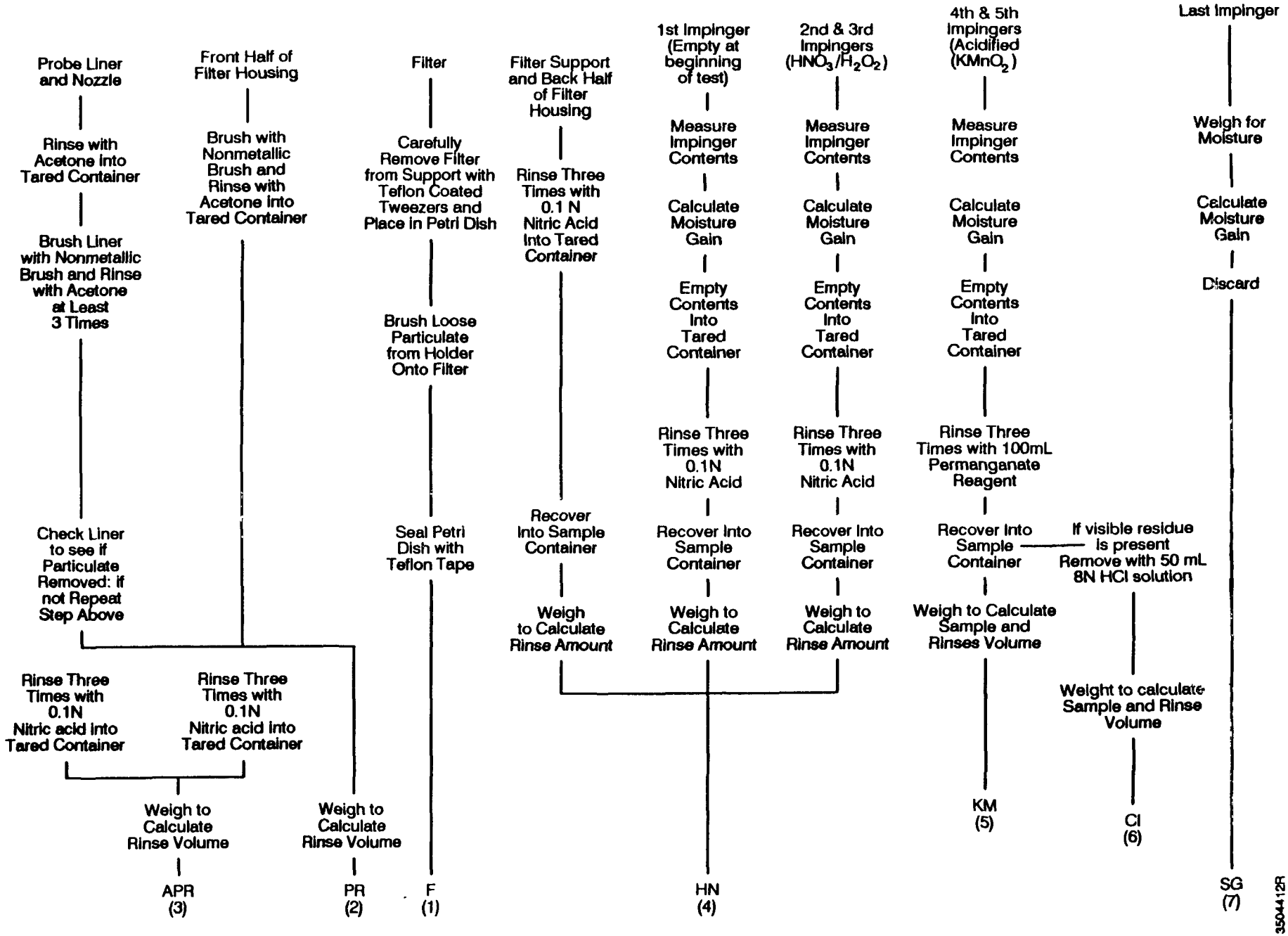

Figure 2-8. Metals sample recovery scheme (see following figure

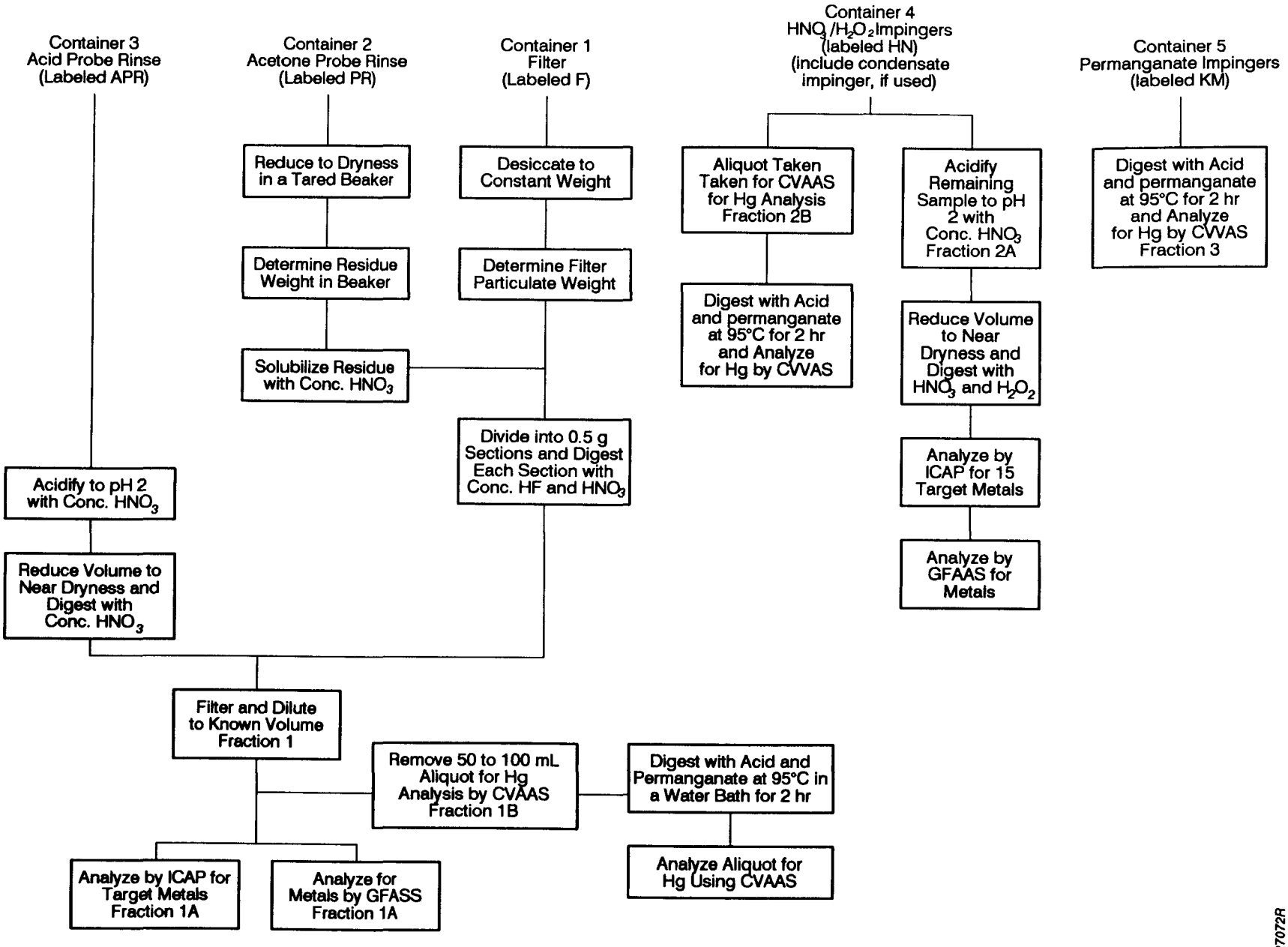

Figure 2-9. Metals Sample Preparation and Analysis Scheme

summarized in Table 2-1. A detailed discussion of the MM sampling and analytical procedures is presented in Section 6.2. A full description of the method is provided in Appendix A.

2.6 Parameters Measured

In addition to Hg, Cd, and Pb emissions, a number of operating parameters were measured. Stack gas flow rate, moisture, oxygen (O_2) concentration, carbon dioxide (CO_2) concentration, and temperature were all measured at the sampling location during each run.

2.6.1 Volumetric Flow Rate Determination by EPA Method 2

Volumetric flow rate was measured according to EPA Method 2. A Type K thermocouple and S-type pitot tube were used to measure flue gas temperature and velocity, respectively.

For EPA Method 2, the pitot tubes were calibrated before use following the directions in the method. Also, the pitots were leak-checked before and after each run.

The parameters that were measured include the pressure difference across the pitots, stack temperature, stack static pressure, and ambient pressure. A computer program was used to calculate the average velocity during the sampling period.

2.6.2 Oxygen and Carbon Dioxide Concentrations by EPA Method 3A

The O_2 and CO_2 concentrations were determined by CEMS following EPA Method 3A. Flue gas was extracted from the duct and delivered to the CEMS through heated Teflon® tubing. The sample stream was then conditioned (particulate and moisture removed) and directed to the analyzers that determine O_2 and CO_2 concentrations on a dry basis. Average concentrations were calculated for each test period.

Only the O_2 values were used for evaluating the data collected for EMB. The O_2 concentration was measured using a Thermox Model WDG III which uses an electrochemical cell. Zirconium oxide contained in the cell conducts electrons when it is hot, due to the mobility of O_2 ions in its crystal

structure. Porous platinum electrodes attached to the inside and outside of the cell provide the instrument voltage response. A difference in O_2 concentration between the sample side of the cell and the reference (outside) side of the cell produces a voltage. This response voltage is proportional to the logarithm of the O_2 concentration ratio. A linearizer circuit board is used to make the response linear. Reference gas is ambient air at 20.9 percent O_2 by volume.

2.6.3 Average Moisture Determination by EPA Method 4

The average moisture content of the flue gas was determined according to EPA Method 4. Before sampling, the initial weight of the impingers was recorded. When sampling was completed, the final weights of the impingers were recorded, and the weight gain was calculated. The weight gain and the volume of gas sampled were used to calculate the average moisture content (percent) of the flue gas. The calculations were performed by computer. Method 4 results were incorporated in all isokinetic sampling methods used during the test.

3.0 METHOD 101A RESULTS

3.1 REVIEW OF DATA

Paired samples for Hg analyses were gathered using the dual Method 101A sampling trains during each of the five operating conditions shown in Table 1-1. Three sampling runs were conducted for each condition, except for Condition 6. During Run 1 of Condition 6, one of the sampling trains was invalidated because it failed the final leak-check. A fourth run was added because of the leak-check problem.

The recovered fractions of each sample were combined and analyzed for Hg content. The results, showing Hg in μg, are shown in Table 3-1. An "R" after the run number notes the second sample collected by the dual train. The Hg recovered from the laboratory filter is also shown in Table 3-1. The Hg results at the outlet varied by test condition, with the highest levels measured during Conditions 4 and 5, which were run without carbon injection. Average Hg levels during Condition 6, 8, and 9 vary with the carbon feed rate.

There were analytical problems that resulted in the exclusion of data from two runs of Condition 4. These problems were caused by illegible labels, smudged in transit. As a result, the impinger contents for the replicate 101A train during Run 2 (2R) of Condition 4 were accidentally switched with the impinger contents of a MM train from the same run. Also during Condition 4, the HCl rinse for the replicate 101A train during Run 3 (3R) was accidentally added to the other Run 3 101A train. As a result, the Hg results from the two outlet trains were added together and reported as a single value for Run 3.

