Draft Project Report

Evaluation and Improvement of Condensable Particulate Matter Measurement

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EPA would like to acknowledge the contributions of all stakeholders in the improvement of the measurement of fine particulate matter. EPA would like to thank George Marson of Environment Canada for his contribution to the initial scoping experiments to quantify the lowest level of condensable particulate matter that could be measured and to minimize the formation of condensable particulate matter artifact. EPA would also like to acknowledge Naomi Goodman and the Electric Power Research Institute for designing and funding additional sampling train experiments to challenge the dry impinger method at higher sulfur dioxide and moisture conditions typical of coal-fired power plants.

ABSTRACT

Method 202 is the current EPA reference method for measuring condensable particulate matter (CPM) in stationary source emissions. EPA invited stakeholder participation in response to comments provided through a proposed rule to implement the fine particle NAAQS (70 FR 65984, November 1, 2005). Based on public comments, EPA initiated an evaluation and improvement of Method 202. EPA focused on artifacts caused by sulfur dioxide (SO_2). Eastern Research Group (ERG), an EPA contractor, evaluated artifact formation from the introduction of SO_2 and nitrogen oxides (NO_x). Two stakeholders—Environment Canada and the Electric Power Research Institute (EPRI)—contributed to the evaluation. This report documents experiments used to identify which modifications to Method 202 should be explored and the results of laboratory-based full-scale stack gas sampling train experiments to evaluate the effectiveness of those modifications versus the best practice Method 202. This report presents the results of ERG's laboratory evaluation of a dry impinger modification to Method 202 and describes the laboratory and quality control procedures that were followed.

EXECUTIVE SUMMARY

On April 25, 2007, EPA promulgated the Clean Air Fine Particle Implementation Rule regarding the Clean Air Act (CAA) requirements for State and Tribal plans to implement the 1997 $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS). These rules require each State that has a $PM_{2.5}$ nonattainment area to submit an attainment demonstration and adopt regulations to ensure the area will attain the NAAQS as expeditiously as practicable. The $PM_{2.5}$ emission inventories and analyses used in the attainment demonstrations must consider filterable and condensable particulate matter (CPM) (i.e., vapor-phase materials that condense or react to form PM immediately upon being emitted from a process vent or stack).

Method 202 in Appendix M of 40 CFR Part 51 is EPA's method for measuring CPM from stationary sources. Method 202, as promulgated in 1991, is a set of sampling procedures for collecting CPM in water-filled impingers, and a set of sample recovery procedures that are performed on the impinger water. The water-filled impingers are nearly identical to the four chilled impingers used in standard stationary source sampling trains for particulate matter (PM) (e.g., Method 5 and Method 17 of Appendix A-3 and A-6, 40 CFR Part 60). Method 202 contains several optional procedures that were intended to accommodate the various test methods used by State and local regulatory entities at the time Method 202 was developed. EPA's preferred operation of the Method 202 requires that the impinger water be purged with nitrogen after the test run to remove dissolved sulfur dioxide (SO_2) gas from the impinger contents. The impinger solution is then extracted with methylene chloride to separate the organic CPM from the inorganic CPM. The organic and aqueous fractions are dried and the residues weighed. The sum of both fractions represents the total CPM.

The preamble to the fine particle implementation rule acknowledged that Method 202 may not provide sufficiently precise measurement of fine PM, including CPM, due to improper application of Method 202 and due to reaction artifacts that can form in the impinger water when SO_2 is present in stationary combustion source emissions

In response to the need for improved measurement of fine PM, EPA and stakeholders performed a series of experiments to assess artifact formation and to refine Method 202. Based upon the results of the various experiments, EPA developed Other Test Method 28 (OTM 28), which is a revision of Method 202. EPA posted OTM 28 on the EPA Web site (www.epa.gov/ttn/emc/prelim.html). OTM 28 achieves at least 90 percent reduction in

SO_2/sulfuric acid artifact formation compared to the current Method 202 using the nitrogen purge option. The proposed method removes options and provides testing contractors with a standardized procedure that improves the precision of the method, and quantifies more accurately direct PM emission to the ambient air.

OTM 28 includes the following changes to the Method 202 sampling train. Figure ES-1 illustrates the improved sampling train.

- Installing a Method 23-type condenser between the filter in the front-half of the sample train and the first impinger to cool the sample gases to less than or equal to 30 ^oC.
- Installing a recirculation pump in the ambient water bath to supply cooling water to the condenser.
- Changing the first two impingers from wet to dry, and placing these two dry impingers in a water bath maintained at less than or equal to 30 ^oC.
- Using a short-stem insert in the first impinger and a standard long-stem insert in the second impinger.
- Requiring the use of a low-temperature filter (i.e., the CPM filter), as described in EPA Method 8, between the second and third impingers (a Teflon filter is used in place of the fiberglass filter described in EPA Method 8).
- Requiring that the temperature of the sample gas drawn through the CPM filter be maintained at or below 30 ^oC.

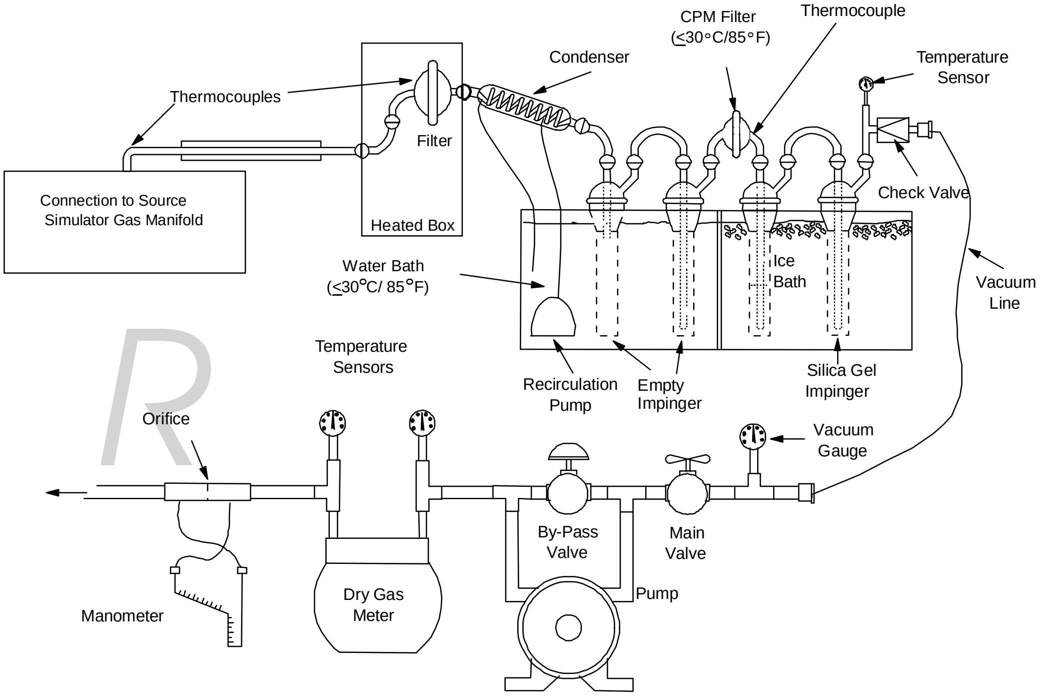

Figure ES-1. OTM 28 Sampling Train

EPA is also proposing the following sample recovery procedures in OTM 28:

- Extracting the CPM filter with water and organic solvent.
- Evaporating the liquid collected in the impingers in an oven or on a hot plate down to a volume of no less than 10 milliliters, instead of all the way to dryness.
- Evaporating the remaining liquid to dryness at ambient temperature prior to neutralization with ammonium hydroxide.
- Reconstituting the sample with 100 milliliters of deionized ultra filtered water.
- Titrating the reconstituted sample with 0.1 normal ammonium hydroxide to achieve a neutral pH of 6.5 to 8.5.
- Evaporating the neutralized liquid sample to a volume of no less than 10 milliliters in an oven or hot plate.
- Evaporating the final sample volume to dryness at ambient temperature.
- Weighing the CPM sample residue to constant weight after allowing a minimum of 24 hours for equilibration in a desiccator.

OTM 28 originated from the following series of experiments performed by EPA, its contract laboratory (Eastern Research Group (ERG)), and two stakeholders (Environment Canada (EC) and the Electric Power Research Institute (EPRI)).

- **Initial scoping experiments** to determine which modifications to Method 202 would offer the most reduction in artifact formation.
- **Phase I ERG simulated stack gas train experiments** to evaluate modifications to EPA Method 202 using full scale sampling equipment to better characterize the precision and bias of CPM measurements.
- **Phase I EPRI simulated stack gas train experiments** to evaluate the performance of the OTM 28 at conditions that represent a wider range of flue gas compositions in coal-fired power plants.
- **Phase II EPRI simulated stack gas train experiments** to evaluate how well two additional methods captured SO_3/SO_4 and whether either method could be used to correct the SO_2 bias in OTM 28.

All Phase I and II laboratory experiments followed the "Laboratory Test Plan and Quality Assurance Project Plan (QAPP) for Method 202 Assessment & Evaluation for Bias and Other Uses" (ERG, 2006) and EPRI's supplement to the EPA Laboratory Test Plan and QAPP (EPRI, 2007).

Initial Scoping Experiments. *Initial scoping experiments were conducted by ERG and EC to determine which modifications to Method 202 that would offer the most reduction in artifact formation.*

The initial laboratory experiments evaluated procedures to reduce the field blank and determine the lowest level of CPM that could be measured. ERG and EC evaluated bench scale sample preparation and analysis procedures to evaluate potential chemical additives (e.g., HCl, H_2SO_4) that might reduce artifacts. ERG and EC also completed several exploratory tests to reduce the CPM originating from field/analytical blanks. In addition, EC modeled the physical and chemical characteristics of typical CPM to optimize the collection temperature, sample drying temperature, and drying time.

How do changes in weighing room air pressure and temperature affect sample weight?

ERG and EC developed and conducted a series of tests to identify/eliminate sources of bias in the analytical procedures. The experiments predicted and demonstrated that changes in weighing room air pressure and temperature affect the measurement of CPM from the samples. EC estimated the effect of changes in weighing room air pressure and temperature on the apparent weight of the 250 mL jars to be the following:

- Effect of 1 kilopascal (kPa) lab pressure change = 0.9 mg, due to air buoyancy
- Effect of 1 °C lab temperature change = 0.6 mg, due to scale thermal sensitivity drift

EC estimated the effect of weighing room air pressure and temperature on the apparent weight of the aluminum weighing pans to be the following:

- Effect of 1 kPa lab pressure change = 0.005 mg, due to air buoyancy
- Effect of 1 °C lab temperature change = 0.003 mg, due to scale thermal sensitivity drift

The weighing room air pressure and temperature effects on the aluminum weighing pans were much lower than the precision of the balance used for these experiments (±0.1 mg). In addition, when samples were weighed in 250 mL glass jars, the average weight of each jar had a standard deviation of 0.5 mg.

EPA concluded the following based on these experiments:

- The 0.5 mg constant weight criterion[1] in Method 202 appears to be appropriate for filters, but appears to be inappropriate for bulky glass jars.
- The quantitative transfer of concentrated condensate to aluminum weighing pans circumvented the problem of weighing small CPM mass in bulky glass weighing containers, and avoids the problem of temperature and pressure grossly affecting the weight of the CPM samples.

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[1] "Constant weight" means a difference of no more than 0.5 mg or l percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings (overnight desiccation is a common practice).

- CPM must be quantitatively transferred to the aluminum weighing pans and samples must be neutral pH between 6.5 and 8.5 to avoid artifact formation with the aluminum.
- The proposed method should require evaporation of the final aqueous sample down to no less than 10 mL, neutralization, and quantitative transfer to aluminum weighing pans for final dry down and weighing.

Do any sulfites remaining after the nitrogen purge oxidize during storage and produce additional inorganic CPM?

Sulfites are formed in Method 202 through SO_2 contact with cold condensed water in the impingers and remain in the condensate after the nitrogen purge. The effect of sample storage on final CPM weight is important since the minimum residual weight anticipated in the revised method from well controlled sources can be on the order of 2 to 3 mg. To investigate this potential contribution to inorganic CPM formation, the aqueous fraction from 10 nitrogen-purged sampling train test runs were split in half, one of which was spiked with three drops of 30 percent hydrogen peroxide (H_2O_2) (approximately 0.15 mL). The peroxide spike oxidizes the residual sulfite and approximates the effect of longer storage times.

Results from subsequent evaporation and jar weighing analyses showed that the spiked jars contained, on average 0.4 mg more CPM, than the unspiked jars.

EPA concluded the following based on these experiments:

- A 0.4 mg increase provides an upper bound indication of potential CPM formation due to extended sample storage.
- Samples improperly purged could show positive bias after storage.

Which CPM would be collected by the Method 202 sampling train based on theoretical calculations of vapor pressure?

As part of the initial scoping experiments, EC completed theoretical calculations to determine which CPM organic compounds would likely be captured as organic CPM in the revised method. Thermodynamic calculations were performed based on vapor pressure, temperature, and drying time to determine retention of organic CPM. These calculations provided the theoretical basis to determine if the sampling and analytical procedures capture the material expected to be CPM in ambient air near a source emission. Results showed the following:

- Method 202 should completely retain compounds with vapor pressure lower than n-heptadecane (C_{17} and heavier hydrocarbons). C_{15} and lighter hydrocarbons are not retained. C_{16} (n-hexadecane: boiling point 287 °C, vapor pressure 0.0011 mmHg @ 21 °C) are only partially retained, representing an arbitrary boundary for organic CPM during sampling episodes collecting approximately 60 dry standard cubic meters of stack gas.

- During the Method 202 nitrogen purge, C_{17} and heavier hydrocarbons are fully retained. C_{16} losses are significant at hydrocarbon concentration levels less than 40 ppmC. Potential loss of lighter compounds is irrelevant, as these compounds are unlikely to be captured.

- During the drying and constant weighing process, the loss rate for C_{16} hydrocarbons equals 0.25 mg/hr. The organic loss rate for C_{17} hydrocarbons was less than the sensitivity of the balance. Hydrocarbons with higher volatility than C_{17} will be lost during the drying and constant weighing process except at sources with heavy hydrocarbon emission concentrations.

- Vapor pressure calculations showed that dilution sampling techniques such as EPA Conditional Test Method 039 (CTM 039) are unable to capture C_{16}-like compounds, based on the typical 20:1 sample dilution specified in the method. Capture of the C_{17} normal chain hydrocarbon in CTM 039 is significantly lower than Method 202 at hydrocarbon concentrations less than 40 ppmC. Outside this narrow range of compounds, the organic CPM collected in OTM 28 and CTM 039 are expected to be comparable.

EPA made the following conclusions based on theoretical calculations of vapor pressure:

- Since the CPM loss rate in OTM 28 is similar to the loss rate in Method 202, EPA determined that weighing to a constant weight is appropriate for both organic and inorganic fractions of the CPM method. Thus, the requirement to weigh samples to constant weight was retained in OTM 28.

- The proposed method should require a sample train condenser and impinger bath temperature to be less than or equal 30 °C (85 °F) to minimize SO_2 absorption into condensed stack moisture.

How do the initial modifications to the sampling train perform under laboratory conditions?

As part of the initial scoping experiments, EC completed 15 full scale sampling train tests in the laboratory. The CPM collection portion of the sampling train consisted of a water-cooled coil, a condensate reservoir (i.e., the first dry impinger), a straight-stem impinger, and a silica gel impinger. All these components were kept in an ice bath, except the condensate reservoir, which was external to the ice box. These experiments evaluated the effectiveness of the nitrogen purge; evaluated the potential CPM artifact contribution due to higher concentrations of SO_2; and compared the drying procedures in single glass containers versus quantitative transfer and weighing in aluminum pans. Table ES-1 shows results of the EC sampling tests.

Table ES-1. Results of EC Tests 1-15

EC Test	SO_2 (ppmd)	H_2O (%)	CPM Jar Weighing (mg/dscm)	CPM Pan Weighing (mg/dscm)
1	253	12.7	4.1	2.8
2	252	11.1	1.5	1.0
3	255	11.2	1.4	1.0
4	258	11.3	1.4	1.1
5	258	11.2	2.0	2.5
Average	255	11.5	2.1	1.7
Stnd. Dev.	2.9	0.7	1.2	0.9
6	25	12.3	3.1	1.9
7	25	11.8	0.5	0.9
8	25	11.7	1.3	1.0
9	25	11.6	1.5	0.8
10	25	10.8	1.0	0.8
Average	25	11.7	1.5	1.1
Stnd. Dev.	0.2	0.5	1.0	0.4
11	123	20.8	-	2.4
12	121	19.7	-	0.9
13	121	19.5	-	0.7
14	121	19.8	-	0.9
15	122	21.0	-	2.0
Average	121	11.7	-	1.1
Stnd. Dev.	1.1	0.7	-	0.7

Results showed the following:

- Nitrogen purge with unfiltered ultra-high purity gas produced a fine black inorganic residue containing iron oxide that was not present in filtered purge gas.

- Three consecutive weight determinations showed differences less than or equal to 0.5 mg and the average standard deviation was estimated to be 0.1 mg.

- Samples dried down in a single glass jar (versus transfer to an aluminum weighing pan) contained 0.4 mg more CPM.

- Samples from runs at 250 ppm SO_2 contained 0.4 mg more CPM than runs at 25 ppm SO_2.

EPA made the following conclusions from EC laboratory train experiments:

- Nitrogen purge at ambient temperature is likely to be more effective than the purge at ice bath temperature.

- Nitrogen purge gas volume of approximately 1 cubic meter drawn through the sampling train is adequate to purge dissolved SO_2 from the sampling train. The nitrogen must be filtered since residual aluminum or iron dust from the purge gas cylinder can add significant mass to the CPM sample.

- A 10-fold increase in SO_2 injected into the test gas mixture caused no measurable increase in inorganic CPM artifact using the revised procedure.

- The inorganic CPM artifact caused by SO_2 may be reduced to approximately 2 mg or less.

These conclusions led to or supported the following changes in the method:

- Require dry impingers at the start of sampling.

- Require the nitrogen purge.

- Filter the nitrogen gas.

- Transfer the samples to aluminum weighing pans for final dry down.

Phase I EPA Sampling Train Experiments. *Phase I EPA simulated stack gas train experiments were completed to evaluate modifications to the sampling and analytical procedures.*

The Phase I EPA sampling train experiments evaluated modifications to the sampling and analytical procedures in Method 202. These Phase I tests compared results from Method 202, operated following EPA's recommended best practice procedures, to results of a dry impinger sampling train assembled according to Richards (Richards, et al, 2005). Tests were performed at gas concentrations typical of stationary source compliance limits. Gases used to simulate stack conditions included SO_2, nitrogen oxides, water, and carbon dioxide.

The first three tests were performed using various modifications to the Richards train. Tests 1-3 showed the artifact produced in the Richards train was significantly less than artifacts produced in Method 202. After Phase I EPA Tests 1-3 demonstrated greater than 90 percent reduction of SO_2 artifact using dry impingers, further refinements were made to the sampling and analytical procedures and EPA Tests 4-8 were completed. Tests 4-8 were performed using the complete set of modifications to the CPM train, which EPA posted on the EPA Web site as OTM 28. Figure ES-2 shows CPM results for EPA Tests 1-8.

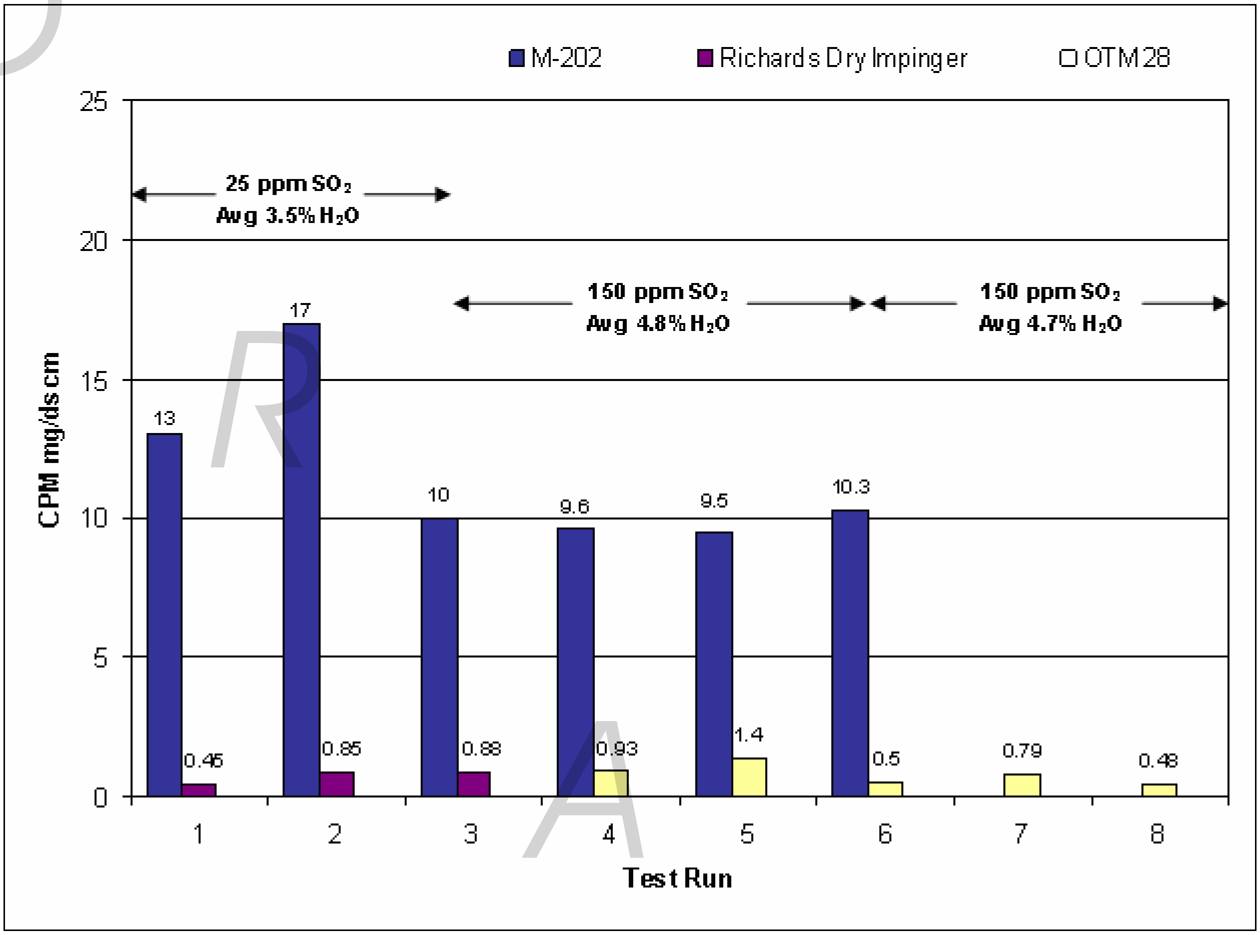

Figure ES-2. Results for Phase I EPA Tests 1-8

Results showed that the additional modifications to sampling train, including elevating the temperature for collection of CPM to 30 °C (85 °F) from ice water temperatures, virtually eliminated the SO_2 artifact. EPA concluded that the CPM remaining in OTM 28 is not SO_2 artifact, but rather typical train blank.

Does OTM 28 produce results with acceptable precision and bias?

OTM 28 was evaluated using the synthetic stack gas manifold operated at 300 °F with gas composed of 150 ppm SO_2, 12 percent carbon dioxide, 50 ppm nitrogen oxides, 8 percent oxygen, and 6-10 percent moisture. A total of eight replicate tests were performed to evaluate the method's precision and bias using the statistical procedures in EPA Method 301. Table ES-2 shows results for the eight replicate tests.

Table ES-2. CPM Results of the Eight Replicate Tests

Replicate Test Run	Organic CPM (mg)	Inorganic CPM (mg)	Ambient Filter CPM (mg)	Total CPM (mg)
1	0.11	2.23	-0.34	2.00
2	0.15	2.88	-0.060	2.97
3	0.090	1.37	0	1.46
4	0.30	1.91	0	2.22
5	0.16	1.54	0.070	1.77
6	0.33	2.19	-0.17	2.34
7	0.080	1.18	0.30	1.56
8	0.020	1.87	0.17	2.06
Blank	-0.020	0.21	0	0.21
Average	0.16	1.90	0	2.05
Std Deviation	0.10	0.51	0.17	0.45
Estimated MDL	0.31	1.54	0.49	1.36

Results demonstrated improved precision and a reduction in the bias from SO_2 artifacts to near the method detection limit (MDL). Based upon comparison of the results to their respective estimated MDLs, the organic and ambient filter fractions were not a measurable source of bias. If the averages of the inorganic and total results are blank-corrected, then they approach the MDL. EPA determined that the inorganic bias had been reduced to the point at which it can be effectively eliminated by OTM 28. Thus, EPA concluded that the precision and bias of OTM 28 under controlled laboratory conditions were improved significantly over any of the options in Method 202. The MDL and supporting laboratory evidence demonstrate that OTM 28 is capable of measuring CPM at sufficiently low levels (1-3 mg).

How does ammonia in the source gas affect OTM 28?

Phase I EPA Tests 16-18 investigated the affect of adding ammonia to the synthetic stack gas stream containing moisture and SO_2. OTM 28 was evaluated using the synthetic stack gas manifold operated at 300 °F with gas composed of 9 ppm ammonia, 22 ppm SO_2, 11 percent carbon dioxide, 45 ppm nitrogen oxides, 7.5 percent oxygen, and 11-12 percent moisture. A 71 °C (160 °F) heated filter was added between the Method 5 train and the OTM 28 train to investigate the formation of filterable ammonium sulfate. The heated filter was designed to capture filterable particulate if it were formed by the reaction of ammonia and SO_2. Results showed no CPM in any of the fractions: 160 °C filter, 71 °C filter, aqueous fraction, or the 30 °C filter.

Results indicated that no CPM formed in either the OTM 28 train or the 71 °C filter on the modified OTM 28 train. EPA concluded that ammonia, under the conditions tested, does not react with SO_2 to form particulate matter. In the absence of particulate formation, it can also be concluded that an artifact is not formed and no additional modifications to the method were necessary due to ammonia artifacts.

Phase I EPRI Sampling Train Experiments. *Phase I EPRI simulated stack gas train experiments were conducted to evaluate the performance of OTM 28 at conditions that represent a wider range of flue gas compositions in coal-fired power plants.*

How does OTM 28 perform at a wider range of conditions expected at coal-fired power plants?

Phase I EPRI Tests 1-12 expanded the EPA test matrix to challenge OTM 28 with higher moisture (10 and 15 percent) and a higher SO_2 concentration (500 ppmv). The EPRI test matrix was intended to help EPA develop a method that would produce accurate results in coal-fired power plants with state-of-the-art particulate controls, on both scrubbed and unscrubbed units, and on coals with a wide range of sulfur content. Thus, to represent the full range of flue gas compositions from coal-fired power plants, EPRI's test matrix included test runs with 500 ppm SO_2 and additional synthetic gas moisture levels of 10 and 15 percent. OTM 28 was compared to the standard EPA Method 202 operated according to EPA's best practice recommended procedures. The objective of these runs was to quantify the SO_2 bias in Method 202 and determine the extent to which OTM 28 mitigates this bias at higher moisture and SO_2 concentrations.

Results from EPRI Tests 1-12 showed the effect of higher SO_2 and moisture conditions on artifact formation in OTM 28. Gravimetric results showed low artifact results that were about the same concentration as the average train blank. Gravimetric results include train blank contribution to mass. Figure ES-3 summarizes the gravimetric results from EPRI Tests 1-12.

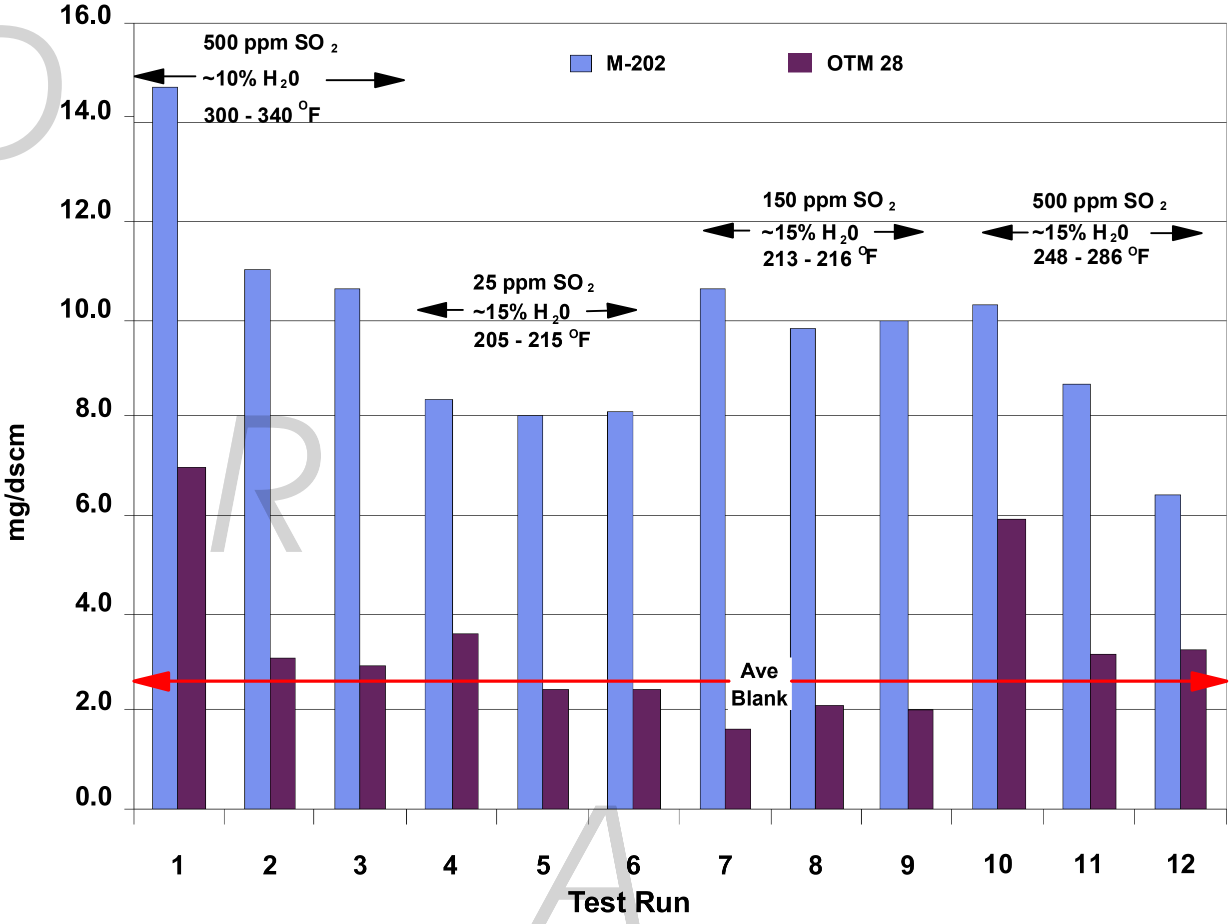

Figure ES-3. Gravimetric Results from Phase I EPRI Tests 1-12

Results from the titration of sulfuric acid performed as part of the analysis procedure gave a clearer evaluation of artifact formation in Method 202 and OTM 28 since train blank contribution to mass is not measured by the titration of sulfuric acid. The average blank in Phase I EPRI Test Runs 1-12 is the average of three complete sampling train blanks that were assembled, recovered, and analyzed without taking any sample from the manifold. Titration results are shown in Figure ES-4.

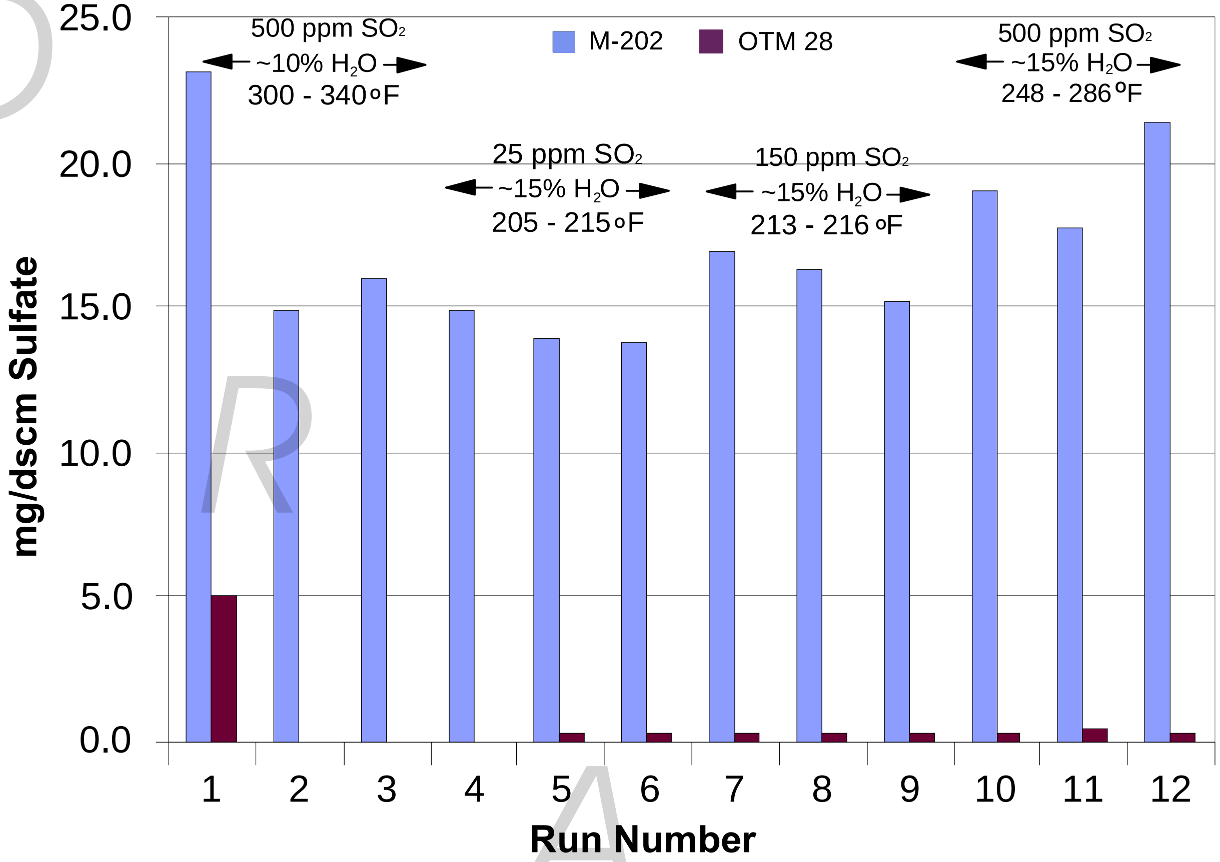

Figure ES-4. Titration Results from Phase I EPRI Tests 1-12

EPA made the following conclusions from EPRI Tests 1-12:

- OTM 28 continues to reduce the artifacts formed by SO_2 during stack gas collection of CPM, even at the additional conditions imposed on the test methods during Phase I EPRI Tests 1-12.

- Based on titration of the sulfuric acid in aqueous train samples, the absolute mass of SO_2 converted to SO_4 artifact in Method OTM 28 is approximately the same in each test run over the SO_2 concentration range of 25 to 500 ppm.

- Data show that there is no difference in the artifact formed in OTM 28 over the range of conditions in this set of tests.

- Calculations of uncertainty (standard deviation) for these results can be expressed with a two standard deviation error for the 98 percent confidence interval, which is significantly different from zero for Method 202 confirming measurable artifact formation above the blank.

- Similar statistical evaluations of OTM 28 show CPM results do not differ statistically from the blank.

Phase II EPRI Sampling Train Experiments. *Phase II EPRI experiments evaluated whether two additional methods could be used to correct the* SO_2 *bias in OTM 28.*

EPRI proposed two other sampling procedures as a potential means to correct the SO_2 bias in OTM 28. These alternatives would identify the SO_2 bias in OTM 28 by providing a separate measurement of the amount of sulfur trioxide/sulfuric acid (SO_3/H_2SO_4) in the flue gas. These extra measurements may allow sulfate artifacts captured in OTM 28 water impinger recoveries to be corrected.