TABLE 3-1. METHOD 101A FRACTIONAL RESULTS

Condition	Run	Measured Mercury (μg) Front Half + Impingers	Analytical Filters	Total	Percentage of Total on Analytical Filters
4	1	201	2.1	203	1%
	1R	164	4.7	168	3%
	2	235	0.3	235	0.1%
	2R	--[a]	0.3	--[a]	
	3	706	24.8	730	3%
	3R	--[b]	--[b]	--[b]	
5	1	361	0.5	361	0.1%
	1R	318	6.0	324	2%
	2	207	3.1	210	1%
	2R	329	0.3	329	0.1%
	3	351	3.2	354	0.9%
	3R	287	5.7	292	2%
6	1	--[c]	--[c]	--[c]	
	1R	22.3	4.4	26.7	16%
	2	32.9	0.4	33.3	1%
	2R	31.7	1.5	33.2	5%
	3	7.8	4.0	11.8	34%
	3R	23.4	2.8	26.2	11%
	4	46.9	1.4	48.3	3%
	4R	37.1	0.7	37.8	2%
8	1	77.8	0.8	78.6	1%
	1R	34.1	2.9	37.0	8%
	2	60.1	2.9	63.0	5%
	2R	45.0	4.5	49.5	9%
	3	24.5	3.8	28.3	13%
	3R	50.5	1.9	52.4	4%
9	1	86.0	1.9	87.9	2%
	1R	148	1.8	149	1%
	2	57.8	2.6	60.4	4%
	2R	96.0	0.7	96.7	0.7%
	3	57.9	4.3	62.2	7%
	3R	79.1	1.2	80.3	1%

[a] Impinger fraction mistakenly switched with $KMnO_4$ fraction from MM train for same run.
[b] Fractions from the paired trains on Condition 4, Run 3 were accidentally combined. Mercury values are therefore the average of the two runs.
[c] Sampling train failed to pass final leak-check.

The Hg content on the laboratory filters varied from 0.3-6.0 μg on all but one run. During Condition 4, Run 3, the Hg level was 24.8 μg. The filters averaged 2.4 percent of the total Hg found in each train, and ranged from less than 1 percent to a high of 34 percent during Condition 6, Run 3. The Hg content of these filters was less than 5 percent of the total on all but 7 of the 29 trains with valid data. All 7 of these trains were from runs during which carbon was being injected and total Hg levels were less than 62 μg. The Hg levels on the laboratory filters during these 7 runs were 2.8-4.5 μg.

Mercury concentrations in the flue gas in μg/dscm at 7 percent O_2 and associated sampling train parameters for each run are shown in Table 3-2. Measured temperatures and O_2 concentrations in the flue gas are also listed in Table 3-2.

3.2 STATISTICAL ANALYSIS

Method 101A was taken to be the standard method for Hg sampling for the purposes of this test. Data from Condition 4, Runs 2 and 3, were not used in the calculation of method variance because of the problems discussed in Section 3.1.

Techniques for determining the precision of the sampling method were taken from the validation protocol. Statistics relative to the sampling method precision are shown in Table 3-3. Precision of the Method 101A data is indicated by the variance of the sample data. Variance is calculated using the following equation:

$$s^2 = \frac{\sum d_i^2}{2n} \qquad (3\text{-}1)$$

where s^2 = the variance of the sample set;

d_i = the difference between the measured Hg concentrations of the paired sample trains in a run; and

n = the number of runs.

The square root of the variance is the standard deviation, which is another common indicator of the precision

TABLE 3-2. MERCURY FLUE GAS CONCENTRATIONS AND OPERATING PARAMETERS
METHOD 101A

Cond	Run	Flue Gas Temp. (°F)	O_2 (%)	CO_2 (%)	Outlet				Outlet R			
					Hg (µg/ dscm)	Flow (dscmm)	H_2O (%)	Iso (%)	Hg (µg/ dscm)	Flow (dscmm)	H_2O (%)	Iso (%)
4	1	276.9	10.7	8.7	322.1	1666	17.5	96.2	270.3	1662	17.7	95.4
	2	275.7	10.0	9.2	354.8	1580	18.9	98.3	--[a]	1568	19.6	96.9
	3	276.1	9.9	9.3	530.7	1649	20.4	97.3	--[b]	1686	18.2	97.6
5	1	280.6	9.1	10.4	538.3	1453	19.7	101.7	505.5	1433	21.0	98.5
	2	281.9	9.0	10.2	310.6	1490	21.9	99.0	470.8	1509	20.6	102.1
	3	278.6	9.1	10.1	491.4	1564	20.6	101.4	425.1	1542	21.9	98.3
6	1	283.9	9.5	10.4	--[c]	--[c]	--[c]	--[c]	40.4	1524	20.8	98.9
	2	285.8	9.5	9.9	48.2	1603	19.5	98.1	47.0	1598	19.8	100.5
	3	284.9	9.6	10.3	16.6	1794	20.1	100.7	37.6	1617	20.7	99.4
	4	284.8	9.0	9.8	65.1	1589	20.2	101.6	52.0	1578	20.9	100.1
8	1	277.0	10.6	8.8	131.7	1642	19.5	100.8	64.4	1478	20.2	97.8
	2	276.7	10.1	9.3	91.6	1836	19.7	99.2	73.9	1680	18.8	95.7
	3	275.7	10.0	9.3	38.5	1802	18.6	107.3	79.3	1609	20.1	97.9
9	1	275.0	10.4	9.1	132.3	1675	18.6	97.5	228.4	1666	19.1	96.8
	2	276.0	10.2	9.3	80.5	1724	19.7	105.7	142.8	1706	20.7	96.4
	3	282.5	11.0	9.3	100.5	1555	20.7	102.8	131.3	1575	19.5	100.5

[a] Sample mistakenly switched with fraction from MM train.
[b] Because fractions were accidentally combined, the average value of the paired trains was calculated and reported in the outlet column of this table.
[c] Concentration is indeterminate due to leak in sampling train.

TABLE 3-3. METHOD 101A PRECISION

Test Condition	No. of Sample Pairs	Average Hg Concentration (μg/dscm)	Variance (μg/dscm)^2	Standard Deviation (μg/dscm)	RSD[a] (%)
Overall	13	188.3	2115	46.0	24.4
Without Carbon Injection (Conditions 4,5)	4	416.8	4227	65.0	15.6
With Carbon Injection (Conditions 6,8,9)	9	86.8	1177	34.3	39.5
High Carbon Injection (Condition 6)	3	44.4	102	10.1	22.8
Medium Carbon Injection (Condition 8)	3	79.9	1085	32.9	41.2
Low Carbon Injection (Condition 9)	3	136.0	2344	48.4	35.6

[a] RSD = relative standard deviation (standard deviation ÷ average concentration).

of a sampling method. The RSD is the ratio of the sample standard deviation to the mean value of the data, and is expressed as a percentage. This statistic is often used as an indicator of precision at a particular concentration level and reflects the need for more precise measurements at low data values. As shown in Table 3-3, Hg concentrations in the stack gas were lower during test conditions in which carbon was injected into the duct ahead of the SD. The variance and standard deviation of the data collected during runs with carbon injection were lower than for the data collected without carbon injection. The RSD, however, was higher with carbon injection. This reflects the impact of the lower mean Hg concentrations when carbon injection occurred. Values shown in Table 3-3 for Conditions 6, 8, and 9 were each calculated using paired sample train data from three runs and, therefore, have less statistical significance than the values derived from the pooled data for all runs with carbon injection.

3.3 CONCLUSIONS

Section 2 of the validation protocol states that "The precision of the method at the level of the emission standard shall not be greater than 50 percent relative standard deviation." As shown in Table 3-3, the RSD for Method 101A was 39.5 percent at an average measured Hg concentration of 86.8 μg/dscm and 15.6 percent at an average of 416.8 μg/dscm. This method therefore meets the RSD criterion for acceptance.

4.0 MULTIPLE METALS METHOD RESULTS

4.1 REVIEW OF DATA

Paired flue gas samples were gathered using dual MM sampling trains for the same five operating conditions during which Method 101A dual trains were used. Three runs were made for each operating condition.

4.1.1 Mercury

Analytical results, showing the amount of Hg in μg collected in each fraction of the sampling train, are shown in Table 4-1. The data show that during most runs, 80-90 percent of the Hg was found in the HNO_3/H_2O_2 impingers, with most of the remainder found in the $KMnO_4/H_2SO_4$ impinger and rinse fraction. The primary exception was Condition 6 (high carbon feed rate) during which the $KMnO_4/H_2SO_4$ impingers accounted for 28-53 percent of the total in three of the six trains. Very little Hg was associated with the front half (FH) or with the empty impinger rinse, except during Condition 5, when Train 3R accounted for roughly 6 percent of the total.

During Condition 4, the empty impinger and rinse samples from Trains 1 and 1R were apparently combined with another fraction, and thus no separate data are available for these two rinses. Also during Condition 4, the probe rinse from Train 2 was combined with the rinse of another train. Because very low Hg levels were found in similar fractions collected during the other runs, the impact of these fractions on total Hg levels during this run is expected to be small. As a result, Hg measurements from the rest of the fractions during these runs were included. Results for Train 2R of Condition 4

TABLE 4-1. MULTIPLE METALS METHOD FRACTIONAL RESULTS

		Hg (μg)				
Condition	Train	Front Half	Empty Impinger Rinse	HNO_3/H_2O_2 Impinger	$KMnO_4/H_2SO_4$ Impinger	Total
4	1	<0.392	--[a]	198	41.6	239.6
	1R	<0.392	--[a]	200	38.2	238.2
	2	<0.392[b]	<0.235	208	51.7	259.7
	2R	<0.392	<0.235	133	--[c]	--[c]
	3	<0.392	0.838[d]	405	139	544.8
	3R	<0.392	0.449[d]	380	125	505.4
5	1	1.32[d]	1.078	275	44.8	322.2
	1R	4.14	<0.221	321	47.8	372.9
	2	0.392	<0.247	226	28.7	255.1
	2R	0.392	1.036[d]	236	50.3	287.7
	3	0.392	0.534[d]	334	38.2	373.1
	3R	19.4	0.768[d]	264	36.7	320.9
6	1	<0.392	<0.216	49.1	7.1[d]	56.2
	1R	<0.392	<0.216	60.5	8.6[d]	69.1
	2	<0.392	<0.071	38.2	8.0[d]	46.2
	2R	<0.392	<0.216	7.9[d]	8.9[d]	16.8
	3	<0.392	<0.227	22.1	9.0[d]	31.1
	3R	<0.392	<0.204	5.2[d]	8.2[d]	13.4
8	1	<0.392	<0.180	68.2	7.8[d]	76.0
	1R	<0.392	<0.255	41.4	6.1[d]	47.5
	2	<0.392	<0.196	112	7.5[d]	119.5
	2R	1.7[d]	<0.204	70.7	6.7[d]	79.1
	3	<0.392	<0.196	80.4	5.7[d]	86.1
	3R	<0.392	<0.243	74.9	4.5[d]	79.4
9	1	<4.34	<0.267	106	<1.8	106
	1R	<0.392	<0.270	114	8.1[d]	122.1
	2	<0.392	<0.212	110	3.0[d]	113
	2R	5.6	<0.286	97.3	10.1	113
	3	<0.392	<0.227	87	2.2[d]	89.6
	3R	<0.392	<0.172	95.5	2.6[d]	98.1

a = No HNO_3 rinse sample sent to lab.
b = Does not include probe rinse fraction.
c = Switched with $KMnO_4$ catch from Method 101A train.
d = Less than five times the detection limit.

were invalidated because the $KMnO_4$ impinger contents and rinse were mistakenly switched with a 101A train.

All of the $KMnO_4/H_2SO_4$ impinger fractions during testing with carbon injection (Conditions 6, 8, and 9) were less than five times the detection limit. The HNO_3/H_2O_2 impingers from Trains 2R and 3R of Condition 6 were also less than five times the detection limit.

The Hg concentrations determined from the analytical data and operating parameters for each run are shown in Table 4-2. The Hg concentrations are on a dry basis and are corrected to 7 percent oxygen.

4.1.2 Cadmium and Lead

Results from the analyses of the MM samples for Cd and Pb are shown in Table 4-3. The levels of these metals in the back half impinger solutions for all of the samples were either below detection limits or less than 5 times the detection limit. In addition, all but 2 of the 27 measurements of Cd on the sampling train filter were less than 5 times the detection limit. Because the total amount of these metals captured was small, the true precision of the measurements is uncertain. Additionally, in many cases, the detection limit of the metal in the impinger solution is relatively large compared to the amount measured on the filter. As a result, the procedure used for handling nondetects will influence statistical estimates of precision based on the dual train measurements.

Concentrations of Cd and Pb in the stack gas were determined using the analytical data and operating conditions for each run. Table 4-4 shows the concentrations assuming that nondetected levels of metals in the sample fractions were zero. Table 4-5 shows these concentrations assuming that sample fractions with metals content below the detection limit contained the metals at the detection limit. These two assumed concentration levels represent the upper and lower bounds on the actual values. Tables 4-4 and 4-5 also contain operating conditions for each run. As opposed to the Hg data,

TABLE 4-2. MERCURY FLUE GAS CONCENTRATIONS AND OPERATING PARAMETERS MULTIPLE METALS METHOD

Cond.	Run	Flue Gas Temp. (°F)	Oxygen (%)	CO_2 (%)	Outlet				Outlet R			
					Hg (μg/dscm)	Flow (dscmm)	H_2O (%)	Iso[a] (%)	Hg (μg/dscm)	Flow (dscmm)	H_2O (%)	Iso[a] (%)
4	1	276.9	10.7	8.7	337.5	1666	17.5	96.2	355.8	1662	17.7	95.4
	2	275.7	10.0	9.2	358.5	1580	18.9	98.3	--[b]	1568	19.6	96.9
	3	276.1	9.9	9.3	710.6	1649	20.4	97.3	700.6	1686	18.2	97.6
5	1	280.6	9.1	10.4	464.5	1453	19.7	101.7	578.1	1433	21.0	98.5
	2	281.9	9.0	10.2	360.7	1490	21.9	99.0	449.5	1509	20.6	102.1
	3	278.6	9.1	10.1	507.5	1564	20.6	101.4	473.6	1542	21.9	98.3
6	1	283.9	9.5	10.4	84.6	1527	19.6	99.1	103.7	1524	20.8	98.9
	2	285.8	9.5	9.9	63.5	1603	19.5	98.1	24.0	1598	19.8	100.5
	3	284.9	9.6	10.3	45.1	1794	20.1	100.7	20.8	1617	20.7	99.4
8	1	277.0	10.6	8.8	128.1	1642	19.5	100.8	75.1	1478	20.2	97.8
	2	276.7	10.1	9.3	171.3	1836	19.7	99.2	126.6	1680	18.8	95.7
	3	275.7	10.0	9.3	130.5	1802	18.6	107.3	121.2	1609	20.1	97.9
9	1	275.0	10.4	9.1	160.3	1675	18.6	97.5	210.0	1666	19.1	96.8
	2	276.0	10.2	9.3	166.8	1724	19.7	105.7	166.0	1706	20.7	96.4
	3	282.5	11.0	9.3	140.8	1555	20.7	102.8	166.4	1575	19.5	100.5

[a] Iso = percent isokinetic.
[b] Total unknown due to switch of $KMnO_4$ impinger fraction with sample from Method 101A train for same run.

TABLE 4-3. MULTIPLE METALS METHOD CADMIUM AND LEAD FRACTIONAL RESULTS

Cond.	Run	Cadmium (μg)			Lead (μg)		
		Front Half	Back Half	TOTAL[a]	Front Half	Back Half	TOTAL[a]
4	1	2.95	0.24[b]	3.19	3.51	(0.33)[c]	3.51
	1R	0.84[b]	0.23[b]	1.07	2.55	0.53[b]	3.08
	2	0.73[b]	0.80[b]	1.53	2.20	(0.33)	2.20
	2R	0.95[b]	(0.22)	0.95	2.55	(0.33)	2.55
	3	0.97[b]	0.40[b]	1.37	2.82	0.78[b]	3 60
	3R	0.88[b]	(0.22)	0.88	2.82	(0.33)	2.82
5	1	--[d]	0.61[b]	--[d]	--[d]	0.45[b]	--[d]
	1R	--[d]	(0.22)	--[d]	--[d]	0.86[b]	--[d]
	2	0.78[b]	(0.22)	0.78	2.00	0.53[b]	2.53
	2R	0.74[b]	(0.22)	0.74	2.27	0.80[b]	3.07
	3	1.27[b]	(0.22)	1.27	3 76	0.53[b]	4.29
	3R	0.65[b]	0.25[b]	0.90	2.14	0.61[b]	2.75
6	1	0.75[b]	0.33[b]	1.08	1.73	0.37[b]	2.10
	1R	0.79[b]	(0.23)	0.79	2.14	0.37[b]	2.51
	2	0.81[b]	(0.22)	0.81	3.03	0.37[b]	3.40
	2R	0.73[b]	0.65[b]	1.38	3.09	0 71[b]	3.80
	3	0.85[b]	0.45[b]	1.30	3.03	(0.33)	3.03
	3R	0.87[b]	(0.22)	0.87	2.68	(0.33)	2.68
8	1	0.91[b]	(0.22)	0.91	4.60	0.36[b]	4.96
	1R	0.97[b]	(0.22)	0.97	4.33	(0.33)	4.33
	2	--[d]	(0.22)	--[d]	--[d]	0.54[b]	--[d]
	2R	0.78[b]	0.32[b]	1.10	2.00	0.36[b]	2.36
	3	0.72[b]	(0.22)	0.72	1.73	0.37[b]	2.10
	3R	1.08	(0.22)	1.08	2.41	(0.34)	2.41
9	1	0.75[b]	(0.22)	0.75	2.40	0.52[b]	2.92
	1R	0.77[b]	(0.22)	0.77	2.27	1.02[b]	3 29
	2	0.78[b]	(0.22)	0.78	2.40	0.94[b]	3.34
	2R	0.98[b]	0.30[b]	1.28	2.81	0.45[b]	3.26
	3	0.72[b]	(0.23)	0.72	2.54	0.70[b]	3.24
	3R	0.74[b]	(0.22)	0.74	2.81	0.68[b]	3.49

[a] Totals are calculated assuming that nondetected values are zero.
[b] Measured value is less than five times the detection limit.
[c] Numbers in parentheses are detection limits for samples in which the analyte was not detected.
[d] Filter could not be analyzed for Cd and Pb due to inadvertent addition of $KMnO_4$ to sample container.

TABLE 4-4. CADMIUM AND LEAD FLUE GAS CONCENTRATIONS BASED ON NONDETECTS AT ZERO MULTIPLE METALS METHOD

Cond.	Run	Flue Gas Temp. (°F)	O_2 (%)	CO_2 (%)	Outlet					Outlet R				
					Cd (μg/dscm)	Pb (μg/dscm)	Flow (dscmm)	H_2O (%)	Iso (%)	Cd (μg/dscm)	Pb (μg/dscm)	Flow (dscmm)	H_2O (%)	Iso[A] (%)
4	1	276.9	10.7	8.7	4.50	4.94	1666	17.5	96.2	1.60	4.60	1662	17.7	95.4
	2	275.7	10.0	9.2	2.11	3.04	1580	18.9	98.3	1.46	3.93	1568	19.6	96.9
	3	276.1	9.9	9.3	1.79	4.70	1649	20.4	97.3	1.22	3.91	1686	18.2	97.6
5	1	280.6	9.1	10.4	--[b]	--[b]	1453	19.7	101.7	--[b]	--[b]	1433	21.0	98.5
	2	281.9	9.0	10.2	1.10	3.58	1490	21.9	99.0	1.16	3.07	1509	20.6	102.1
	3	278.6	9.1	10.1	1.73	5.84	1564	20.6	101.4	1.33	4.06	1542	21.9	98.3
6	1	283.9	9.5	10.4	1.62	3.16	1527	19.6	99.1	1.19	3.77	1524	20.8	98.9
	2	285.8	9.5	9.9	1.11	4.66	1603	19.5	98.1	1.98	5.44	1598	19.8	100.5
	3	284.9	9.6	10.3	1.89	4.39	1794	20.1	100.7	1.35	4.16	1617	20.7	99.4
8	1	277.0	10.6	8.8	1.53	8.36	1642	19.5	100.8	1.53	6.85	1478	20.2	97.8
	2	276.7	10.1	9.3	--[b]	--[b]	1836	19.7	99.2	1.75	3.77	1680	18.8	95.7
	3	275.7	10.0	9.3	1.09	3.18	1802	18.6	107.3	1.65	3.68	1609	20.1	97.9
9	1	275.0	10.4	9.1	1.14	4.42	1675	18.6	97.5	1.33	5.66	1666	19.1	96.8
	2	276.0	10.2	9.3	1.15	4.92	1724	19.7	105.7	1.88	4.79	1706	20.7	96.4
	3	282.5	11.0	9.3	1.13	5.10	1555	20.7	102.8	1.26	5.92	1575	19.5	100.5

[a] Iso = percent isokinetic.
[b] Cd and Pb concentrations not available due to unanalyzable filter.

TABLE 4-5. CADMIUM AND LEAD FLUE GAS CONCENTRATIONS BASED ON NONDETECTS AT DETECTION LIMIT MULTIPLE METALS METHOD

Cond.	Run	Flue Gas Temp. (°F)	O_2 (%)	CO_2 (%)	Outlet					Outlet R				
					Cd (μg/dscm)	Pb (μg/dscm)	Flow (dscmm)	H_2O (%)	Iso[a] (%)	Cd (μg/dscm)	Pb (μg/dscm)	Flow (dscmm)	H_2O (%)	Iso[a] (%)
4	1	276.9	10.7	8.7	4.50	5.41	1666	17.5	96.2	1.60	4.60	1662	17.7	95.4
	2	275.7	10.0	9.2	2.11	3.50	1580	18.9	98.3	1.80	4.44	1568	19.6	96.9
	3	276.1	9.9	9.3	1.79	4.70	1649	20.4	97.3	1.52	4.36	1686	18.2	97.6
5	1	280.6	9.1	10.4	--[b]	--[b]	1453	19.7	101.7	0.35	--[b]	--[b]	21.0	98.5
	2	281.9	9.0	10.2	1.42	3.58	1490	21.9	99.0	1.50	3.07	1509	20.6	102.1
	3	278.6	9.1	10.1	2.03	5.84	1564	20.6	101.4	1.33	4.06	1542	21.9	98.3
6	1	283.9	9.5	10.4	1.62	3.16	1527	19.6	99.1	1.53	3.77	1524	20.8	98.9
	2	285.8	9.5	9.9	1.42	4.66	1603	19.5	98.1	1.98	5.44	1598	19.8	100.5
	3	284.9	9.6	10.3	1.89	4.88	1794	20.1	100.7	1.70	4.68	1617	20.7	99.4
8	1	277.0	10.6	8.8	1.90	8.36	1642	19.5	100.8	1.89	7.38	1478	20.2	97.8
	2	276.7	10.1	9.3	--[b]	--[b]	1836	19.7	99.2	1.75	3.77	1680	18.8	95.7
	3	275.7	10.0	9.3	1.43	3.18	1802	18.6	107.3	1.99	4.19	1609	20.1	97.9
9	1	275.0	10.4	9.1	1.46	4.42	1675	18.6	97.5	1.71	5.66	1666	19.1	96.8
	2	276.0	10.2	9.3	1.48	4.92	1724	19.7	105.7	1.88	4.79	1706	20.7	96.4
	3	282.5	11.0	9.3	1.49	5.10	1555	20.7	102.8	1.62	5.92	1575	19.5	100.5

[a] Iso = percent isokinetic.
[b] Cd and Pb concentrations not available due to unanalyzable filter.

there is no apparent difference in Cd and Pb levels during the individual test conditions.