Could other sampling methods be used to correct the SO_2 bias in OTM 28?

Phase II EPRI tests evaluated how well two methods captured SO_3/SO_4.

Controlled Condensate Method. EPRI Tests 19-24 and 31-36 measured the ability of OTM 28 and the controlled condensate method to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at relatively high and low concentrations. The percent recovery of each train type measured by IC was compared to the theoretical SO_3/H_2SO_4 concentration added to the synthetic stack gas manifold. Figure ES-5 summarizes the results of Phase II EPRI Tests 19-24 and 31-36.

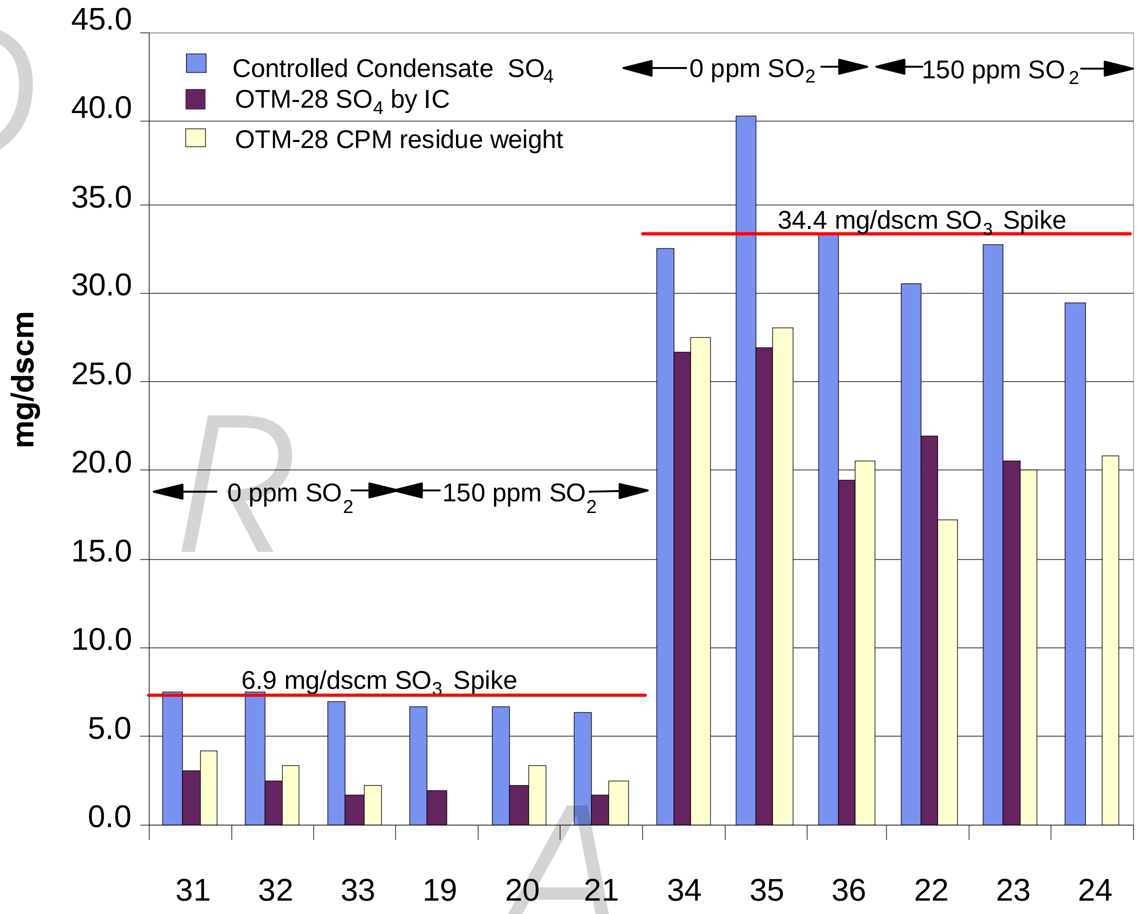

Figure ES-5. Results of OTM 28 vs. Controlled Condensate Method Sulfuric Acid Challenge

Results showed the following:

- OTM 28 SO_4 recovery at the 6.9 mg/dscm (1.75 ppm) spike level ranged from 32-58 percent, with an average recovery of 41 percent compared to the spiked amount.

- OTM 28 SO_4 recovery at the 34.4 mg/dscm (8.75 ppm) spike level ranged from 58-81 percent, with an average recovery of 65 percent compared to the spiked amount.

- Controlled condensate percent recovery of SO_4 ranged from 86-117 percent, with an average recovery of 99 percent compared to the spiked amount.

The controlled condensate method accurately measures sulfate under the test conditions for experiments performed in this evaluation. Recovery of sulfuric acid from synthetic stack gas was lower for OTM 28 compared to the controlled condensate method or the theoretical spike level. SO_2 did not appear to contribute artifact to either method under these test conditions. When SO_2 is added, OTM 28 recovers less SO_4. Therefore, EPA concluded that additional artifact is not formed in the presence of SO_2.

EPRI concluded that if the controlled condensate method were used to measure sulfuric acid, and if sulfuric acid results were substituted for sulfate measured in OTM 28, then the total CPM results would be higher than OTM 28 results alone.

Low-temperature filter method. Phase II EPRI Tests 13-15 and 25-27 measured the ability of OTM 28 and the low-temperature filter methods to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at a relatively low concentration. Results in Figure ES-6 show that the 160 °F filter does not capture all of the SO_3. Some sulfate, in the form of sulfuric acid mist, passes through the 160 °F filter and is found in both the impinger water and the CPM (ambient) filter.

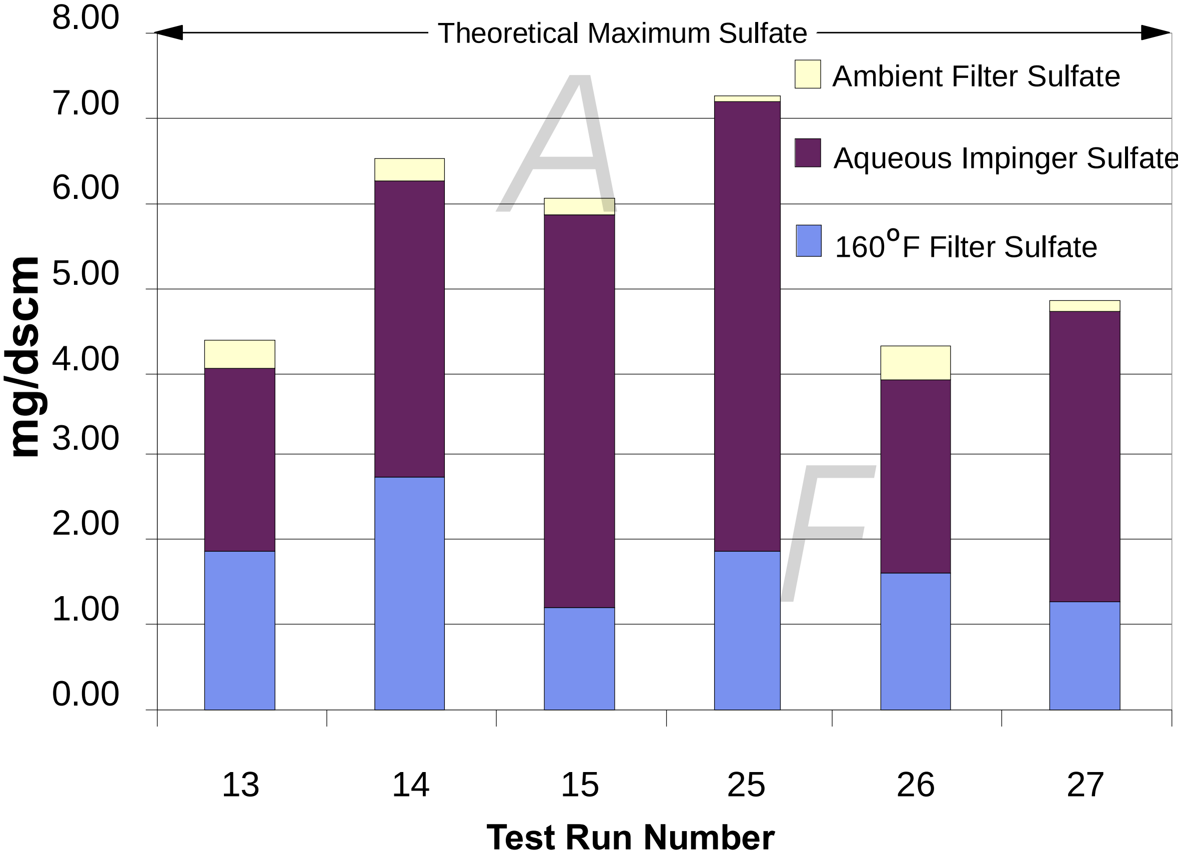

Figure ES-6. Low-Temperature Sampling Train Results by Fraction

EPRI concluded that addition of the 160 °F low-temperature filter makes the train slightly more efficient at collecting H_2SO_4 than OTM 28. The trains perform similarly over the range of SO_2 concentrations.

EPA concluded that since all of the H_2SO_4 was not collected on the 160 °F low-temperature filter, the low-temperature filter train can not provide correction for SO_2 artifact.

REFERENCES

EPRI, 2007. EPRI Supplement to EPA Laboratory Test Plan and Quality Assurance Project Plan Method 202 Assessment and Evaluation for Bias and other Uses. Prepared by URS Corporation for EPRI. February 2007.

ERG, 2006. U.S. EPA. Laboratory Test Plan and Quality Assurance Project Plan For Method 202 Assessment & Evaluation for Bias and Other Uses. Prepared by Eastern Research Group, Inc. for U.S. EPA under Contract 68-D-02-079. 2006.

Richards, et al, 2005. Richards, J.; Holder, T.; Goshaw, D.; Optimized Method 202 Sampling Train to Minimize the Biases Associated with Method 202 Measurement of Condensible Particulate Matter Emissions, Air & Waste Management Association Hazardous Waste Combustion Specialty Conference, St. Louis, Missouri, November 2-3, 2005.

1.0 INTRODUCTION AND OBJECTIVES

The U.S. Environmental Protection Agency (EPA) manages ambient air quality through the National Ambient Air Quality Standards (NAAQS). States must complete emissions inventories and analyses to demonstrate compliance with NAAQS. Such emission inventories include the National Emissions Inventory (NEI), State Implementation Plans (SIP), and the periodic emissions inventories required under the Consolidated Emissions Reporting Rule (CERR), which include the reporting of PM emissions. For EPA to effectively manage ambient air quality, the test methods that are used to develop emission inventories, demonstrate attainment, develop emission factors, and demonstrate compliance with an emission limit must yield results that are unbiased, accurate, and precise.

On April 25, 2007 (70 FR 20586), EPA promulgated the rules regarding the Clean Air Act (CAA) requirements for the development of State and Tribal plans to implement the 1997 fine particle NAAQS and to ensure that the areas will attain these standards no later than 2015. The promulgated rule to implement the fine particle NAAQS required the measurement of both the filterable and condensable fractions of particulate emissions that are 2.5 micrometers in diameter and smaller ($PM_{2.5}$) from stationary sources. These measurements are used to develop the emission inventories, analyses, and emission factors that States use to demonstrate compliance with the fine particle NAAQS. To quantify the condensable particulate matter (CPM) fraction of fine particle emissions, EPA, States, and emission sources rely on EPA Method 202, Determination of Condensable Particulate Emissions from Stationary Sources, which was promulgated in 1991 and published in Appendix M of 4O CFR part 51.

EPA acknowledged in the preamble to the April 25, 2007 final rule that Method 202 and its various hardware and analytic options described are sometimes applied inappropriately, which can lead to inaccurate and imprecise CPM measurements. EPA is also aware that application of Method 202 can produce inaccurate CPM measurements when sampling emission sources containing sulfur dioxide (SO_2) due to reaction artifacts that form in the sampling train. In addition, commenters on the November 1, 2005 (70 FR 65984) proposed rule highlighted imprecision and biases associated with Method 202, the lack of a method to size the filterable particulate matter, and the need for publishing methods in the Federal Register.

Method 202 is known to produce artifacts when sampling emissions sources with sulfur dioxide (SO_2). This artifact that forms in the Method 202 impingers produces a positive bias in the inorganic CPM emissions. In some compliance test reports, SO_2 related material was shown to be the major source of reportable CPM. When used to develop emission factors, these biases result in biases in the emissions factors. The use of biased emissions factors in turn produces biased national, regional, and facility-specific PM emissions inventories reported in the NEI, SIPs, and periodic reports required by the CERR.

The April 25, 2007 final rule established a transitional period for developing emission limits and regulations for condensable $PM_{2.5}$. During this transitional period, EPA committed to devote resources toward assessing and improving the available test methods for CPM and EPA invited stakeholder participation to evaluate Method 202.

This report summarizes part of EPA's efforts to evaluate and improve Method 202. Beginning in 2006, ERG—an EPA subcontractor—and stakeholder Environment Canada (EC) completed exploratory laboratory bench chemistry tests and simulated stack gas train experiments to evaluate Method 202 and the Electric Power Research Institute (EPRI) funded tests by ERG to evaluate method performance in an expanded test matrix. Field evaluation of the method to assess precision and bias at an operating stationary source is not addressed in this report. The laboratory studies focused on investigation and reduction of Method 202 artifacts caused by SO_2 in the stack gas. Specifically, this report documents the following experiments:

- Initial scoping experiments conducted by ERG and EC to determine which modifications to Method 202 would offer the most reduction in artifact formation.

- Simulated stack gas train experiments to evaluate modifications to EPA Method 202 using full scale sampling equipment to better characterize precision and bias of CPM measurements.

- Stack gas train experiments to evaluate the performance of the dry impinger method at conditions that represent a larger range of flue gas compositions in coal-fired power plants (500 ppm SO_2 and additional synthetic gas moisture levels of 10 and 15 percent).

- Stack gas train experiments comparing the performance of the dry impinger method and two additional methods—controlled condensate method and a low-temperature filter method to evaluate how well the methods captured SO_3/SO_4 and whether either method could be used to correct the SO_2 bias in the dry impinger method.

Laboratory experiments followed the “Laboratory Test Plan and Quality Assurance Project Plan (QAPP) for Method 202 Assessment & Evaluation for Bias and Other Uses” (ERG, 2006) (Appendix A) and EPRI’s supplement to the EPA Laboratory Test Plan and QAPP (EPRI, 2007) (Appendix D).

1.1 Previous Laboratory Experiments

Since the promulgation of Method 202 in 1991, air emission testing experience within the regulated industry and regulatory agencies has demonstrated the potential for variations in measured CPM emissions. Potentially significant problems affecting Method 202 accuracy include the following:

1. Artifacts formed by dissolved SO_2 and nitrogen oxides in water with subsequent oxidation to form sulfates and nitrates in the impingers.
2. Gas phase homogeneous reactions between ammonia and hydrogen chloride and/or between ammonia and SO_2 in the cold, water-filled impingers.
3. Loss of dissolved semivolatile organic compounds when impinger water is evaporated at an elevated temperature.
4. Penetration of submicrometer sized condensed particles (e.g., sulfuric acid mist) through the impingers of the Method 202 sampling train.

The SO_2 absorbed in the impinger water has been reported as one of the major causes of artifacts. Further oxidation of SO_2 in the presence of water allows formation of sulfuric acid or sulfate salts. This sulfuric acid is measured as an inorganic condensable particulate artifact that does not form immediately after the release of the stack gases to the ambient air. This artifact formed in the Method 202 impingers translates into a positive bias in the inorganic condensable PM emissions. Thus, EPA sought to verify and refine Method 202 to minimize the potential for artifact formation.

As early as 1989, results of laboratory and field evaluations in “Laboratory and Field Evaluation of the EPA Method 5 Impinger Catch for Measuring Condensible Matter from Stationary Sources” (DeWees, et al, 1989) led to several conclusions and recommendations:

1. A nitrogen purge should be conducted at the rate of 20 liters per minute for 60 minutes at the end of a test run when SO_2 is present in the gas being sampled. An air purge was not recommended.

2. The sample should be dried at 105 °C prior to the addition of ammonium hydroxide (NH_4OH). If this procedure were followed, then the sample could be analyzed for chlorine ions (Cl^-) following the final CPM weight determination, which would be subtracted from the final CPM weight and reported as secondary condensable matter.

3. The weight of ammonia added to the sample may be determined by (1) using the ion chromatography (IC) analysis for SO_4 according to EPA Method 5F, or (2) titrating the sample to a pH of 7.0 using 0.1 N NH_4OH and a pH meter.

4. The organic matter from the aqueous impinger contents should be extracted using methylene chloride. The use of ether-chloroform would also be acceptable.

5. When the determination of condensable matter includes both organic and inorganic fractions, the pH of the sample need not be adjusted prior to extraction, and the extraction should be repeated three times.

In September 2005, EPA completed a "Laboratory Evaluation of Method 202 to Determine Fate of SO_2 in Impinger Water" (Battelle, 2005), which replicated some of the earlier EPA work and addressed some additional issues. The report concluded that nitrogen purge was between 90 and 95 percent effective in reducing SO_2 artifact.

In November 2005, a "dry impinger" modification to Method 202 demonstrated in a significant additional reduction in the sulfate artifact. The modification was presented by a private testing contractor (Air Control Techniques, P.C) at the Air and Waste Management Association (AWMA) specialty conference. The modification was based on a decision that it is inappropriate to use water-filled impingers to cool the sample gas stream for CPM combustion sources having SO_2, NO_2, and/or soluble organic compounds (Richards, et al, 2005). Laboratory tests (Richards, et al, 2005) conducted using a conventional water filled impinger sampling train on a simulated combustion source gas stream confirmed that Method 202 is subject to a substantial positive bias due to SO_2 absorption and aqueous phase oxidation. Sulfur dioxide artifact reaches equilibrium with gas phase SO_2 in the purged Method 202 system resulting in as much as 30 to 40 mg of artifact. However, this bias can be substantially reduced by first passing the sample gas stream through a water-cooled indirect condenser, a dry knock-out impinger, and two empty impingers in an ice bath. This provides sufficient heat exchange to cool the sample gas stream below 68 ºF and to condense all vapor phase material to form CPM. The condensed particulate matter is captured in the condensed stack moisture or on a high-efficiency filter following the third and final sample collection impinger.

1.2 Current Laboratory Experiments

In 2006, after initial stakeholder results (Richards, et al, 2005) showed that removing the water from the impingers reduced artifacts caused by SO_2, EPA sponsored a series of laboratory tests to confirm the SO_2 artifact reduction between Method 202 and the dry impinger modification to Method 202. Under a contract with EPA, ERG completed additional experiments and consolidated results of stakeholder experiments.

Initial laboratory experiments helped determine which modifications to Method 202 would offer the reduction in artifact formation. Laboratory experiments started with bench scale sample preparation and analysis procedures to evaluate potential chemical additives (e.g., HCl, H_2SO_4) that might reduce artifacts. ERG and stakeholder EC also completed several exploratory tests to reduce the CPM originating from field/analytical blanks. In addition, EC modeled the physical and chemical characteristics of typical CPM to optimize the collection temperature, sample drying temperature, and drying time.

Simulated stack gas train experiments were conducted to evaluate modifications to EPA Method 202 and to better characterize precision and bias of CPM measurements. ERG completed simulated stack gas tests with full scale sampling equipment and a synthetic stack gas simulator manifold. ERG and EC performed tests that included evaluation of the performance of full scale sampling trains collecting condensable particulate material under a variety of conditions typical of well-controlled stationary source emissions. Based upon the results of the various experiments, EPA developed Other Test Method 28 (OTM 28), which is a revision of Method 202. EPA posted OTM 28 on the EPA Web site (www.epa.gov/ttn/emc/prelim.html) (also see Appendix C). In addition, EPRI provided test matrices that included the wider range of SO_2 concentrations and moisture levels that are found in the electric power industry. EPRI's stack gas train experiments also compared the performance of OTM 28 and two additional methods—controlled condensate method and a low-temperature filter method to evaluate how well the methods captured SO_3/SO_4 and verify the adequacy of capture of sulfuric acid by each of the CPM measurement techniques.

1.3 Organization of this Report

The remainder of this report is organized as follows.

- Section 2 presents the conclusions and recommendations of the tests that are described in this report beginning with the preliminary laboratory experiments followed by the full laboratory sampling train experiments.
- Section 3 presents the details of the preliminary laboratory experiments that explored potential improvements to the Method 202 and led to OTM 28.
- Section 4 describes a series of full scale laboratory experiments to evaluate OTM 28.
- Section 5 presents the details of experiments to determine whether a separate measurement of sulfur trioxide/sulfuric acid may allow sulfate artifacts captured in OTM 28 water impinger recoveries to be corrected.

2.0 CONCLUSIONS AND RECOMMENTATIONS

ERG and EC designed and completed a series of initial laboratory tests to determine the source of potential bias in CPM measurements using Method 202. The completed experiments achieved the following:

- Evaluated the dry down and weighing procedures in a single glass container versus transfer to aluminum weighing pans (Section 3.1.1)
- Determined the potential CPM contribution of sulfites that remain in the impinger condensate after the nitrogen purge (Section 3.1.2)
- Evaluated CPM residue retention to determine what CPM would be retained and would be measured during the analytical portion of the method (Section 3.1.3)
- Evaluated the nitrogen purge and evaluated dry down using aluminum pans (Section 3.1.4)

ERG and EC then completed laboratory test runs of modifications to Method 202. The completed tests achieved the following:

- Evaluated the effectiveness of the nitrogen purge (Section 3.2.1)
- Evaluated the potential CPM contribution due to higher concentrations of SO_2 (Section 3.2.2)
- Further compared the dry down procedures in a single glass container versus transfer to aluminum weighing pans (Section 3.2.3)

2.1 Initial Scoping Experiments

Through a series of initial scoping experiments, ERG and EC reduced the field blank and evaluated the lowest level of CPM that could be measured. ERG and EC developed and conducted a series of tests to reduce the CPM originating from field/analytical blanks. In addition, EC modeled the physical and chemical characteristics of typical CPM to optimize the collection temperature, sample drying temperature, and drying time.

2.1.1 Evaluation of CPM Mass Weighing Procedures

The experiments described in Section 3.1.1 predicted and demonstrated that changes in weighing room air pressure and temperature affect the measurement of CPM from the samples.

EC estimated the effect of weighing room air pressure and temperature on the apparent weight of the 250 mL jars to be the following:

- Effect of 1 kilopascal (kPa) lab pressure change:
  1 kPa/101.3 kPa*0.0012 g/mL *78 mL = 0.9 mg, due to air buoyancy
- Effect of 1 °C lab temperature change:
  1 °C*2.5 ppm per °C/1,000,000 * 204 g = 0.6 mg, due to scale thermal sensitivity drift

In two direct weighing experiments, samples remained in 250 mL glass beakers. Results showed that the average weight of each jar had a standard deviation of 0.5 mg. However, the average weight differences of consecutively weighed jars had a standard deviation of 0.2 mg.

In the indirect weighing experiments, samples were transferred to a secondary weighing vessel. Aluminum weighing pans were used as a secondary weighing vessel. The effect of common environmental differences on the apparent weight of the aluminum weighing pans was estimated to be the following:

- Effect of 1 kPa lab pressure change:
  1 kPa/101.3 kPa * 0.0012 g/mL * 0.44 mL = 0.005 mg, due to air buoyancy
- Effect of 1 °C lab temperature change:
  1 °C * 2.5 ppm per °C/1,000,000 *1.2 g = 0.003 mg, due to scale thermal sensitivity drift

Results showed that the weighing room air pressure and temperature effects were much lower than the precision of the balance (±0.1 mg) used for the experiments using aluminum weighing pans as the final weighing vessel.

EPA made the following conclusions based on the experiments described in Section 3.1.1:

- The 0.5 mg consistency criterion in Method 202 appears to be appropriate for filters, but appears to be inappropriate for bulky glass jars.
- The drying and weighing of condensate in large glass jars or beakers would require additional blank correction procedures to compensate for the effects of changes in air pressure and temperature in the weighing room.

- The quantitative transfer of concentrated condensate to aluminum weighing pans circumvented the problem of weighing small CPM mass in bulky glass weighing containers, and avoids the problem of temperature and pressure grossly affecting the weight of the CPM samples.

- CPM must be quantitatively transferred to the aluminum weighing pans and samples must be pH neutral between 6.5 and 8.5 to avoid artifact formation with the aluminum.

These conclusions led to/supported the following changes in Method 202:

- The proposed method should require evaporation of the final aqueous sample down to no less than 10 mL, neutralization and quantitative transfer to aluminum weighing pans for final dry down and weighing.

2.1.2 Evaluation of Sample Storage

The experimental approach is described in Section 3.1.2. Experiments were performed to confirm that any sulfites remaining after the nitrogen purge oxidize during storage and produce additional inorganic CPM. Sulfites are formed in Method 202 through SO_2 contact with cold condensed water and remain in the condensate after the nitrogen purge. The effect of sample storage on final CPM weight is important since the minimum residual weight anticipated in the dry impinger method from well controlled sources can be on the order of 2 to 3 mg.

Results from subsequent evaporation and jar weighing analyses showed that the spiked jars contained on average 0.4 mg more CPM than the unspiked jars.

EPA made the following conclusions based on the experiments described in Section 3.1.2.

- A 0.4 mg increase provides an upper bound indication of potential CPM formation upon extended sample storage.

- Samples improperly purged could show positive bias after storage.

2.1.3 Retention of Organic Condensable Particulate

EC evaluated CPM residue retention to determine which CPM would be collected by the revised sampling train based on theoretical calculations of vapor pressure. These calculations provided the theoretical basis to determine if the sampling and analytical procedures capture the material expected to be CPM in ambient air near a source emission. The theoretical calculations answered the following questions:

- Which organic compounds are likely to be captured as organic CPM in EPA Method 202? (Section 3.1.3.1)
  - Results showed that C_{17} and heavier hydrocarbons are fully retained by condensation. C_{15} and lighter hydrocarbons are for the most part not retained. Results showed that C_{16} (n-hexadecane: boiling point 287 °C, vapor pressure 0.0011 mmHg @ 21 °C) represents an arbitrary boundary for organic CPM levels less than approximately 60 dry standard cubic meter.

- How much of the captured organic CPM is likely to be lost during the nitrogen purge of Method 202? (Section 3.1.3.2)
  - Results showed that C_{17} and heavier hydrocarbons are fully retained. C_{16} losses are significant at HC concentration levels less than 40 ppm, as methane (23 mg/ DSCM of Organic CPM). Potential loss of lighter compounds is irrelevant, as these compounds are unlikely to be captured.

- Should the Method 202 constant weight criterion for inorganic CPM apply to organic CPM? (Section 3.1.3.3)
  - Loss rate C_{16} (mg/hr) = 0.25 mg/hr
  - The organic loss rate for C_{17} hydrocarbons was less than the sensitivity of the balance, therefore constant weight criterion for organic CPM was recommended. Hydrocarbons with higher volatility than C_{17} will be lost during the drying and constant weighing process except at sources with heavy hydrocarbon emission concentrations.

- How do organic CPM results from a manual non-dilution sampling train compare to organic CPM results from a dilution sampling CTM 039 train (Measurement of $PM_{2.5}$ and PM_{10} Emissions by Dilution Sampling (Constant Sampling Rate Procedures)) when testing non-polar organic compounds? (See Section 3.1.3.4.)
  - Vapor pressure calculations showed that the dilution sampling techniques such as EPA Method CTM 039 are unable to capture C_{16}-like compounds, based on the typical 20:1 sample dilution specified in the method. Capture of the C_{17} normal chain hydrocarbon in CTM 039 is significantly lower than Method 202 at hydrocarbon concentrations less than 40 ppmC.
  - Outside this narrow range of compounds, the organic CPM collected in OTM 28 and CTM 039 results are expected to be comparable.

EPA made the following conclusions based on the experiments described in Section 3.1.3:

- Since the CPM loss rate in OTM 28 is similar to the loss rate in Method 202, EPA determined that weighing to a constant weight is appropriate for both organic and inorganic fractions of the CPM method. Thus, the requirement to weigh samples to constant weight was retained in OTM 28.

- The proposed method should require a sample train condenser and impinger bath temperature to be less than or equal 30 °C (85 °F) to retain condensable organic compounds.

2.1.4 Environment Canada Laboratory Experimental Test Matrix

EC completed 15 full scale sampling train tests described in Section 3.2 using conventional stack sampling equipment. These experiments were designed to evaluate the effectiveness of the nitrogen purge; evaluate the potential CPM contribution due to higher concentrations of SO_2; and further compare the dry down procedures in a single glass container versus quantitative transfer to aluminum weighing pans.

Results of the experiments described in Section 3.2 showed the following:

- Three consecutive weight determinations showed differences less than or equal to 0.5 mg and the average standard deviation was estimated to be 0.1 mg.

- Samples dried down in a single glass jar (versus transfer to an aluminum weighing pan) contained 0.4 mg more CPM.

- Samples from runs at 250 ppm SO_2 contained 0.4 mg more CPM than runs at 25 ppm SO_2.

Conclusions from EC Laboratory Experiments (Section 3.2) are the following:

- Nitrogen purge at ambient temperature is likely to be more effective at removing dissolved SO_2 from stack moisture than the prescribed purge at ice bath temperature.

- Nitrogen purge with unfiltered ultra-high purity (UHP) gas produced in a fine black inorganic residue containing iron oxide that was not present in filtered purge gas.

- Nitrogen purge gas volume of approximately 1 cubic meter drawn through the sampling train is adequate to purge dissolved SO_2 from the dry impinger train. The nitrogen must be filtered since residual aluminum or iron dust from the purge gas cylinder can add significant mass to the CPM sample.

- A 10-fold increase in SO_2 level caused no measurable increase in inorganic CPM artifact.

- The inorganic CPM artifact caused by SO_2 may be reduced to approximately 2 mg or less by the dry impinger version of Method 202.

- Weighing samples in glass jars or beakers is subject to higher variability due to changes in temperature and pressure.

These conclusions supported the following recommendations for changes in the method:

- Require dry impingers.
- Require the nitrogen purge.
- Filter the nitrogen gas.
- Operate and purge the sampling train at less than or equal to 30 °C (85 °F).
- Transfer to aluminum weighing pans for final dry down.

2.2 Phase I Sampling Train Experiments to Evaluate Artifact Formation

The Phase I sampling train experiments compared Method 202, operated following EPA's recommended best practice procedures (see Appendix B), to the dry impinger sampling train. The tests showed the difference between Method 202 and the dry impinger modification to Method 202 in reducing the SO_2 artifact at SO_2 concentrations that are typical of stationary source compliance limits.

2.2.1 Phase I EPA Tests 1-8

After Phase I EPA Tests 1-3 demonstrated greater than 90 percent reduction of SO_2 artifact using the dry impinger modification, further refinements were made to the sampling and analytical procedures of the dry impinger method and EPA Tests 4-8 were completed. The refined method was then tested in replicate eight times to evaluate the precision and bias of the new procedures.

Results showed that the modifications to the dry impinger train (Richards et al, 2005), including elevating the temperature for collection of CPM to 30 °C (85 °F) from ice water temperatures, virtually eliminated the SO_2 artifact.

- The inorganic CPM artifact caused by SO_2 may be reduced to approximately 2 mg or less by the dry impinger modification of Method 202.

- The CPM remaining in the modified method is not SO_2 artifact, but rather typical train blank.

- The precision and bias of the modified method determined under controlled laboratory conditions were improved significantly over any of the options in Method 202.

Thus, EPA recommended the following changes to the standard Method 202 train and procedures:

- Require the filtered nitrogen purge.
- Require dry impingers, rather than wet impingers.
- Operate a condenser at a temperature of <30 °C (<85 °F) to cool the stack gas.
- Install a recirculation pump in the ambient water bath to provide cooling water to the condenser.
- Collect samples at ≤30 °C (≤85 °F), rather than at ice bath temperatures.
- Use ultra-filtered deionized water.
- Use an out-of-stack, low-temperature filter between the second and third impingers
- Use a Teflon® CPM filter after the second impinger.
- Extract the CPM filter with ultra-filtered deionized water.
- Use methylene chloride with less than 1 ppm condensable residue.
- Use acetone with less than 1 ppm condensable residue.
- Titrate reconstituted inorganic CPM with ammonium hydroxide to stabilize sulfuric acid.
- Evaporate the neutralized liquid to a minimum volume of 10 mL in an oven or hot plate; evaporate the final volume to dryness at ambient temperature.
- Correct inorganic CPM to include sulfuric acid weight with no waters of hydration.
- Evaporate the liquid collected in the impingers in an oven or on a hot plate down to a minimum volume of 10 mL, instead of all the way to dryness.
- Evaporate the final 10 mL of aqueous CPM sample at ambient temperatures.
- Evaporate organic CPM at ambient temperature.

These revised sampling procedures are consistent with the sampling procedures that EPA posted as OTM 28 (www.epa.gov/ttn/emc/prelim.html) (also see Appendix C), except a 110 mm fiberglass filter was used for these tests instead of a Teflon® filter. OTM 28 requires a 110 mm Teflon® filter instead of the fiberglass filter used in tests for this report.

Replicate test results demonstrated improved precision from the new procedures and reduction in the bias from SO_2 artifacts to near the method detection limit (MDL) of OTM 28. OTM 28 was evaluated using the synthetic stack gas manifold operated at 300 °F with gas composed of 150 ppm SO_2, 12 percent carbon dioxide, 50 ppm nitrogen oxides, 8 percent oxygen, and 6-10 percent moisture. The estimated MDL demonstrates that the dry impinger method is capable of measuring CPM at sufficiently low levels to meet regulatory requirements. Stakeholders were concerned that EPA's Method 202 was not valid for measuring CPM because it could not measure CPM at sufficiently low levels. The MDL and supporting laboratory evidence demonstrate that OTM 28 is capable of measuring CPM at sufficiently low levels (1-3 mg).

Based upon comparison of the results to their respective estimated MDLs, the organic and ambient filter fractions were not a measurable source of bias. If the averages of the inorganic and total results are blank-corrected, then they approach the MDL. EPA concluded that the inorganic bias has been reduced to the point at which it can be effectively eliminated by OTM 28 as described in this report.

EPA concluded that the precision and bias of OTM 28 under laboratory conditions were improved significantly over any of the options in Method 202. The MDL and supporting laboratory evidence demonstrate that OTM 28 is capable of measuring CPM at sufficiently low levels (1-3 mg).

2.2.2 Phase I EPA Tests 16-18

Phase I EPA Tests 16-18 investigated the affect of adding ammonia to the synthetic stack gas stream containing moisture and SO_2. OTM 28 was evaluated using the synthetic stack gas manifold operated at 300 °F with gas composed of 9 ppm ammonia, 22 ppm SO2, 11 percent carbon dioxide, 45 ppm nitrogen oxides, 7.5 percent oxygen, and 11-12 percent moisture. A 71 °C (160 °F) heated filter was added between the Method 5 train and the OTM 28 train to further investigate the formation of filterable ammonium sulfate under the test conditions for these matrix elements. The heated filter was designed to capture filterable particulate if it were formed by the reaction of ammonia and SO_2. Results show no CPM in any of the fractions: 160 °C filter, 71 °C filter, aqueous fraction, or the 30 °C filter.

Results indicated that no CPM formed in either the OTM 28 train or the 71 °C modified dry impinger train. EPA concluded that ammonia, under the conditions tested, does not react with SO_2 to form an artifact and no additional modifications to OTM 28 were necessary.

2.2.3 Phase I EPRI Tests 1-12

EPRI Tests 1-12 expanded the EPA test matrix to challenge OTM 28 with higher moisture (10 and 15 percent) and a higher SO_2 concentration (500 ppmv). OTM 28 was compared to the standard EPA Method 202 operated according to EPA's recommended procedures.

EPRI Tests 1-12 showed that OTM 28 reduced CPM artifact at the range of SO_2 conditions submitted by EPRI. Results showed that OTM 28 continues to reduce the artifacts formed by SO_2 during stack gas collection of condensable particulate, even at the additional conditions imposed on the test methods during EPRI Tests 1-12.

- The average blank in Phase I EPRI Test Runs 1-12 is the average of three complete sampling train blanks that were assembled, recovered, and analyzed without taking any sample from the manifold.
- Based on titration of the sulfuric acid in aqueous train samples, the absolute mass of SO_2 converted to SO_4 artifact in Method OTM 28 is approximately the same in each test run over the SO_2 concentration range of 25 to 500 ppm.
- Data show that there is no difference in the artifact formed in OTM 28 over the range of conditions in this set of tests.