4.2 STATISTICAL ANALYSIS

4.2.1 Mercury

The MM data were evaluated for precision using techniques in the validation protocol. Statistics relative to the precision of sampling method are shown in Table 4-6. The precision of the method is indicated by the variance of the sample data. This was calculated across the range of sampling conditions using equation 3-1. The standard deviation and RSD were calculated as described in Section 3.2.

Mercury concentrations in the stack gas were lower during test conditions in which carbon was injected into the duct. As shown in Table 4-6, the variance and standard deviation of the data collected during periods of carbon injection were lower than for the data collected during the baseline condition without carbon injection. The RSD, however, was higher during carbon injection. This reflects the impact of low Hg concentrations on RSD values. Note also that the RSD values increased as average Hg concentrations decreased during individual test conditions, again reflecting the impact of low Hg concentrations on calculated RSD values.

4.2.2 Cadmium and Lead

The precision of the measurements of Cd and Pb concentrations in the stack gas was calculated using the same method as for the Hg data. Statistical indicators of the precision of Cd and Pb measurements are shown in Table 4-6. Because carbon injection had no apparent effect on the concentration of these metals in the stack gas, the data were pooled to estimate overall precision numbers. The values were calculated using two alternative assumptions concerning sample fractions in which either Cd or Pb was not detected. The first assumption is that the level of nondetected analytes is zero. The second assumption is that nondetected analytes are present at the detection limit. Because of the low overall levels of Cd and Pb measured in the samples, the choice of

TABLE 4-6. MULTIPLE METALS METHOD PRECISION

Test Condition	No. of Sample Pairs	Average Concentration (μg/dscm)	Variance $(\mu g/dscm)_2$	Standard Deviation (μg/dscm)	RSD (%)
Mercury					
Overall	14	251.5	1175	34.3	13.6
Without Carbon Injection (Conditions 4,5)	5	493.8	2236	47.3	9.6
With Carbon Injection (Conditions 6,8,9)	9	116.9	585	24.2	20.7
High Carbon Injection (Condition 6)	3	57.0	419	20.5	35.9
Medium Carbon Injection (Condition 8)	3	125.5	817	28.6	22.8
Low Carbon Injection (Condition 9)	3	168.4	520	22.8	13.5
Cadmium					
Overall, Nondetects are zero	13	1.54	0.373	0.611	39.6
Overall, Nondetects are D.L.	13	1.76	0.339	0.582	33.0
Lead					
Overall, Nondetects are zero	13	4.56	0.254	0.504	11.1
Overall, Nondetects are D.L.	13	4.71	0.240	0.489	10.4

assumptions regarding nondetects affects the values of the precision statistics.

4.3 CONCLUSIONS

Section 2 of the EPA protocol states that "The precision of the method at the level of the emission standard shall not be greater than 50 percent relative standard deviation." This criterion is the basis for evaluating the precision of the MM train for measuring Hg, Cd, and Pb.

4.3.1 Mercury

As shown in Table 4-6, the RSD for the MM method was 20.7 percent at an average Hg concentration of 117 μg/dscm with carbon injection and 9.6 percent at an average Hg concentration of 494 μg/dscm without carbon injection. The use of this proposed method for measurement of Hg therefore appears to meet the EPA precision criterion for acceptance on the basis of RSD. For the three test conditions with carbon injection, the RSD values increase with decreasing average Hg levels.

4.3.2 Cadmium and Lead

When assuming that Cd and Pb concentrations in nondetected samples were zero, the RSD of the Cd concentration measurements was 39.6 percent at an average stack gas concentration of 1.5 μg/dscm. The RSD of the Pb concentration measurements was 11.1 percent at an average stack gas concentration of 4.6 μg/dscm. When using the alternative assumption that Cd and Pb are present in nondetected samples at the detection limit, the RSD of the Cd concentration measurements was 33.0 percent at an average stack gas concentration of 1.8 μg/dscm. The RSD for Pb was 10.4 percent at an average stack gas concentration of 4.7 μg/dscm. RSD's under both assumptions were within the validation protocol requirement of 50 percent.

5.0 INTER-METHOD COMPARISON FOR MERCURY

The results of the Method 101A testing and the simultaneous MM method testing were compared to assess the relative precision and the difference in measured Hg concentrations between the two methods. These comparisons were based on the procedures in the validation protocol.

5.1 STATISTICAL ANALYSIS

5.1.1 Precision

Precision is an indicator of the ability of a measurement method to achieve similar results under identical operating conditions (i.e., reproducibility). Table 5-1 summarizes the statistics comparing the precision of Method 101A and MM method trains that are presented in Sections 3.0 and 4.0. Figure 5-1 is a plot of the RSD statistics for the two sampling methods based on the runs conducted with and without carbon injection. Based on these data, the MM train appears to have better precision (i.e., less variability) than Method 101A and satisfies the requirement in the validation protocol that requires an alternative method (in this case, MM) to have less variance than the established method (Method 101A).

A one-tailed F test was used to determine whether the lower variance in the MM data is statistically significant. The F test assesses the likelihood that the difference in variances of two data sets could be due to random chance by comparing the F statistic, which is the ratio of the data set variances, to the known distribution of F. The F statistic for the MM and Method 101A data sets is:

TABLE 5-1. VARIABILITY OF MULTIPLE METALS AND METHOD 101A MERCURY DATA

Statistic	Units	101A	MM
No. of Observations			
Overall		13	14
With Carbon Injection		9	9
Without Carbon Injection		4	5
Average Hg Concentration	µg/dscm		
Overall		188.3	251.5
With Carbon Injection		86.8	116.9
Without Carbon Injection		416.8	493.8
Variance	$(\mu g/dscm)^2$		
Overall		2115	1175
With Carbon Injection		1177	585
Without Carbon Injection		4227	2236
Standard Deviation	µg/dscm		
Overall		46.0	34.3
With Carbon Injection		34.3	24.2
Without Carbon Injection		65.0	47.3
RSD	percent		
Overall		24.4	13.6
With Carbon Injection		39.5	20.7
Without Carbon Injection		15.6	9.6

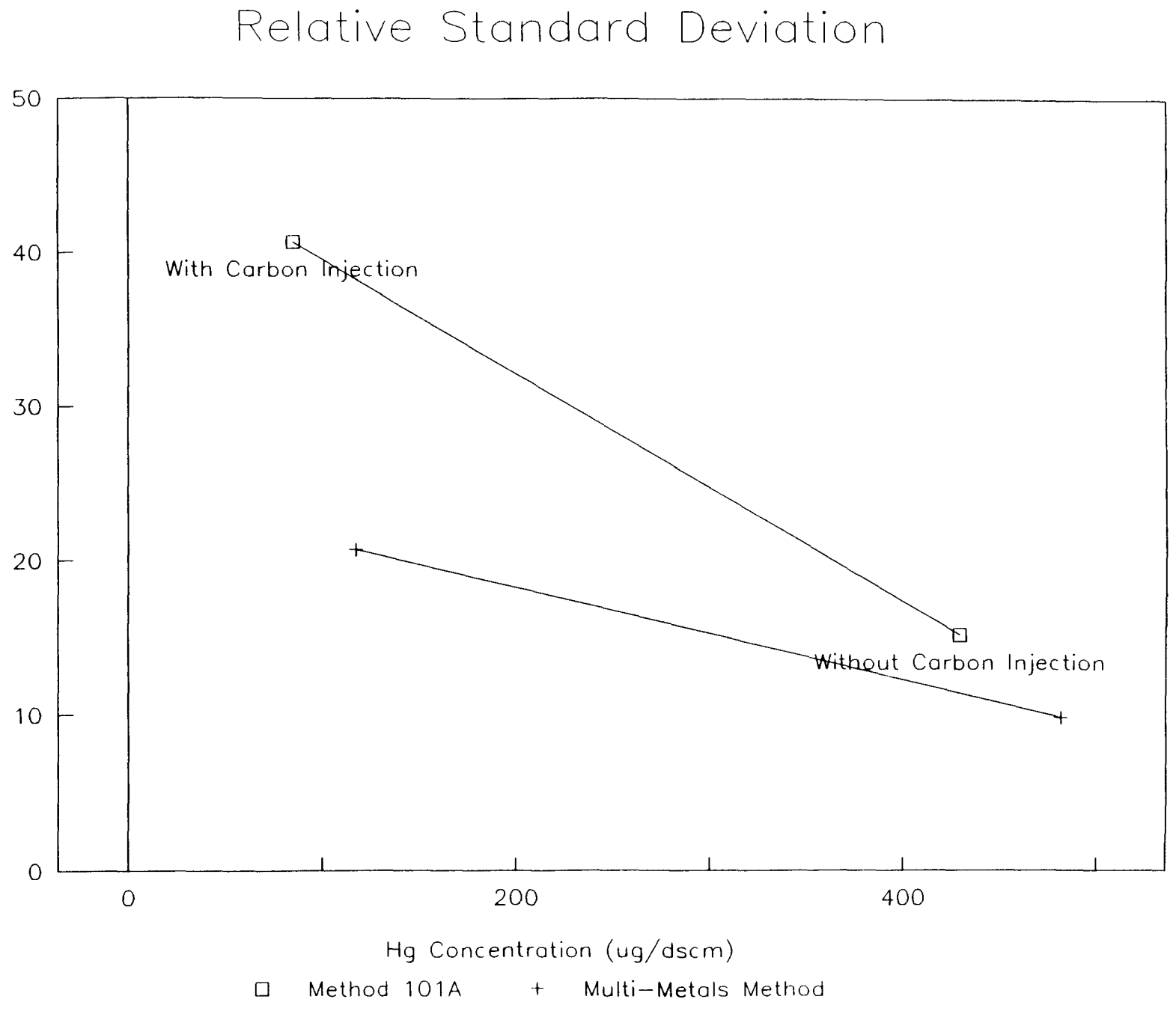

Figure 5-1. Comparison of RSD values for both mercury

$$\frac{s^2_p}{s^2_v} \qquad (5\text{-}1)$$

where s^2_p = the variance of the MM data; and
s^2_v = the variance of the Method 101A data.

The F distribution is dependent on the number of observations in the two data sets being compared. Values for F distributions associated with variance observation numbers are tabulated at specific percentage points in most statistics texts.