The uncertainty (standard deviation) of EPRI Tests 1-3 results for Method 202 at 500 ppm SO_2 and 10 percent water was 2.3 mg/dscm. The average Method 202 results can be expressed with a two standard deviation error for the 98 percent confidence interval was 12 ± 4.6 mg/dscm, which is significantly different from zero, confirming measurable artifact formation. Similar evaluation of the Method 202 results for other test series demonstrate significant artifact formation.

Similar calculations of uncertainty for OTM 28 for EPRI Tests 1-3 show a standard deviation of 2.3 mg/dscm. The average Method 202 results can be expressed with 98 percent confidences as 4.3 ± 4.6 mg/dscm. These results indicate there is no statistically significant artifact captured by OTM 28 at the 98 percent confidence level. Similar statistical evaluations of OTM 28 show results do not differ statistically from the blank.

2.3 Phase II Sampling Train Experiments to Quantify Inorganic CPM

EPRI proposed two other sampling procedures as potential alternatives to correct the SO_2 bias in OTM 28. These alternatives would identify the SO_2 bias in OTM 28 by providing a separate measurement of the amount of sulfur trioxide/sulfuric acid (SO_3/H_2SO_4) in the flue gas. These extra measurements may allow sulfate artifacts captured in OTM 28 water impinger recoveries to be corrected.

2.3.1 Phase II EPRI Tests 19-24 and 31-36

Phase II EPRI Tests 19-24 and 31-36 measured the ability of OTM 28 and the controlled condensate methods to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at a relatively high and low concentrations. The percent recovery of each train type measured by IC was compared to the theoretical SO_3/H_2SO_4 concentration added to the synthetic stack gas manifold.

The data showed that SO_2 did not appear to contribute artifact to either method under these test conditions. The controlled condensate method accurately measure sulfate under the test conditions for experiments performed in this evaluation. Recovery of sulfuric acid from synthetic stack gas was lower for OTM 28. Elevated SO_2 reduces the recovery of sulfuric acid by OTM 28.

The controlled condensate method accurately measures sulfate under the test conditions for experiments performed in this evaluation. Recovery of sulfuric acid from synthetic stack gas was lower for OTM 28 compared to the controlled condensate method or the theoretical spike level. SO_2 did not appear to contribute artifact to either method under these test conditions. When SO_2 is added, OTM 28 recovers less SO_4. Therefore, EPA concluded that additional artifact is not formed in the presence of SO_2.

EPRI concluded that if the controlled condensate method were used to measure sulfuric acid, and if sulfuric acid results were substituted for sulfate measured in OTM 28, then the total CPM results would be higher than OTM 28 results alone.

2.3.2 Phase II EPRI Tests 13-15 and 25-27

Phase II EPRI Tests 13-15 and 25-27 measured the ability of OTM 28 and the low-temperature filter methods to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at a relatively low concentration.

The data showed that the 160 °F filter does not capture all of the SO_3. Some sulfate, in the form of sulfuric acid mist passes through the 160 °F low-temperature filter and is found in both the impinger water and the CPM filter. EPRI concluded that addition of the 160 °F low-temperature filter makes the train slightly more efficient at collecting H_2SO_4 than OTM 28. The trains perform similarly over the range of SO_2 concentrations. Collection of sulfuric acid mist in both trains is a worst-case test since most dry stationary source stack samples contain solid particles that could adsorb or react with sulfate reducing the amount of sulfuric acid mist that is too fine for the sampling train to collect.

The data showed the following:

- Addition of the 160 °F filter makes the train more efficient at collecting H_2SO_4.
- The trains perform similarly under the range of SO_2 concentrations.
- EPRI concluded that addition of the 160 °F filter makes the train more efficient at collecting H_2SO_4 than OTM 28.

EPA concluded that since all of the H_2SO_4 was not collected on the 160 °F low-temperature filter, the low-temperature filter train does not provide correction for SO_2 artifact.

3.0 DETAILS OF PRELIMINARY LABORATORY EXPERIMENTS

This section describes the details of preliminary laboratory experiments completed by ERG and EC to evaluate the effect of sulfur dioxide (SO_2) on Method 202. Tests included bench experiments to evaluate sample preparation and recovery, followed by 15 full scale sampling train experiments to test proposed improvements to EPA Method 202. Each laboratory test evaluated a specific issue and resulted in information that guided subsequent refinements and helped design sampling train tests of the method.

The ERG and EC preliminary laboratory test series had the following purposes: to quantify the lowest level of CPM that could be measured; to minimize the formation of SO_2 artifact; and to evaluate the effectiveness of the nitrogen purge. The following laboratory test approaches and results are described in detail in this section of the report:

- <u>3.1 Initial Scoping Experiments</u> completed by EC to reduce the CPM found in field/analytical blank and to quantify the lowest measurable level of CPM.
- <u>3.2 Train Evaluation-EC Tests 1-15</u> completed by EC to evaluate the effectiveness of the nitrogen purge; to evaluate the potential CPM contribution due to higher concentrations of SO_2; and further to compare the dry down procedures.

3.1 Initial Scoping Experiments

To quantify the lowest level of CPM that could be measured and to minimize the formation of CPM artifacts, ERG and EC evaluated the fundamental and theoretical chemical and physical constraints that affect the formation of CPM. ERG developed an experimental test design and conducted tests to evaluate and improve CPM sampling and analysis. Then, the method was modified and tested to confirm improvement and performance of the revised test method.

3.1.1 Evaluation of Residual Mass Weighing Procedures

The mass of CPM can be determined using two approaches: (a) direct and (b) indirect.

3.1.1.1 Direct CPM Determination in a Single Glass Container

Direct CPM measurement can be made in a single glass container. This alternative has the fewest steps since residue remains in a single container until final weighing. However, the weighing process is challenging because it is difficult to precisely weigh large glass containers. This investigation was initiated by EC, a stakeholder in the Method 202 revision process. EC examined evaporation/drying in pre-cleaned 120 mL and 250 mL clear wide-mouth jars that weighed approximately 114 g and 204 g, respectively. EC used a Mettler-Toledo AL204 balance with a capacity of 210 g ±0.0001 grams (210,000 mg ±0.1 mg) readability and 2.5 ppm/°C sensitivity drift.

Because air pressure and temperature in the weighing room change from day to day, differences were noted between the initial weight of the empty glass container (taring) and subsequent weights for the same empty containers. EC estimated the effect of air pressure and temperature on the apparent weight of the 250 mL jars to be the following:

- Effect of 1 kilopascal (kPa) lab pressure change:
  1 kPa/101.3 kPa*0.0012 g/mL *78 mL = 0.9 mg, due to air buoyancy

- Effect of 1 °C lab temperature change:
  1°C*2.5 ppm per °C/1,000,000 *204 g = 0.6 mg, due to scale thermal sensitivity drift

The effect of air pressure and temperature on final CPM weight is important since the minimum residual weight anticipated in the dry impinger method is on the order of 2 to 3 mg.

Two weighing experiments were carried out to examine the limitations of conventional weight-before-and-after approach for the determination of inorganic CPM in 250 mL glass jars. In the first direct weighing experiment, empty glass jars were cleaned, dried, and weighed. Final weighing of the evaporation residues were taken two or more days after initial taring, which would allow adequate time for sample evaporation and drying. Four sets of 24 jars each were weighed in a given order six times over a 4-day period.

Results showed that the average weight of each jar had a standard deviation of 0.5 mg. However, the average weight differences of consecutive jars had a standard deviation of 0.2 mg. This appears to be due to the fact that the environmental conditions during the weighing of consecutive jars were more consistent than the conditions from weighing the same jar on different days. The Method 202 consistency criterion for acceptance of consecutive weightings in Method 202 (<0.5 mg over 6 hours) was often exceeded, even though the weight was stable with respect to the preceding glass jar. The data showed that the 0.5 mg consistency criterion in Method 202 appears to be appropriate for filters, but appears to be inappropriate for bulky glass jars. Based on these observations, a second weighing experiment evaluated an alternative weighing scheme for weighing CPM samples in glass jars.

In the second direct weighing experiment, a set of 24 jars was tared by multiple weighings greater than 6 hours apart. Each time the jars were weighted in the same order. Every second jar in the set was used to contain and evaporate samples from Method 202 experiments. The remaining jars remained empty and served as reference for the jar in the set that was weighted immediately before or after. In this manner, the final CPM weight could be corrected for the weighing room air pressure and temperature effects.

Results showed that the average weight of each jar had a standard deviation of 0.5 mg. Consistent with the first weighing experiment, results showed that the average standard deviation resulting from weighing multiple inorganic CPM samples in this manner was estimated to be 0.2 mg.

3.1.1.2 Indirect CPM Determination by Drying the Sample in a Large Glass Container Followed by Wet Quantitative Transfer to a Weighing Pan for Final Dry Down

In the indirect weighing experiment, aluminum weighing pans were used as a secondary weighing vessel. Residual mass was determined using the same weighing equipment used for the glass jars.

Based on the size of the aluminum pans and the thermal characteristics of the aluminum, the effect of common environmental differences on the apparent weight of the aluminum weighing pans was estimated to be the following:

- Effect of 1 kPa lab pressure change:
  1 kPa/101.3 kPa*0.0012 g/mL *0.44 mL = 0.005 mg, due to air buoyancy
- Effect of 1 ^{o}C lab temperature change:
  1^{o}C*2.5 ppm per ^{o}C/1,000,000 *1.2 g = 0.003 mg, due to scale thermal sensitivity drift

Results showed that the weighing room air pressure and temperature effects were much lower than the precision of the balance used for the experiments (±0.1 mg). In this respect, the data show that the indirect weighing alternative appears to be the preferred method to determine residual mass. However, the CPM must be quantitatively transferred to the secondary weighing container and no artifact can result from the interaction of the transferred liquid with the aluminum and the sample pH should be 6.5 to 8.5 to prevent interaction of the sample with the aluminum.

3.1.2 Evaluation of Sample Storage Time

EPA Method 202 does not specify the maximum time between when a sample is collected and when a sample is analyzed. Sulfites may remain in the condensate after the nitrogen purge and can oxidize during longer storage and produce additional inorganic CPM. To investigate this potential contribution to inorganic CPM formation, the aqueous fraction from 10 nitrogen purged sampling train test runs were split in half, one of which was spiked with three drops of 30 percent hydrogen peroxide (H_2O_2)(approximately 0.15 mL). The peroxide spike oxidizes the residual sulfite and approximates the effect of longer storage times.

Results from subsequent evaporation and jar weighing analyses showed that the spiked jars contained on average 0.4 mg more CPM than the unspiked jars. This increase provides an upper bound indication of potential CPM formation upon extended sample storage.

The effect of sample storage on final CPM weight is important since the minimum residual weight anticipated in the dry impinger method from well controlled sources can be on the order of 2 to 3 mg.

3.1.3 Organic Condensable Particulate Matter

EC evaluated CPM residue retention to determine which CPM would be collected by the sampling train based on theoretical calculations of vapor pressure. This helped EPA evaluate which CPM would be retained and measured through the analytical portion of the method.

During the review of using Method 202 for measuring emissions of CPM from stationary sources, the following questions were raised:

- Which organic compounds are likely to be captured as organic CPM in EPA Method 202 or its replacement? (See Section 3.1.3.1.)

- How much of the captured organic CPM is likely to be lost during the nitrogen purge of Method 202? (See Section 3.1.3.2.)

- Should the Method 202 constant weight criterion (<0.5 mg change over 6 hours) for inorganic CPM apply to organic CPM? (See Section 3.1.3.3.)

- How do organic CPM results from a manual non-dilution sampling train compare to organic CPM results from a dilution sampling CTM 039 train (Measurement of $PM_{2.5}$ and PM_{10} Emissions by Dilution Sampling (Constant Sampling Rate Procedures)) when testing non-polar organic compounds? (See Section 3.1.3.4.)

3.1.3.1 Evaluation of Organic Compound Capture Efficiency

The purpose of this set of theoretical calculations was to determine which organic compounds would likely be captured as organic CPM in Method 202. The capture of organic CPM in the Method 202 train depends on various factors including compound vapor pressure, concentration, sample volume, and water solubility. These calculations are based on the following typical conditions:

- Sample containing a single n-alkanes compound
- Hydrocarbon (HC) levels 0-100 ppm as methane
- Sample and purge volume 1.2 dry standard cubic meter

The fate of hydrocarbon vapors within the Method 202 train was modeled on the basis of the vapor pressure of C_{10}-C_{20} normal alkane hydrocarbons, which were estimated as a function of temperature from Antoine parameters applicable to the 0.004 to 10 mmHg range. The estimated capture of these hydrocarbons as organic CPM (O-CPM) is shown in Figure 3-1 as a function of concentration and carbon chain length.

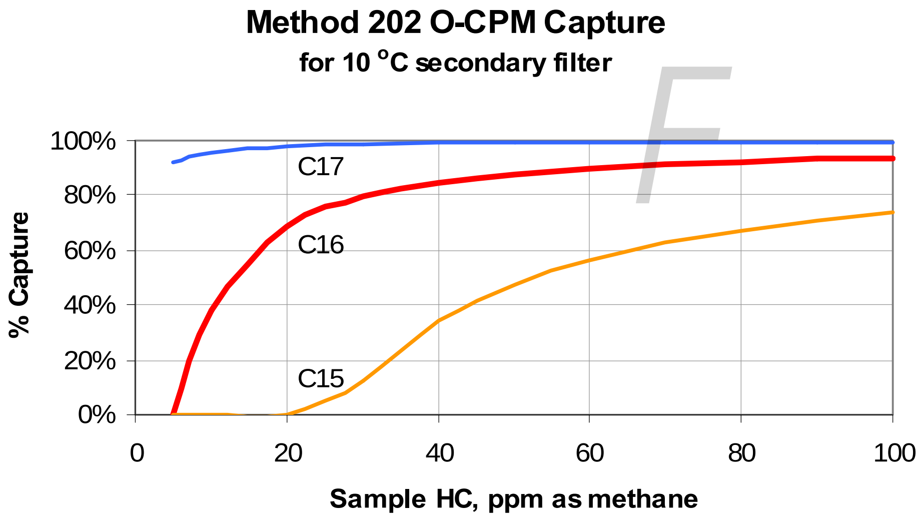

Figure 3-1. Predicted Capture of Organic CPM as a Function of Concentration

Results showed that C_{17} and heavier hydrocarbons are fully retained by condensation. C_{15} and lighter are for the most part not retained. Results showed that C_{16} (n-hexadecane: boiling point 287 °C, vapor pressure 0.0011 mmHg @ 21 °C) represents an arbitrary boundary for organic CPM retention in the dry impinger sampling procedure.

3.1.3.2 Evaluation of Organic Compound Retention

A second set of calculations was performed to test how much organic CPM would be lost during the nitrogen purge of Method 202. The retention of the organic catch during the nitrogen purge depends on the volatility of the organic CPM, its temperature and quantity. The loss of normal hydrocarbons as result of the nitrogen purge is shown in Figure 3-2, as a function of concentration and carbon chain length.

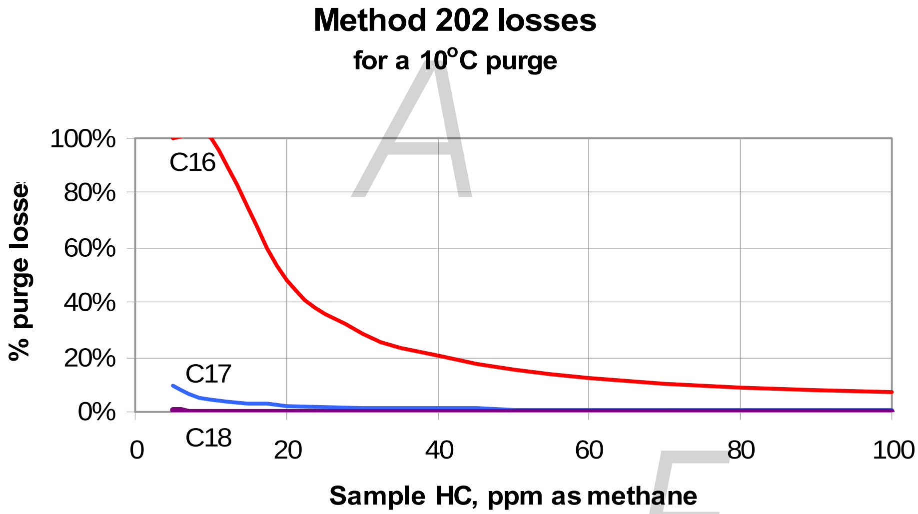

Figure 3-2. Predicted Loss of Organic CPM During the Nitrogen Purge Process

Results showed that C_{17} and heavier hydrocarbons are fully retained. C_{16} losses are significant at HC concentration levels less than 40 ppm, as methane (23 mg/dscm O-CPM). Potential loss of lighter compounds is irrelevant, as these compounds are unlikely to be captured in the sampling train based as shown in Figure 3-1.

3.1.3.3 Evaluation of the Inorganic/Organic Constant Weight Criteria

The purpose of this experiment was to determine whether the Method 202 constant weight criterion (<0.5 mg change over 6 hours) for inorganic CPM should apply to organic CPM. Following solvent extraction, the residue of the methylene chloride must be determined gravimetrically according to Method 202. The methylene chloride solution is evaporated at ambient temperature and the residue weighted to constant weight (<0.5 mg change in 6 hours) consistent with EPA Method 315.

Following the evaporation of methylene chloride, the residue may also evaporate, although at much lower rate. The loss rate of semivolatile residue can be estimated from the vapor pressure (VP) and molecular weights (MW), with a relationship experimentally tested with naphthalene-methylene chloride solutions.

$$\text{Loss rate}_{\mathbf{CX}}\ (\text{mg/hr}) = \text{Loss rate}_{\mathbf{MC}}\ (\text{mg/hr}) * (VP_{\mathbf{CX}} / VP_{\mathbf{MC}}) * (MW_{\mathbf{CX}} / MW_{\mathbf{MC}})$$

Where:

$VP_{\mathbf{CX}}$ = vapor pressure of compound x
$C_{\mathbf{X}}$ = compound x
MC = methylene chloride
MW = molecular weight

As experimentally determined, under laboratory fume hood conditions, methylene chloride evaporates from 5.7 cm aluminum pans at an average rate of 6,650 mg/hr. The methylene chloride vapor pressure is approximately 400 mmHg. Therefore, the loss rate of C_{16} hydrocarbons is estimated as follows:

$$\begin{aligned} \text{Loss rate}\mathbf{C}_{16}\ (\text{mg/hr}) &= 6{,}650\ \text{mg/hr} * (0.0011\ \text{mmHg} / 400\ \text{mmHg}) * (226 / 97) \\ &= 0.04\ \text{mg/hr} * 6\ \text{hours} \\ &= 0.25\ \text{mg in 6 hours} \end{aligned}$$

Since the loss rate is similar to the Method 202 constant weight criterion for inorganic CPM (<0.5 mg change over 6 hours), these calculations showed that weighing to a constant weight was appropriate.[2] Therefore, evaporation of CPM samples was written into OTM 28 to require measuring residue weights to constant weight of ± 0.5 mg.

3.1.3.4 Evaluation of Condensable Particulate Retention Comparability

The purpose of this calculation was to compare organic CPM results from a manual non-dilution sampling train to organic CPM results from a dilution sampling train (e.g., EPA Conditional Test Method (CTM) 039 train). Specifically, the net capture (capture and retention) of Method 202 and CTM 039 for sampling hydrocarbon vapors were compared. The results are shown in Figures 3-3 and 3-4, respectively.

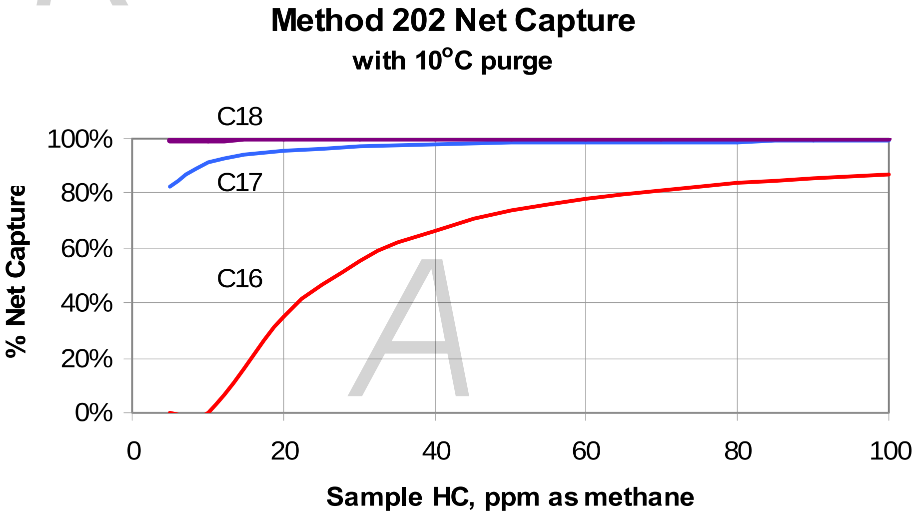

Figure 3-3. Improved Method 202 Net Capture with 10 °C Purge

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[2] In Method 315, the term “constant weight” means a difference of no more than 0.5 mg or l percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings (overnight desiccation is a common practice). If a third weighing is required and it agrees within ±0.5 mg, then the results of the second weighing should be used. For quality assurance purposes, record and report each individual weighing; if more than three weighings are required, note this in the results for the subsequent MCEM results.

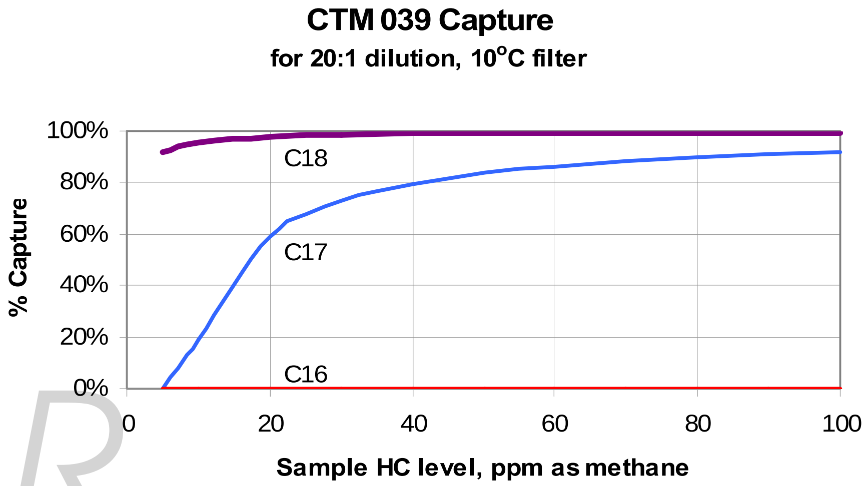

Figure 3-4. CTM039 Capture for 20:1 Dilution, 10 °C Filter

Results showed that Method CTM 039 was unable to capture C_{16}-like compounds, based on the typical 20:1 sample dilution specified in the method. Capture of the C_{17} normal chain hydrocarbon is significantly lower than Method 202 at hydrocarbon concentrations less than 40 ppm, as methane. Outside this narrow range of compounds, the O-CPM and CTM-039 results are expected to be comparable.

3.2 Environment Canada Laboratory Full Scale Train Evaluation

EC completed 15 full scale sampling train laboratory tests that were designed to evaluate the effectiveness of the nitrogen purge; evaluate the potential CPM artifact contribution due to higher concentrations of SO_2; and compared the drying procedures with quantitative transfer to aluminum weighing pans versus dry down in a single glass container.

3.2.1 Experimental Apparatus – EC Laboratory Full Scale Train Evaluation

EC completed the laboratory runs using conventional stack testing equipment as shown in Figure 3-5. Ambient air was aspirated through a 3-inch glass fiber filter and then humidified by bubbling the air through a water impinger housed within the oven of a Method 5 sampling train as shown in Figure 3-6. This impinger was fitted with a 250-watt heating tape, which was equipped with an adjustable rheostat. Moisture levels were varied by altering the oven temperature as well as the power to the heating tape.

Figure 3-5. Environment Canada Laboratory Test Stand for Method 202

Figure 3-6. Environment Canada Method 202 Gas and Moisture Introduction System

An analyzed mixture of SO_2 in nitrogen (2,000 to 4,000 ppm) was added at constant rate to the moisturized air stream. The SO_2 flow started approximately 15 seconds after the start of the air flow and was stopped 15 seconds before the end of the 1-hour laboratory run.

The CPM collection portion of the sampling train consisted of a water-cooled coil, a condensate reservoir (dry impinger), a straight-stem impinger, and a silica gel impinger as shown in Figure 3-7. All these components were kept in an ice bath, except the condensate reservoir, which was external to the ice box.

Figure 3-7. Environment Canada M-202 Sampling Train

The sampling train was connected to the corresponding control module and operated at a flow rate of approximately 0.6 standard cubic feet per minute (scfm). Results showed that approximately 94 percent of the moisture gain was collected in the dry impinger, 1 percent in the second impinger, and the remainder in the silica gel impinger.

3.2.2 Experimental Design – EC Full Scale Train Evaluation (Evaporation and Weighing of Inorganic CPM)

At the completion of each run, the condensate was transferred to a Greenburg-Smith impinger and its contents were purged at room temperature with a total of 1.2 scfm of nitrogen (Praxair, ultra-high purity) over 1 hour. A black fine particle residue was observed on some preliminary runs, therefore, a 47 mm glass fiber filter was installed in the low pressure nitrogen line and in the SO_2 mixture line. Black CPM residue was not encountered on subsequent test runs.

Method 202 requires the evaporation of considerable amounts of water for the gravimetric determination of the evaporation residue. Even with the dry impinger version of Method 202, it is necessary to evaporate approximately 200 mL for a 1-hour test run on a 20 percent moisture source. For these tests, samples are placed in glass containers and dried in an oven at 105° C.

The residues of the 15 Method 202 laboratory runs were transferred into 1.2 gram aluminum pans by three successive rinses, each with 2 mL deionized water. In Runs 1 through 10, the condensate was evenly split into two jars; therefore, the total water volume loaded into the weighing pans was approximately 12 mL. The tared weighing pans were dried overnight.

3.2.3 Results and Discussion – EC Tests 1-15

Results from the 15 Method 202 laboratory runs (inorganic CPM determinations) are summarized in Table 3-1.

Table 3-1. Results of EC Tests 1-15

EC Test	SO_2 (ppmd)	H_2O (%)	CPM Jar Weighing (mg/dscm)	CPM Pan Weighing (mg/dscm)
1	253	12.7	4.1	2.8
2	252	11.1	1.5	1.0
3	255	11.2	1.4	1.0
4	258	11.3	1.4	1.1
5	258	11.2	2.0	2.5
Average	255	11.5	2.1	1.7
Stnd. Dev.	2.9	0.7	1.2	0.9
6	25	12.3	3.1	1.9
7	25	11.8	0.5	0.9
8	25	11.7	1.3	1.0
9	25	11.6	1.5	0.8
10	25	10.8	1.0	0.8
Average	25	11.7	1.5	1.1
Stnd. Dev.	0.2	0.5	1.0	0.4
11	123	20.8	-	2.4
12	121	19.7	-	0.9
13	121	19.5	-	0.7
14	121	19.8	-	0.9
15	122	21.0	-	2.0
Average	121	11.7	-	1.1
Stnd. Dev.	1.1	0.7	-	0.7

Results showed the following:

- Values for tare and final weighing were the average of three consecutive weights conducted 6 or more hours apart, resulting in a weight difference of less than or equal to 0.5 mg.

- The average standard deviation resulting from weighing multiple inorganic CPM samples in this manner was estimated to be 0.1 mg.

- Nitrogen purge with unfiltered ultra-high purity gas produced a fine black inorganic residue containing iron oxide that was not present in filtered purge gas.

- Three consecutive weight determinations showed differences less than or equal to 0.5 mg and the average standard deviation was estimated to be 0.1 mg.

- Samples dried down in a single glass jar (versus transfer to an aluminum weighing pan) contained 0.4 mg more CPM.

- Samples from runs at 250 ppm SO_2 contained 0.4 mg more CPM than runs at 25 ppm SO_2.

EPA made the following conclusions from EC laboratory train experiments:

- Nitrogen purge at ambient temperature is likely to be more effective than the purge at ice bath temperature.
- Nitrogen purge gas volume of approximately 1 cubic meter drawn through the sampling train is adequate to purge dissolved SO_2 from the dry impinger train. The nitrogen must be filtered since residual mass from the purge gas cylinder can add significant mass to the CPM sample.

Based on theoretical calculations, laboratory bench experiments, and initial sampling train runs, the following refinements to the method were recommended:

- Add a condenser to cool stack gas prior to the knock out impinger.
- Require dry impingers at the start of sampling.
- Use a “knock out” impinger with short stem to collect condensed stack liquid.
- Purge the train at 20 liters/minute or ΔH@ for 1 hour.
- Filter the nitrogen gas.
- Transfer the samples to aluminum weighing pans for final dry down.

Other modifications were recommended for evaluation in ERG full train experiments:

- Use ice bath vs. 30 °C water bath or impinger sample collection.
- Use backup CPM filter following CPM impingers.

4.0 DETAILS OF PHASE I LABORATORY SAMPLING TRAIN EXPERIMENTS

This section contains the details of a series of full scale laboratory sampling train experiments completed by ERG and EC to evaluate improvements to the Method 202 sampling train. These tests were based on the initial scoping experiments described in Section 3. The purpose of the Phase I laboratory experiments (EPA Tests 1-12 and 16-18 in the QAPP (ERG, 2006)(See Appendix A) and EPRI Tests 1-12 (EPRI, 2007)(See Appendix D) was to compare Method 202, operated according to EPA's recommended procedures, to the improved (dry impinger) sampling train configuration that resulted from the initial scoping experiments described in Section 3. The comparison was intended to show the efficacy of the dry impinger modification to Method 202 in reducing the SO_2 artifact under simulated stack conditions.

Paired sampling runs of these two sampling train configurations were completed to compare the formation of SO_2 artifact in both trains under various simulated stack gas conditions. These tests are described in this section and include the following:

- 4.1 Phase I Laboratory Experiments-EPA Tests 1-8
    - Evaluate SO_2 artifact formation in the best practice Method 202 sampling train and the dry impinger sampling train at a range of SO_2 concentrations that are typical of stationary source compliance limits
    - Determine the precision and bias of the dry impinger modification from eight replicate tests

- 4.2 Phase I Laboratory Experiments-EPA Tests 16-18
    - Evaluate the effects of ammonia on the dry impinger sampling train

- 4.3 Phase I Laboratory Experiments-EPRI Tests 1-12
    - Challenge the dry impinger modification with higher a SO_2 concentration (500 ppmv) and higher moisture (10 and 15 percent) level, which represent the range of conditions at coal-fired power plants

4.1 Phase I Sampling Train Experiments – EPA Tests 1-8

Phase I EPA Tests 1-8 were completed to evaluate SO_2 artifact formation in the standard Method 202 sampling train and the dry impinger sampling train at a range of SO_2 concentrations that are typical of stationary source compliance limits. These tests corresponded with QAPP Runs 1-12 (ERG, 2006). Eight additional replicates dry impinger train tests were completed to evaluate the best practice precision and bias of the dry impinger modification.

4.1.1 Matrix

The test matrix shown in Table 4-1 includes tests at two levels of SO_2 to simulate low level SO_2 concentrations (target of 25 ppm) typically observed in gas-fired turbines and high-level SO_2 concentrations (target of 150 ppm) typically observed in coal-fired power plants. These conditions were selected after review of regulatory limits and typical SO_2 emission concentrations from these sources. In addition to varying the SO_2 concentration, ERG added other components to the gas compositions to evaluate potential interferences from water, nitrogen oxides, and carbon dioxide.

Table 4-1. Phase I EPA Tests 1-8 Experimental Matrix Test Conditions and Gas Composition

Phase I EPA Test	Paired Methods*	Sulfur Dioxide (ppm)	Effective Ammonia (ppm)	Carbon Dioxide (%)	Oxygen (%)	Water (%)	Nitrogen Oxides (ppm)
1	A, B	25	0	12	8	5	50
2	A, B	25	0	12	8	5	50
3	A, B	25	0	12	8	5	50
4	A, C	150	0	12	8	5	50
5	A, C	150	0	12	8	5	50
6	A, C	150	0	12	8	5	50
7	C	150	0	12	8	5	50
8	C	150	0	12	8	5	50

* Methods
A = Method 202
B = Richards dry impinger method
C = OTM 28

4.1.2 Sampling Equipment and Approach

A standard Method 202 train and the dry impinger train were paired and evaluated in the laboratory using a synthetic stack gas generator manifold. Several gas components were spiked into the stack gas simulator, including SO_2 and nitrogen oxides (NO/NO_2).

For the first three paired tests (Phase I EPA Tests 1-3), ERG assembled and operated the dry impinger train similarly to the dry impinger train described in the Richards study (Richards, et al, 2005), which had ice water in the impinger sample collection box. After Phase I EPA Tests 1-3 demonstrated a significant reduction of SO_2 artifact using the dry impinger modification, further refinements were made to the sampling and analytical procedures of the dry impinger method to reduce the SO_2 artifact further. For EPA Phase I Tests 4-8, the condenser and first two impingers were cooled to ambient temperature 25-30 °C (77-86 °F) using a water bath. Tests 4-8 were performed using the complete set of modifications to the CPM train, which EPA posted on the EPA Web site as Other Test Method 28 (OTM 28) (www.epa.gov/ttn/emc/prelim.html). Results for Phase I Tests 1-8 are presented in Section 4.1.5.

Once the Phase I EPA Tests 4-8 were completed and a reduction of more than 90 percent in SO_2 artifact was observed for OTM 28 compared to the best practice Method 202 results, ERG completed eight replicate test runs to determine whether the precision and bias of OTM 28 were acceptable. Results of the eight replicate tests are presented in Section 4.1.5. This series of eight Replicate Tests were completed under the high-SO_2 train (150 ppm) conditions similar to Phase I EPA Tests 4-8 to evaluate the precision and bias of OTM 28 under controlled laboratory conditions.

4.1.2.1 Synthetic Stack Gas Generation

During each sampling run, SO_2 and nitrogen oxides (NO/NO_2) gases were introduced into a mixing chamber of the laboratory source gas simulator through three mass flow controllers. Gases were dynamically spiked into the stack gas simulator from certified gas cylinders. Higher flow gas additions were added through calibrated rotameters. Calibration of the mass flow controllers was verified with a National Institute of Standards and Technology (NIST)-traceable Buck flow monitor. A cross section of the manifold mixing chamber is shown in Figure 4-1. An example of the gas mixture flow rates is shown in Table 4-2.

Gases were injected separately into the manifold through a seven-port injection module. Gas was delivered from the injection module into a pair of sequential mixing chambers prior to entering the sampling manifold. Gases were mixed as they passed from the injection ports through these two gas mixing chambers. Sufficient gas volume was added in the correct proportions through the injection and mixing modules to generate a synthetic stack gas flow rate up to 50 liters per minute (L/min) or 1.8 standard cubic feet per minute (scfm). The gas stream was heated to ensure all components remained in the gas phase.

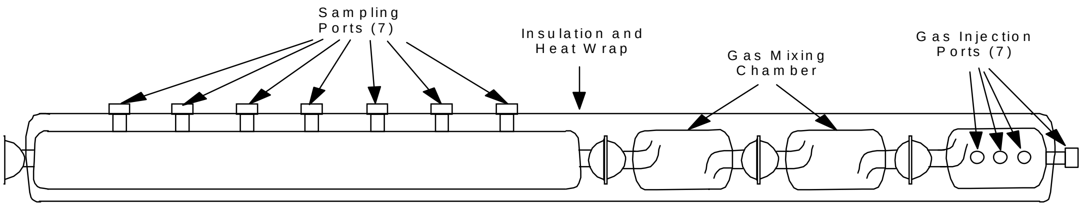

Figure 4-1. Cross Section of Stack Gas Sampling Manifold

Table 4-2. Example Gas Mixture for Laboratory Stack Gas Generator

Gas Type	Cylinder Concentration	Gas Flow (mL/min)	Final Gas Concentration
Carbon Dioxide	60%	10,000	11.41%
NO/NO_2 (in N_2)	15,000 ppm	170	48.5 ppm
Sulfur Dioxide (in N_2)	2%	64	24.3 ppm
Oxygen (in air)	21%	20,000	8.0%
Nitrogen*	100%	10,000	19%
Water (in N_2)	9.2 mL/min	10,000	11.8%
Total Gas Flow		52,577 mL/min	

* Nitrogen in certified gas cylinders makes up the remainder of the final manifold gas mixture.

Dry nitrogen (N_2) was used as the primary diluent at a flow rate of 20 L/min. To provide a moisture content between 5 and 10 percent, compressed air was bubbled through a heated stainless steel chamber containing water before entering the inlet manifold at 10 L/min. Carbon dioxide (CO_2) was injected into the manifold through a separate port at 10 L/min. Nitrogen oxides (NO/NO_2) and SO_2 were also individually injected into the module as pollutants at rates shown in Table 4-2. Steam transported by the nitrogen diluent was used for tests above 8 percent moisture.

Gases in the simulator and sampling probe temperatures were maintained at 160 ± 5°C (320 ± 9 °F) for the Phase I EPA Tests 1-8 and corresponding replicates. This temperature is 35 °C (95 °F) higher than the minimum temperature required by EPA Method 5. The elevated temperature ensured all components remained in the gas phase and helped minimize premature reactions between gaseous components added to the source gas simulator. Gases in the simulator and sampling probe temperatures were maintained at 300 °C (572 °F) for EPRI Tests 1-12, except EPRI Tests 4-9. For Phase I EPRI Tests 4-9, the 98 °C (210 °F) temperature was chosen to represent sources operating at near the saturation point of water without condensing in the gas manifold.

Each sampling train was connected to the heated manifold port on the laboratory source gas simulator. Sampling train glass nozzles were connected through 5/8-inch SV threaded fittings and silicon septa on the manifold. Trains were operated with glass-lined probes and standard Method 5 heated filter boxes. Sufficient flow from the combination of cylinders and humidified zero air was generated to produce excess gas (>34 L/min). Two sampling trains were operated at a sampling flow rate of approximately 14.5 L/min (0.5 scfm). Phase I EPA Tests 1-8 were conducted for 1 hour, allowing collection of approximately 1 cubic meter of gas. Phase I EPRI Tests 1-12 were conducted for 2 hours, allowing collection of approximately 2 cubic meters of gas. Excess simulated stack gas and sample train exhaust was vented into a standard laboratory fume hood.

4.1.2.2 Method 202 Train

The EPA reference Method 202 train was assembled according to Method 202 (40 CFR Part 51, Appendix M). The Method 202 sampling train was equipped with three impingers each filled with 100 mL of deionized water and a fourth impinger containing silica gel (see Figure 4-2). The first impinger was connected directly to a Method 5 heated 110 mm filter holder. Both the Method 5 probe and hot filter box were maintained at 160°C. The Method 5 probe and 110 mm filter preconditioned the test gas mixture and collected any filterable PM exiting the manifold. For the 25 ppm SO_2 runs (Phase I EPA Tests 1-3), all four impingers were chilled by an ice water bath as required by Method 202. The standard Method 202 sampling train was operated following EPA's best practice recommended procedures to obtain the best measurement of particulate matter resulting from the dilution cooling of the sampled gas stream (see Appendix B and www.epa.gov/ttn/emc/methods/method202.html).

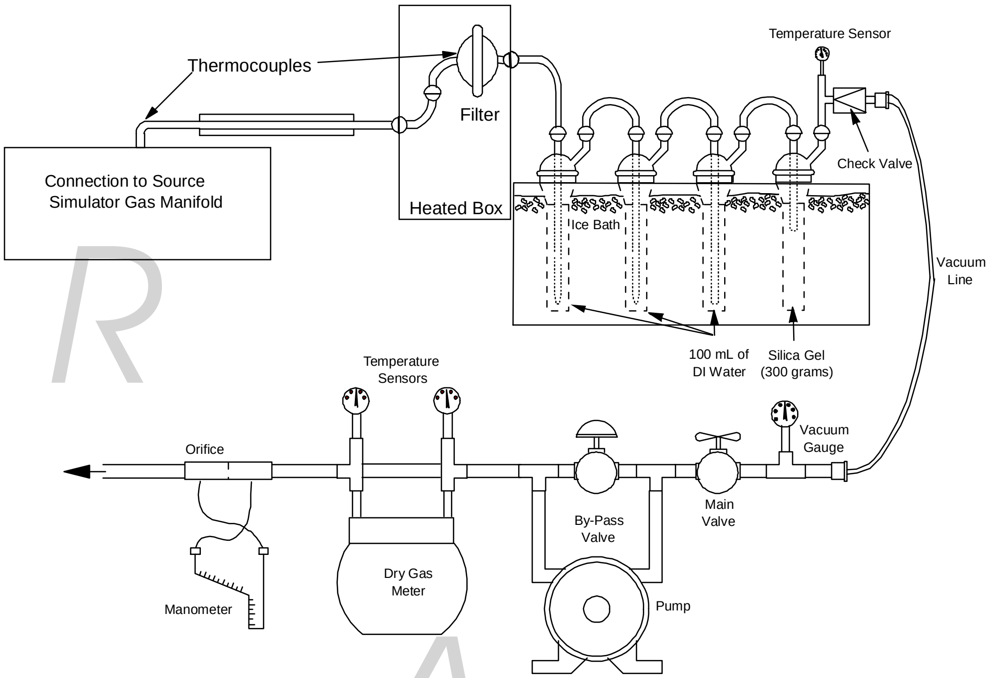

Figure 4-2. Standard EPA Method 202 Sampling Train

4.1.2.3 Dry Impinger Train

The dry impinger train was assembled as described by Richards (Richards, et al, 2005). The Richards dry impinger train consisted of a Method 23 type coil condenser and four impingers connected to a Method 5 probe and 110 mm filter, both heated to 160 °C (see Figure 4-3). The coil condenser connected the heated filter to the impingers and cooled the gas stream via recirculating water. The gas stream flowed from the condenser into the first knockout impinger. The first knockout impinger was not charged with water prior to the sample run and featured a shortened stem to separate the source gas from water condensed out of the gas stream. The next two impingers were also not charged with water but were equipped with long-stem bubbler tubes. The final impinger contained silica gel.

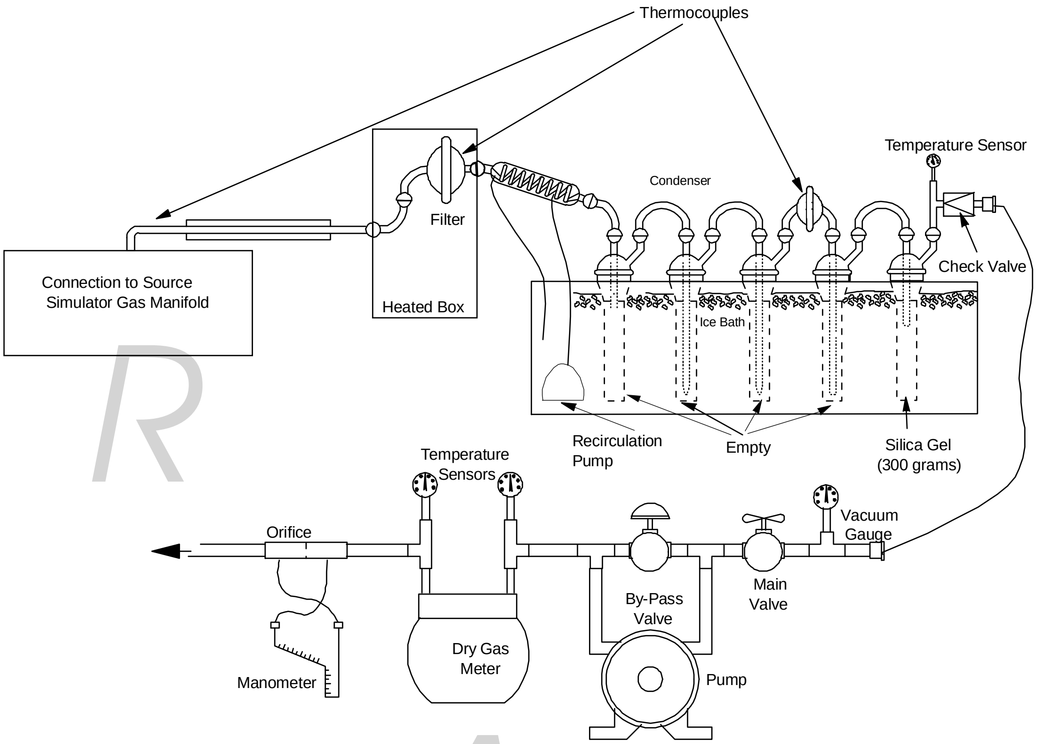

Figure 4-3. Richards Dry Impinger Train

4.1.2.4 Revised Sampling Procedures for the Dry Impinger Train

For the Phase I EPA Tests 1-3, all of the impingers were cooled with ice water similar to the Richards study (Richards, et al, 2005) to maintain the gas exiting the CPM filter at approximately 20 °C (68 °F). For Phase I EPA Tests 4-8 and the corresponding replicates, the first two impingers were operated at an ambient temperature of 25-30 °C (77-86 °F) using a water bath. The water bath also supplied cooling water for the condenser.

After Phase I EPA Tests 1-3 demonstrated a significant reduction of SO_2 artifact using the Richards dry impinger modification, further refinements were made to the sampling and analytical procedures to reduce the SO_2 artifact further. For Phase I EPA Tests 4-8 (150 ppm SO_2), the following sampling steps were modified. Figure 4-4 shows the OTM 28 sampling train.

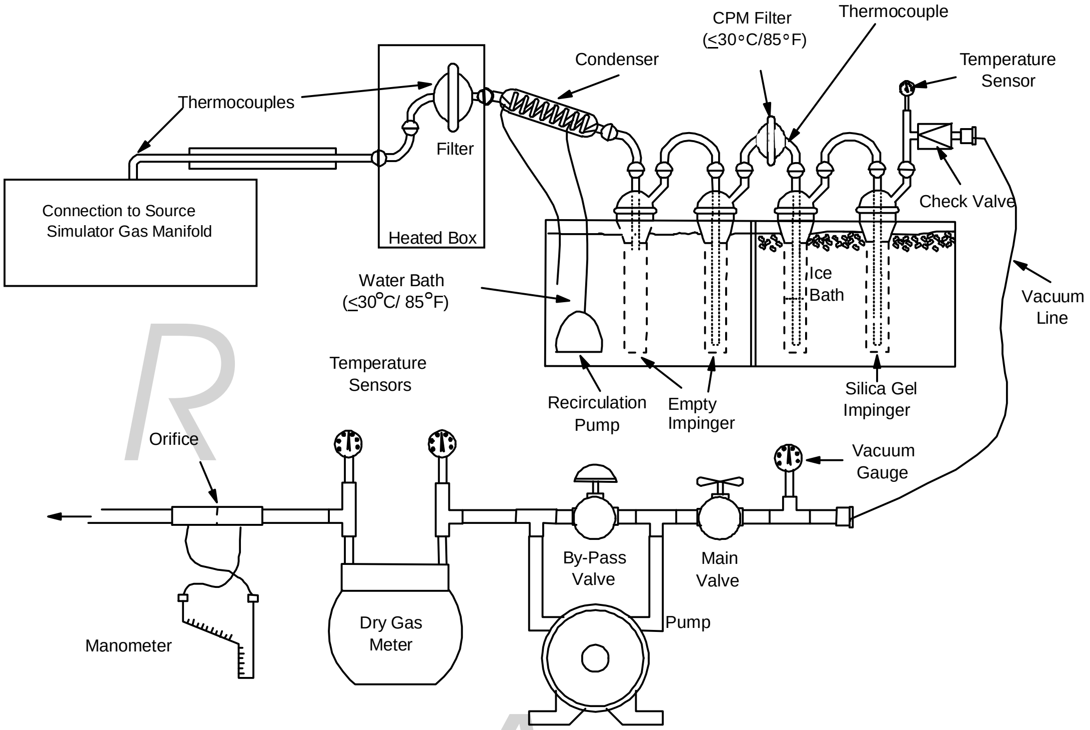

Figure 4-4. OTM 28 Sampling Train

- The first two impingers were cooled to ambient temperature 25-30 °C (77-86 °F) using an ambient water bath. (In Phase I EPA Tests 1-3, which were operated consistent with the Richards study (Richards, et al, 2005), the impingers were chilled with an ice bath to maintain gas collection temperature at approximately 20 °C.)

- A separate or divided water bath was added to accommodate the remaining impingers, which were cooled by ice water.

- An unheated 110 mm fiberglass filter was added after the last impinger in the 30 °C water bath (i.e., between the second and third impinger).

- The water and filter temperatures were monitored during the runs: ERG regulated the impingers' temperature using a pump that recirculated water from the water bath to the condenser to maintain the exit temperature of the CPM filter at 29 °C (85 °F) or less. Water temperature surrounding the first two impingers was maintained between 25 °C and 30 °C by adding small amounts of ice as necessary.

- The two impingers that followed the 110 mm fiberglass filter were cooled by ice water and were used together with the silica gel filled impinger to measure moisture.

These revised sampling procedures are consistent with the sampling procedures that EPA posted as OTM 28 (www.epa.gov/ttn/emc/prelim.html) (also see Appendix C), except a 110 mm fiberglass filter was used instead of a Teflon® filter. OTM 28 requires a 110 mm Teflon® filter instead of the fiberglass filter used in tests for this report.

4.1.3 Sampling Train Recovery – Method 202 and Dry Impinger Samples

Samples were collected from the synthetic stack gas manifold following Method 5/ Method 202 procedures including pre- and post-sampling leak checks. Method 202 and dry impinger sampling trains collected gas simultaneously from the source gas simulator for 1 hour at a collection rate of 0.5 scfm. Immediately following each post-run leak check, the knockout impinger from the dry impinger train was weighed to determine the amount of water collected. The short stem impinger insert was replaced with a modified Greenburg-Smith long stem impinger insert and the impinger was refitted to the train.

Both trains were then purged for 1 hour with nitrogen by drawing gas from an ultra-high purity (UHP) nitrogen supply at a flow rate of 15 L/min. Nitrogen from the UHP supply was to deliver 4 L/min more than the sampling trains required. Excess nitrogen was vented to an exhaust hood. Each train was then recovered using procedures described in EPA Method 202 by rinsing three times with deionized water followed by rinsing three times with acetone and three rinses with methylene chloride. Figure 4-5 shows the nitrogen flush manifold.

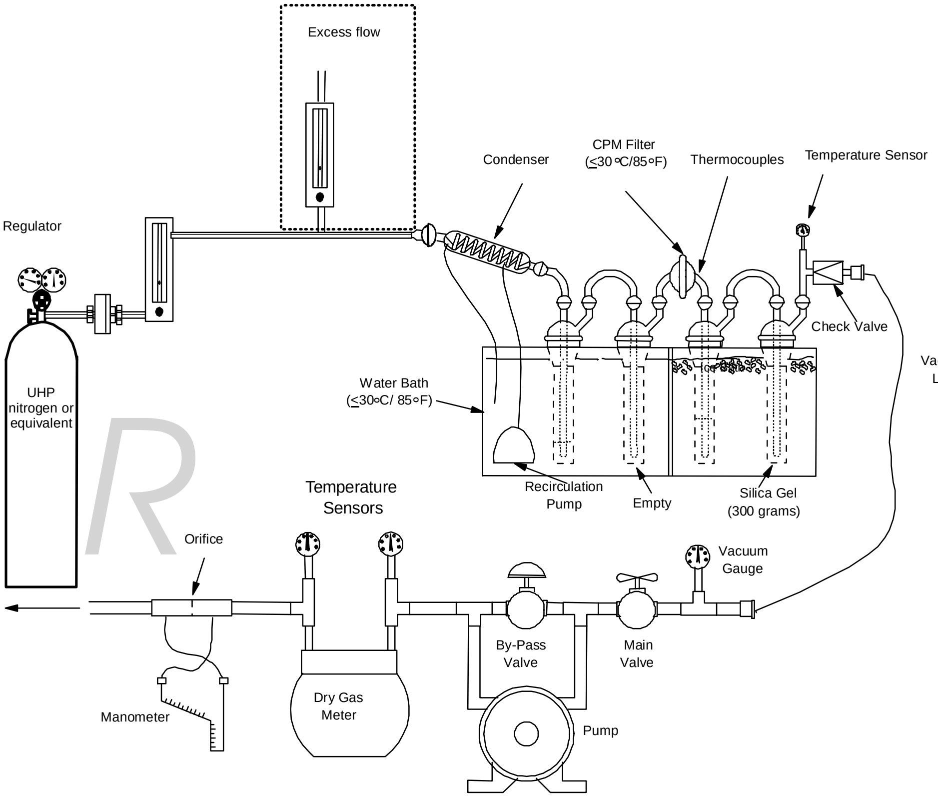

Figure 4-5. Nitrogen Flush Manifold

4.1.4 Analytical Procedures – Phase I EPA Tests

In Phase I EPA Tests 1-3, samples recovered from both trains were processed and analyzed gravimetrically to determine the amount of SO_2 artifact that would be measured as condensable particulate matter in each train. In addition, aliquots of the impinger samples were analyzed by ion chromatography (IC) to measure sulfate as sulfuric acid in the samples.

For gravimetric analysis, the aqueous fractions were extracted using the organic rinses recovered from each train. The organic extraction was repeated twice with fresh methylene chloride after the initial extraction with the train organic rinse. Each of the organic fractions was evaporated to 10 to 25 mL at ambient temperature in clean 300 mL laboratory beakers. The final evaporation of approximately 10 to 25 mL was done by quantitative transfer from 300 mL beakers into 50 mL aluminum weighing pans. The residue in the pans was dessicated to constant weight and weighed to 0.01 ± 0.05 mg.

The aqueous fractions were evaporated to dryness in a convection oven at 105 °C (221 °F). The dried aqueous fractions were reconstituted in 100 mL deionized water and neutralized with ammonium hydroxide, using phenolphthalein as a titration indicator. The aqueous fractions were again dried at 105 °C (221 °F), dessicated and weighed to 0.01 ± 0.05 mg.

4.1.4.1 Revised Analytical Procedures for the Dry Impinger Method

After Phase I EPA Tests 1-3 demonstrated a significant reduction of SO_2 artifact using the dry impinger modification, further refinements were made to the sample preparation and analytical procedures of the dry impinger method to reduce the SO_2 artifact further. The revised analytical procedures are consistent with the analytical procedures that EPA posted as OTM 28 (www.epa.gov/ttn/emc/prelim.html) (also see Appendix C). Specifically, for the Phase I EPA Tests 4-8 (150 ppm SO_2 tests), the sample preparation and analysis steps were modified as follows:

- The ambient filters were dried, dessicated, and weighed.
- Following extraction, the aqueous fractions were evaporated at an elevated temperature on a hot plate to less than 25 mL. The remaining liquid was evaporated at ambient temperature.
- The aqueous fractions were reconstituted in 100 mL of ASTM Type II water.
- A 1 mL aliquot was removed for IC analysis to determine ammonium and sulfate content.
- The remaining liquid was titrated using 0.1N ammonium hydroxide to pH 7 measured with a pH meter.
- The aqueous fractions were evaporated again to less than 25 mL on a hot plate with the remaining liquid evaporated at ambient temperature.
- The dried samples were dessicated and weighed. Following gravimetric analysis, the samples were reconstituted in 100 mL deionized water. A 1 mL aliquot was removed from each for IC ammonium and sulfate analysis.

<u>Organic Extraction – Method 202 and Dry Impinger Samples</u>. The impinger sample was combined with the organic rinses and serially extracted with methylene chloride using a separatory funnel. Solvents were HPLC grade or equivalent. Once extracted, the sample was dried using anhydrous sodium sulfate, concentrated to no less than 10 mL, quantitatively transferred to a preweighed aluminum pan and evaporated to dryness at room temperature (<30 °C or <86 °F). Final residue weights were determined by allowing the organic residue to

attain constant weight in a desiccator. Method 202 requires that weights are measured to the nearest 0.1 mg, which requires a standard analytical balance capable of measuring 0.0001 g. Since this project focuses on reducing artifacts to zero, residual mass was determined to the nearest 0.00001 ±0.00005 g, requiring a balance capable of measuring 0.00001 g.

Inorganic CPM Preparation – Method 202 and Dry Impinger Samples. The aqueous inorganic phase and rinse from the impingers of each train was evaporated to approximately 10 mL in a glass beaker on a hot plate. The final 10 mL of sample was taken to dryness at ambient temperature not to exceed 30 °C (86 °F), reconstituted to approximately 10 mL with water, and neutralized by titration with ammonium hydroxide. The neutralized aqueous inorganic material was evaporated to approximately 10 mL, transferred to a preweighed aluminum pan and allowed to dry at ambient temperature (<30 °C or <86 °F). Residue weights were determined by allowing samples to attain constant weight in a desiccator. Weights were recorded to the nearest 0.00001 ±0.00005 g in an environmentally controlled room meeting filterable particulate weighing specifications.

4.1.5 Results and Discussion – Phase I EPA Tests 1-8 and Replicates

Each experimental design test run consisted of a Method 202 and a dry impinger train (i.e., Method 202 and dry impinger trains were paired). The first three test runs (Phase I EPA Tests 1-3) were performed using the Method 202 operated according to the best practice procedures (Appendix B) and the dry impinger sampling method operated as described in the Richards study (Richards, et al, 2005). The next test runs (Phase I EPA Tests 4-8) were performed using Method 202 operated according to the best practice procedures and OTM 28 according to the sampling and analytical procedures in Sections 4.1.2.4 and 4.1.4.1.

Results showed that the dry impinger modification to Method 202 significantly reduced artifact. Results for Phase I Tests 1-8 are shown in Figure 4-6 (see Appendices E and F for raw data and moisture calculations).

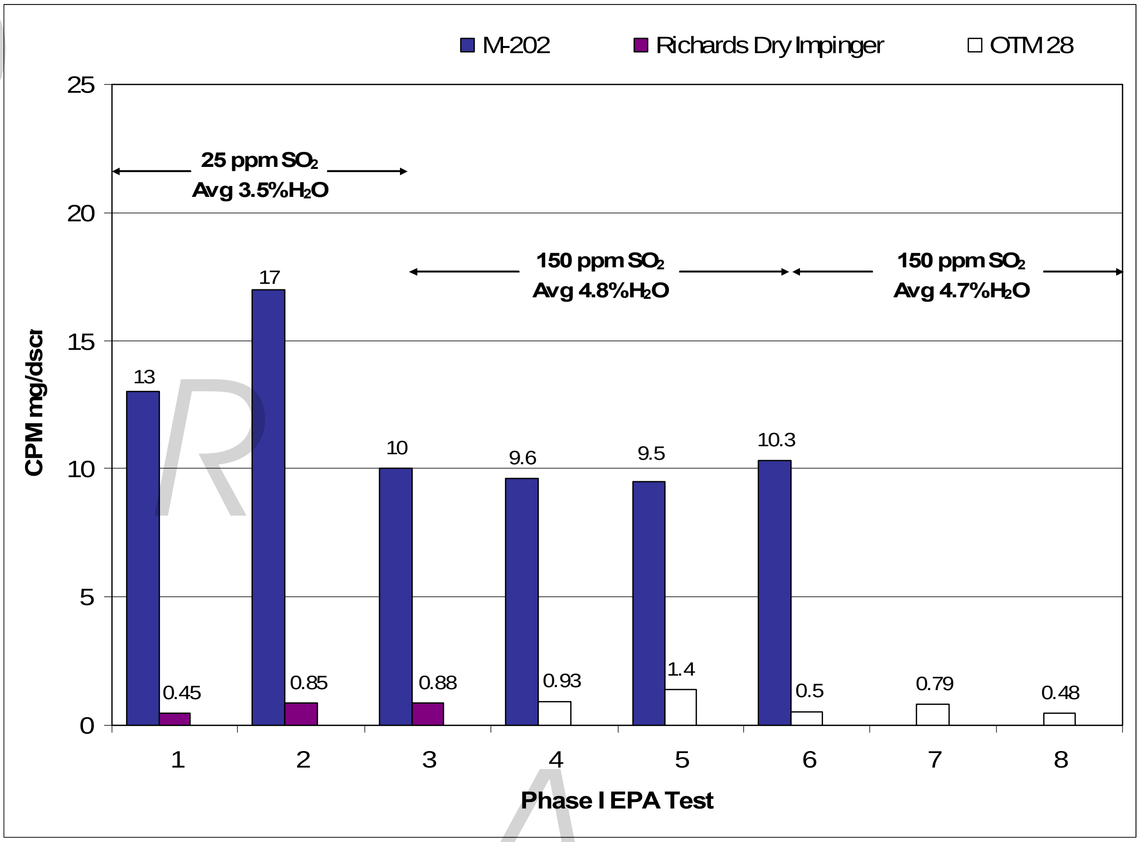

Figure 4-6. Results for Phase I EPA Tests 1-8

4.1.5.1 Results and Discussion – Phase I EPA Tests 1-3

The Phase I Tests 1-3 were designed to confirm SO_2 artifact in the best practice Method 202 sampling train and to confirm that the Richards dry impinger modification to Method 202 significantly reduced SO_2 artifact. Results confirmed that the Richards dry impinger modification achieved greater than 90 percent reduction in SO_2 artifact.

4.1.5.2 Results and Discussion – Phase I EPA Tests 4-8

After initial results (Phase I EPA Tests 1-3) from operating the dry impinger sampling train according to the Richards study (Richards, et al, 2005) demonstrated a significant reduction of SO_2 artifact, further refinements were made to the sampling and analytical procedures of the dry impinger method and Phase I EPA Tests 4-8 were completed. Phase I EPA Tests 4-8 were performed to determine if further improvements could be made to reduce the SO_2 artifact and to demonstrate that the reduction in artifact was reproducible. Results for Phase I EPA Tests 4-8 are shown in Figure 4-6. Results in these tables are based on ion chromatographic analysis of train samples to isolate the SO_2 artifact formation from the baseline blank contamination inherent to each of the methods.

Results for Phase I EPA Tests 4-8 showed a significant decrease in SO_2 artifact in OTM 28, even at higher SO_2 concentrations. OTM 28 appears to be equally effective in controlling artifact formation in both the low- and high-SO_2 concentration gas streams. The standard Method 202 train generated consistently higher amounts of artifact in the low- and high-SO_2 concentration samples.

Results also showed that during the evaluation of the two train configurations, the gravimetrically determined blank values of the OTM 28 train were near the CPM values resulting from OTM 28 tests. For replicate tests of OTM 28 (Section 4.1.5.3), improved preparation and clean up procedures and the use of deionized ultra-filtered water reduced the blank level to near the method detection limit (MDL).

4.1.5.3 Results and Discussion – Phase I EPA Eight Replicate Tests

ERG completed eight Replicate Tests under the high-SO_2 train (150 ppm) conditions similar to Phase I EPA Tests 4-8 to determine whether the precision and bias of OTM 28 were acceptable. Specifically, ERG evaluated the performance of OTM 28 using the statistical procedures in EPA Method 301. Replicate tests demonstrated that properly cleaned OTM 28 sampling trains could be used to reach an MDL of approximately 1 to 2 mg over a range in SO_2 concentrations up to 150 ppm. Results for the eight Replicate Test runs are shown in Table 4-3 (see Appendix G for raw data).

Table 4-3. OTM 28 Replicate Results Summary

Replicate Test Run	Organic CPM (mg)	Inorganic CPM (mg)	Ambient Filter CPM (mg)	Total CPM (mg)
1	0.12	2.26	-0.36	2.12
2	0.16	2.99	-0.06	3.09
3	0.09	1.44	0.00	1.54
4	0.31	1.98	0.00	2.30
5	0.17	1.65	0.07	1.89
6	0.39	2.58	-0.20	2.77
7	0.08	1.24	0.31	1.64
8	0.02	1.94	0.18	2.14
Blank	-0.02 mg	0.21 mg	0 mg	0.21 mg
Average	0.17	2.02	-0.01	2.18
Std Deviation	0.12	0.59	0.21	0.53
Estimated MDL	0.37	1.78	0.63	1.60

The averages were not blank-corrected. Negative filter weights were used in the calculation of the average filter weight and filter weight standard deviation. The estimated MDL were calculated as three times the standard deviation.

The distribution of condensed water was also recorded during the eight Replicate Tests. Most stack moisture was collected in the knockout impinger or the ice-chilled moisture train after the CPM filter. Less water was collected in the second impinger. Water condensed on the surfaces of all the ambient temperature components. Water also soaked the ambient temperature filter. Results for water distribution in the impingers are shown in Table 4-4 (see Appendix H for moisture calculations). Results also showed that the condenser easily cooled the 160 °C (320 °F) gas to less than 29 °C (84 °F) if the water bath temperature was operated at approximately 27 °C (80 °F). The majority of CPM was found in the aqueous fraction and careful attention to controlling or reducing contamination was crucial to reaching the lowest level of detectable CPM.

Table 4-4. Distribution of Moisture in OTM 28 Replicate Tests

Phase I EPA Test	Knockout Impinger (g)	1st Impinger (g)	Moisture Impinger (g)	Silica Impinger (g)	Total Moisture (g)	Percent Moisture (%)
1	39	0	22.9	19.7	81.6	10.31
2	36	~0.1	25.8	20.5	82.6	10.26
3	24	0.7	24.9	17.9	67.5	8.64
4	23.8	0.3	22.6	20.1	66.8	8.47
5	28.2	1.6	23	16.9	69.7	9.05
6	27.9	0.7	22.9	18	69.5	9.86
7	11.7	0.2	22.6	15.9	50.4	6.57
8	9.9	0.2	19.5	16.4	46.0	5.99

In addition to separating the gas components from the condensed water, OTM 28 operated at a higher collection temperature reduces the solubility of SO_2 in water. The combined affect of less water, not bubbling or sparging the stack gas through the water, and lower SO_2 solubility explains the reduction in artifact formation. Ion chromatography results also showed that both methods produce some sulfite (SO_3) and sulfate (SO_4) in the aqueous fraction. Sulfite is unstable during analysis and converts to sulfate with increased time and temperature. The total sulfite and sulfate mass in each of the Eight Replicate tests was less than the detection limit of the analytical balance (0.00001 g) used for these experiments.

4.2 Phase I Sampling Train Experiments with Ammonia – EPA Tests 16-18

The purpose of Phase I EPA Tests 16-18 was to determine the effects of ammonia (NH_3) on the formation of SO_2 artifact when applying OTM 28 in the absence of sulfuric acid or hydrochloric acid gas. Specifically, the purpose of Phase I EPA Tests 16-18 was to determine if NH_3 catalyzes SO_2 to sulfate (SO_4), thus forming CPM at a target temperature before it reaches the OTM 28 sampling train. These tests corresponded with QAPP Tests 16-18 (ERG, 2006)(Appendix A).

4.2.1 Matrix

The test matrix for Phase I EPA Tests 16-18 was similar to Phase I EPA Tests 1-3, including a target 25 ppm SO_2 concentration. However, Phase I EPA Tests 16-18 included the addition of ammonia gas at approximately 9 ppm. Tests were also performed at a higher moisture content (target 11-12 percent rather than 8 percent) to simulate the emissions of source types for which ammonia would be added. The actual test conditions are listed in Table 4-5.

Table 4-5. Actual Phase II Test Conditions

Phase I EPA Test	Paired Methods	Sulfur Dioxide* (ppm)	Ammonia* (ppm)	Carbon Dioxide* (%)	Oxygen (%)	Water ** (%)	Nitrogen Oxides* (ppm)
16	A, B	22	9	10.7	7.5	12	44.8
17	A, B	22	9	10.7	7.5	11.9	44.8
18	A, B	22	9	10.7	7.5	11.2	44.8

* Based on gas dilution calculations
** Measured Moisture
A = OTM 28
B = OTM 28 with a 71 °C (160 °F) filter between the Method 5 filter (320 °F) and the condenser

4.2.2 Sampling Equipment and Approach

The OTM 28 sampling train was paired with another OTM 28 sampling train with a low-temperature heated filter added. Specifically, for Phase I EPA Tests 16-18, a 71 °C (160 °F) filter was added after the Method 5 filter 160 °C (320 °F) and before the condenser of the OTM 28 sampling train. The additional filter was designed to capture filterable particulate if it were formed by the reaction of ammonia and SO_2. The target temperature of 71 °C (160 °F) was chosen because it was cold enough for ammonia to react with the SO_2, but warm enough to prevent water from condensing. This "low-temperature" filter modification is shown in Figure 4-7.

The sampling approach for Phase I EPA Tests 16-18 was the same as the sampling approach for Phase I EPA Tests 4-8 as described in Section 4.1:

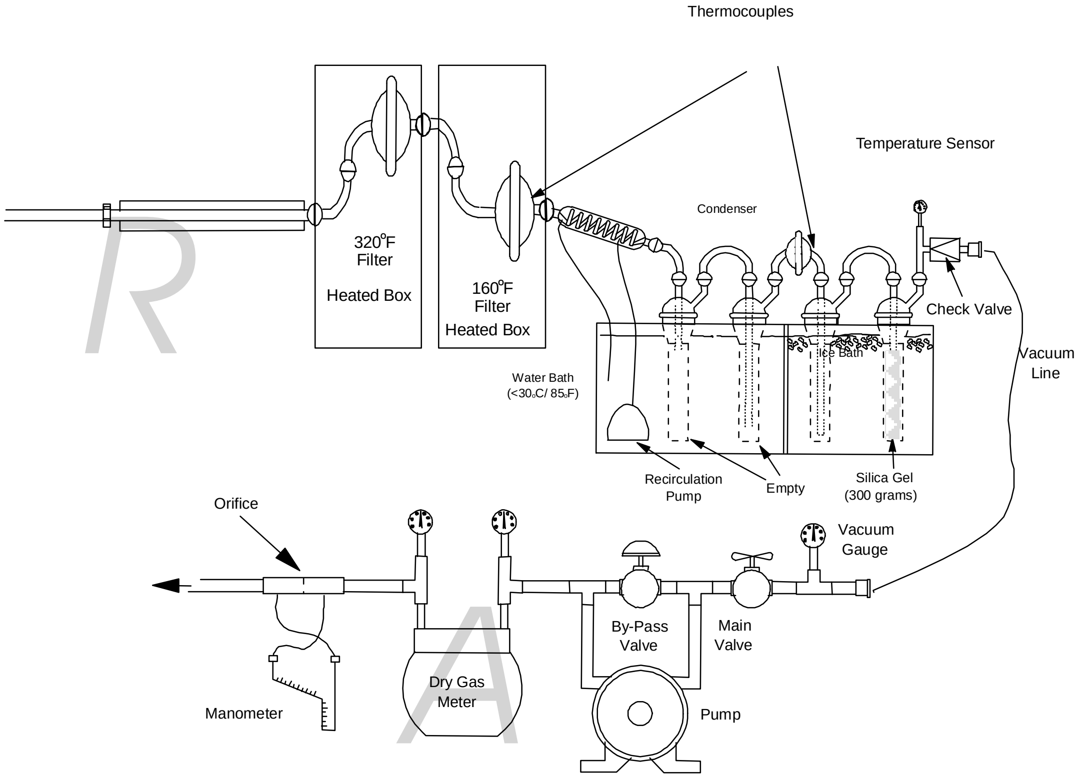

Figure 4-7. OTM 28 Sampling Train with an Added 160 °F Filter

- Sampling trains were evaluated using the stack gas simulator manifold described in Section 4.1.2.1.

- Sampling trains collected gas from the source gas simulator for 1 hour at a collection rate of 0.5 scfm.

- Sampling trains were operated according to the revised sampling procedures described in Section 4.1.2.4.

4.2.3 Sampling Train Recovery – Method 202 and Dry Impinger Samples

The sampling train recovery procedures for Phase I EPA Tests 16-18 were the same as the sampling train recovery procedures described in Section 4.1.3.