As shown in Table 5-2, the calculated F statistics for the overall data set and for the runs with and without carbon varied from 0.508 to 0.555. Due to the differences in the number of data points (observations) within each data set, the F statistics represent points on different F distributions. The F statistics for each data set were compared with critical values of the appropriate F distribution at different confidence levels. The results for all three data sets indicate that the variance of the MM method cannot be said to be smaller than the variance of Method 101A with 90 percent confidence. However, the assertion can be made that the variance of the MM method is smaller with 75 percent confidence for the overall data set and for the data set based on carbon injection, but not for the data set without carbon injection. As a result, there appears to be a reasonable chance that the lower variability of the MM train measurements is due to random chance in the measurements, rather than to an actual difference.

5.1.2 Inter-method Difference in Measured Mercury Concentrations

The test data were analyzed for systematic difference in values measured by the two measurement methods by comparing the mean value of the pair of measurements made by one sampling method during a single run with the mean value of the pair of measurements made by the other sampling method in the

TABLE 5-2. COMPARISON OF VARIANCES FOR MULTIPLE METALS AND METHOD 101A MERCURY DATA

Conditions	Calculated F	Confidence Level for Critical Value of F		
		75%	90%	95%
All	0.555	0.680	0.476	0.385
With Carbon Injection	0.508	0.610	0.386	0.291
Without Carbon Injection	0.529	0.488	0.239	0.152

same run. This comparison was made for all runs when the two dual trains were run simultaneously. As shown in Table 5-3, there were a total of 13 data points, 8 with carbon injection and 5 without carbon injection.

The difference, d_i, in measured Hg levels between the two methods during each run was calculated as:

$$d_i = \frac{(V_{1i} - V_{2i})}{2} - \frac{(P_{1i} - P_{2i})}{2} \qquad (5\text{-}2)$$

where V_{1i} and V_{2i} = the measured values from the two dual trains using Method 101A during the i-th test; and

P_{1i} and P_{2i} = the measured values from the dual MM trains.

The mean difference was calculated for each test condition by calculating the mean of the d_i's from runs in that test condition. Test conditions were then grouped into those with carbon injection, those without carbon injection, and the overall data set. The mean difference for each of the grouped data sets was calculated by averaging the d_i's of all runs and conditions. As shown in Table 5-3, the average measured Hg levels are higher using the MM method than when using Method 101A. The average difference in measured Hg concentration for all of the data was 39 µg/dscm. The average difference is 54 µg/dscm during tests without carbon injection, but is strongly influenced by the large d_i calculated for Run 3 of Condition 4. The other values of d_i obtained during testing without carbon injection appear similar to the values measured during testing with carbon injection. Based on the limited number of data points, particularly for tests conducted without carbon injection, it is uncertain whether the differences calculated for subgroups with and without carbon injection are real or due to small sample size.

The statistical significance of the difference in measured values was determined using a t test. The t statistic for the data was calculated using the formula:

TABLE 5-3. COMPARISON OF DIFFERENCES IN AVERAGE MERCURY CONCENTRATIONS FOR MULTIPLE METALS METHOD AND METHOD 101A

Cond.	Run	101A (μg/dscm)	MM (μg/dscm)	d_i (μg/dscm)	Avg d_i
4	1	296.2	346.7	-50.4	-112.7
	2	177.4	--	--	
	3	530.7	705.6	-174.9	
5	1	521.9	521.3	0.6	-15.4
	2	390.7	405.1	-14.4	
	3	458.2	490.6	-32.3	
6	1	--	94.2	--	-1.0
	2	47.6	43.8	3.9	
	3	27.1	33.0	-5.9	
	4	58.5	--	--	
8	1	98.1	101.6	-3.5	-45.6
	2	82.8	149.0	-66.2	
	3	58.9	125.9	-67.0	
9	1	180.3	185.15	-4.8	-32.4
	2	111.7	166.4	-54.8	
	3	115.9	153.6	-37.7	
Average:					
w/o Carbon Injection (4,5)		439.6	493.9		-54.3
w/Carbon Injection (6,8,9)		90.3	119.8		-29.5
Overall		224.6	263.7		-39.0

$$t = \frac{d_m}{\left[\frac{s_p}{\sqrt{n}}\right]} \qquad (5\text{-}3)$$

where d_m = the mean of the d_i's of each run;

s_p = the standard deviation of the measured concentrations using the MM method; and

n = the total number of paired samples.

As specified in the validation protocol, the calculated t statistic was compared to the appropriate critical value for t at an 80 percent confidence level in each test case. In all cases, as shown in the upper half of Table 5-4, the calculated t statistic exceeded the critical value for t at a confidence level of 80 percent. As a result, the difference between methods is considered statistically significant in all cases.

The table also shows the tabulated t values at more stringent confidence levels. These additional t values represent the highest confidence level for which tabulated critical t values are lower than the calculated t statistics for the actual test data. For example, these data indicate that the difference in mean concentrations for all of the runs are statistically different at the 99 percent confidence level.

Since the inter-method bias was shown to be statistically significant, a correction factor (CF) was calculated according to the validation protocol for the MM method data using the equation:

$$CF = \frac{1}{1 + \frac{d_m}{V_m}} \qquad (5\text{-}4)$$

where V_m = the mean of the Method 101A Hg measurements.

As shown in the lower half of Table 5-4, the CF is 1.14 for the data without carbon injection (during which Hg levels typically exceeded 200 µg/dscm) and 1.49 for the data with carbon injection (during which Hg levels were less than

TABLE 5-4. t STATISTICS AND CORRECTION FACTORS FOR AVERAGE MERCURY CONCENTRATIONS

	Value	Critical Value	Confidence Level
t Statistic			
Overall	4.106	1.356	80%
		3.055	99%
With Carbon Injection	3.448	1.415	80%
		2.998	98%
Without Carbon Injection	2.568	1.638	80%
		2.353	90%
Correction Factor[a]			
Overall	1.21	1.1	--
With Carbon Injection	1.49	1.1	--
Without Carbon Injection	1.14	1.1	--

[a] Correction Factor was calculated using only data from runs which yielded values from all four sampling trains.

200 μg/dscm). The large variation in these two values suggests that the CF may vary with Hg concentration, rather than being constant as is normally assumed. Both values exceed the criteria in the validation protocol that CF values should be between 0.9 and 1.1.

5.2 CONCLUSIONS

Although not statistically significant at the 90 percent confidence level, the calculated precision of the MM method sample values, as indicated by the sample variances, was greater than precision of the Method 101A values, both when grouped by control options (with and without carbon injection) and for the overall data set. This meets the EPA protocol for method precision when comparing a proposed to a validated method. There is a reasonable likelihood that the lower variance of the MM method is due to random variation and is not real.

The MM method measured higher Hg concentrations than Method 101A. Comparison of the calculated inter-method bias t statistics to the critical values of the t distribution indicates the difference in measured values is statistically significant at or above the 90 percent confidence level in all cases. The fact that the MM method measures higher concentrations of Hg raises the question of whether all the Hg in the flue gas is being captured and recovered in the Method 101A train. This, coupled with the indication that the MM method appears to have better precision than Method 101A, may be good reason to further investigate the two methods.

6.0 SAMPLING AND ANALYTICAL PROCEDURES

This section provides additional information on the equipment preparation, sampling, and analytical procedures used with Method 101A and the MM method during the OMSS test program.

6.1 METHOD 101A

Mercury emissions were tested by Method 101A as specified in 40 CFR Part 61, Appendix B. The method calls for isokinetic extraction of flue gas using a sampling train similar to the Method 5 train. Use of a sampling train filter is optional; however, for this test program, a filter was used at all sample locations.

In Method 101A, flue gas is extracted, passed through the filter, and bubbled through acidified $KMnO_4$. There are two fractions of the sampling train: the probe rinse/impinger catch and the sampling train filter. Following sample recovery, the $KMnO_4$ and filter solutions were shipped back to the laboratory for analysis. The analytical preparation procedure consisted of filtering the $KMnO_4$ and filter solutions and analyzing the filtrates by CVAAS. Because of concern that the laboratory filtering procedure may remove a portion of the collected Hg, the laboratory filters were re-extracted and analyzed separately from the $KMnO_4$ solution, and the results are reported separately.

The following sections briefly describe the Method 101A testing procedures. A full description is given in the reference method located in Appendix A.

6.1.1 Sampling Equipment

The Method 101A sampling train, including the optional heated filter, is shown in Figure 2-4. The front half of this train is similar to Method 5 train, incorporating all isokinetic sampling apparatus. A glass nozzle/probe liner unit was used so that the sample stream did not touch any metal surfaces. The filter was a low-metals glass fiber filter. Four impingers were used in the train. The first three contained 50 ml, 100 ml, and 100 ml, respectively, of acidified 4 percent $KMnO_4$. The last impinger was filled with silica gel to remove water prior to the sampling train meter and pump. All reagent preparation followed strict QA/QC guidelines as dictated in the Method 101A protocol.

6.1.2 Equipment Preparation

All sampling equipment was calibrated in accordance with EPA Method 5 guidelines. This included dry gas meters, pitot tubes, and nozzle orifices. All glassware was cleaned as follows:

- Soaked in 10 percent HNO_3 acid bath;
- Rinsed three times with 50 percent HNO_3;
- Rinsed three times with tap water;
- Rinsed three times with 8N hydrochloric acid (HCl);
- Rinsed three times with tap water; and
- Rinsed three times with deionized/distilled (or equivalent) water.

Glassware was then sealed with Parafilm™, wrapped in bubble wrap, packed, and shipped to the test site.

All nozzles and probe liners were cleaned on site between runs by following the above rinsing procedures. Nozzle calibration was checked on site.

6.1.3 Reagent Preparation

The following reagents were used during sampling operations:

- 8N HCl = 67 ml concentrated HCl/100 ml deionized (DI) water (H_2O);

- 4 percent $KMnO_4$ = 4 percent solution in H_2O and H_2SO_4; specific instructions for preparation can be found in Section 2.3.2.

- 50 percent HNO_3 = equal parts acid and DI H_2O.

Blank samples were taken of all reagents used, to determine if Hg contamination was present.

6.1.4 Sample Train Operation

The Method 101A sampling train was operated similarly to an EPA Method 5 train. Care was taken to determine the proper isokinetic sampling rate below 1.0 cfm. Actual rates were approximately 0.5 cfm. Temperatures of the stack gas, oven (filter skin), silica gel impinger, and inlet and outlet to the gas meter were monitored. Additional recordings of dry gas meter readings, velocity head (ΔH), orifice pressure (Δp), and sample vacuum were taken. The above data were collected at each sample point every 5 minutes. Total sampling times for each run were approximately 60 minutes.

Leak-checks of the sampling train were performed prior to the test, following train removal from a port (port change), and following completion of the test. The maximum acceptable leak rate is 0.02 cfm or 4 percent of the average sample rate, whichever is less.

6.1.5 Sample Recovery

The Method 101A flue gas samples were recovered as shown in Figure 2-5. The first step after completion of the post-test leak-check was to dismantle and seal the train into the following components:

- Probe nozzle and liner,

- Filter holder, and

- Impinger train.

These components were transported back to the laboratory trailer for recovery operations. The impingers were then weighed to determine flue gas moisture levels.

The contents of the $KMnO_4$ impingers were poured into a 950-ml sample bottle. The nozzle and probe were then brushed and rinsed three times with fresh 4 percent $KMnO_4$ and placed

in a 200-ml bottle. Although no visible deposits were observed during any of the runs, a small amount of 8N HCl was used to rinse the glassware used during Conditions 4, 5, and 6. The rinse was placed in a separate 125-ml bottle. The glassware used during Conditions 8 and 9 was not rinsed with HCl.