4.2.4 Analytical Procedures – Phase I Test Runs 16-18

The analytical procedures for Phase I EPA Tests 16-18 were the same as the revised analytical procedures for Phase I EPA Tests 4-8 as described in Section 4.1.4.1. In addition, ERG used IC to determine if NH_3 or SO_4 was present in samples from the 71 °C (160 °F) filter or the aqueous impinger solutions. Analytical steps included the following:

- Dry and reconstitute samples in water
- Remove an aliquot for analysis by IC
- Analyze for anions and cations by IC
- Add ammonia to neutralize samples and remove sulfate waters of hydration
- Dry samples and weigh residue

4.2.5 Results and Discussion – Phase I EPA Tests 16-18

Table 4-6 contains the IC results by fraction of each train for Tests 16-18. Table 4-7 summarizes gravimetric results by individual train for Tests 16-18 (see Appendix I for raw data).

Table 4-6. OTM 28 Train with 71 °C (160 °F) Filter – IC Results by Fraction

Phase I Test Run	Method 5 filter (160 °C) (mg)	Low-temp filter (71 °C) (mg)	Aqueous (mg)	Organic (mg)	Ambient filter (30 °C) (mg)	Total (mg)
NH_3						
16	ND	ND	ND	NA	ND**	ND
17	ND	ND	ND	NA	ND**	ND
18	ND	ND	ND	NA	ND**	ND
Train Blank 1	ND	NA	ND	NA	NR	ND
Train Blank 2	ND	NA	ND	NA	NR	ND
Train Blank 3	ND	NA	ND	NA	NR	ND
Reagent Blank	NA	NA	ND	NA	NR	ND
SO_4						
16	180	160	ND	NA	ND*	340
17	146	201	ND	NA	ND*	347
18	181	156	ND	NA	ND*	337
Train Blank 1	147	142	ND	NA	NR	289
Train Blank 2	147	102	ND	NA	NR	249
Train Blank 3	150	NA	ND	NA	NR	150*
Reagent Blank	NA	NA	ND	NA	NR	ND

ND = Not detectable above 27.6 total micrograms
NR = Not run
* Missing 71 °C Filter Fraction
ND** = Not detected in gravimetric analysis of filter
NA = Not applicable

Table 4-7. OTM 28 Train – IC Results by Fraction

Phase I Test Run	Method 5 filter (160 °C) (mg)	Low-temp filter (71 °C) (mg)	Aqueous (mg)	Organic (mg)	Ambient filter (30 °C) (mg)	Total (mg)
NH_3						
Test Run 16	ND	NA	ND	NA	ND	
Test Run 17	ND	NA	ND	NA	ND	
Test Run 18	ND	NA	ND	NA	ND	
SO_4						
Test Run 16	474	NA	ND	NA	ND	
Test Run 17	276	NA	ND	NA	ND	
Test Run 18	477	NA	ND	NA	ND	

ND = Not detectable above 27.6 total micrograms of ammonia as ammonium ion
NA = Not applicable

Results showed no CPM in any of the fractions: 160 °C filter, 71 °C filter, aqueous fraction, or the 30 °C filter. Results indicated that no CPM formed in either the OTM 28 train or the 71 °C (160 °F) filter on the OTM 28 train.

4.3 Phase I Sampling Train Experiments – EPRI Tests 1-12

EPRI Tests 1-12 expanded the EPA test matrix to challenge OTM 28 with higher moisture (10 and 15 percent) and a higher SO_2 concentration (500 ppmv), which represent the range of conditions at coal-fired power plants. OTM 28 was compared to the standard EPA Method 202 operated according to EPA's best practice recommended procedures (Appendix B). Like EPA Tests 1-8, the standard Method 202 sampling train was operated following EPA's best practice recommended procedures to obtain the best measurement of particulate matter resulting from the dilution cooling of the sampled gas stream (www.epa.gov/ttn/emc/methods/method202.html) (Appendix B). The objective of these runs was to quantify the SO_2 bias in Method 202 and determine the extent to which OTM 28 mitigates this bias at higher moisture and SO_2 concentrations.

4.3.1 Matrix

Higher water (moisture) content was included in the matrix to test the possibility that more condensed water in the sampling train would capture more SO_2 and ultimately produce more sulfate artifact.

Two inlet gas temperatures were proposed: 300 °F and 140 °F. Different temperatures were selected because the inlet sample gas manifold temperature could impact where in the dry impinger train the flue gas moisture condenses, and correspondingly how much water is available to absorb SO_2 from the flue gas. All of the 10 percent moisture runs represent unscrubbed flue gas, which would most likely be sampled at air heater outlet temperatures in the range of about 270 °F to 320 °F. These runs were conducted at 300 °F as a mid-point for this range.

The 15 percent moisture runs were primarily intended to represent scrubbed flue gas, which would be nearly or completely saturated with moisture. These flue gases would typically be sampled at temperatures ranging from 120 °F (saturated) to about 160 °F (with significant reheat or when sampling a semi-dry scrubber). However, the manifold was operated at temperatures to maintain water in the gaseous phase. To perform this set of tests, the moisture generation system was modified using a precision digital pump to add water to a tubular stainless steel heat exchanger. The heat exchanger temperature was controlled to 300 °F to ensure water was converted to steam. Nitrogen gas was added through this heat exchange tube to transport moisture to the sampling manifold injection port.

Several preliminary tests were performed to ensure all of the water was gaseous and collected before this test sequence was officially started. The primary indicator was complete vaporization of moisture in the manifold, as indicated by no condensation in the manifold. A temperature of ~210 °F was necessary to avoid condensation in the manifold when this test matrix was generated.

Table 4-8. Phase I EPRI Tests 1-12 Experimental Matrix Test Conditions and Gas Composition

Phase I EPRI Test	Methods*	SO_2 (ppmv)	NH_3 (ppmv)	CO_2 (%)	O_2 (%)	H_2O (%)	Nitrogen Oxide Mix (ppmv)	SO_3/ Sulfuric Acid (ppmv)	Inlet Gas Temperature, (^oF)
1	A, B	500	0	12	8	10	50	0	300
2	A, B	500	0	12	8	10	50	0	300
3	A, B	500	0	12	8	10	50	0	300
4	A, B	25	0	12	8	15	50	0	140

Table 4-8. Phase I EPRI Tests 1-12 Experimental Matrix Test Conditions and Gas Composition (Continued)

Phase I EPRI Test	Methods*	SO_2 (ppmv)	NH_3 (ppmv)	CO_2 (%)	O_2 (%)	H_2O (%)	Nitrogen Oxide Mix (ppmv)	SO_3/ Sulfuric Acid (ppmv)	Inlet Gas Temperature, (°F)
5	A, B	25	0	12	8	15	50	0	140
6	A, B	25	0	12	8	15	50	0	140
7	A, B	150	0	12	8	15	50	0	140
8	A, B	150	0	12	8	15	50	0	140
9	A, B	150	0	12	8	15	50	0	140
10	A, B	500	0	12	8	15	50	0	300
11	A, B	500	0	12	8	15	50	0	300
12	A, B	500	0	12	8	15	50	0	300

* Methods
A = Method 202
B = OTM 28

4.3.2 Sampling Equipment and Approach

The sampling approach for Phase I EPRI Tests 1-12 was the same as the sampling approach for Phase I EPA Tests 4-8 as described in Section 4.1:

- Sampling trains were evaluated using the stack gas simulator manifold described in Section 4.1.2.1.
- Sampling trains were operated according to the OTM 28 sampling procedures described in Section 4.1.2.4.

The EPRI sampling trains collected gas from the source gas simulator for 2 hours at a collection rate of 0.5 scfm. Glass fiber filter media was used as the CPM filter in all EPRI tests.

4.3.3 Sampling Train Recovery – Method 202 and Dry Impinger Samples

The sampling trains were recovered according to the procedures described in Section 4.1.3.

4.3.4 Analytical Procedures

The analytical procedures for Phase I EPRI Tests 1-12 were similar to the OTM 28 analytical procedures for Phase I EPA Tests 4-8 as described in Section 4.1.4.1.

An aliquot of selected aqueous fractions was set aside for ion chromatography analysis. Sulfate concentration was determined by ion chromatography following EPA SW-846 Method 9056.

4.3.5 Results

Phase I EPRI Tests 1-12 quantified the SO_2 bias in Method 202 and determined the extent to which OTM 28 mitigates this bias at higher moisture and SO_2 concentrations. Results are compared to the average of three blank trains and standard deviation of blank results to determine the significance of the comparison.

The comparison of Method 202 to OTM 28 are based on the actual test run conditions shown in Table 4-9.

Table 4-9. Actual Test Run Conditions for Tests 1-12

Phase I EPRI Test	Methods*	SO_2 (ppmv)	NH_3 (ppmv)	CO_2 (%)	O_2 (%)	H_2O (%)	Nitrogen Oxide Mix (ppmv)	SO_3/ Sulfuric Acid (ppmv)	Average Inlet Gas Temperature, (°F)
1	A, B	445	0	10	7	10	59	0	344
2	A, B	445	0	10	7	10	59	0	302
3	A, B	445	0	10	7	10	59	0	298
4	A, B	21	0	10	7	12	57	0	205
5	A, B	21	0	10	7	13	57	0	215
6	A, B	21	0	10	7	14	57	0	208
7	A, B	134	0	7	7	14	57	0	214
8	A, B	134	0	7	7	14	57	0	214
9	A, B	134	0	7	7	14	57	0	216
10	A, B	424	0	10	7	15	56	0	286
11	A, B	424	0	10	7	15	56	0	286
12	A, B	424	0	10	7	14	56	0	284

*Methods:
A = Method 202
B = OTM 28

Gravimetric results for Method 202 tests for these conditions are shown in Table 4-10; gravimetric results for OTM 28 for these conditions are shown in Table 4-11. Results have been converted to units of milligrams per dry standard cubic meter (mg/dscm) to allow comparison between the different sampling volumes collected during the experimental tests.

Table 4-10. Gravimetric Method 202 Results for Phase I EPRI Tests 1-12

Phase I EPRI Test	Organic CPM (mg)	Inorganic CPM (mg)	Filter (mg)	Total CPM (mg)	Total CPM (mg/dscm)
1	ND	28	NA	28	14.7
2	0.46	21	NA	22	11.0
3	0.05	21	NA	21	10.6
4	0.28	16	NA	16	8.3
5	0.31	16	NA	16	8.0
6	0.12	16	NA	16	8.1
7	0.25	21	NA	21	10.6
8	ND	19	NA	19	9.8
9	ND	20	NA	20	10.0
10	ND	20	NA	20	10.3
11	ND	17	NA	17	8.7
12	ND	13	NA	13	6.4
TB1	0.19	4	NA	5	2.4
TB2	ND	5	NA	5	2.6
TB3	6.44	1	NA	7	3.7

TB = train blank

Table 4-11. Gravimetric OTM 28 Results for Phase I EPRI Tests 1-12

Test	Organic CPM (mg)	Inorganic CPM (mg)	Filter (mg)	Total CPM (mg)	Total CPM (mg/dscm)
1	0.35	12.9	12.9*	26	6.9*
2	0.45	5.51	ND	6	3.1
3	0.34	5.22	ND	6	2.9
4	0.72	5.84	0.2	7	3.6
5	0.55	3.98	0.1	5	2.4
6	0.3	4.31	ND	5	2.4
7	0.21	2.9	ND	3	1.7
8	0.36	3.57	ND	4	2.1
9	0.25	2.92	0.6	4	2.0
10	6.83	4.35	0.0	11	5.9
11	0.34	5.5	0.3	6	3.2
12	0.57	4.52	1.1	6	3.2
TB1	0.13	4.23	0.0	4	2.3
TB2	0.74	4.73	0.0	5	2.9
TB3	0.97	2.21	0.0	3	1.7

* CPM filter result failed the two standard deviation test and was excluded from data set.
TB = train blank

Table 4-12. Side-by-Side Comparison of Total CPM Results for Method 202 and OTM 28

Test	Method 202-Total CPM (mg/dscm)	OTM 28 -Total CPM (mg/dscm)	Difference (mg/dscm)
1	14.7	6.9*	7.8
2	11.0	3.1	7.9
3	10.6	2.9	7.7
4	8.3	3.6	4.7
5	8.0	2.4	5.6
6	8.1	2.4	5.7
7	10.6	1.7	8.9
8	9.8	2.1	7.7
9	10.0	2.0	8
10	10.3	5.9	4.4
11	8.7	3.2	5.5
12	6.4	3.2	3.2
TB1	2.4	2.3	NA
TB2	2.6	2.9	NA
TB3	3.7	1.7	NA

* CPM filter was excluded from data set because it was an outlier.

Results for EPRI Tests 1-12 showed consistent reduction of artifacts even at conditions that represent some of the extremes in water and SO_2 concentrations at coal-fired power plants. The SO_2 bias in Method 202 ranged from 6.4 to 14.7 mg/dscm, with an average of 9.7 mg/dscm. The SO_2 bias in OTM 28 ranged from 1.7 to 5.9 mg/dscm, with an average of 3.85 mg/dscm. OTM 28 reduced SO_2 artifact by 66 percent on average or better compared to the best practice Method 202.

The three replicate blank trains are a small sample of the expected blank population. Estimates of the precision of the blanks indicate the average blank measured for Method 202 trains was 3 mg/dscm with a standard deviation of 0.7 mg/dscm. The three replicate train blanks suggest the blank for Method 202 is 3 ± 1.4 mg/dscm. The average blank for OTM 28 was 2 mg/dscm with a standard deviation of 1 mg/dscm. The three replicate train blanks suggest that the train blank for OTM 28 is 2 ± 2 mg/dscm. There is more mass in the Method 202 train blank than in OTM 28 because Method 202 uses more solvent and more glassware.

Figure 4-8 compares the CPM collected by these two methods. The figure shows a line representing the average blank CPM for all trains (2.6 mg/dscm). OTM 28 CPM results were close to the average blank level of 2 mg/dscm. Method 202 results were significantly greater than the average Method 202 train blank of 3 mg/dscm.

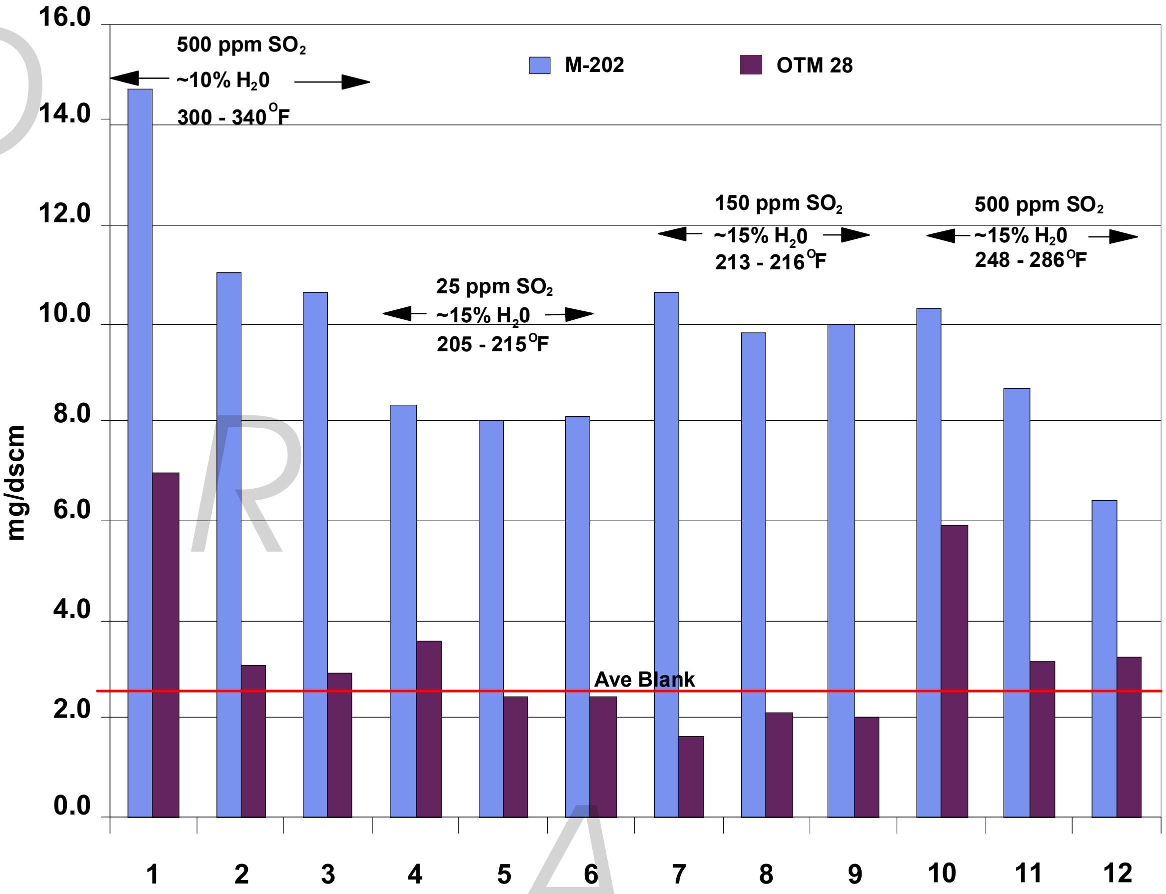

Figure 4-8. Comparison of Method 202 and OTM 28 CPM

Results from the titration of sulfuric acid performed as part of the analysis procedure gave a clearer evaluation of artifact formation in Method 202 and OTM 28 since train blank contribution mass is not measured by the titration of sulfuric acid. The average blank in Phase I EPRI Test Runs 1-12 is the average of three complete sampling train blanks that were assembled, recovered, and analyzed without taking any sample from the manifold. Titration results are presented in Table 4-13 and are shown in Figure 4-9.

Table 4-13. Titration Results from Phase I EPRI Tests 1-12

Run Number	SO_2 Concentration (ppm)	Moisture (%)	Method 202 Sulfuric Acid by Titration (mg/dscm)	OTM 28 Sulfuric Acid by Titration (mg/dscm)
1	500	10	23.1	5.0
2	500	10	14.9	0
3	500	10	16.0	0
4	25	15	14.8	0
5	25	15	13.9	0.25
6	25	15	13.8	0..25
7	150	15	16.9	0.25
8	150	15	16.3	0.26
9	150	15	15.3	0.26
10	500	15	18.9	0.25
11	500	15	17.8	0.51
12	500	15	21.3	0.25

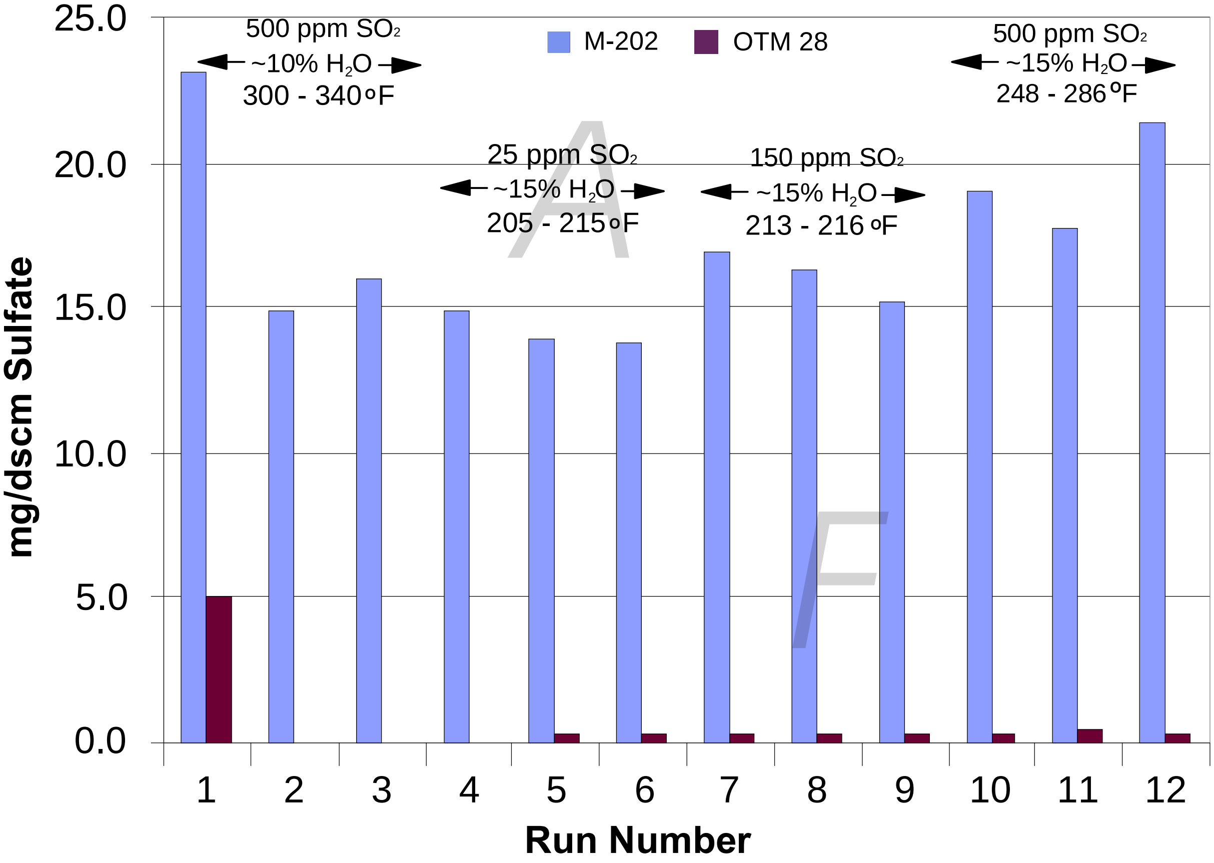

Figure 4-9. Titration Results from Phase I EPRI Tests 1-12

5.0 DETAILS ON PHASE II EPRI LABORATORY SAMPLING TRAIN EXPERIMENTS

This section contains details of Phase II laboratory experiments. EPRI proposed two other sampling procedures as potential alternatives to OTM 28. These alternatives would identify the SO_2 bias in OTM 28 by providing a separate measurement of the amount of sulfur trioxide/sulfuric acid (SO_3/H_2SO_4) in the flue gas. These extra measurements may allow sulfate artifacts captured in the OTM 28 water impinger recoveries to be corrected.

The additional EPRI tests evaluated collection efficiency of measurable amounts of SO_3/H_2SO_4 in the synthetic gas mixture. Because the relative proportions of SO_3 and H_2SO_4 in the gas depend on the gas temperature and moisture content, test runs included different concentrations of SO_3/H_2SO_4 and inlet gas temperatures. These tests would determine the ability of each method to quantify inorganic CPM present at known concentrations in the synthetic stack gas.

- 5.1 Phase II Laboratory Experiments-EPRI Controlled Condensate
  - Tests 19-24 and 31-36 to measure the ability of OTM 28 and controlled condensate methods to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at relatively high and low concentrations.
- 5.2 Phase II Laboratory Experiments-EPRI Low-temperature Filter
  - Tests 13-15 and 25-27 to measure the ability of OTM 28 and low-temperature filter methods to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at a relatively low concentration.

5.1 Phase II Laboratory Experiments – EPRI Controlled Condensate Tests 19-24 and 31-36

The controlled condensation method was tested in parallel with OTM 28 to provide a more accurate measure of flue gas CPM. The controlled condensation result was to be used to provide a direct measurement of the amount of SO_3/sulfuric acid spiked into the flue gas simulator. The total CPM from SO_3 spiked test runs is assumed to be sulfate. Therefore, the controlled condensation method is assumed to be the referee method to evaluate the OTM 28 SO_3/sulfuric acid recovery.

5.1.1 Matrix

The test matrix shown in Table 5-1 includes tests at two levels of SO_2 matched up to two levels of SO_3. Tests 19-24 and 31-36 included 2 ppmv and 10 ppmv inlet SO_3/sulfuric acid concentrations to measure the ability of each method to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at relatively high and low concentrations. The actual range of SO_3/sulfuric acid in coal flue gases can vary from undetectable (less than 0.1 ppmv) to upwards of 60 ppmv.

Table 5-1. Phase II EPRI Controlled Condensate Tests – Experimental Matrix Test Conditions and Gas Composition

Phase II EPRI Test	Paired Methods*	Sulfur Dioxide (ppm)	Effective Ammonia (ppm)	Carbon Dioxide (%)	Oxygen (%)	Water (%)	SO_3/Sulfuric Acid (ppmv)
31	B, C	0	0	12	8	10	2
32	B, C	0	0	12	8	10	2
33	B, C	0	0	12	8	10	2
34	B, C	0	0	12	8	15	10
35	B, C	0	0	12	8	15	10
36	B, C	0	0	12	8	15	10
19	B, C	150	0	12	8	10	2
20	B, C	150	0	12	8	10	2
21	B, C	150	0	12	8	10	2
22	B, C	150	0	12	8	15	10
23	B, C	150	0	12	8	15	10
24	B, C	150	0	12	8	15	10

* Methods
B = OTM 28
C = Controlled condensation method

Tests 19-24 compared the OTM 28 train to the controlled condensate method with the addition of 150 ppmv SO_2. These tests evaluated each method's ability to discriminate between sulfuric acid/SO_3 in stack gas and the sulfuric acid formed as an artifact of SO_2. Tests 19-24 included a 150 ppmv mid-point SO_2 concentration and Tests 25-36 included 0 ppmv SO_2. Of the tests at a 150 ppmv SO_2 concentration, the first three (Tests 19-21) were proposed at concentrations representing low-sulfur-coal, unscrubbed flue gas (10 percent moisture, 300 °F), and a relatively low inlet SO_3/sulfuric acid concentration of 2 ppmv. While this is higher than the SO_3 concentration typically measured in most low-sulfur-coal flue gas, it was proposed at 2 ppmv to ensure that a readily measurable SO_3 concentration was present.

Tests 31-36 also compared OTM 28 to the controlled condensate system method. Tests 31-36 repeated the conditions of Tests 19-24, but without SO_2 in the synthetic flue gas matrix. These tests compared the collection efficiency of OTM 28 to a sampling method specifically designed to collect sulfuric acid and SO_3, without any potential SO_2-related bias. That is, in the runs with SO_2 in the gas matrix, it is likely that some of the sulfate-related CPM reported by one or more methods could be due to SO_2 artifacts. Repeating these runs with no SO_2 in the synthetic gas matrix would allow any such bias to be measured by difference, and would allow a direct measurement of the efficiency of the methods to retain SO_3/sulfuric acid.

Six of the 12 tests with SO_2 at 150 ppmv included moisture conditions (15 percent) intended to replicate scrubbed flue gas (Tests 22-24 and 34-36). The 300 °F gas temperature maintains both water and sulfuric acid above the estimated acid dew point (287 °F) of this gas mixture. At 140 °F, virtually all of the sulfuric acid in the synthetic gas mixture would be condensed. Although all of the sulfuric acid in the synthetic gas mixture would be condensed when sampling scrubber outlet flue gas (all of the sulfuric acid is present as sub-micron-diameter acid mist), it is difficult to simulate this condition at the bench scale. The 10 ppmv SO_3/sulfuric acid concentration is in the typical range for high-sulfur-coal, scrubbed flue gas.

5.1.2 Sampling Equipment and Approach

OTM 28 and the controlled condensate trains were paired and evaluated in the laboratory using a synthetic stack gas generator manifold. Several gas components were spiked into the stack gas simulator. The following interfering compounds were spiked into the stack gas simulator: SO_2, nitrogen oxides (NO/NO_2), and SO_3/sulfuric acid.

5.1.2.1 Sulfur Trioxide Synthetic Gas Generator

ERG developed an SO_3 synthetic gas generator based on a design proposed by EPRI. EPRI's original design passes a small amount of compressed gas containing SO_2, nitrogen, and oxygen across a vanadium catalyst coated on an inorganic substrate held at high temperature (>800 °F) in a tube furnace. The resulting reaction assumes 100 percent conversion of the SO_2 to SO_3. The catalyst method must be precise and accurate in the amount of SO_3/sulfuric acid delivered to the sampling manifold.

Initial tests of an EPRI supplied vanadium catalyst did not work. ERG modified the original design to use a platinum black catalyst in a quartz wool bed following the procedures described by Cheney (Cheney, 1978), in place of the vanadium catalyst.

The quartz reactor tube dimensions of approximately 30 cm long by 14 mm in diameter fit the cavity of the tube furnace and allowed efficient heat transfer to the catalyst. Quartz ball joints were used to connect the reactor tube to the inlet gases and the outlet quartz transfer line leading to the gas simulator manifold mixing chamber used for sampling experiments. The tube furnace was operated at 1,000 °F and the temperature was monitored during the reactor operation. The exit temperature of the quartz transfer line between the tube furnace and the mixing chamber was maintained at 300 °F.

Reactor make-up gases included the following:

- Nitrogen (ultra-high purity or UHP)
- Air (scientific grade)
- SO_2 (2 percent certified; N_2 balance)

Nitrogen and air were added through a moisture trap containing molecular sieves. Connections at ambient temperature were made with Swagelok stainless steel fittings. Nitrogen and air at appropriate ratio were allowed to flow through the reactor as the tube furnace heats.

Sulfur dioxide was added after the moisture trap and can be turned on or off with an inline valve. Sulfur dioxide flow was started after the furnace and make-up gases are flowing and have reached operating temperature.

The gas mixture entered the reaction tube filled with quartz wool. As the gas mixture entered the reaction tube it initially passed through untreated glass wool and heats before contacting the platinum black catalyst. The tube dimensions fill the inside of the tube furnace (at about 13 mm wide and 14 cm long). Approximately 1.5 g of platinum black catalyst has been "dispersed" in several segments of the glass wool. The ball joint exit of the reaction tube attached to a thick wall quartz tube that was actively heated to bring the gas temperature entering the mixing manifold to 300 °F. A thermocouple mounted in a PFTE cross connector is used to measure the gas temperature as it exits the transfer tube. Gas passes straight through the cross connector and approximately 1 inch of Teflon® line connected to the gas mixing manifold.

Reactor operating conditions necessary to generate approximately 1 L/min of SO_3 at the outlet are the following:

- Nitrogen flow ~800 mL/min
- Air flow ~200 mL/min

- SO_2 flow set to generate desired concentration.

The SO_2 gas is added to generate 70 and 400 ppm reactor outlet concentration, which produces a range of 2 to 10 ppm in the gas mixing manifold after dilution.

ERG used certified calibration gas containing 2 percent SO_2 as the source of SO_2 to the catalyst. The flow rate of this stream was maintained using a mass flow regulator to maintain a precise SO_3 injection rate. A compressed zero grade air was added upstream of the SO_2 addition and used as the oxidizer and primary carrier gas. The dry SO_3 stream exiting the catalyst was added to the synthetic gas stack gas manifold. Figure 5-1 illustrates the reactor setup.

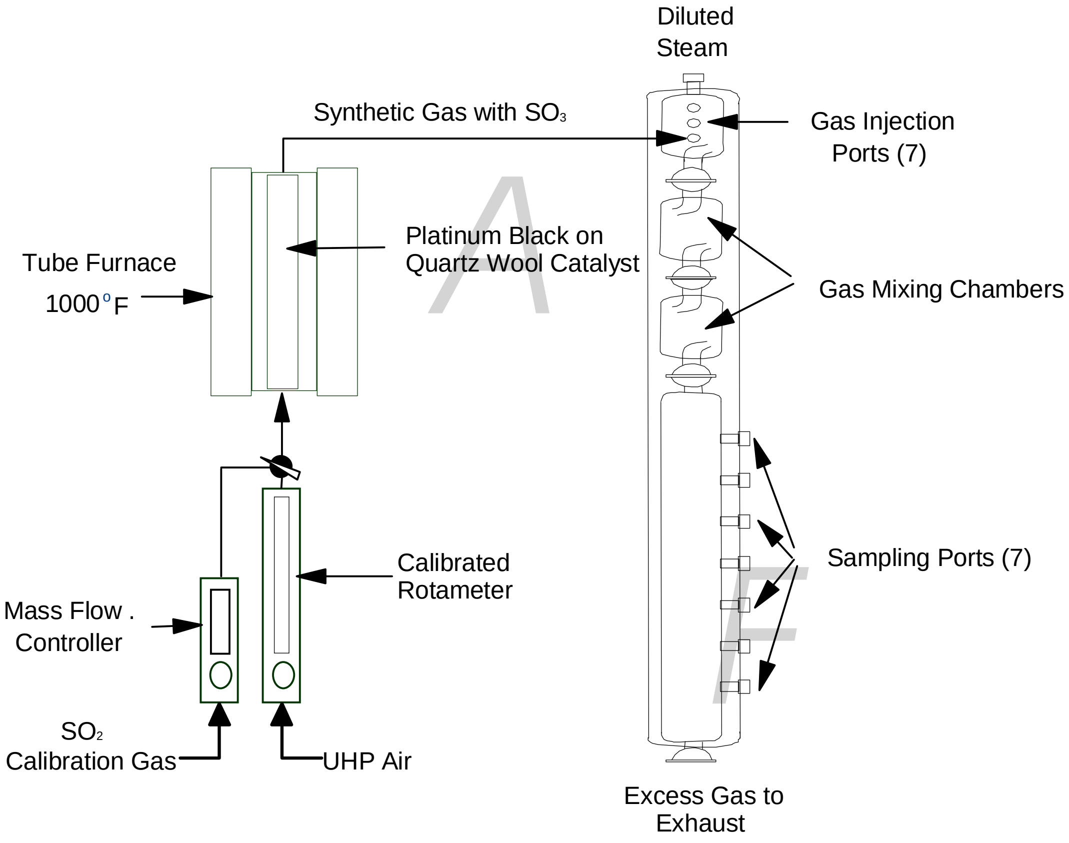

Figure 5-1. Catalyst-Based SO_3 Injection Setup

Sulfur Trioxide/Sulfuric Acid Generator Validation. Fourier transform infrared spectroscopy (FTIR) was used as a preliminary check of the SO_3 gas generator efficiency to performing the tests in the experimental matrix. A heated PTFE line led anhydrous gas directly from the generator gas transfer line to a heated multipass FTIR cell. The FTIR cell was maintained at 185 °C. Both SO_3 and SO_2 were measured simultaneously. FTIR indicated approximately 89 percent conversion efficiency from the reactor chamber.

5.1.2.2 OTM 28 Train

The OTM 28 train was assembled and operated according to the revised sampling procedures described in Section 4.1.2.4 and illustrated in Figure 4-5.

5.1.2.3 Controlled Condensate Train

The basic approach employed by this method is to collect a particulate-free sample of sulfuric acid in a temperature controlled condenser. Samples are collected through a quartz-lined probe and thimble filter heated between 550 and 600 °F. Figure 5- 2 illustrates the controlled condensation method sampling train. The sample is filtered across a heated (550 °F) quartz thimble, then passes through a water-cooled glass condenser. The condenser is controlled by water bath at a temperature about 20 °F above the flue gas moisture dew point, in this case 167 °F ± 5 °F. The large surface area of the glass condenser ensures that most of the sulfuric acid condenses rather than nucleating as sub-micron droplets that remain in the sample gas. From the condenser, the sample gas flows through a chilled impinger filled with 60 percent hydrogen peroxide and a silica filled impinger to condense moisture and remove other acid gases, prior to entering a dry gas meter.

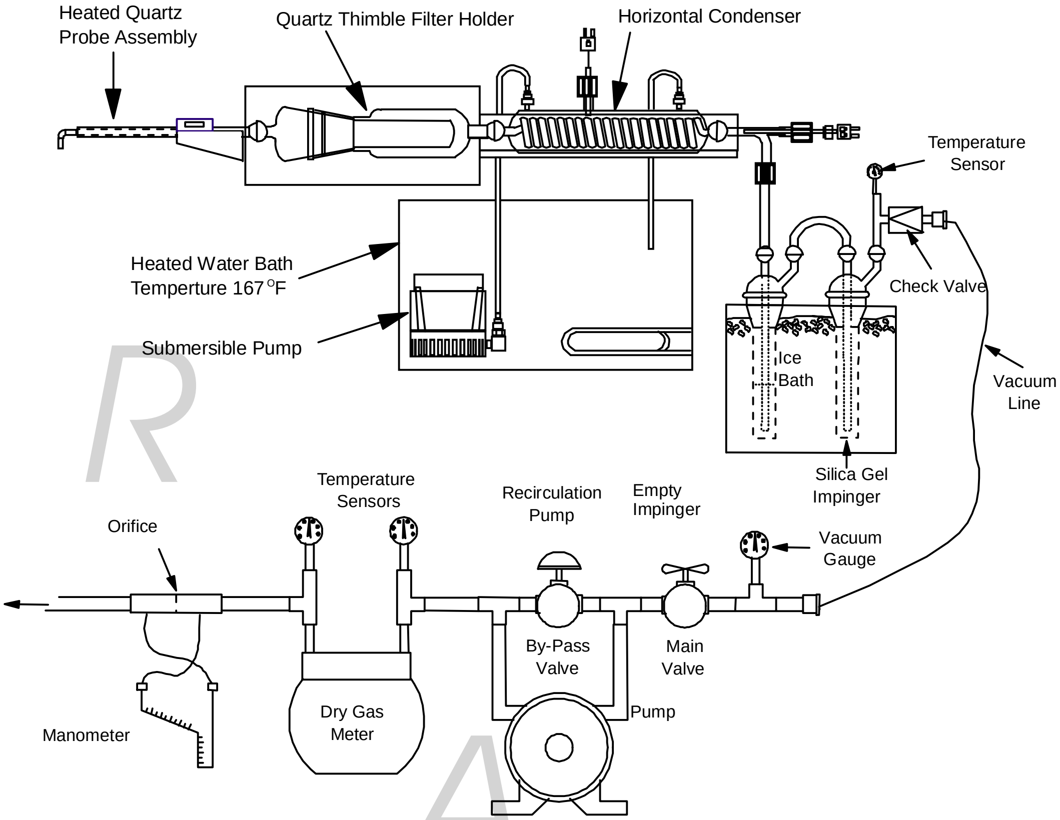

Figure 5-2. Controlled Condensation Sampling Train

5.1.3 Sampling Train Recovery

5.1.3.1 Sampling Train Recovery – EPA Dry Impinger Method

Samples from the Phase II EPRI Tests 19-24 and 31-36 were recovered from OTM 28 using the sampling train recovery procedures described in Section 4.1.3. The sampling procedures were consistent with the revised sampling procedures that EPA posted as OTM 28 (www.epa.gov/ttn/emc/prelim.html) (also see Appendix C).

5.1.3.2 Sampling Train Recovery – Controlled Condensate Method

For methods comparison, a heated (550 °F) quartz thimble, located in a hot box between the probe and condenser was used to be consistent with the configuration of current controlled condensation trains in field use. Adsorption of SO_3 on the quartz thimble or glass surfaces was avoided by conducting a "conditioning" run with a new, clean thimble in these tests. The conditioning run duration was 1 hour with approximately 10 ppm SO_3 in the gas manifold gas mixture. This conditioning allowed the components of the train to reach adsorption equilibrium with the sample gas.

At the end of the run, the condensed acid was rinsed from the condenser coil, collected and analyzed for sulfate content. Dividing the total sulfate by the total gas volume allowed calculation of the SO_3/sulfuric acid concentration per dry standard cubic meter or ppm.

Sample recovery for the controlled condensate method consisted of the following steps:

- Disconnect probe and hot filter from the sampling train
- Disconnect impingers from condenser
- Recover and rinse impingers
    - Record sample volume
    - Analyze sample by IC (or titration) for sulfate
    - Calculate SO_2 or equivalent concentration
- Recover and rinse condenser coil with ~10 mL DI water each time
    - Record liquid sample volume
    - Analyze sample by IC (or titration) for sulfate

The downstream impingers were recovered to confirm sample gas moisture content, and analyzed for sulfate content to provide a measure of the sample gas SO_2 content. These moisture and SO_2 analyses provide a level of QC on the integrity of the sample gas, by determining whether representative values were measured for the sample gas.

The analysis of the condenser catch was conducted by IC since IC results are more sensitive and accurate than alternatives such as titration.

5.1.4 Analytical Procedures – Phase II EPRI Tests 19-24 and 31-36

5.1.4.1 Analytical Procedures – OTM 28

Samples from OTM 28 were analyzed using the revised analytical procedures described in Section 4.1.4.1. An aliquot of selected aqueous fractions was set aside for IC analysis. Sulfate concentration was determined by IC following EPA SW-846 Method 9056.

5.1.4.2 Analytical Procedures – Controlled Condensate Method

An aliquot of the aqueous fraction recovered from the condenser coil was analyzed for sulfate by IC analysis. Sulfate concentration was determined by IC following EPA SW-846 Method 9056.

Measuring the concentration of H_2SO_4 aerosol in µg/m^3 used the following calculations:

$C_{\mu g/mL}$ = total µg/mL $SO_4^{=}$ reported from ion chromatography (condenser rinse)

DSCF = Volume of gas sampled in cubic feet

$$\text{DSCF} \times \frac{28.3\ \mathbf{l}}{\text{SCF}} = \text{Volume of gas sampled } (\mathbf{l})$$

V_T = total condenser rinse volume in mL

$C_{\mu g/mL} \times V_T = \mu g\ H_2SO_4$

$\text{DSCF} \times 0.283\ m^3/\text{CF} = m^3$

$$\frac{\mu g H_2SO_4}{m^3\ sampled} = \frac{\mu g\ H_2SO_4}{m^3}$$

$$\frac{\mu g\ H_2SO_4}{m^3} \div \frac{1000 \mu g}{mg} = \frac{mgH_2SO_4}{m^3}$$

5.1.5 Results and Discussion – Phase II EPRI Tests 19-24 and 31-36

The goal of Phase II EPRI Tests 19-21 and 31-36 was to measure the ability of each method to quantitatively capture and measure known flue gas SO_3/sulfuric acid concentrations at relatively high and low concentrations. Tests were conducted with and without the addition of SO_2 to evaluate artifact formation in each train. Overlayed on the SO_2 addition were tests at low (~2 ppmv) and high (~10 ppmv) sulfuric acid addition to the test gas mixture. These tests would help determine if the controlled condensate method could be used to correct OTM 28 for SO_4 formed as an artifact. Results of the controlled condensate method and OTM 28 are based on the actual run conditions and gas concentrations shown in Table 5-2.

Table 5-2. Actual Test Run Conditions for Comparison of OTM 28 with Controlled Condensate Method

Phase II EPRI Test	Methods *	SO_2 (ppmv)	NH_3 (ppmv)	CO_2 (%)	O_2 (%)	H_2O (%)	Nitrogen Oxide Mix (ppmv)	SO_3/ Sulfuric Acid (ppmv)**	Inlet Gas Temperature, (˚F)
31	B, C	0	0	12	9	9	56	1.8	282
32	B, C	0	0	12	9	9	56	1.8	289
33	B, C	0	0	12	9	9	56	1.8	294
34	B, C	0	0	12	8	11	53	1.8	294
35	B, C	0	0	12	8	12	53	1.8	294
36	B, C	0	0	12	8	15	53	1.8	294
19	B, C	148	0	12	9	9	55	1.8	296
20	B, C	148	0	12	9	8	55	1.8	294
21	B, C	148	0	12	9	8	55	1.8	290
22	B, C	155	0	12	8	16	53	8.8	297
23	B, C	155	0	12	8	15	53	8.8	298
24	B, C	155	0	12	8	15	53	8.8	300

*Methods:
B = OTM 28
C = Controlled condensate method
** Theoretical based on gas flows assuming 100 percent SO_2 conversion in reactor.

Gas concentrations reported in Table 5-2 were calculated based on the final gas mixture. Moisture content was measured in OTM 28. The actual SO_3 gas concentration delivered to the stack gas manifold was less than the theoretical since the reactor efficiency was not 100 percent. The sulfuric acid concentration in the manifold was corrected for the gas reactor generator performance based on FTIR measurements of the reactor gas output.

Results from OTM 28 tests and analyses for Phase II EPRI Tests 19-21 and 31-33 are shown in Table 5-3. All results have been converted to units of milligrams per dry standard cubic meter (mg/dscm) to allow comparison of results from different sampling trains. The OTM 28 results include the gravimetric analysis for sample fractions processed according to the proposed version of the test method. Gravimetric measurement of the CPM filter from OTM 28 could not be completed accurately for Tests 22-24 because the samples contained sulfuric acid and would not reach constant weight. Therefore, the CPM filters from all tests were extracted with reagent grade water in a sonic bath, filtered to remove glass shards, and analyzed by IC for sulfate.

Table 5-3. Dry Impinger Method Sulfuric Acid Challenge Results – Gravimetric CPM Results

Phase II EPRI Test	Actual SO_4 (mg/dscm)	Organic (mg/dscm)	Corrected Inorganic (mg/dscm)*	CPM Filter** (mg/dscm)	Total (mg/dscm)	Sulfate Recovery (%)
31	6.9	0.40	3.4	0.6	4.4	63
32	6.9	0.41	2.8	0.5	3.7	53
33	6.9	0.42	1.9	0.3	2.6	37
34	34.4	0.37	14.6	12.9	27.9	79
35	34.4	0.22	15.1	12.9	28.2	80
36	34.4	0.18	12.5	8.2	20.9	59
19	6.9	0.40	1.4*	0.4	2.2	32
20	6.9	0.22	3.1	0.2	3.6	51
21	6.9	0.22	2.1	0.2	2.5	36
22	34.4	0.65	8.9	8.5	18.0	51
23	34.4	0.21	13.5	6.6	20.3	58
24	34.4	0.48	12.7	8.1	21.3	61
TB1	0.0	0.70	1.8	0.0	2.5	NA
TB2	0.0	0.20	1.5	0.0	1.7	NA

* For this sample, sulfuric acid titration results were used.
** Filters were extracted and analyzed by IC for sulfate.

Percent recovery of SO_4 ranged from 32-80 percent, with an average recovery of 55 percent compared to the spiked amount. Test 19 inorganic results were considered to be an outlier because the gravimetric result for the inorganic fraction was almost 15 times higher than the corresponding IC results. This difference indicates this sample was contaminated during sampling or analysis. The IC result for sulfate were used in place of the weigh of this sample.

Sulfate (H_2SO_4) analysis was performed by IC on all fractions from OTM 28 tests. Analysis of sulfate by IC measures only sulfate and allowed recovery of sulfate to be compared directly between the sampling trains. Results for the sulfate analysis of the OTM 28 tests are summarized in Table 5-4.

Table 5-4. OTM 28 Sulfuric Acid Results

Phase II EPRI Test	Actual SO_4 (mg/dscm)	Inorganic IC (mg/dscm)	Filter IC (mg/dscm)	Total Sulfate by IC + Organic (mg/dscm)	Dry Impinger Recovery (%)
31	6.9	2.2	0.64	2.9	42
32	6.9	2.0	0.46	2.4	35
33	6.9	1.4	0.32	1.7	25
34	34.4	13.8	12.9	27	78
35	34.4	14.2	12.9	27	79
36	34.4	11.3	8.18	20	57
19	6.9	1.5	0.39	1.9	27
20	6.9	1.8	0.21	2.0	30
21	6.9	1.4	0.17	1.6	23
21	6.9	1.4	0.17	1.6	23
22	34.4	13.6	8.48	22	64
23	34.4	14.0	6.63	21	60
24	34.4	0.0	8.11	8.1	24

Results from the controlled condensate tests and analyses for Phase II EPRI Tests 19-24 and 31-36 are shown in Table 5-5. All results have been converted to units of milligrams per dry standard cubic meter (mg/dscm) to allow comparison of results from different sampling trains. The controlled condensate train results include IC analysis of SO_4 from only the condenser fraction of the sampling train.

Table 5-5. Controlled Condensate Sulfuric Acid Results

Phase II EPRI Test	Actual SO_4 (mg/dscm)	Total Sulfate by IC (mg/dscm)	Controlled Condensate Recovery (%)
31	6.9	7.5	109
32	6.9	7.6	111
33	6.9	6.9	100
34	34.4	32.7	95
35	34.4	40.2	117
36	34.4	33.5	9
19	6.9	6.7	98
20	6.9	6.7	97
21	6.9	6.4	92
22	34.4	30.8	89
23	34.4	32.9	95
24	34.4	29.6	86

Results show that the controlled condensate method collected on average 99 percent of the sulfate (H_2SO_4) spiked into the system. OTM 28 was less effective, capturing on average only 47 percent of the sulfate. The OTM 28 train was less effective at the lower sulfate concentrations and when SO_2 was added to the test gas at lower concentrations, but was more effective (67 percent) at capturing sulfate at higher concentrations.

Comparison of the CPM collected by these two methods is shown in Figure 5-3. This figure shows that OTM 28 results were less than the controlled condensate method for all test runs. Recoveries at the low sulfate spiking levels are near or at the detection limit for OTM 28. Recovery from the controlled condensate train was always higher than OTM 28. Sulfur dioxide did not appear to contribute artifact to either method under these test conditions.

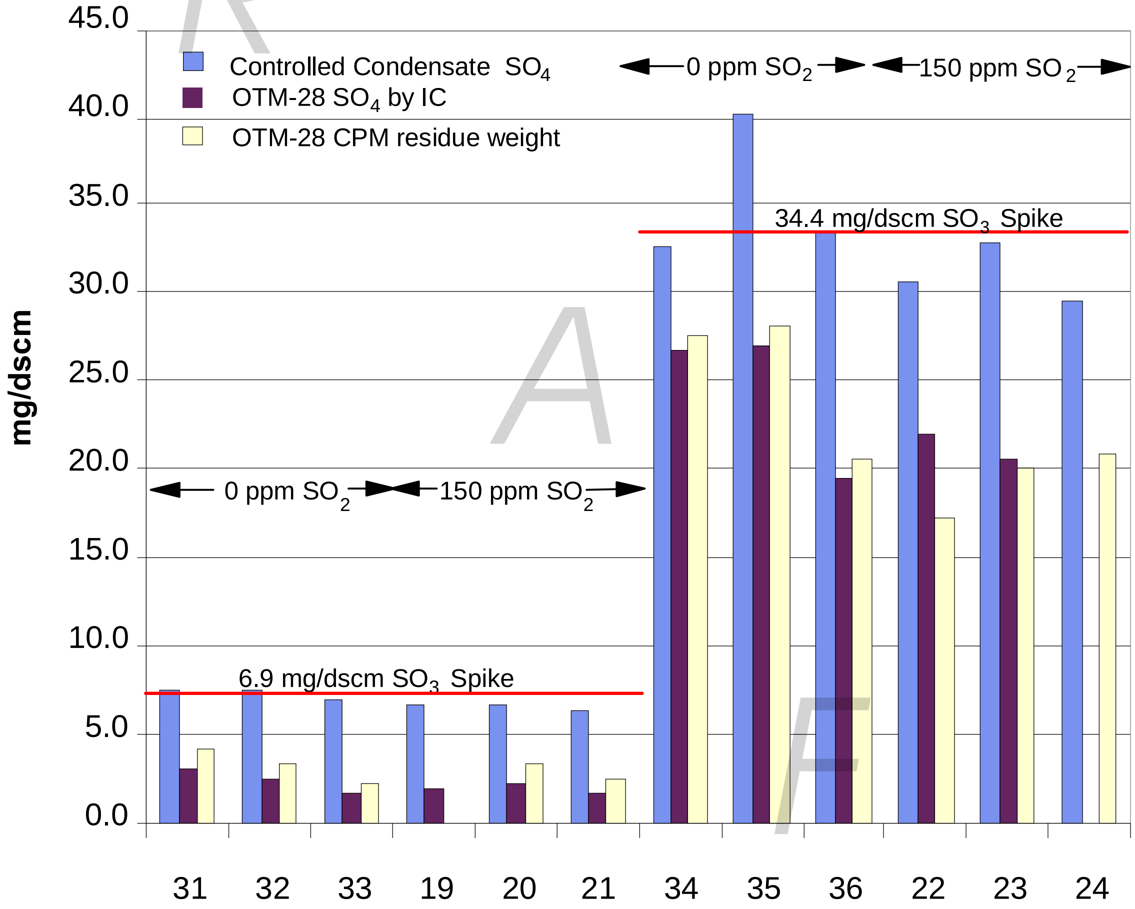

Figure 5-3. Results of OTM 28 vs. Controlled Condensate Method Sulfuric Acid Challenge

The three replicate train samples of each type were a small number of samples to perform statistical evaluation. Estimates of the precision of replicate runs shows an average uncertainty (standard deviation) for OTM 28 low sulfate spiking runs of 0.85 mg/dscm compared to 0.3 mg/dscm for the controlled condensate train. At higher sulfate spiking levels, the uncertainty in OTM 28 is 5.9 mg/dscm compared to an uncertainty of 2.9 mg/dscm for the controlled condensate method. Under all conditions in this set of test runs, the controlled condensate sampling train is more precise than the OTM 28 train.

5.2 Phase II Laboratory Experiments – EPRI Low-temperature Filter Tests 13-15 and 25-27

Phase II EPRI Tests 13-15 and 25-27 were designed to measure the ability of OTM 28 and the low-temperature filter method to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at a relatively low concentration. The EPRI low-temperature filter method was tested in parallel with OTM 28 to provide a more accurate measure of flue gas CPM. The EPRI low-temperature filter method result was to be used to provide a direct measurement of the amount of SO_3/sulfuric acid spiked into the flue gas simulator. The total CPM from SO_3 spiked test runs is assumed to be sulfate. Therefore, for these tests, the EPRI low-temperature filter method is assumed to be the referee method to evaluate OTM 28 SO_3/sulfuric acid recovery.

5.2.1 Matrix

The test matrix shown in Table 5-6 includes tests at two levels of SO_2 matched up to two levels of SO_3. Tests 19-24 and 31-36 included 2 ppmv and 10 ppmv inlet SO_3/sulfuric acid concentrations to measure the ability of each method to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at relatively high and low concentrations. The actual range of SO_3/sulfuric acid in coal flue gases can vary from undetectable (less than 0.1 ppmv) to upwards of 60 ppmv.

Table 5-6. Phase II EPRI Low-temperature Filter Tests – Experimental Matrix Test Conditions and Gas Composition

Phase II EPRI Test	Paired Methods*	Sulfur Dioxide (ppm)	Effective Ammonia (ppm)	Carbon Dioxide (%)	Oxygen (%)	Water (%)	SO_3/Sulfuric Acid (ppmv)
25	B, D	0	0	12	8	10	2
26	B, D	0	0	12	8	10	2
27	B, D	0	0	12	8	10	2
13	B, D	150	0	12	8	10	2

Table 5-6. Phase II EPRI Low-temperature Filter Tests – Experimental Matrix Test Conditions and Gas Composition (Continued)

Phase II EPRI Test	Paired Methods*	Sulfur Dioxide (ppm)	Effective Ammonia (ppm)	Carbon Dioxide (%)	Oxygen (%)	Water (%)	SO_3/Sulfuric Acid (ppmv)
14	B, D	150	0	12	8	10	2
15	B, D	150	0	12	8	10	2

* Methods
B = OTM 28
D = controlled condensation method

Tests 13-15 and 25-27 included a 2 ppmv inlet SO_3/sulfuric acid concentration to measure the ability of each method to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at a relatively low concentration. The goal of this comparison was to determine if SO_2 interfered with either sampling procedure and if the low-temperature filter method was a viable option for correcting SO_2 artifact formation in wet or dry impinger sampling systems.

Tests 13-15 compared the OTM 28 train to the low-temperature filter method and continued with the 150 ppmv mid-point SO_2 concentration. Sulfur trioxide at 2 ppmv and SO_2 at 150 ppm were added to evaluate the formation of SO_2 artifact in the OTM 28. These tests evaluated the ability of the low-temperature filter method to determine a correction factor between sulfuric acid/SO_3 in stack gas and the sulfuric acid formed as an artifact of SO_2. These test runs were completed at 10 percent moisture levels.

Tests 25-27 repeat the conditions of Tests 13-15, but without SO_2 in the synthetic flue gas matrix. This gas mixture evaluated the assumption that all the SO_3/sulfuric acid in the gas mixture is captured at 160 °F and any sulfuric acid found in the impinger samples is an artifact of SO_2 reactions. The purpose of these runs was to determine the accuracy of each method in quantifying sulfuric acid actually present in the sample gas, without any potential SO_2-related bias.

5.2.2 Sampling Equipment and Approach

The OTM 28 and the EPRI low-temperature trains were paired and evaluated in the laboratory using a synthetic stack gas generator manifold. Several gas components were spiked into the stack gas simulator. The following interfering compounds were spiked into the stack gas simulator: SO_2, nitrogen oxides (NO/NO_2), and SO_3/sulfuric acid.

5.2.2.1 Sulfur Trioxide Synthetic Gas Generator

The SO_3 synthetic stack gas simulator was prepared and calibrated according to the procedures described in Section 5.1.2.

5.2.2.2 OTM 28 Train

The OTM 28 train was assembled and operated according to the revised sampling procedures described in Section 4.1.2.4 and illustrated in Figure 4-5. The sampling procedures were consistent with the revised sampling procedures that EPA posted as OTM 28 (www.epa.gov/ttn/emc/prelim.html) (also see Appendix C), except a 110 mm fiberglass filter was used instead of a Teflon® filter.

5.2.2.3 EPRI Low-temperature Filter Train

The EPRI low-temperature filter train was assembled the same as the OTM 28 train, but with additional heated fiberglass particulate filter inserted between the 320 °F filter and the condenser. The sampling probe and heated filter of the low-temperature filter modified sampling train is similar to that of a conventional Method 5b sampling train. At the exit of the Method 5b filter, a second, fiberglass particulate filter in a temperature-controlled hot box was inserted. This filter operates at 160 °F, which should be well below the sulfuric acid gas dew point. The gas exiting the 160 °F filter enters the OTM 28 sampling train. Figure 5-4 illustrates the low-temperature filter modification to the OTM 28 train.

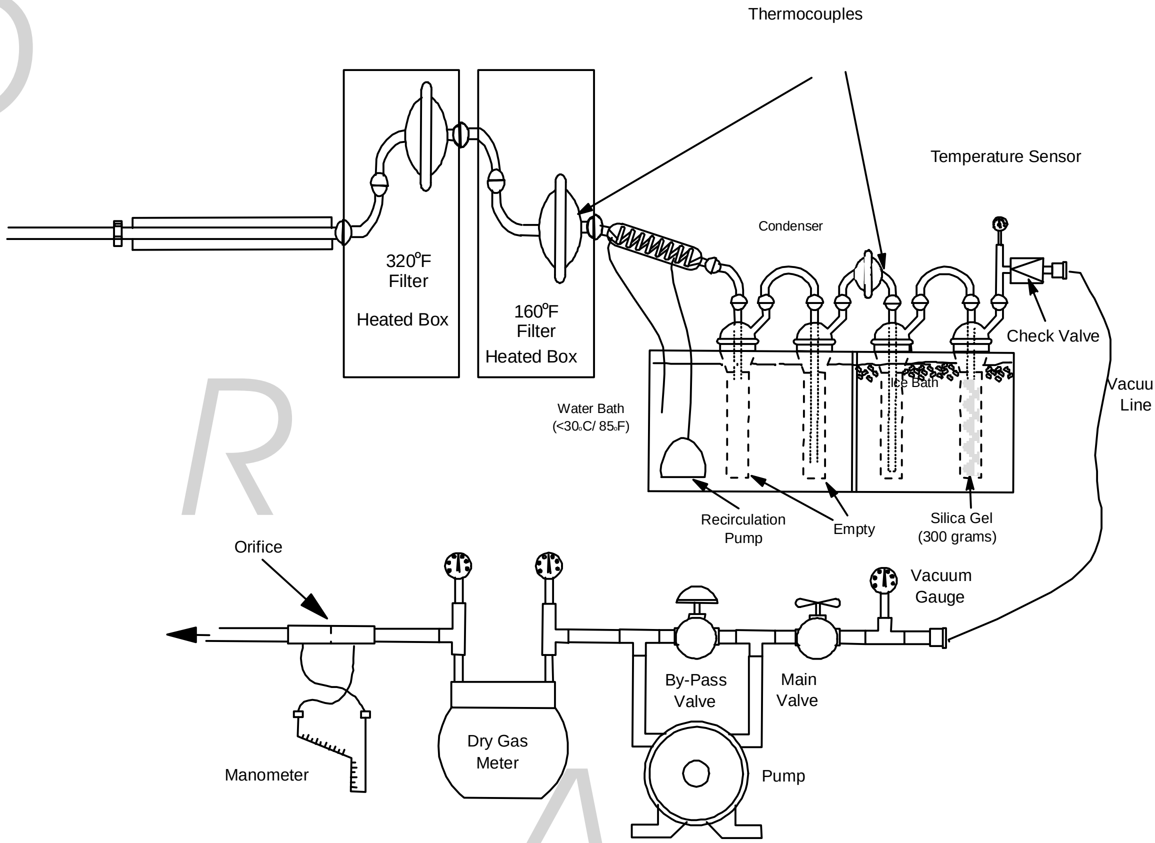

Figure 5-4. EPRI Low-temperature Filter Sampling Train

5.2.3 Sampling Train Recovery

5.2.3.1 Sampling Train Recovery – EPA Dry Impinger Method

Samples from the Phase II EPRI Tests 13-15 and 25-27 were recovered from OTM 28 using the sampling train recovery procedures described in Section 4.1.3.

5.2.3.2 Sampling Train Recovery – EPRI Low-temperature Filter Method

The low-temperature filter train has several fractions that require recovery, preparation, and analysis, including the following:

- Probe rinse
- High temperature filter (from the 310 °F filter box)
- Low-temperature filter (from the 160 ºF filter box)
- CPM train impingers (combined short stem and long stem impinger catch)
- CPM filter

C Moisture train components

The procedures used to prepare each of these sample fractions are described in Section 5.2.4.2.

5.2.4 Analytical Procedures

5.2.4.1 Sampling Train Analysis – EPA Dry Impinger Method

Samples from OTM 28 were analyzed using the analytical procedures described in Section 4.1.5.2.

5.2.4.2 Sampling Train Analysis – Controlled Condensate Method

The following procedures were used to prepare each of these sample fractions from the low-temperature filter sampling train.

<u>Probe Rinse and High Temperature Filter</u>. The probe rinse and high temperature filter were recovered consistent with the procedure in EPA Method 5. These two fractions were archived and were not analyzed.

<u>Low-Temperature Filter Extraction</u>. The low-temperature filter was extracted with deionized ultra-filtered (DIUF) water. Each filter was folded and inserted into a vial and covered with deionized ultra-filtered water (about 10 mL) and then extracted in a sonic bath for 2 minutes. This step was repeated two times and the extract was poured into a clean glass beaker. The extract was evaporated on a hot plate until about 10 mL of water was left, and then allowed to go to dryness at room temperature.

The low-temperature filter residue was then re-constituted with 100 mL of DIUF water. To ensure complete re-constitution, the sample was heated and stirred for about 10 minutes and then allowed to cool to room temperature. A 10 mL aliquot was set aside for IC analysis; the remainder was titrated with NH_4OH to a pH of 7. The remainder of the sample was evaporated to approximately 10 mL in a 105 ºC oven or on a hot plate. The sample was quantitavely transferred to a clean, tared weighing pan and evaporated to dryness at room temperature. Once the pan appears dried, it was placed in a dessicator until it reached constant weight.

<u>OTM 28 Impingers</u>. OTM 28 train impinger catch was recovered and analyzed identical to the procedures described in Section 4.1.4.1.

<u>CPM Filter Extraction</u>. The CPM filter was treated differently from OTM 28. The filter used for the EPRI studies was a fiberglass mat meeting EPA Method 5 specifications. The filter

was removed from the holder and extracted with DIUF water as described in the low-temperature filter extraction section. Each filter was folded and placed in a vial, then covered with 10 mL of DIUF water and sonicated for 2 minutes three times. The extract was then transferred to a tared vial for IC analysis. This sample was not evaporated to dryness or titrated/weighed.

Table 5-7 shows the analytical methods and sample fractions for the low-temperature filter modification tests.

Table 5-7. Analytical Methods and Sample Fractions for Low-temperature Filter Modification Tests*

Sample Fraction	Media	Analysis	Result
1. In-Stack Nozzle Wash*	Acetone Rinse	Archived	None
2. In-Stack Filter*	Fiberglass Filter	Archived	None
3. Probe wash	Water	Archived	None
4. Reduced temperature filter	Fiberglass Filter	Extract with water, analyze for sulfate	Inorganic condensable H_2SO_4 Inorganic condensable H_2SO_4
5. Impinger Water Fraction	Water	Collect aliquot for IC analysis. Evaporate, add NH_4OH to convert H_2SO_4 to $(NH_4)_2SO_4$, evaporate, weigh, correct final weights	Condensable inorganics, corrected for sulfuric acid content.
6. Impinger Organic Fraction	MeCl2 Rinse and extraction	Evaporate at room temperature, weigh	Organic CPM.
7. Pseudo-particulate Sulfate Correction	Residue from water impinger fraction	Determined by ion chromatography	Inorganic condensable H_2SO_4

5.2.5 Results and Discussion – Phase II EPRI Tests 13-15 and 25-27

The goal of this set of tests was to measure the ability of each method to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at relatively high and low concentrations. These tests would help determine if the low-temperature filter method could be used to correct OTM 28 for SO_4 formed as an artifact.

Results of OTM 28 and low-temperature filter method are based on the actual run conditions and concentrations shown in Table 5-8. Target gas concentrations in the experimental design matrix were calculated based on the final gas mixture including water vapor introduced into the gas sampling manifold. The actual SO_3 gas concentration was corrected using the initial SO_3 reactor generator performance measured by FTIR and the amount of SO_2 measured in the reactor stream.

Table 5-8. Experimental Test Matrix for Comparison of the Dry Impinger Method and the Low-Temperature Filter Method

Phase II EPRI Test	Methods *	SO_2 (ppmv)	NH_3 (ppmv)	CO_2 (%)	O_2 (%)	H_2O (%)	Nitrogen Oxide Mix (ppmv)	SO_3/ Sulfuric Acid (ppmv)	Inlet Gas Temperature, (°F)
13	B, D	148	0	12	9	8	55	1.8	335
14	B, D	148	0	12	9	9	55	1.8	332
15	B, D	148	0	12	9	10	55	1.8	332
25	B, D	0	0	12	8	8	56	1.8	369
26	B, D	0	0	12	8	9	56	1.8	369
27	B, D	0	0	12	9	9	56	1.8	342

* Methods: B = OTM 28
D = EPRI Low-temperature Filter Modification to M-202

Tests 13-15 and 25-27 involved challenging the sampling trains with approximately 2 ppmv SO_3/sulfuric acid to measure the ability of each method to quantitatively capture and measure flue gas SO_3/sulfuric acid concentrations at a relatively low concentration. Tests 25-27 duplicated the flue gas conditions of Tests 13-15, without SO_2 added to the gas mixture.

These tests compared the performance of the low-temperature filter method and OTM 28. Specifically, these tests were intended to verify the adequacy of capture of sulfate by each of these CPM measurement techniques. The goal of this comparison was to determine if SO_2 interfered with either sampling procedure and if the low-temperature filter method was a viable option for correcting SO_2 artifact formation in wet or dry impinger sampling systems.

The reactor and gas mixing manifold were assessed prior to this set of test runs using the controlled condensate method. Results from the controlled condensate test showed the reactor was delivering approximately 50 percent of the expected sulfuric acid to the gas mixing manifold. This lower recovery of sulfuric acid indicated the beginning of a catalyst bed failure to completely convert SO_2 to SO_3. Tests were conducted at the 2 ppm spiking concentration under the assumption that the conversion efficiency would be constant for the first six test matrix elements.

Generation of SO_3 was evaluated at the end of the low sulfate spiking series before moving on to the higher SO_3 (10 ppm) series. Recovery of sulfate was erratic between tests as shown by the percent recovery of sulfate for each train. The erratic recovery indicated the SO_2 reactor was beginning to fail. The test series at 10 ppm sulfate challenge concentrations were not performed due to poor conversion efficiency of the reactor.

Results from total mass recovery from the OTM 28 train are shown in Table 5-9. Results from the sulfate recovery from the low-temperature filter addition to the OTM 28 sampling train are shown in Table 5-10. Results are also shown in bar chart form in Figure 5-5. Condensable particulate and sulfate analyses of the organic extract of train samples were all nondetectable or contained insignificant mass and are not reported in these tables.

Table 5-9. OTM 28 CPM Results

Phase II EPRI Test	SO_2 (ppm)	Theoretical SO_4 max (mg/dscm)	Actual H_2O (%)	Aqueous Impinger mass (mg/dscm)	Ambient Filter Sulfate (mg/dscm)	Total* (mg/dscm)
13	148	6.9	9.4	1.96	0.44	2.40
14	148	6.9	8.9	0.50	0.47	1.49
15	148	6.9	10	5.49	0.72	6.21
25	0	6.9	8.4	4.89	0.11	5.00
26	0	6.9	8.9	1.75	0.37	2.12
27	0	6.9	8.7	2.61	0.14	2.75

Table 5-10. EPRI Low-Temperature Filter CPM Results

Phase II EPRI Test	SO_2 (ppm)	Theoretical SO_4 max (mg/dscm)	Actual H_2O (%)	160 °F Filter mass (mg/dscm)	Aqueous Impinger Sulfate (mg/dscm)	Ambient Filter Sulfate (mg/dscm)	Total* (mg/dscm)
13	148	6.9	8.4	1.90	2.10	0.35	4.35
14	148	6.9	8.9	2.73	3.54	0.25	6.53
15	148	6.9	9.0	1.18	4.65	0.22	6.05
25	0	6.9	8.4	1.85	5.32	0.12	7.29
26	0	6.9	8.9	1.59	2.32	0.37	4.28
27	0	6.9	8.7	1.27	3.43	0.15	4.85

Results for total mass of CPM recovered from each train in a test matrix run were determined by adding the gravimetric results from the aqueous impinger samples to the sulfate mass measured in the CPM filter extract. These results contain sulfate and any interference or blank contamination present in samples recovered from the respective sampling train. Results for total CPM mass determined in this manner are higher than the mass of the sulfate alone that was recovered from the sampling trains.

The mass recovered from each train was compared to the total sulfate mass theoretically captured by each sampling train. The mass recover as a percent of the amount spiked is reported in Table 5-11.

Table 5-11. OTM 28 Train vs. LTF Train CPM Recovery

Phase II EPRI Test	OTM 28 Total Mass Recovery (%)	LTF + OTM 28 Total Mass Recovery (%)
13	35	63
14	14	95
15	90	88
25	72	106
26	31	62
27	40	70

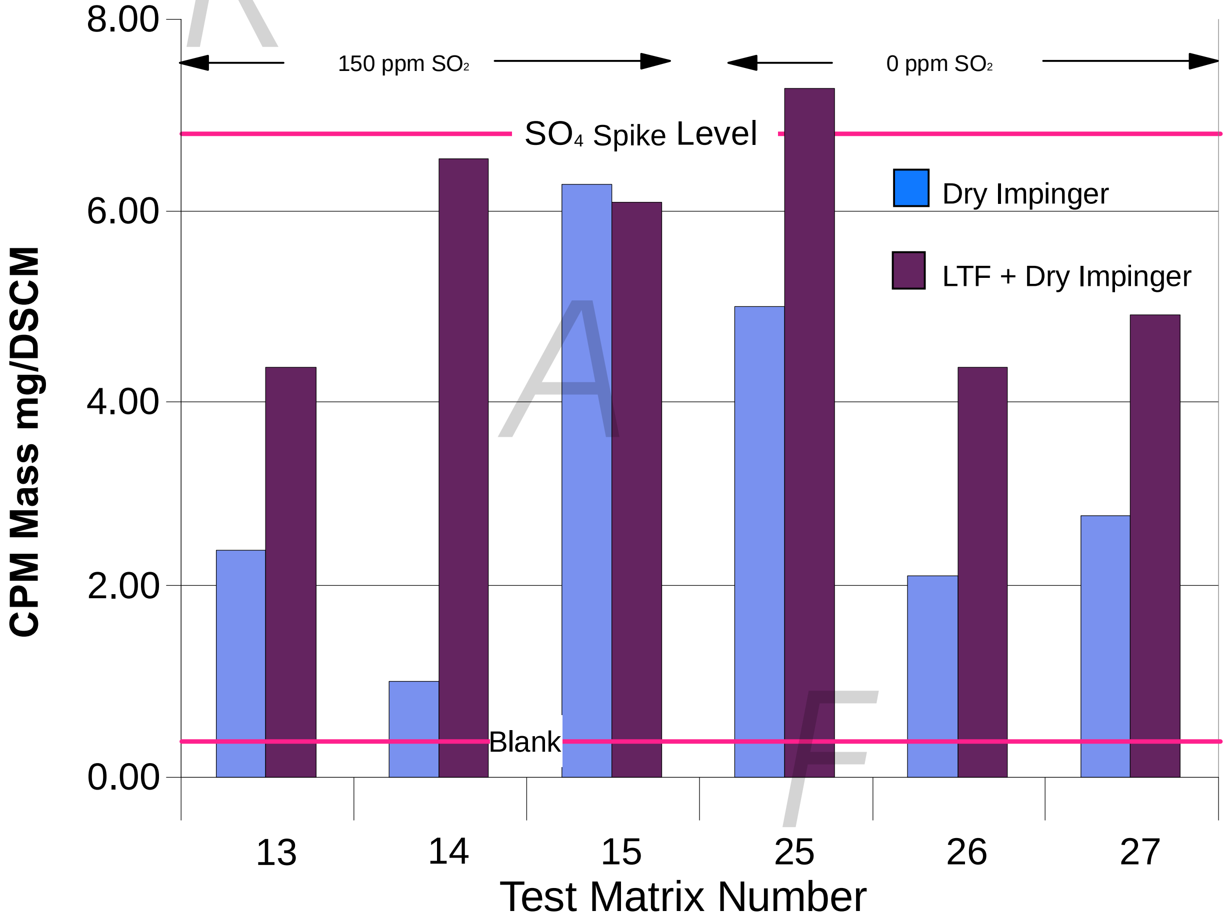

Figure 5-5. OTM 28 vs. EPRI Low-Temperature Filter Total Mass Recovery

Results for total sulfate recovered from each train in a test matrix run were determined by adding the IC analysis results for the filter(s), and inorganic train fraction results from the aqueous impinger samples. Results were corrected for sample recovery volume and converted to mg/dscm for each sampling train run. These results contain sulfate without interference or blank contamination present in samples recovered from the respective sampling train. Results for total sulfate mass determined in this manner are lower than the mass of the gravimetric mass of train samples due to the blank nonsulfate inorganic mass.