The sampling train filter was carefully placed in a 500-ml sample jar and 50 to 100 ml of fresh 4 percent $KMnO_4$ was added. Any residual filter pieces left on the filter holder were quantitatively removed using a sharpened edge blade and/or nylon bristle brush and added to this container.

A filter and reagent blank were also collected. Following recovery operations, the samples were fully labeled, logged in the sample logbook, and chain of custody forms were filled out.

6.1.6 Analytical Preparation

After the samples were received by the laboratory, the chain of custody forms were signed and fluid levels checked to determine if any sample loss occurred during transport. As stated in the previous section, three to four sample containers were generated from each train. The preparation scheme used for each of these fractions is shown in Figure 2-6.

Prior to analysis, the front half rinse and impinger fractions were combined and filtered through a Whatman 40 filter. If an HCl rinse fraction was generated, it was also filtered through the same filter. Finally, the filter was washed with the HCl and $KMnO_4$ and the rinsings were combined with the filtrate for analysis.

The sampling train filter sample was transferred to a beaker, placed in a steam bath, and evaporated down to where most of the liquid had disappeared (not dryness). Then, 20 ml of concentrated HNO_3 was then added and placed on a hot plate (with watch glass cover) and heated for two hours at 70°C. This solution was allowed to cool and then was filtered using the same laboratory filter discussed above. The filtrate was

then combined with the front half rinse/impinger sample filtrate prior to analysis.

At this point, the laboratory filter is normally discarded. For this test program, however, the laboratory filter from each run was digested with 25 ml of 8N HCl. The resulting digestion solution was then filtered, the filter was rinsed with 8N HCl and $KMnO_4$, and the resulting filtrate was analyzed separately to determine the fraction of Hg captured on the laboratory filter.

6.1.7 Analysis

The $KMnO_4$ samples were brought up to a known volume using DI water. A sample aliquot was removed and placed in 25 ml of DI H_2O already in the aeration bottle. First, 4 ml of 5 percent $KMnO_4$ was added, then 5 ml of 15 percent HNO_3 was added, followed by addition of 5 ml of 5 percent $KMnO_4$. The solution was mixed thoroughly with the exit arm stopcock closed. The reducing agents, sodium chloride hydroxylamine and tin (II), were added as specified in the method and aeration was initiated. Absorbance was then read using CVAAS at 253.7 nanometers. The same analysis was done on the lab filter solution. Each analytical reading had a corresponding printout of the absorbing Hg peaks. These graphs are included with the data package in Appendix D.

6.2 MULTIPLE METALS METHOD

Sampling for metals was performed according to an EPA draft protocol entitled "Methodology for the Determination of Metals Emissions in Exhaust Gases from Incineration and Similar Combustion Processes." The protocol is presented in the Appendix A. Analyses of the OMSS test samples were performed for Hg as well as As, Cd, Cr, Ni, and Pb. Results for Hg, Cd, and Pb are presented in this report.

6.2.1 Sampling Equipment

The methodology calls for using the sampling train shown in Figure 2-7. The seven-impinger train consists of a glass nozzle and glass probe liner followed by a heated filter assembly with a Teflon® filter support, a series of impingers,

the usual Method 5 meterbox, and vacuum pump. The sample is not exposed to any metals surfaces in this train. The contents of the sequential impingers are: two impingers with a 5 percent HNO_3/10 percent H_2O_2 solution, two impingers with a 4 percent $KMnO_4$/10 percent H_2SO_4 solution, and one impinger containing silica gel. Empty knockout impingers are added both before and after the HNO_3 impingers. The impingers are connected together with clean glass U-tube connectors. Sampling train components were recovered and analyzed in separate front and back half fractions according to the described method.

6.2.2 Equipment Preparation

Glassware was washed in hot soapy water, rinsed three times with tap water and then rinsed three times with deionized distilled water. The glassware was then subjected to the following series of soaks and rinses:

- Soaked in a 10 percent HNO_3 solution for a minimum of 4 hours,
- Rinsed three times with DI distilled water rinse, and
- Rinsed with acetone rinse.

The cleaned glassware was allowed to air dry in a contamination-free environment. The ends were then covered with Parafilm™. All glass components of the sampling train, and any sample bottles, pipets, Erlenmeyer flasks, petri dishes, graduated cylinders, and other laboratory glassware used during sample preparation, recovery, and analysis were cleaned according to this procedure.

6.2.3 Reagent Preparation

The acids and H_2O_2 used were Baker "Instra-analyzed" grade. The H_2O_2 was purchased specifically for this test site and was kept cold until it was opened.

The reagent water was Baker "Analyzed HPLC" grade. The lot number, manufacturer, and grade of each reagent used was recorded in the laboratory notebook.

The HNO_3/H_2O_2 absorbing solution and the acidic $KMnO_4$ absorbing solution were prepared daily according to Sections 4.2.1 and 4.2.2 of the reference method. Each reagent had its own designated transfer and dilution glassware. This glassware was marked for identification with a felt tip glass marking pen and used only for the reagent for which it was designated.

The analyst prepared the acidic $KMnO_4$ solution using the following procedure, beginning at least one day before the reagent was needed:

- Quantitatively remove 400 ml from a 4-liter bottle of Baker "Analyzed HPLC" water so that 3.6 liters remain in the bottle. Label this bottle 4.4 percent $KMnO_4$ in water.

- Quantitatively add 160 g of $KMnO_4$ crystals to the bottle; stir with a Teflon® stirring bar and stirring plate as thoroughly as possible. This reagent will be stored on the counter in a plastic tub at all times.

- Each morning the acidic reagent is needed, decant 900-ml of $KMnO_4$ solution into a 1000 ml volumetric flask. Carefully add 100 ml of concentrated H_2SO_4 and mix. This reagent is volatile and must be mixed cautiously. Hold the flask cap on the flask, mix once, vent quickly. Complete the mixing slowly until the mixture is homogenous. Allow the solution to cool and bring the final volume to 1000 ml with H_2O.

- Carefully filter this reagent through Whatman 541 filter paper into another volumetric flask or 2-liter amber bottle. Label this bottle "4 percent acidic $KMnO_4$ absorbing solution." Vent the top and store the reagent in a plastic tub at all times.

The remaining equipment preparation tasks included calibration and leak checking of all train equipment as specified in Method 5. Equipment that was calibrated included probe nozzles, pitot tubes, metering system, probe heater, temperature gauges, metering system, and barometer.

6.2.4 Sample Train Operation

The sampling operations used for metals testing are virtually the same as those listed in EPA Method 5. Detailed

instructions for assembling the metals sampling train are found beginning on page 14 of the reference method.

6.2.5 Sample Recovery

The recovery procedures began as soon as the probe was removed from the stack and the post-test leak check was completed. To facilitate transfer from the sampling location to the recovery trailer, the sampling train was disassembled into three sections: the nozzle/probe liner, filter holder, and impingers in their bucket. Each of these sections was capped with Teflon® tape or Parafilm™ before transport to the recovery trailer.

Once in the trailer, the sampling train was recovered as separate front and back half fractions, as shown in Figure 2-8. No equipment with exposed metal surfaces was used in the sample recovery procedure. The weight gain in each of the impingers was recorded to determine the moisture content in the flue gas.

Following weighing of the impingers, the front half of the train was recovered, which included the filter and all sample-exposed surfaces forward of the filter. The probe liner was rinsed with acetone by tilting and rotating the probe while spraying acetone into its upper end so that all inside surfaces were wetted. The acetone was quantitatively collected into a tared bottle. This rinse was followed by additional brush/rinse procedures using a non-metallic brush to remove any residual particulate matter; the probe was held in an inclined position and acetone was sprayed into the upper end as the brush was pushed through with a twisting action. All of the acetone and particulate were caught in the sample container. This procedure was repeated until no visible particulate remained and finished with a final acetone rinse of the probe and brush. The front half of the filter was also rinsed with acetone and brushed until all visible particulate was removed. After all front half acetone washes were collected, the cap was tightened, the liquid level marked, and the bottle weighed to determine the acetone rinse volume.

The nozzle/probe liner and front half of the filter holder were then rinsed three times with 0.1N HNO_3 and the rinse solution was placed into a separate bottle. The bottle was capped tightly, the weight of the combined rinse recorded, and the liquid level marked. The filter was placed in a clean, well-marked glass petri dish and sealed with Teflon® tape.

The contents of the knockout impinger were recovered into a preweighed, prelabeled bottle with the contents from the HNO_3/H_2O_2 impingers. These impingers and connecting glassware were rinsed thoroughly with 0.1N HNO_3, the rinse was collected in the appropriate impinger contents bottle, and a final weight was taken.

The impingers that contained the $KMnO_4/H_2SO_4$ solution were poured together into a preweighed, prelabeled bottle. The impingers and connecting glassware were rinsed with at least 100 ml of the $KMnO_4/H_2SO_4$ solution (from the same batch used for sampling) a minimum of three times. Rinses were added to the sample recovery bottle. A final 50 ml 8N HCl rinse was conducted and placed into the sample recovery bottle. A final weight was recorded and the liquid level was marked on the bottle. The bottle cap was replaced loosely enough to allow venting.

A reagent blank was recovered in the field from each of the following reagents:

- Acetone blank - 100 ml sample size;
- 0.1N HNO_3 blank - 1000 ml sample size;
- 5 percent HNO_3/10 percent H_2O_2 blank - 200 ml sample size;
- 4 percent $KMnO_4$/10 percent H_2SO_4 blank - 1000 ml sample size; this blank should have a vented cap;
- 8N HCl blank - 50 ml sample size;
- Dilution water; and
- Filter blank - one each.

Each reagent blank was from the same lot used during the sampling program. Each lot number and reagent grade was recorded on the field blank label.

The liquid level of each sample container was marked on the bottle in order to determine if any sample loss occurred during shipment. No sample loss was observed for any of the samples collected during the OMSS test.

6.2.6 Metals Analytical Procedures

A diagram illustrating the sample preparation and analytical procedure for the target metals is shown in Figure 2-9. Approximate detection limits for the various metals of interest are summarized in Table 2-1.

The front half fractions were digested with concentrated HNO_3 and HF in a microwave pressure vessel. The microwave digestion takes place over a period of approximately 10 to 12 minutes in intervals of 1 to 2 minutes at 600 Watts. The digested filter and the digested probe rinses were combined to yield the front half sample fraction. The fraction was diluted to a specified volume with water and divided for analysis by applicable instrumentation.

The absorbing solutions from the HNO_3/H_2O_2 impingers were combined. An aliquot was removed for the analysis of Hg by CVAAS, and the remainder was acidified and evaporated to near dryness. The sample was then digested with 50 percent HNO_3 and 3 percent H_2O_2 by microwave digestion. After the fraction had cooled, it was filtered and diluted to a known volume with water.

Each sample fraction was analyzed by ICP using EPA Method 6010. If iron and aluminum were present, the sample was diluted to reduce their interferences on Pb. Graphite Furnace Atomic Absorption Spectroscopy was used to analyze for Pb by EPA Method 7421. Matrix modifiers, such as specific buffering agents, may be added to these aliquots to react with and tie up interfering agents. The total volume of the absorbing solutions and rinses for the various fractions were measured and recorded in the field notebook.