Results from total sulfate mass recovered from OTM 28 are shown in Table 5-12. Results from the sulfate recovered from the low-temperature filter addition to OTM 28 are shown in Table 5-13. Results are also shown in bar chart form in Figure 5-6. Sulfate analyses of the organic extract of train samples were all nondetectable and are not reported in these tables.

The sulfate mass recovered from each train was compared to the total sulfate mass theoretically possible from sampling the spiked manifold gas. The sulfate mass recovery as a percent of the amount spiked is reported in Table 5-14.

Results showed that the 160 °F filter does not capture all of the SO_3. Some sulfate, in the form of sulfuric acid mist passes through the 160 °F and is found in both the impinger water and the CPM filter. Recovery of mass was always higher for the low-temperature filter train samples. Sulfate mass recovered by either train was always less than the theoretical maximum sulfate mass.

Table 5-12. OTM 28 Sulfate Results

Phase II EPRI Test	SO_2 (ppm)	Theoretical SO_4 max (mg/dscm)	Actual H_2O (%)	Aqueous Impinger mass (mg/dscm)	Ambient Filter Sulfate (mg/dscm)	Total* (mg/dscm)
13	148	6.9	9.4	0.36	0.44	0.80
14	148	6.9	8.9	0.47	0.47	0.97
15	148	6.9	10	3.84	0.72	4.56
25	0	6.9	8.4	2.56	0.11	2.67
26	0	6.9	8.9	0.87	0.37	1.23
27	0	6.9	8.7	0.49	0.14	1.56

Table 5-13. EPRI Low-Temperature Filter Sulfate Results

Phase II EPRI Test	SO_2 (ppm)	Theoretical SO_4 max (mg/dscm)	Actual H_2O (%)	160 °F Filter mass (mg/dscm)	Aqueous Impinger Sulfate (mg/dscm)	Ambient Filter Sulfate (mg/dscm)	Total* (mg/dscm)
13	148	6.9	8.4	0.66	0.45	0.35	1.46
14	148	6.9	8.9	2.96	2.34	0.25	5.55
15	148	6.9	9.0	0.91	3.85	0.22	4.98
25	0	6.9	8.4	1.14	1.43	0.12	2.69
26	0	6.9	8.9	1.14	0.41	0.37	1.92
27	0	6.9	8.7	0.89	0.52	0.15	1.56

Table 5-14. OTM 28 Train vs. LTF Train Sulfuric Acid Recovery

Phase II EPRI Test	Dry Impinger Sulfate Recovery (%)	LTF Sulfate Recovery (%)
13	12%	21%
14	14%	80%
15	66%	72%
25	39%	39%
26	18%	28%
27	9%	23%

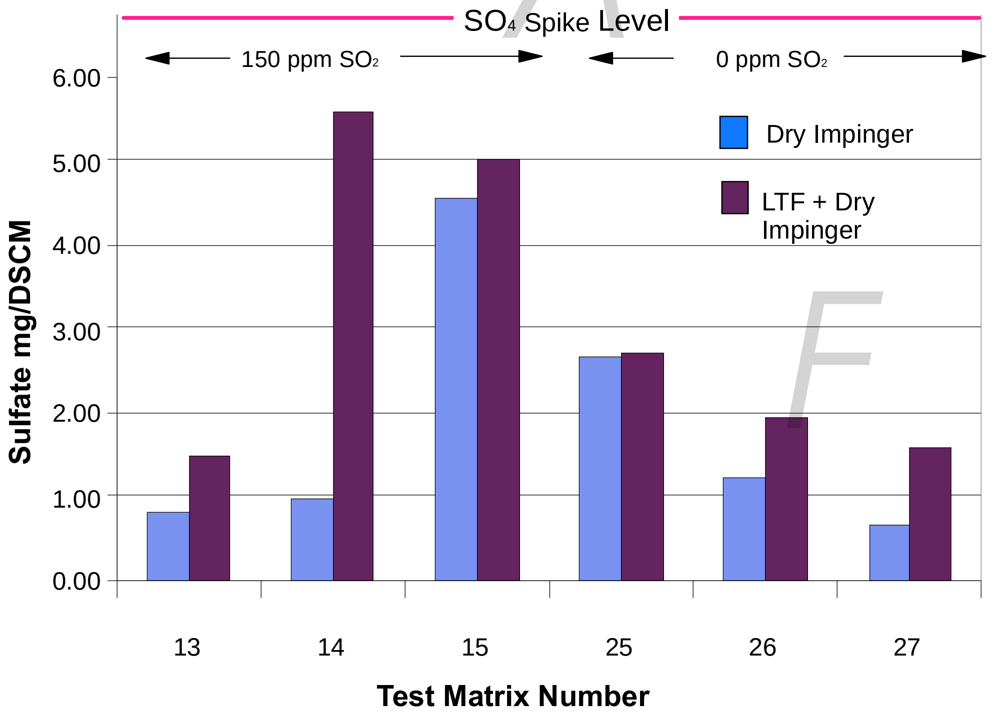

Figure 5-6. OTM 28 vs. EPRI Low-Temperature Filter Sulfate Mass Recovery

One reason for comparing the performance of the low-temperature filter addition to OTM 28 was to validate the ability of the 160 °F filter to collect the sulfate in the flue gas sample. Figure 5-7 compares the mass collected in each of the low-temperature filter sampling train fractions (i.e., 160 °F filter, aqueous impinger, final CPM filter). The 160 °F filter does not capture all of the SO_3. Some sulfate, in the form of sulfuric acid mist, passes through the 160 °F filter and is found in both the impinger water and the CPM filter.

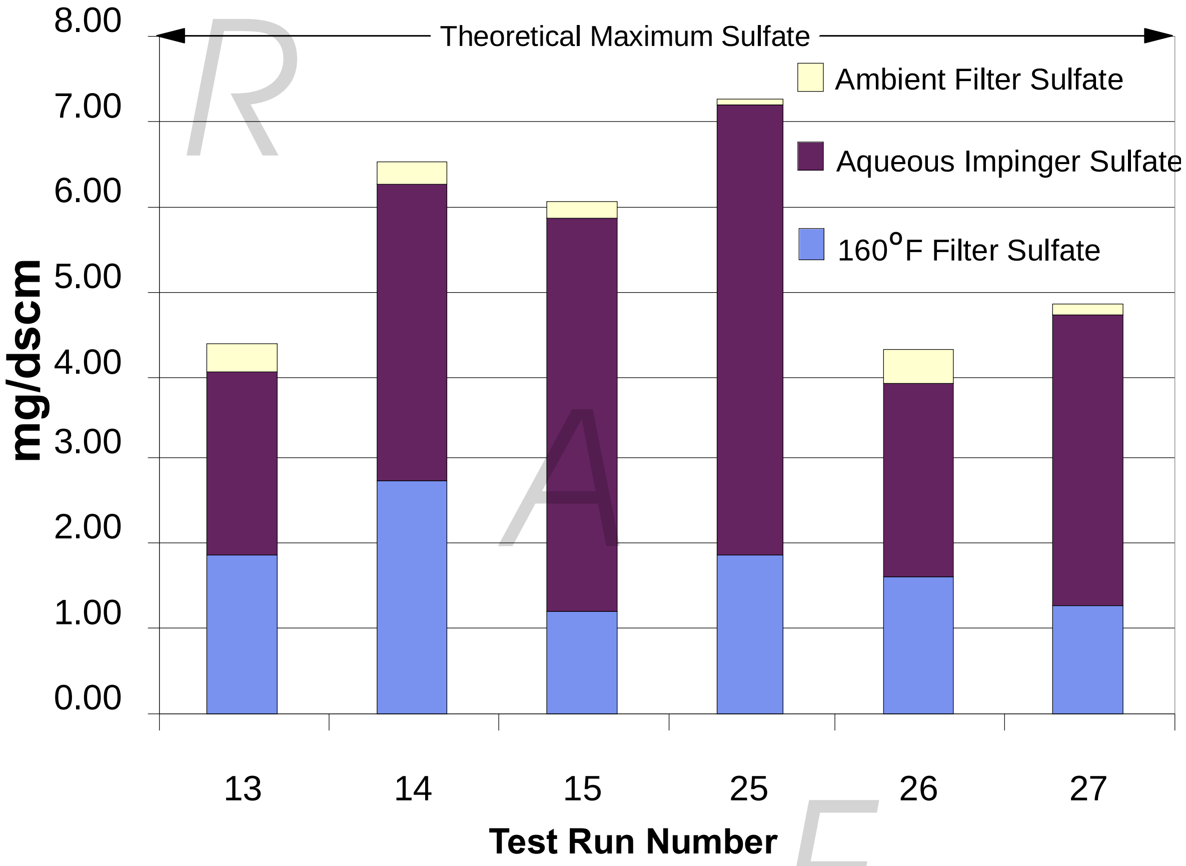

Figure 5-7. Low-Temperature Sampling Train Results by Fraction

6.0 QUALITY ASSURANCE

This section describes the achievement of overall data quality objectives (DQOs) of experiments to evaluate methods to sample and analyze condensable particulate matter (CPM). The quality assurance/quality control (QA/QC) procedures described in this section apply to the full scale sampling train experiments completed by ERG and EPRI.

All Phase I and II laboratory tests followed the "Laboratory Test Plan and Quality Assurance Project Plan (QAPP) for Method 202 Assessment & Evaluation for Bias and Other Uses" (ERG, 2006) and "EPRI Supplement to EPA Laboratory Test Plan and Quality Assurance Project Plan for Method 202 Assessment and Evaluation for Bias and Other Uses" (EPRI, 2007). The documents are included as Appendices A and D of this report. ERG also followed the QA procedures specified in methods used to analyze samples from these tests. ERG documented findings that were outside the expected norms for each method.

All QA/QC procedures were performed and were satisfactory. Results of QA/QC procedures are discussed in this section.

The primary goal of these experiments was to evaluate modifications to EPA Method 202 and supplementary methods that are expected to reduce the formation of CPM artifacts resulting from sulfur dioxide (SO_2) in the stack gas. Several sets of tests were completed at various stack gas compositions. EPA made several modifications to the Method 202 sampling train and analytical procedures that led to Other Test Method 28 (OTM 28), which EPA posted on its Web site (www.epa.gov/ttn/emc/prelim.html) (also see Appendix C).

The following sets of tests were completed:

> Phase I ERG Tests 1-8 simulated stack gas train experiments to evaluate modifications to EPA Method 202 using full scale sampling equipment to better characterize the precision and bias of CPM measurements.
>
> Phase I EPRI Tests 1-12 compared the best practice EPA reference Method 202 to OTM 28. Three sampling runs were performed for each test condition to establish an initial comparison of Method 202 and OTM 28 at conditions closer to the stack gas composition that would be encountered at coal-fired combustion units. The two methods were operated simultaneously at each of the simulated stack gas conditions to generate 12 paired test runs. Results of EPRI Phase I Tests 1-12 combined with results from ERG Phase I Replicate Tests 1-8 present a data set useful to draw conclusions about the behavior of the dry impinger sampling method. Quality Control in EPRI Phase I included triplicate field train blanks.

Phase II EPRI Tests 19-24 and 31-36 challenged the controlled condensate method and OTM 28 with known concentrations of a condensable inorganic particulate material (sulfuric acid). The controlled condensate method served as both a referee method and as a potential approach for correction of artifacts formed if the OTM 28 train formed unacceptable artifact mass at the more extreme stack gas compositions in these tests.

Phase II EPRI Tests 13-15 and 25-27 also challenged two methods (low-temperature filter method and OTM 28) with known concentrations of sulfuric acid. The tests evaluated the addition of a lower temperature filter (~160 °F) to the dry impinger train as a means to eliminate the SO_2 artifact bias by trapping the sulfuric acid before the stack gas moisture was condensed. If such an approach were successful, then the sulfuric acid found in OTM 28 could be designated as an artifact that would not be included in the CPM for the sample. For this approach to be valid, 100 percent of the sulfuric acid from the synthetic flue gas must be captured on the low temperature filter.

The targets for the measurement quality objectives (MQOs) originate in Method 202. ERG evaluated the performance of the modified CPM method (OTM 28) using EPA's general requirements for method performance found in EPA Method 301. Since these tests focus on reducing artifacts to zero residual weight, the mass recovered from samples in these tests was recorded to the nearest 0.00001 ±0.00005 grams (g) requiring a balance capable of measuring 0.00001 g.

Special weighing procedures were put into place that required balance quality checks with weights approximately equal to the sample residue pan weights and checks requiring addition of 1.0 mg weights to confirm that the balance could accurately detect sample weights anticipated in this set of tests.

6.1 Sampler Operation QC

6.1.1 General QC

Standard quality control measures used during this series of tests include:

- Method 202, dry impinger, and the low-temperature filter trains, sampling probes were maintained at a temperature of 320°F ±25°F.
- Ice was added to the front impinger box as necessary to maintain the correct method temperature (<30°C (85°F)) for dry impinger trains, 68°F for Method 202 trains).
- Dry impinger method final "cold" filter temperature was monitored and recorded in 10 minute intervals and maintained at or below 30°C (85°F).
- Moisture collection and silica gel impinger gas temperatures were maintained below 20°C (68°F).
- Final meter readings were recorded.

- Final leak checks of sampling trains were completed at maximum vacuum experienced during the test. All trains passed final leak checks.
- Data sheets were checked for completeness and typographical errors. Impinger bucket identification was verified on the data sheets. Abnormal conditions were noted in the field log notebook.

6.1.2 Sampling Train Recovery QC

Standard quality control measures for sampling train recovery were used during this series of tests:

- Disassembled trains and cap sections.
- Confirmed data sheets are completely filled out, legible.
- For dry impinger modification trains, replaced the first impinger insert with a modified Greenburg-Smith impinger.
- Performed nitrogen purge of impinger catch for one (1) hour at or above sample collection flow rate.
- Completed purge data sheets. Ensured sheets were completely filled out and were legible.

6.1.3 Sample Recovery QC

New Certified I-Chem bottles were used to recover and store samples prior to preparation and analysis. Final impinger weights were determined and recorded. Train samples were recovered immediately after sample collection and train purge completion. The train rinse samples were then collected in the following fractions:

- Filter recovered and stored in a clean petri dish.
- Impinger solutions were weighed and processed according to Method 202 or dry impinger method requirements.
- Silica impinger and contents were weighed and recycled.
- Moisture collected by each train was calculated and compared, moisture agreed within 2 percent for all tests.

6.2 Laboratory QC

Specific QC measures performed during laboratory evaluation of sampling train performance are described below. Because the results of this investigation focused on low-level weight and sulfate concentration gains, the QC measures included field blanks, frequent balance calibration checks, and QC for sulfate analyses by ion chromatography (IC). These QC measures are outlined below in Table 6-1 for the recovery/analytical effort.

EPRI stakeholder contributions included additional QC for mass from analytical balance measurements. Mass measurements were checked in a way to evaluate small mass increases above the base weigh of the aluminum weighing pans used in this study. Mass was recorded for a 10 g weight and the subsequent addition of small (i.e., 1 and 5 mg) Class S weights to the 10 g weight. This additional QC step and the acceptance criteria for the control are described in Table 6-1.

Table 6-1. Laboratory Test QC Activities

Parameter	QC Check	Frequency	Acceptance Criteria	Corrective Action
Particulate Mass Gain	Balance Calibration Check	Each Day Used	Within ±0.1% of true value	Remove balance from service until repaired
	EPRI Additional Mass Increase Check: For typical sample pan weights, check reading with increase of 1 mg and 5 mg.	Each Day Used	1 mg addition must be within ±0.1 mg 5 mg addition must be within ±0.3 mg	Remove balance from service until repaired
Sulfate by Ion Chromatography	Calibration Curve – Five Point	Each Day Used	Correlation Coefficient of 0.999 or greater	Recalibrate, if necessary repair instrument and recalibrate
	Analyze second source standard	Initially, and after every ten samples	90-110% recovery	Reanalyze any samples not bracketed by acceptable second source standards
	Duplicate analysis	Every 10th sample	10% RPD	1. Reanalyze sample and duplicate 2. Reanalyze batch of 10 3. Recalibrate and reanalyze all samples from the day
	Matrix Spike and Matrix Spike Duplicate (MS/MSD)	Every 10 samples	85-115% recovery 15% RPD	1. Reanalyze MS and MSD 2. Dilute all samples of a similar concentration, re-prepare MS/MSD, analyze diluted samples 3. Flag data

RPD = relative percent difference

Table 6-2 describes additional reagent and sampling train QC requested by stakeholder EPRI for full scale train tests in their portion of the study.

Table 6-2. Reagent and Field Train Blank QC Samples

QC Check	Frequency	Action
Reagent Blanks	Three for every lot of reagent or solvent	Hold portion for possible investigation of contamination issues
Field (Laboratory) Blank Trains	Recover one blank train for every five sampling trains run or three train blanks per similar experimental matrix test sequence. Blanks should include all steps for the accompanying test, including recovery of the appropriate sampling glassware and/or filter, sample preparation, and analysis. Alternate blank collection times (some morning runs and some afternoon runs)	Analyze these trains with the measurement run samples. Compare magnitude of blank values to measured values*

*Report all blank values greater than 10 percent of measured values in data tables

6.2.1 Blank(s)

6.2.1.1 Reagent Blanks

Aliquots of each lot of solvent were collected for analysis as reagent blanks. Aliquots were prepared and analyzed in the same manner as the test samples. Results of reagent blanks are shown in Table 6-3 and 6-4. Reagent blanks were an insignificant contribution to samples or field train blanks.

Table 6-3. Reagent Blanks Results from EPA Studies

Reagent Blank	Mass in 100 mL (mg)	Sulfate Mass by in 100 mL (mg)
EPA Tests 1-8 Dry Impinger – M-202 Comparison		
Acetone	N/A	N/A
Methylene Chloride	-0.05	N/A
Water	10.6	0
Water (Duplicate)	8.24	N/A
Aluminum Pan	Dry-0.25	NA
EPA Tests 1-8 – Eight Replicate MDL Tests		
Acetone	N/A	N/A
Methylene Chloride	-0.06	N/A
Water	0.21	0

Table 6-4. Reagent Blanks Results from EPRI Additional Studies

Reagent Blank	Mass of 100 mL (mg)
EPRI Tests 1-12 Dry Impinger – M-202 Comparison	
Acetone	-0.99
Methylene Chloride	-0.16
Water	0.24
EPRI Tests 19-24 and 31-36 Dry Impinger – Controlled Condensate Comparison	
Acetone	0.34
Methylene Chloride	0.25
Water	0.30
EPRI Tests 13-15 and 25-27 Low Temperature Filter – Dry Impinger Comparison	
Acetone	0.11
Methylene Chloride	1.43
Water	0.07

6.2.1.2 Train Blanks

During the train sample collection phase of the study at several sets of train blanks were prepared. Field train blank samples were composed of samples recovered from a sampling train fully assembled as it was used for test samples. Each train was leak checked. The sampling trains were recovered in the same manner as their respective test train samples. Table 6-5 shows results of field train blanks for EPA tests.

Table 6-5. Field Train Blank Results for EPA Tests

Train Blank No.	Method	Organic (mg)	Inorganic (mg)	Filter (mg)	Total (mg)	Total Equivalent (mg/DSCM)**
EPA Tests 1-12						
TB1	Dry Impinger				10.7	10.7
TB1	M-202				19.5	19.5
EPA Replicate MDL Tests*						
TB1	Dry Impinger	-0.11	0.46	-0.34	0.46*	0.46
TB2	Dry Impinger	0.14	1.02	-0.55	1.16	1.16
TB3	Dry Impinger	-0.075	0.53	-0.85	0.53	0.53

* Negative numbers not included in field train blank total

** Assumes 1.0 DSCM total volume

6.2.1.3 Train Blanks Specific to EPRI Tests

Triplicate field train blanks samples were collected for EPRI Tests 1-12. Table 6-6 shows the field train blanks for EPRI Tests 1-12.

Table 6-6. Field Train Blank Results for EPRI Tests 1-12

Train Blank No.	Method	Organic (mg)	Inorganic (mg)	Filter (mg)	Total (mg)	Total Equivalent (mg/DSCM)*
TB1	Dry Impinger	0.13	4.23	0.0	4.36	2.3
TB2	Dry Impinger	0.74	4.73	0.0	5.74	2.9
TB3	Dry Impinger	0.97	2.21	0.0	3.18	1.7
Average	Dry Impinger	0.61	3.72	0.0	4.33	2.3
TB1	M-202	0.19	4.5	0.0	4.69	2.4
TB2	M-202	0.0	5.03	0.0	5.03	2.6
TB3	M-202	6.44	0.82	0.0	7.26	3.7
Average	M-202	3.32	3.45	0.0	5.66	2.9

* Assumes 2.0 DSCM total volume

The uncertainty at 98 percent confidence in the average recovery of the dry impinger train suggest results from the low level SO_2 spiking tests are at or near the detection limit of the method.

All the sample results for reference Method 202 were significantly higher than blank results of 2.9 mg/DSCM.

6.2.1.4 Train Blanks for EPRI Tests 19-24 and 31-36

Duplicate sample dry impinger train blanks were prepared for EPRI Tests 19-24, 31-36. Results of the Phase 2 field train blanks are shown in Table 6-7. Dry impinger train blanks were consistent with the results found during the comparison of the dry impinger method to Method 202.

Table 6-7. Field Train Blanks for EPRI Tests 19-24 and 31-36

Train Blank No.	Method	Organic (mg)	Inorganic (mg)	Filter (mg)	Total (mg)	Total Equivalent (mg/DSCM)
TB4	Dry Impinger	1.3	3.4	0.0	4.7	3.4
TB5	Dry Impinger	0.38	2.8	0.0	3.1	2.8
Average	Dry Impinger	0.84	3.1	0.0	3.9	3.1

6.2.1.5 Train Blanks for EPRI Tests 13-15 and 25-27

Duplicate sample dry impinger and low temperature filter train blanks were prepared for EPRI Tests 13-15 and 25-27. Gravimetric measurements were made for the organic and inorganic fractions from these field blank trains. Results of the Phase 2 field train gravimetric blanks are shown in Table 6-8. Sulfate analysis was run on the field train blank aqueous extract samples IC was used to screen field train blanks for traces of sulfate. The results of the sulfate blank for EPRI Tests 19-24 and 31-36 are shown in Table 6-9.

Table 6-8. Field Train Blanks for EPRI Tests 19-24 and 31-36

Train Blank No.	Method	Organic (mg)	Inorganic (mg)
TB6	Dry Impinger	0.95	ND
TB7	Dry Impinger	0.43	2.32
Average	Dry Impinger	0.69	1.16
TB6	LTF-Dry Impinger	0.59	ND
TB7	LTF-Dry Impinger	0.30	0.0
Average	LTF-Dry Impinger	0.45	0.0

Table 6-9. Field Train Sulfate Blanks for EPRI Tests 19-24 and 31-36

Train Blank No.	Method	Low Temperature Filter (mg)	Inorganic (mg)	Filter (mg)	Total (mg)
TB6	Dry Impinger	N/A	0.14	0.18	0.32
TB7	Dry Impinger	N/A	0.0	0.26	0.26
Average	Dry Impinger	N/A	.07	0.18	0.43
TB6	LTF-Dry Impinger	0.18	0.32	0.20	0.7
TB7	LTF-Dry Impinger	0.52	0.0	0.51	1.0
Average	LTF-Dry Impinger	0.35	0.16	0.36	0.87

7.0 REFERENCES

Battelle, 2005. Laboratory Evaluation of Method 202 to Determine Fate of SO_2 in Impinger Water. Prepared by Battelle for EPA, Contract No. 68-D-02-061, Work Assignment 3-14.

Cheney, 1978. Cheney, J. and J. Homolya. Characterization of Combustion Source Sulfate Emissions with a Selective Condensation Sampling System" in Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, Vol. 1, Measurements Technology, EPA 600/9-78-020a. NTIS PB287-436. 1978.

Dewees, et al, 1989. Laboratory and Field Evaluation of the EPA Method 5 Impinger Catch for Measuring Condensible Matter from Stationary Sources. Proceedings of the 1989 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Publication VIP-13. EPA Report No. 60019-89-0601. Air & Waste Management Association, Pittsburgh, PA.

EPRI, 2007. EPRI Supplement to EPA Laboratory Test Plan and Quality Assurance Project Plan Method 202 Assessment and Evaluation for Bias and other Uses. Prepared by URS Corporation for EPRI. February 2007.

ERG, date. Personal communication between Ray Merrill (Eastern Research Group) and George Marson (Environment Canada). Date.

ERG, 2006. U.S. EPA. Laboratory Test Plan and Quality Assurance Project Plan For Method 202 Assessment & Evaluation for Bias and Other Uses. Prepared by Eastern Research Group, Inc. for U.S. EPA under Contract 68-D-02-079. 2006.

Richards, et al, 2005. Richards, J.; Holder, T.; Goshaw, D.; Optimized Method 202 Sampling Train to Minimize the Biases Associated with Method 202 Measurement of Condensible Particulate Matter Emissions, Air & Waste Management Association Hazardous Waste Combustion Specialty Conference, St. Louis, Missouri, November 2-3, 2005.

U.S. EPA, 1988. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Source Specific Methods Section 3.16 EPA/600/4-77/027b. 1988.

Appendix A

Laboratory Test Plan and Quality Assurance Project Plan For Method 202 Assessment and Evaluation for Bias and Other Uses

ERG No.: 0173.03.006.002
EPA No.: 68-D-02-079

Laboratory Test Plan and Quality Assurance Project Plan for Method 202 Assessment & Evaluation for Bias and Other Uses

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November 02, 2006

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Appendix Template

Section 1.0
Problem Background/Project Description

Problem Background

Emission Inventories for the National Emissions Inventory (NEI), State Implementation Plans (SIPs), and the Consolidated Emissions Reporting Rule (CERR) require the reporting of primary PM emissions, including both the filterable and condensible components. The NEI, the SIP emissions inventories, and the periodic emissions inventories required under the CERR measurements must contain accurate data for government agencies to effectively manage ambient air quality. These emission inventories are based on a combination of emission factors and site-specific test results, when test results are available. Site-specific test results provide a direct measurement of emissions and are conducted primarily to demonstrate compliance with an existing emission limitation. Emission factors are based on the averages of several site-specific tests. Thus, both emission factor development and emissions inventory reporting depend on site-specific tests. Results of site-specific compliance tests must be unbiased and have known uncertainty.

The test method used to quantify condensible PM emissions is EPA Method 202, *Determination of Condensible Particulate Emissions from Stationary Sources*, as published in Appendix M of 40 CFR part 51. Method 202 is a set of procedures performed on the water placed in and collected by chilled impingers used in standard stationary source sampling trains for PM (e.g., Method 5, Method 17). Method 202, as promulgated in 1991, includes a recommendation to bubble nitrogen through the water contained in these chilled impingers to purge SO_2 from the water. Since the promulgation of Method 202 in 1991, air emission testing experience has shown that it is inappropriate to use water-filled impingers to cool the sample gas stream for condensible particulate matter (CPM) combustion sources having sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and/or soluble organic compound emissions.[1] These gaseous contaminants can be partially absorbed in the impinger solutions and chemically oxidize to form material counted as CPM in Method 202. These "artifact" reaction products are not related to the primary emission of CPM from the source. The potentially significant problems affecting Method 202 accuracy include the following:

1. Dissolved sulfur dioxide and nitrogen oxides in water with subsequent oxidation to form sulfates and nitrates in the impingers;
2. Dissolved semivolatile organic compounds into water;
3. Penetration of submicrometer-sized condensed particles through the impingers of the Method 202 sampling train; and
4. Gas-phase homogeneous reactions between ammonia and hydrogen chloride and/or between ammonia and sulfur dioxide in the cold, water-filled impingers.

The SO_2 absorbed in the impinger water has been reported as one of the major causes of artifacts. The SO_2 slowly converts to $SO_{3,}$ forming sulfurous acid in the water.

$$SO_2\ (g) > SO_2\ (aq)$$

$$SO_2\ (aq) + H_2O > H_2SO_3 > HSO_3^{G} + H^{+}$$

Further oxidation, addition of water, and consumption of excess H^+ allows formation of sulfuric acid or sulfate salts. This sulfuric acid is an inorganic particulate artifact that does not form immediately after the release of the stack gases to the ambient air. This artifact formed in the Method 202 impingers translates into a bias in the inorganic condensible PM emissions reported in the compliance test reports. In some tests, SO_2 related material was shown to be the major source of reportable condensible particulate. When used to develop emissions factors, these biases result

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[1] Optimized Method 202 Sampling Train to Minimize the Biases Associated with Method 202 Measurement of Condensible Particulate Matter Emissions, John Richards, Tom Holder, and David Goshaw, Air Control Techniques, P.C., Cary, North Carolina.

in biases in the emissions factors. The use of biased emissions factors in turn produce biased national, regional, and facility-specific PM emissions inventories reported in the NEI, SIPs, and periodic reports required by the CERR.

In a laboratory study during FY05 by Battelle[2], it was determined that without the nitrogen purge, the mass of particulate artifact formed was about 400 to 500 milligrams per liter (mg/L) of water when gas with 300 parts per million (ppm) of SO_2 was bubbled through the water. At lower concentrations of SO_2 and extended sampling times, only 150 to 200 mg/L of artifact formed. Because conversion of SO_2 to SO_3 begins when sampling starts and the nitrogen purge does not start until the sampling is completed, some artifact remains. Several studies have characterized the efficiency of the nitrogen purge and document that this purge is between 90 and 95 percent effective. The Battelle study also indicated that the nitrogen purge was between 90 and 95 percent effective. At least one recent study has proposed modifications to Method 202 glassware and procedures reducing further the formation of inorganic particulate artifact[1].

On November 1, 2005 (70 FR 65984), EPA proposed a rule establishing minimum requirements for the preparation, adoption, and submittal of acceptable SIPs for fine PM. The preamble to the proposed rule discussed requirements for emissions inventories, source test methods, and emissions reporting of primary PM emissions. These discussions identified the need to report both the filterable and the condensible fraction of PM emissions. Numerous public comments described problems with Method 202 in measuring the condensible fraction of PM emissions. The comments highlighted imprecision and biases in the condensible test method both with and without nitrogen purge. Lastly, some commenters suggested that biases and variability of the method were due to the presence of ammonia in the emissions gas. These commenters recommended subtracting the ammonium collected in the test method to eliminate the bias.

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[2] EPA Contract No. 68-D-02-061, Work Assignment 3-14.

Project Description

In this work assignment, ERG will confirm that Method 202 performance operated under the “best” EPA recommended conditions generates SO_2 related CPM artifacts. ERG will also evaluate a dry impinger modification to Method 202 sampling trains. The objective of this work assignment is to perform a laboratory assessment of modification(s) to Method 202 that will reduce artifact reaction products that are not related to the primary emission of CPM from the source. Laboratory tests are planned to determine method precision and bias of the modified EPA Method 202 train with the compounds of interest.

In addition to ERG’s evaluation of the dry impinger modification, stakeholders will complete additional evaluations of modifications to Method 202. This Quality Assurance Project Plan (QAPP)/Test Plan describes the approach and quality control procedures that will be used to evaluate modifications to Method 202 conducted by both ERG and stakeholders.

Stakeholders will follow the approach and quality control procedures of this QAPP/Test plan. In addition, stakeholders will identify point of contact, provide the equivalent of Section 4, “Laboratory Spiking Equipment and Sampling Procedure,” and Section 6, “Analytical Procedures,” and identify any deviations from the base QAPP. Stakeholder contributions to the QAPP/Test Plan will be included as appendices. In those sections, stakeholders will describe the specific modification to Method 202, the type of source characterized or simulated, and the desired outcome (e.g., artifact reduction from sources with high moisture or sulfuric acid).

Sections 4 and 6 of this QAPP/Test plan describe the equipment and the sampling and analytical procedures of the dry impinger modification. For the dry impinger modification, an EPA Method 202 sampling train will form the basis of the sampling hardware. Sampling train modifications will be evaluated by collecting gaseous pollutants from a stack gas generation system as described in Section 4.2. The sampling trains are described in Section 4.3. Samples are recovered and analyzed according to the procedures in Method 202 described in Sections 4 and 6.

The suspect interfering gases will be spiked into the stack gas generation system under controlled laboratory conditions. The sampling manifold simulates stationary source emission components and concentrations offering a background matrix of water vapor and carbon dioxide. Sulfur dioxide, nitrogen oxides, and ammonia can be spiked at concentrations described in the experimental matrix in Section 4.1.

In Phase 1 of the evaluation a minimum of three valid sampling runs will be collected for Method 202 operated under "best conditions" as recommended by EPA. If the dry impinger modification to Method 202 shows significant reduced interference from SO_2 compared to the baseline Method 202, additional replicate tests will be conducted in Phase 2 of the project to establish the bias and precision of the method modification under laboratory test conditions.

This QAPP/test plan is divided into 14 sections. These sections follow the requirements for Quality Assurance Project Plans found in EPA's QA/R-5. This QAPP/test plan is written for a research and development project at "level 3" since procedures and quality control/quality assurance requirements for the method are being developed through this effort.

Table 1-1. Candidate Compounds for Method 202 Assessment and Evaluation Study

Interfering Target Compounds	CAS No.	Boiling Point °C
Sulfur dioxide	7446-09-05	-10°C
Ammonia	7664-41-7	33°C
Nitrogen Oxides (NO)	10102-43-9	-152°C
Stack Gas Simulants		
Carbon Dioxide	124-38-9	-78°C (sublimes)
Water Vapor	7732-18-5	100°C
Oxygen	7782-44-7	-183°C

Section 2.0
Project Organization and Responsibility

The Project Manager, Dr. Raymond G. Merrill, Jr., will have ultimate authority and accountability for implementing the program. In addition, Dr. Merrill will keep senior ERG management informed of the status and progress of the program. The project organization for the entire program to assess and evaluate Method 202 for bias and other uses is shown in Figure 2-1.