To prepare for Hg analysis by CVAAS, aliquots from the $KMnO_4$ impingers, HNO_3/H_2O_2 impingers, filter digestion, and front half rinses were digested with acidic reagents at 95°C in capped BOD bottles for approximately 3 hours. Hydroxylamine hydrochloride solution and stannous chloride were added immediately before analysis. The AAS analysis for Hg followed EPA Method 7470.

6.2.7 Mercury Standards and Quality Control

An intermediate Hg standard was prepared weekly; working standards were prepared daily. The calibration curve was made with at least six points. Quality control samples were prepared from a separate 10 micrograms per milliliter (µg/ml) standard by diluting it into the range of the samples.

A quality control sample must agree within 10 percent of the calibration, or the calibration will be repeated. A matrix spike on 1 of every 10 samples from the HNO_3/H_2O_2 back half sample fraction must be within 20 percent or the samples will be analyzed by the method of standard addition.

7.0 QUALITY ASSURANCE/QUALITY CONTROL

Specific QA/QC procedures were strictly adhered to during this test program to ensure the production of useful and valid data throughout the course of the project. As discussed in Section 7.2, the system of QC procedures is a collection of routine "checks" performed to ensure data quality. The QA parameters presented in this section are a collection of data quality indicators used to assess actual data quality. Detailed QC procedures for all manual flue gas sampling, process sample collection, and CEM operations are presented in the OMSS Test Plan.

Section 7.1 presents a brief summary of the test program quality assurance. Section 7.2 presents the QA/QC definitions and data quality objectives. Section 7.3 presents manual flue gas sampling and recovery QA parameters for the outlet sampling location. Section 7.4 presents method-specific analytical QA parameters. Section 7.5 discusses data variability.

7.1 QA/QC SUMMARY

The QA/QC objectives and achievements are summarized in Table 7-1. Precision, accuracy, and completeness objectives are presented. All objectives were met. Based on test design, precision and accuracy results for parameters which are solely based on field measurements (i.e., flue gas flow, flue gas moisture, etc.) cannot be determined. As an indicator of data variability within each test condition, a coefficient of variation (CV) or an RSD value was also calculated for all test measurements. These values do not reflect on the precision of the test measurements because they

TABLE 7-1. SUMMARY OF ESTIMATED PRECISION, ACCURACY, AND COMPLETENESS OBJECTIVES AND RESULTS

Parameter (Method)	Precision		Accuracy		Data Completeness	
	Objective (%)	Result (%)	Objective (%)	Result (%)	Objective (%)	Result (%)
Method 101A Hg Concentrations	±20[a]	±6.2[b]	±30[c]	±0.4[d]	90	96[e]
Multi-Metals Hg Concentrations	±20[a]	±4.0[f]	±30[c]	±2.2	90	96
Gas Flow Rate (Method 1 & 2)	±6[g]	NA[h]	±10[g]	NA	90	100
Moisture Content (Method 4)	±20[g]	NA	±10[g]	NA	90	100
Molecular Weight (O_2 & CO_2 by CEMS)	±4	NA	±10[g]	NA	90	100
O_2 Concentration (CEMS)	±10	NA	±20	NA	90	100

[a] Analytical only, percent difference between replicate samples.
[b] Average deviation between matrix spike (MS) and matrix spike duplicate (MSD) results for total train Hg results.
[c] Analytical only, measured versus expected value of laboratory control sample (LCS) analyses.
[d] Average laboratory control sample (LCS) results for total train Hg results.
[e] EPA Method 101A - Condition 13 Run 3, Condition 7 Run 1 were invalidated, MM - Condition 5 run 1 and Condition 8 Run 2 were invalidated.
[f] Average deviation between MS and MSD Hg results for all fractions.
[g] Precision and accuracy based on EPA collaborative tests.
[h] NA = Not Applicable.

NOTE: All QA analytical results are shown in Appendix D and are briefly discussed in Section 7.4.

also incorporate plant operation variability as well as variability in the waste feed itself. Each condition's CV and pooled CV values are given in Section 7.5.

There were 32 Method 101A runs conducted at the FF outlet duct (stack). All test runs met the QA/QC isokinetic criterion of ±10 percent of 100 percent isokinetic. One run was invalidated due to a sampling problem: a post-test leak check problem occurred at the stack during Condition 6, Run 1. The invalidated run was repeated.

There were approximately 116 Method 101A sample fractions sent to Radian's PPK laboratory for Hg analysis. Sample control problems with a small number of these fractions occurred, which resulted in invalidated or modified test results. Most of these problems were due to illegible labels, smudged during transit. During Condition 4, the impinger contents from outlet 101A Run 2R and MM Run 2R were switched and therefore invalidated data from both trains. A similar problems occurred for Condition 4 Run 3 with the outlet 101A HCl rinse for Train 3R being added to the outlet Run 3 sample. These results were added together and reported as one run (Run 3). A brief synopsis of these anomalies are presented in Table 7-2.

The MM tests were conducted at the stack during 15 runs (3 runs times 5 conditions). After reviewing the sampling data, all of these test runs were accepted as valid, with one run having to be leak corrected with a final (2nd half) leak check at 0.03 cfm. However, after reviewing the analytical data, two MM test runs (Condition 5, Run 1 and Condition 8, Run 2) were invalidated for Pb and Cd due to placement of the sampling train filters in $KMnO_4$. All MM test runs met the isokinetic criterion.

7.2 QA/QC DEFINITIONS AND OBJECTIVES

The overall QA/QC objective is to ensure precision, accuracy, completeness, comparability, and representativeness for each major measurement parameter in the test program. For

TABLE 7-2. SAMPLING, SAMPLE CONTROL, AND ANALYTICAL ERRORS WITH ASSOCIATED CORRECTIVE ACTIONS OMSS, CROWS LANDING, CA (1991)

Condition	Run	Method	Sample Location	Error	Corrective Action
4	2R & 2R	101A & MM	Outlet	$KMnO_4$ impinger contents switched.	Results for both trains invalidated.
4	3 & 3R	101A & 101A	Outlet	HCl rinse from Run 3R added to Run 3.	Results for Runs 3 and 3R were added together.
5	1 & 1R	MM (Cd & Pb)	Outlet	Filters placed in $KMnO_4$.	Run invalidated (Cd & Pb only).
6	1	101A	Outlet	Severely bad leak check.	Run invalidated and repeated.
8	2	MM (Cd & Pb)	Outlet	Filters placed in $KMnO_4$.	Run invalidated (Cd & Pb only).

this test program, QC, QA, and data quality are defined as follows:

- Quality Control: The overall system of activities whose purpose is to provide a quality product or service. The QC procedures are routinely followed to ensure high data quality.

- Quality Assurance: A system of activities whose purpose is to provide assurance that the overall quality control is being done effectively. Assessments can be made from QA parameters on what degree of data quality was achieved.

- Data Quality: The characteristics of a product (measurement data) that bear on its ability to satisfy a given purpose. These characteristics are defined as follows:

  - Precision: A measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. Precision is best expressed in terms of the standard deviation and in this report will be expressed as the RSD or CV.

  - Accuracy: The degree of agreement of a measurement (or an average of measurements of the same thing), with an accepted reference or true value.

  - Completeness: A measure of the amount of valid data obtained from a measurement system compared with the amount that was expected to be obtained under prescribed test conditions.

  - Comparability: A measure of the confidence with which one data set can be compared with another.

  - Representativeness: The degree to which data accurately and precisely represent a characteristic of a population (actual condition).

7.3 MANUAL FLUE GAS SAMPLING AND RECOVERY PARAMETERS

The following section reports method-specific sampling QA parameters used to assess the quality of emissions test data produced from manual tests during the test program.

7.3.1 Mercury by Method 101A Sampling Quality Assurance

Successful completion of the post-test leak-checks ensures that no dilution of the sampled stack gas was

occurring during the test. Leak-checks were completed after completion of each change in the flue gas duct. All reported 101A test runs at the outlet met the leak rate criterion, except Condition 6, Run 1. Data from this run was invalidated and the test repeated. No results were reported for the invalidated run. All leak check results are shown on the field data run sheets shown in Appendix B.

Tables 7-3 presents the isokinetic sampling rates for the 101A outlet sampling trains. The acceptance criterion is that the average sampling rate must be within 10 percent of 100 percent isokinetic. All test runs met the isokinetic criterion.

All dry gas meters are fully calibrated every 6 months against an EPA intermediate standard. The full calibration factor or meter Y is used to correct the metered sample volume to true sample volume. To verify the full calibration, a post-test calibration is performed. The full and post-test calibration coefficients must be within 5 percent to meet Radian's internal QA/QC acceptance criterion. As can be seen from Table 7-4, the post-test calibration factors for meter boxes used for all manual flue gas testing were well within 5 percent of the full calibration factor.

Field blanks were collected to verify the absence of any sample contamination. A sample filter field blank in $KMnO_4$ and a $KMnO_4$ solution field blank were analyzed. Relatively small amounts of Hg were detected in the filter/$KMnO_4$ and $KMnO_4$ blanks; 0.7 and 0.4 total μg, respectively (58.8 and 31.3 total ng/L). These levels are very small compared to test run values which averaged 124 total μg at the outlet. (Average outlet FH/BH fractions = 120 total μg; average outlet filter catch fractions = 3.5 total μg.) Because of the small amount of Hg in the sample blanks as compared to the total sample, and because there is unknown consistency of any Hg contamination in the reagent blanks, no blank corrections were employed. Analytical blank results are discussed in Section 7.4.

TABLE 7-3. ISOKINETIC RESULTS FOR THE STACK MERCURY (101A) TESTS; OMSS, CROWS LANDING, CA (1991)

	Isokinetic Rates			
Condition	Run 1	Run 2	Run 3	Run 4[a]
4	96.2	98.3	97.3	--
4R	101	96.9	97.6	--
5	102	99	102	--
5R	98.5	102	98.3	--
6	98.1	101	102	--
6R	98.9	101	99.4	100
8	101	99.2	107	--
8R	97.8	95.7	97.4	--
9	97.5	106	103	--
9R	96.8	96.4	100	--

[a] A fourth run was only conducted for Condition 6.

TABLE 7-4. DRY GAS METER CALIBRATION CHECK;
OMSS, CROWS LANDING, CA (1991)

Meter Box I.D. No.	Sampling Location	Full Calibration Factor	Post-Test Calibration Factor	Deviation[a] (%)
N-31	Stack, FF[b]	1.0060	1.0385	3.2
14	Stack	0.9973	0.9590	-3.8
7	Stack	1.0022	0.9845	-1.8
A-36	Stack	1.0254	1.0307	-0.5
8	Stack	1.0065	NC[c]	--

[a] $\frac{\text{Post Test - Full}}{\text{Full}} \times 100$

[b] FF = Fabric Filter Inlet
[c] NC = Not Completed

7.3.2 Multiple Metals Sampling Quality Assurance

All MM leak-checks passed the leak-check criterion of 0.02 cfm, except for Condition 8, Run 3 at the stack. A post-test leak rate of 0.03 cfm was measured. The sample volume for this run was leak corrected according to method protocols. The isokinetic sampling rates for the MM trains are listed in Table 7-5. All isokinetic values were within 10 percent of 100 percent.

The post-test dry gas meter calibration checks for boxes used for the MM sampling are shown in Table 7-5. The results are well within the 5 percent acceptance criterion.

The Hg analyses were completed on three MM reagent blank samples. No Hg was detected on the HNO_3 rinse solution, HNO_3/H_2O_2 impinger solution, or the DI with reagent blanks. The detection limits were <0.6, <0.5, and <1.0 total μg, respectively (<2.0 $\mu g/L$ for each of the three fractions).

7.4 ANALYTICAL QUALITY ASSURANCE

The following section reports QA parameters for the Hg 101A and MM analytical results.

7.4.1 Mercury by Method 101A Analytical Quality Assurance

The analysis of all flue gas impinger and filter samples was completed at Radian's PPK laboratory. An EPA-approved modification to the Method 101A sample preparation procedure was incorporated into the analytical protocol for this test program. This was based on recent information revealing that possible removal of sampled Hg could be occurring during the laboratory filtering process. Therefore, the laboratory filters were also analyzed and the results included into the Hg emission calculations. A breakdown of the amounts of Hg collected in each sample fraction is given in Table 3-1. The analysis was completed using normal Method 101A protocols employing CVAAS. More detail on these procedures is presented in Section 2.2.

Laboratory method blanks were analyzed to verify the absence of Hg contamination originating in the laboratory. Table 7-6 presents the results from those analyses. Out of

TABLE 7-5. ISOKINETIC RESULTS FOR THE STACK MULTIPLE METALS TESTS; OMSS, CROWS LANDING, CA (1991)

	Isokinetic Rates		
Condition	Run 1	Run 2	Run 3
4	99.3	101	103
4R	94.8	96.9	98.1
5	105	106	103
5R	99.2	97.6	97.0
6	99.1	103.7	105
6R	99.1	99.3	98.4
8	96.9	106	97.3
8R	102	96.5	96.9
9	104	100	105
9R	92.4	102	99.6

TABLE 7-6. MERCURY 101A METHOD BLANK RESULTS
OMSS, CROWS LANDING, CA (1991)

Analytical Batch (Condition)	Sample Type	No. of Samples Run	No. of Method Blanks	No. of Positive Detections	Average Detection Limit (total μg)
1-4, 6	101A Train	35	6	0	<7.3
3, 7-8	101A Train	26	4	0	<4.1
7, 8	101A Train	25	5	0	<22.5
6, 8	101A Train	25	5	0	<18.6
7	101A Train	8	2	0	<16.9
1-4, 6	Lab Filter	35	0	0	<0.02
6-8, 3	Lab Filter	22	4	0	<0.03
7, 8	Lab Filter	22	4	0	<0.01
7, 8, 3	Lab Filter	22	4	0	<0.01
7, 8	Lab Filter	18	4	0	<0.01
	Total	238	44	0	<6.9

Note: See Analytical Results in Appendix D for Individual Method Blank Values.

the 44 method blanks analyzed (1 for every 10 samples analyzed), no detections were found. The results for each blank analysis are given in the analytical results in Appendix D.

Possible analytical matrix interferences were investigated by conducting matrix spike analyses. A known amount of Hg was added to a series of samples and the recovery calculated. Radian's internal QA criterion for matrix spike recoveries is ±20 percent of 100 percent. Table 7-7 presents the Method 101A matrix spike recovery results. All recoveries were within 20 percent of 100 percent. In addition to matrix spike (MS) analyses, matrix spike duplicate (MSD) analyses were also completed. The QA criterion for MSD recoveries results are within 10 percent of the MS value. The individual MSD results are listed in Appendix D. All MSD results met the QA criterion.

Laboratory Control Samples (LCS) were also analyzed to verify the continuing accuracy of the spectrometer calibration curve. A known concentration of Hg prepared from a source of Hg separate from the calibration Hg stock was submitted for analysis. Acceptable results of LCS analyses were to be within 10 percent deviation from the actual LCS value. Table 7-8 presents the Method 101A LCS range of results. All LCS samples met the acceptance criterion. Individual LCS results are given in Appendix D.

7.4.2 Multiple Metals Analytical Quality Assurance

Table 7-9 presents the method blank metals results for the Multi-Metals flue gas samples. Results are given for both the FH and BH fractions. A small amount of Hg was found in one of the method blanks analyzed with the Condition 5 samples. This value was 5.9 total μg for a FH fraction. Typical FH amounts of Hg collected in the test samples were less than 1 μg. (Total FH/BH Hg collected averaged 181 total μg.) Therefore, the level of Hg found in the method blanks does not appear to be significant. Lead was not detected in

TABLE 7-7. MERCURY 101A MATRIX SPIKE RESULTS
OMSS, CROWS LANDING, CA (1991)

Analytical Batch (Condition)	Sample Type	No. of Samples Run	No. of Matrix Spikes (including MSD)[a]	Range of Recovery Values (%)
1-4, 6	101A Train	35	6	85.3-104
3, 7-8	101A Train	26	4	94.5-102
7, 8	101A Train	25	4	94.5-102
6, 8	101A Train	25	4	95.2-103
7	101A Train	8	2	94-98
1-4, 6	Lab Filter	35	4	96.8-99.9
6-8, 3	Lab Filter	22	6	88.6-107
7, 8	Lab Filter	22	4	92.4-103
7, 8, 3	Lab Filter	22	2	89.9-96
7, 8	Lab Filter	18	4	97.8-102
	Total	238	40	

[a] MSD = Matrix Spike Duplicates

Note: Acceptance criterion for matrix spikes is ±20 percent. The MSD criterion is ±10 percent of the duplicate result. (See Analytical Results in Appendix D for individual MS and MSD values.)

TABLE 7-8. MERCURY 101A LABORATORY CONTROL SAMPLE RESULTS
OMSS, CROWS LANDING, CA (1991)

Analytical Batch (Condition)	Sample Type	No. of Samples Run	No. of LCS Samples	Range of Recovery Values (%)
1-4, 6	101A Train	35	3	94.8-106
3, 7-8	101A Train	26	4	96.2-105
7, 8	101A Train	25	7	95.8-106
6, 8	101A Train	25	8	93.2-106
7	101A Train	8	3	97.3-101
1-4, 6	Lab Filter	35	3	93.8-101
6-8, 3	Lab Filter	22	4	99.7-103
7, 8	Lab Filter	22	4	92-110
7, 8, 3	Lab Filter	22	4	92-101
7, 8	Lab Filter	18	4	91.5-107
	Total	238	44	

LCS = Laboratory Control Sample acceptance criterion is ±10 percent of 100.

TABLE 7-9. MULTIPLE METALS METHOD BLANK, MATRIX SPIKE, AND LABORATORY CONTROL SAMPLE RESULTS OMSS, CROWS LANDING, CA (1991)

Analytical Batch (Condition)	Fraction[a]	Method Blank (total μg)			Matrix Spike (%)		
		Pb	Cd	Hg	Pb MS/MSD	Cd MS/MSD	Hg MS/MSD
4, 6, 8	FH	<0.3	0.36	<0.4	106/103	95.6/94.8	100/97
5, 9	FH	<0.3	0.31	5.6	110/110	91.3/91.2	94/95
4, 6, 8	PR	NA	NA	<0.2	-	-	106/104
5, 9	PR	NA	NA	<0.2	-	-	103/94.4
4, 6, 8	BH	<0.3	<0.2	<5.0	100/100	105/104	106/94
5, 9	BH	<0.3	<0.2	<5.2	97/98.6	97.9/97.6	102/100
4, 6, 8	KM	NA	NA	<1.8	-	-	102/99.3
5, 9	KM	NA	NA	<1.7	-	-	98.1/94.3
4, 6, 8	PR				-	-	105/104
					Laboratory Control Sample (%)		
5, 9	BH				103	103	99.2
4, 6, 8	KM				-	-	96.5
5, 9	KM				-	-	99.2

[a] FH = Front Half
PR = Probe Rinse
BH = Back Half
KM = $KMnO_4$ Fraction

Note: MS = Matrix Spike
MSD = Matrix Spike Duplicate

any of the method blanks, however, a small amount of Cd (approximately 0.3 μg) was found in two samples.

Table 7-9 also presents the MS results for the metals analyses. All spiked recoveries were within the QA allowance of ±20 percent of 100 percent. All MSD recoveries were within 10 percent of the MS value for Pb, Cd, and Hg except one BH Hg sample (MS = 106 percent, MSD = 94 percent). With 17 MSD recoveries meeting the 10 percent criterion, and only one MSD value not meeting it, the MM analytical QA appears to be acceptable.

LCS values are also shown in Table 7-9. All results are within 10 percent of 100 percent thereby meeting the QA criterion.

7.5. DATA VARIABILITY

Simple CV values are presented in Table 7-10. These values do not reflect on the precision of the sampling and analytical method since they do not compare duplicate trains as was done in previous sections. The following values are presented as indicators of data variation within each test condition. Pooled CV values are also presented.

7.5.1 Overview

Coefficients of variation were calculated for all the final stack gas pollutant concentrations. The CV or RSD is calculated by dividing the standard deviation by the mean and expressed as a percentage. The CV values expressed in the following tables are not intended to represent sampling/analytical precision. They are more a reflection of the variability of the data as a whole, including process caused emission variability, as well as variability in the waste feed. The CV values presented here should not be compared to any acceptability criterion. They are only shown to provide insight into the variability of the data.

The CV values for each test condition are calculated as follows:

TABLE 7-10. COEFFICIENTS OF VARIATION FOR THE OUTLET FLUE GAS CONCENTRATIONS OMSS, CROWS LANDING, CA (1991)

Outlet Sampling Location										
							101A		Multiple Metals	
Cond	Flow (%)	H_2O (%)	CO_2 (%)	O_2 (%)	Cd (%)	Pb (%)	Hg (%)	Hg R (%)	Hg (%)	Hg R (%)
4	2.8	7.7	3.5	4.3	52.8	24.5	27.9		44.7	46.2
5	3.8	5.4	1.5	0.6	35.7	49.5	26.9	8.6	17.0	13.7
6	8.4	1.6	2.6	0.8	25.6	19.7	56.9	14.7	35.2	94.9
8	5.9	2.9	3.2	3.1	60.7	74.0	53.6	10.4	17.2	26.3
9	5.2	5.3	1.3	4.1	0.9	7.3	25.0	31.9	8.7	14.0
Outlet Pooled	5.3	5.8	4.2	4.6	41.0	42.4	47.4	17.8	27.9	49.6
			Combined 4.4				Combined 42.4		Combined 39.9	

NOTE: All values were based on concentrations corrected to 7 percent O_2.

$$CV = \frac{S}{M} \times 100 \qquad (7\text{-}1)$$

where CV = Coefficient of variation;

S = Standard deviation (using n-1 in the denominator where n = number of data points); and

M = mean.

The CV's from several distinct groups of data can be combined into a "Pooled CV." Pooled CV's presented for all test conditions are calculated as follows:

$$CV_p = \sqrt{\frac{\sum (CV_i)^2 \, n_i}{\sum n_i}} \qquad (7\text{-}2)$$

where CV_p = pooled coefficient of variation;

CV_i = Coefficient of variation for a simple sample set i; and

n_i = Number of data points in that sample set.

7.5.2 Test Program Data Variation

Tables 7-10 presents the CV's for all measured flue gas concentrations at the APCD outlet. Values are presented for each individual condition which was composed of two to four runs. Condition CV values are presented for each parameter at the outlet sample location. Pooled CV values are presented for each parameter inclusive of all test conditions.

Duplicate trains (side by side nozzles/trains) were operated during five test conditions for both the Method 101A Hg train and the MM train. Assessments of precision of the 101A train and the MM train was completed in Sections 3.0 - 5.0. The CV values for Hg concentrations are presented here without any statistical comparisons made.