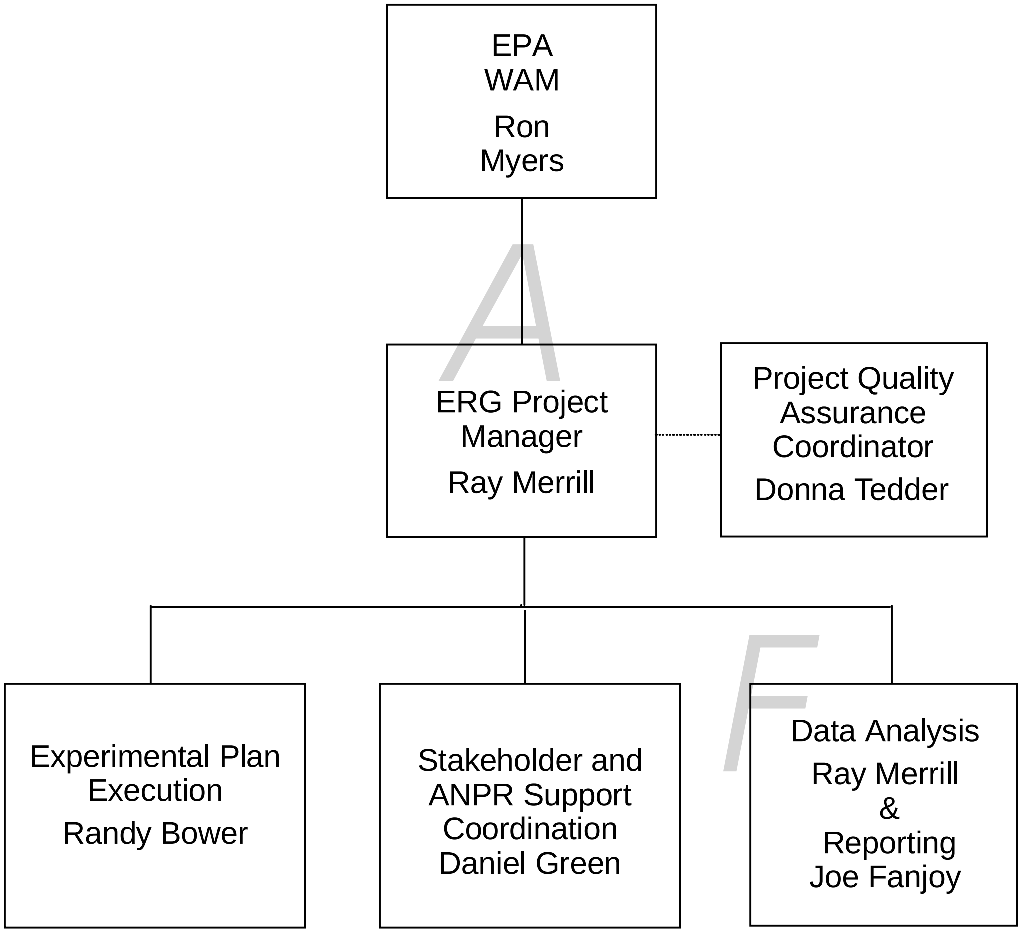

Figure 2-1. Project Organization and Responsibility

The Quality Assurance (QA) Project Coordinator, Donna Tedder, will ensure the quality of the data generated from laboratory testing and sample analysis. She is responsible for reviewing the QA Project Plan/Test Plan (QAPP/Test Plan), evaluating the internal quality control (QC) program, coordinating performance and systems audits, and documenting the results of all QA/QC activities to ensure that the QC procedures are being followed and that the data quality is correctly and adequately documented. She will ensure that QA objectives for the project are met.

The Laboratory Studies Coordinator, Randy Bower, will lead day-to-day effort of laboratory studies, supervise sample preparation and analyses, and coordinate the preparation of the project final report. Mr. Bower is also responsible conducting the laboratory spiking and sampling task. He will be assisted by Dave Dayton, Mark Owens, Mitch Howell, Thomas McKenzie, and Joe Fanjoy.

Mr. Dayton will assemble the source simulator spiking manifold and assist Mr. Bower in spiking compressed and dilution gases in the manifold.

Mr. Owens will coordinate preparation of the sampling trains. Mr. Owens will assure that the test equipment is in good working order and properly operated and will assure that tests are performed according to the procedures outlined in this combined QAPP/Test Plan. He will also note and record any conditions that may have an impact on the quality of the data.

Mr. Bower will coordinate the recovery and distribution of samples to the laboratory analysis team in the most timely manner possible, and ensure that the sample custody records are correctly documented and transferred with the samples.

Mr. Howell is responsible for ion chromatographic analysis of samples. He will coordinate the analysis review for this procedure.

Mr. McKenzie is responsible for sample residue preparation and gravimetric analysis.

The Data Analysis Task Leader, Ray Merrill, will perform the statistical analyses required to evaluate the applicability of the methods to the analyses listed in Table 4-1. Dr. Merrill will also report accurately and completely on all statistical procedures used to evaluate the data.
Mr. Fanjoy will assist Mr. Bower and Dr. Merrill in outlining and writing the final report.

In a non-laboratory/non-analytical effort, Danny Greene is responsible for coordinating activities with stakeholders, including conference calls, information gathering, and responding to public comments.

The Project Secretary, Jody Tisano, is responsible for permanent records and correspondence for the project. Ms. Tisano will prepare reports in accordance with ERG and EPA specifications.

Section 3.0
Data Quality Objectives

This section describes the overall data quality objectives (DQOs) of the work assignment and the method DQOs for the measurements made in the laboratory evaluation tests of the baseline and modified Method 202 sampling trains. The primary goal of this work assignment is to evaluate modifications to EPA Method 202 that are expected to reduce the formation of artifacts from SO_2.

3.1 Work Assignment DQO

Phase 1 of the experimental effort will provide an initial assessment of the dry impinger modifications to Method 202. Three sampling runs will be performed for each method to establish an initial comparison between Method 202 and the dry impinger modification to Method 202. The two methods will be operated simultaneously at each of the three different simulated stack gas conditions (nine baseline runs). The number of replicate sampling train runs planned during Phase 1 of this project will not be sufficient for an exhaustive statistical verification. However, if the dry impinger test runs show an improvement of 50 percent reduction of the artifact condensible particulate matter (CPM) from SO_2, then additional test runs will be performed to characterize the dry impinger modification precision and bias. A minimum of eight valid additional dry impinger modified method tests will be performed and evaluated to determine if the improvement is statistically significant.

3.2 Measurement Precision and Bias Targets

The targets for the measurement quality objectives (MQO) originate from Method 202[1] and EPA's general requirements for method performance found in EPA Method 301[2]. Since this project focuses on reducing artifacts to zero residual weight, the mass recovered from samples in these tests will be recorded to the nearest 0.00001 ±0.00005 grams (g) requiring a balance capable of measuring 0.00001 g. The need to require balance sensitivity 10 times lower than Method 202 will be assessed at the end of the experimental effort.

For the eight replicate tests, precision is determined, at the minimum, using paired test results under identical conditions. The precision of the method at the level of the standard must not be greater than 50 percent relative standard deviation. For a modified method to show equivalency, the precision of the proposed test method must be as precise as the validated method for acceptance. Bias is established by comparing the method's recovery against a reference value. Since no CPM will be added to samples in the preliminary evaluation or the eight replicate tests, bias will be determined by the amount of artifact mass measured under the assumption that the method should generate 0.000 g/scm under the test conditions in this plan.

Section 13 describes the precision, accuracy (bias), and completeness calculations that will be performed on the laboratory sampling data for both the Method 202 baseline and the dry impinger modified method evaluation.

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[1] EPA Method 202. Determination of Condensible Particulate Emissions from Stationary Sources. U. S. Environmental Protection Agency, http://www.epa.gov/ttn/emc/methods/method202.html.

[2] EPA Method 301. Method Validation Protocol. U.S. Environmental Protection Agency, http://www.epa.gov/ttn/emc/promgate.html.

Section 4.0
Laboratory Spiking Equipment and Sampling Procedures

This section describes the laboratory spiking equipment and sampling procedures that ERG will apply in the evaluation of the dry impinger modification to Method 202. Appendices to this document contain descriptions of the laboratory spiking equipment and sampling procedures that stakeholders will apply in evaluation of their respective modification to Method 202.

4.1 Experimental Design

In the laboratory test program, ERG will perform an initial comparison of the formation of artifacts in EPA Method 202 and a modification to Method 202 that cools the emission gases and collects condensible particulate matter (CPM) in "dry" impingers (dry impinger modification). Artifacts are know to be caused by SO_2 at the conditions described in this section. Initial measurements will be made under laboratory controlled conditions using simulated stack gas mixtures that approximate low level (e.g., gas-fired turbine) and elevated (e.g., coal-fired power plant) SO_2 emissions. These conditions were selected after review of regulatory limits and typical SO_2 emission concentrations from these sources. Other conditions may be evaluated by stakeholders or EPA in later phases of this program.

Replicate gas samples will be collected from an atmosphere generator to determine potential artifact formation in each method. The test will consist of at least three test runs at each condition. Each test run will consist of an independent sampling train, such that three full sets of train samples can be collected and evaluated. While the replicate samples are not sufficient to demonstrate Method 301 precision and accuracy, they will be sufficient to compare performance of the proposed Method 202 dry impinger modification to the baseline "best practice" application of Method 202. The experimental matrix with key emission gas concentrations is shown in Table 4-1.

Additional tests of the dry impinger modification will be conducted if the modification demonstrates at least 50 percent reduction in artifact formation during baseline tests. A minimum of eight additional tests that replicate conditions in Test 7 or 16 of the baseline tests (Table 4-1) will be collected to evaluate bias and precision of the dry impinger modified method. Final test conditions will be determined after evaluation of the baseline test data.

Table 4-1. Method 202 Baseline Evaluation Experimental Matrix

Test	**Method**	**Effective SO_2 (ppm)**	**Effective Ammonia (ppm)**	**Carbon Dioxide (%)**	**Oxygen (%)**	**Water (%)**	**Nitrogen oxide mix (ppm)**
1	M-202	25	0	12	8	5	50
2	M-202	25	0	12	8	5	50
3	M-202	25	0	12	8	5	50
4	M-202	150	0	12	8	5	50
5	M-202	150	0	12	8	5	50
6	M-202	150	0	12	8	5	50
7	Dry Impinger Mod	25	0	12	8	5	50
8	Dry Impinger Mod	25	0	12	8	5	50
9	Dry Impinger Mod	25	0	12	8	5	50
10	Dry Impinger Mod	150	0	12	8	5	50
11	Dry Impinger Mod	150	0	12	8	5	50
12	Dry Impinger Mod	150	0	12	8	5	50
Optional Tests							
13	M-202	25	10	12	8	5	50
14	M-202	25	10	12	8	5	50
15	M-202	25	10	12	8	5	50
16	Dry Impinger Mod	25	10	12	8	5	50
17	Dry Impinger Mod	25	10	12	8	5	50
18	Dry Impinger Mod	25	10	12	8	5	50
1A	Dry Impinger Mod	150	10	12	8	5	50
2A	Dry Impinger Mod	150	10	12	8	5	50
3A	Dry Impinger Mod	150	10	12	8	5	50

4.2 Special Equipment

Several stack gas simulants will be spiked into the stack gas simulator described in Section 4.2.1. In Phase 1 testing, the following interfering compounds will be spiked into the stack gas simulator: sulfur dioxide (SO_2), and nitrogen oxides (NO/NO_2). The affect of adding ammonia will be evaluated after the initial tests with SO_2 and NO/NO_2.

The compounds will be dynamically spiked into the stack gas simulator from certified gas cylinders. During each sampling run, these gases will be introduced into a mixing chamber of the laboratory source gas simulator through three mass flow controllers. Calibration of the mass flow controllers will be verified with a NIST-traceable Buck flow monitor. The flow rate of the spike into each mixing chamber will be sufficient to generate the concentrations listed in Table 4-1. Gases in the simulator and sampling probe temperatures will be maintained at 160 ± 5°C. This temperature is 35°C higher than EPA Method 5 requires. The elevated temperature will help minimize premature reactions between gaseous components added to the source gas simulator. Each sampling train will be connected to a heated manifold port on the laboratory source gas simulator. Sufficient flow from the combination of cylinders and humidified zero air will be generated to produce excess gas. Two sampling trains will be operated at approximately 14.5 liter/minute (L/min)(0.5 standard cubic feet per minute (scfm)) for 1 hour allowing collection of approximately 1 cubic meter of gas. Excess simulated stack gas and sample train exhaust will be vented into a standard laboratory fume hood.

4.2.1 <u>Laboratory Spiking Equipment and Dynamic Gaseous Spiking</u>

For the laboratory evaluation, sample gas stream will be collected from the stack gas simulator shown in Figure 4-1. A cross section of the manifold mixing chamber is shown in Figure 4-2. The manifold delivery system will generate synthetic stack gas at a flow rate in excess of 40 L/min (1.5 scfm). Gas will be delivered into the humidification chamber prior to the gas mixing chambers. The gas stream will be heated to ensure all components remain in the gas

Figure 4-1. Source Gas Simulator Manifold

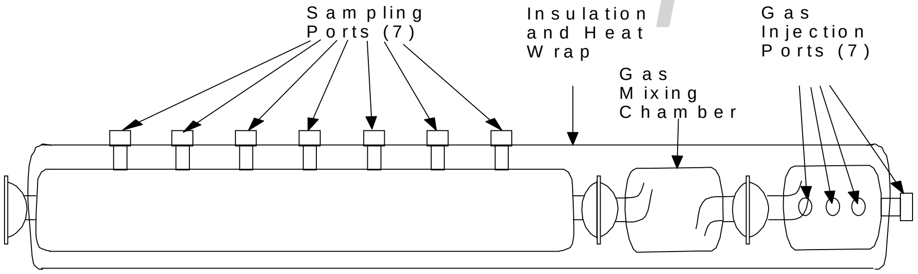


Figure 4-2. Cross Section of Simulator Manifold Mixing Chamber

phase. The Method 202 and the dry impinger modified Method 202 will collect gas from the manifold at approximately 14 L/min for approximately 1 hour. The resulting gas volume collected by each train will be approximately 1 dry standard cubic meter (dscm).

4.3 Sampling Preparation

4.3.1 Method 202 Equipment Preparation

Glassware Preparation

All glassware used for sampling will be thoroughly cleaned prior to use. This includes the probe, filter holders, impingers, all sample bottles, and all utensils used during sample recovery. All glassware will be washed with hot soapy water, rinsed with hot tap water, rinsed with distilled water, and dried. The glassware will be triple rinsed with methanol followed by triple rinsing with methylene chloride.

4.3.2 Method 202 Train Preparation

Train preparation includes assembly and leak checking meter boxes, nozzles, and umbilicals and transfer lines. For the baseline Method 202 experiments, a single Method 5/Method 202 train will be assembled following the requirements in Method 202 as shown in Figure 4-3. Reference calibration procedures will be followed when available, and the results will be properly documented and retained.

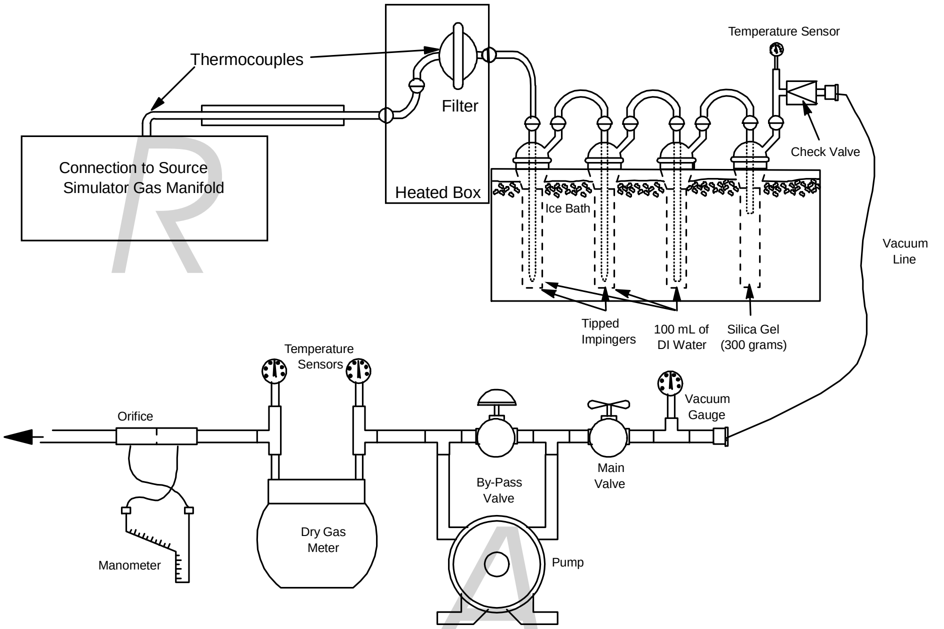


Figure 4-3. Schematic of Condensible Particulate Sampling Train (Method 202)

Dry Gas Meter Calibration

Dry gas meters (DGMs) will be used in the sample trains to measure the sample volume. All DGMs will be calibrated to document the volume correction factor. Post-test calibration checks will be performed as soon as possible after testing. Pre-and post-test calibrations should agree within 5 percent.

Prior to calibration, a positive pressure leak check of the system will be performed using the procedure outlined in Section 3.3.2 of EPA's Quality Assurance Handbook. The system will be placed under approximately 10 inches of water pressure and a gauge oil manometer will be used to determine if a pressure decrease can be detected over a one-minute period. If leaks are detected, they will be eliminated before actual calibrations are performed.

After the sampling console is assembled and leak checked, the pump will be allowed to run for 15 minutes to allow the pump and DGM to warm up. The valve is then adjusted to obtain the desired flow rate. For the pre-test calibrations, data will be collected at the orifice manometer settings ()H) of 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 in H_2O. Gas volumes of 5 ft^3 are used for the two lower orifice settings, and volumes of 10 ft^3 are used for the higher settings. The individual gas meter correction factors (($_i$) are calculated for each orifice setting and averaged. The method requires that each of the individual correction factors fall within ±2 percent of the average correction factor or the meter will be cleaned, adjusted, and recalibrated. In addition, ERG requires that the average correction factor be within 1.00 ±1 percent. For the post-test calibration, the meter will be calibrated three times at the average orifice setting and vacuum that were used during the actual test. Dry gas meter calibrations will be performed by Apex Environmental, Inc.

4.3.3 Dry Impinger Equipment Preparation

A single dry impinger modification train (Method 5/Method 202) will be assembled as shown in Figure 4-4. Preparation of the sample train will follow Method 202 requirements, which are summarized in Section 4.3. The sample trains will be assembled in the ERG laboratory from components commonly used in EPA Method 5 and Method 23.

The dry impinger modification to Method 202 includes inserting a Method 23 type stack gas condenser and a condensate collection impinger without bubbler tube between the hot box filter assembly and the first Method 202 impinger (Figure 4-4). At the start of the tests, impingers in the modified train will be clean, without any water or reagent added.

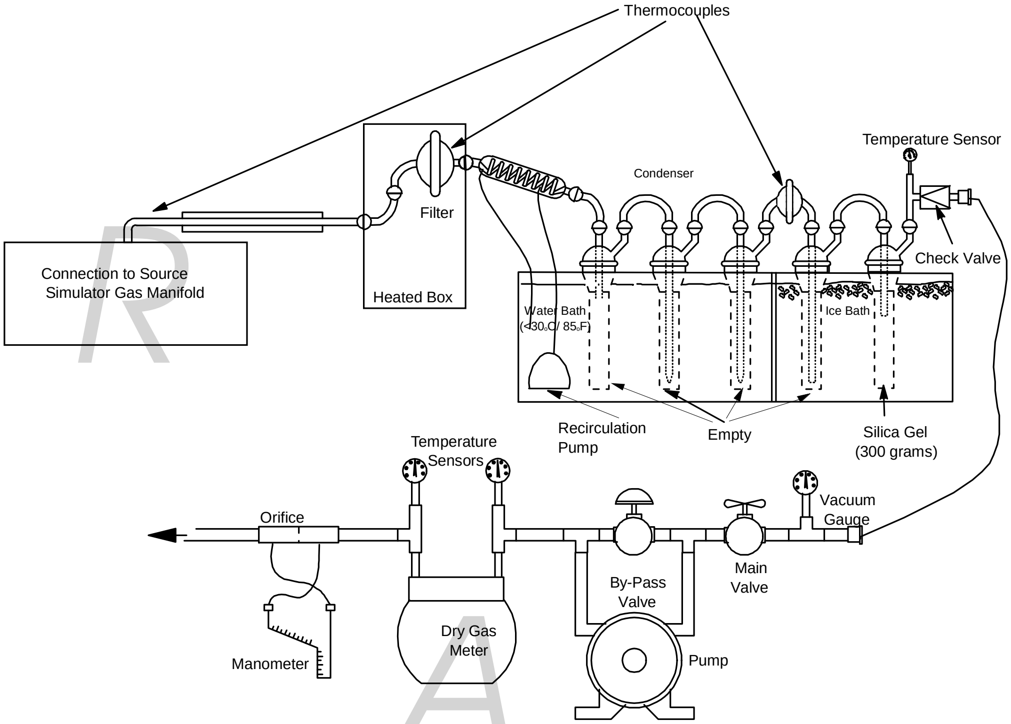


Figure 4-4. Dry Impinger Modification to Method 202

4.3.4 Sampling Operations

The sample trains will be assembled in the ERG laboratory in the special projects/preparation area. Thermocouples will be attached to measure the gas generation system temperature and probe outlet and impinger outlet temperatures. The probe heaters will be turned on and allowed to stabilize at 160 ± 16°C (320 ± 32°F). The standard impinger configuration for EPA Method 202 will be followed. Crushed ice will be added to each impinger bucket.

Each sampling train will be leak checked after sampling is complete as required in EPA Method 5/202. If a piece of glassware needs to be emptied or replaced, a final leak check will be performed before the glassware piece is removed. An initial leak check will be performed after the train is re-assembled.

To leak check the assembled train, the nozzle end is capped off and a vacuum of 15 in. Hg is pulled in the system. When the system is evacuated, the volume of gas flowing through the system will be timed for 60 seconds. The leak rate is required to be less than 0.02 acfm (ft^3/min) or 4 percent of the average sampling rate, whichever is less. After the leak rate is determined, the cap is slowly removed from the nozzle end until the vacuum drops off, and then the pump is turned off. If the leak rate requirement is not met, the train will be systematically checked by first capping the train at the filter, at the first impinger, etc., until the leak is located and corrected.

In the event that a final leak rate is found to be above the minimum acceptable rate (0.02 acfm or 4 percent of the average sampling rate) upon removal from the test port, the results of the run would typically be void.

The leak rates and sampling start and stop times will be recorded on the sampling task log. Also, any other events that occur during sampling will be recorded on the task log (such as pitot cleaning, thermocouple malfunctions, heater malfunctions, and any other unusual occurrences).

After sample collection, each train will be purged with dry zero grade nitrogen for 1 hour at the sampling rate used to collect source simulator gases. A long stem impinger insert will replace the short impinger insert in the dry impinger modification train. The impinger stem tip will extend approximately 1 cm below the sample surface. If sufficient water is not collected in the first dry impinger, degassed reagent grade water will be added to ensure the impinger tip extends below the sample surface. During the eight sample replicate tests ultra high purity nitrogen will be filtered prior to the first impinger. The total purge gas volume will be at least 1 cubic meter. A checklist for sampling is included in Figure 4-5. Sampling train data will be recorded every five minutes on standard data forms.

4.3.5 Sample Recovery

The sample bottles containing the impinger contents and filters for each of the sampling trains will be prepared in an adjacent hood to the sampling system to avoid contamination. Final impinger weights will be determined and recorded. The train rinses sample will then be collected in the following fractions:

- Filter recovered and stored in a clean petri dish.
- Impinger solutions, weighed and processed according to Method 202.
- Silica impinger and contents, weighed and recycled.

Each train sample fraction will be carefully removed from the train assembly, sealed and moved to ERG's sample preparation laboratory.

Recovery procedures are detailed in this section. **NOTE: No methanol or acetone will be used in sample recovery.**

Before test starts:

1. Check impinger sets to verify the correct order, contents, orientation, and number of impingers.

2. Check that the correct pieces of glassware are available and in good condition. Have at least one spare probe liner, probe sheath, and meterbox ready.

3. Verify that a sufficient number of appropriate data sheets are available. Complete required preliminary information including ambient temperature, barometric pressure, and static pressure.

4. Examine meter boxes - level as necessary, zero the manometers and confirm that pumps are operational.

5. Check thermocouples - make sure they are reading correctly.

6. Perform initial leak checks; record leak rate and vacuum on sampling log.

7. Turn on variacs/heaters and check to see that the heat is increasing.

8. Add ice to impinger buckets.

9. Record the initial dry gas meter reading.

During test:

1. Notify Sampling Task Lead of any sampling problems ASAP. Trained operator should fill in sampling log and document any abnormalities.

2. Position the train assembly at the sampling location. Maintain probe temperature at 320°F ±25°F. Keep temperature as steady as possible. Add ice to the front impinger box as necessary to maintain a temperature of <85°F at cold filter outlet. If the stack gas temperatures or the moisture level are high , the ice will melt rapidly.

3. Check dry impinger method final “cold” filter temperature every 1/4 hour, maintain at or below 30°C (85°F).

4. Check impinger solutions every 1/4 hour; if the first impinger is approaching full, stop test, empty it into a pre-weighed bottle, for Method 202 add an additional 200 mL of preweighed reagent (water), and replace the impinger in the train. For the dry impinger method replace the empty impinger in the train.

5. Check impinger silica gel every 1/4 to 1/2 hour; if indicator color begins to fade, request a pre-filled, pre-weighed impinger from the recovery trailer.

6 Check the ice in the rear impinger bucket frequently. If the stack gas temperatures are high, the ice will melt at the bottom rapidly. Maintain silica gel impinger gas temperatures below 85°F.

Figure 4-5. Sampling Checklist

After test is completed:

1. Record final meter readings.
2. Do final leak check of sampling trains at maximum vacuum during test.
3. Check completeness of data sheet. Verify the impinger bucket identification is recorded on the data sheets. Note any abnormal conditions.
4. Reserved for field tests leak check pitot tubes and inspect for tip damage.
5. Disassemble trains and cap sections.
6. Reserved for field test probe sample recovery.
7. Reserved for field test probe cap and storage.
8. Make sure data sheets are completely filled out, legible, and give them to the Sampling Task Leader
9. Replace the first impinger insert with a modified Greenburg Smith Perform nitrogen purge of impinger catch for one (1) hour at or above sample collection flow rate.
10. Make sure the
11. Repeat “During Test” QC checks
12. Complete purge data sheets. Ensure sheets are completely filled out, legible, and give them to the Sampling Task Leader.

Figure 4-5. Continued

4.4 Blank(s)

4.4.1 Train Blanks

During the eight replicate train sample collection phase of the study at least three sets of train blanks will be prepared. A sampling train will be assembled in the staging area, and leak checked. The sampling train will be recovered in the same manner previously described.

4.4.2 Laboratory Water Blanks

Accompanying the eight replicate train samples in the precision study, analysis of laboratory blanks will indicate any SO_2 contributions attributable to laboratory procedures. Three water blanks of 100 mL each will be prepared, evaporated to dryness using the procedures described in Section 6, and weighed.

4.4.3 Reagent Blanks

Aliquots of each lot of methylene chloride and water will be collected for analysis as reagent blanks. Aliquots will be prepared and analyzed for extractable organic residue as described in Section 6.

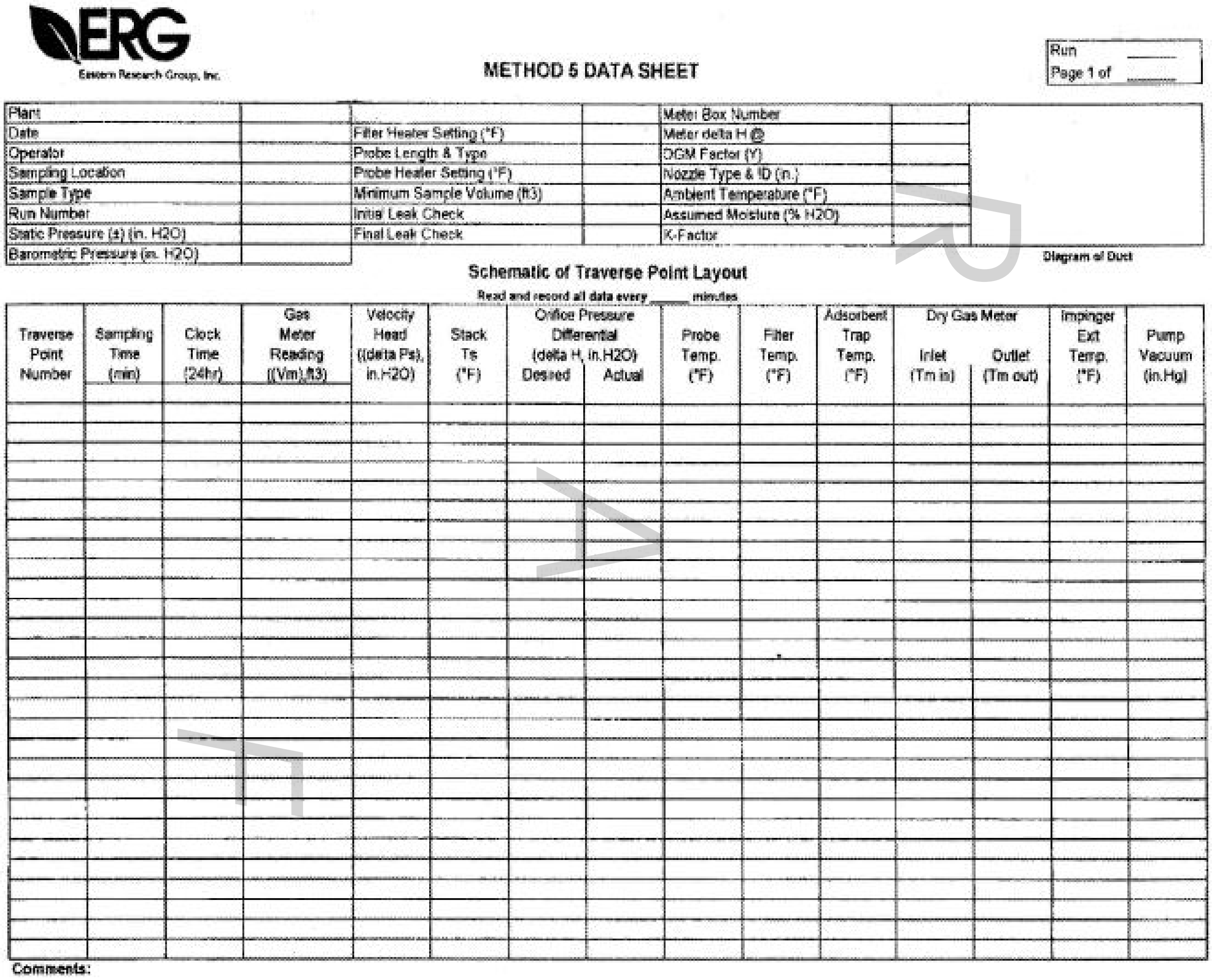
Section 5.0
Sample/Data Custody

Sample and data custody records will be kept in permanent, hardbound dedicated laboratory notebooks. Each sample will be given a unique identification number that will be recorded in a laboratory notebook and on each sample container. The information kept on the sampling sheet will include the following:

- Sample identification number
- Sample date
- Spiking System temperature
- Run number
- Barometric pressure
- Gas mixture control settings
- Initials of the person taking the sample

The data sheets used for each run are shown in Figures 5-1 and 5.2. The sampling data sheet contains the information given above, plus additional data that will be used for each run.

The Sampling and Analysis Task Leader will be responsible for ensuring that all samples taken are accounted for and that proper custody and documentation procedures are followed for the field sampling efforts. A master sample logbook will be maintained to provide a hard copy of all sample collection activities. Manual flue gas sampling data will also be maintained by the Recovery Task Leader. Copies of the field data sheets and chain of custody records will accompany the samples to the laboratory for analysis. The sampling train components will be recovered and individually labeled. The liquid levels in rinse containers will be marked on each bottle. The individual sample labels will be recorded on the sample label and in the sample logbook. Sample bottle lids will be sealed on the outside with Teflon® tape to



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METHOD 5 DATA SHEET

Run ______
Page 1 of ______

Plant				Meter Box Number	
Date		Filter Heater Setting (°F)		Meter delta H @	
Operator		Probe Length & Type		DGM Factor (Y)	
Sampling Location		Probe Heater Setting (°F)		Nozzle Type & ID (in.)	
Sample Type		Minimum Sample Volume (ft3)		Ambient Temperature (°F)	
Run Number		Initial Leak Check		Assumed Moisture (% H2O)	
Static Pressure (±) (in. H2O)		Final Leak Check		K-Factor	
Barometric Pressure (in. H2O)					

Diagram of Duct

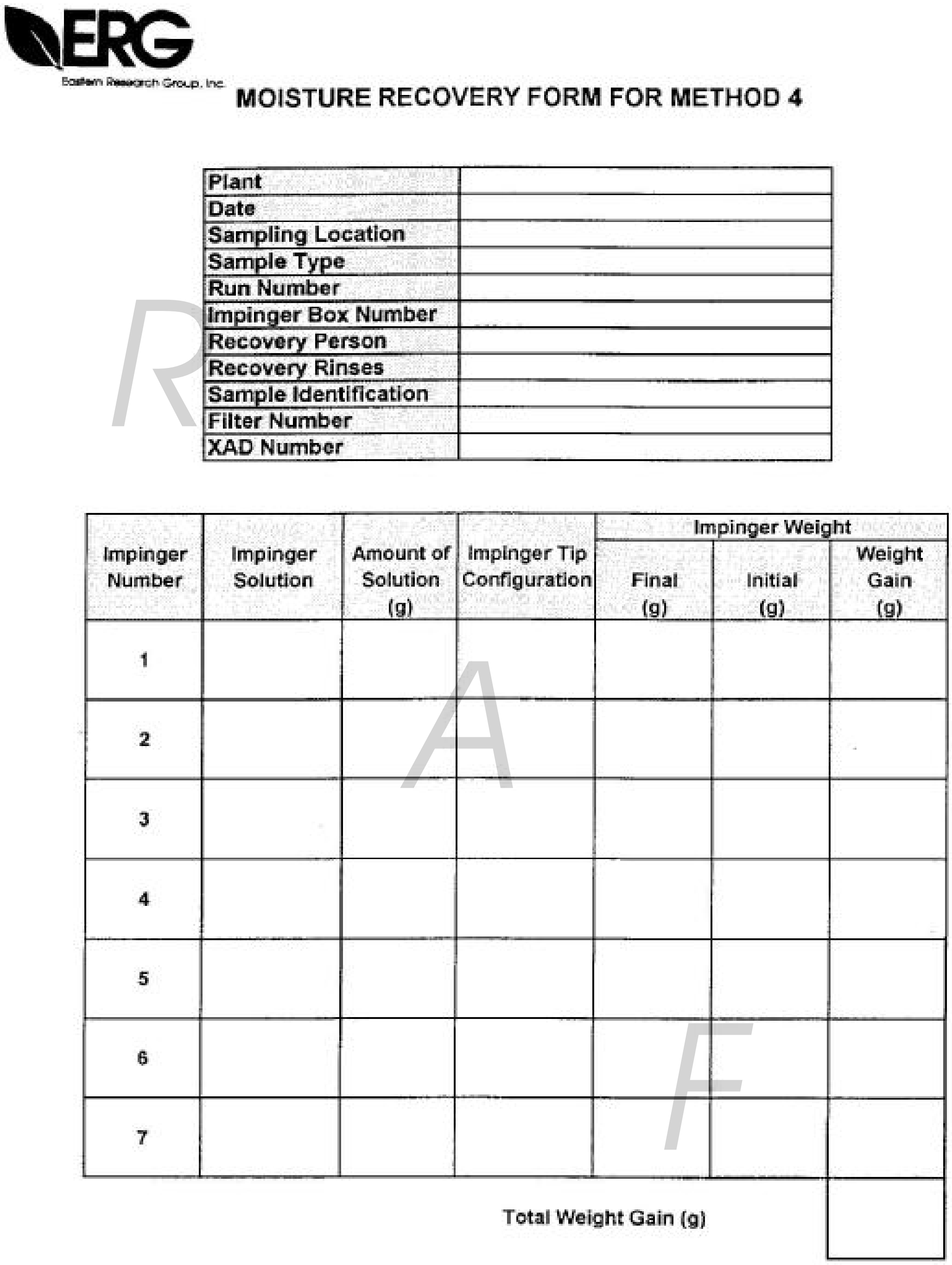
Schematic of Traverse Point Layout

Read and record all data every ______ minutes

Traverse Point Number	Sampling Time (min)	Clock Time (24hr)	Gas Meter Reading ((Vm),ft3)	Velocity Head ((delta Ps), in.H2O)	Stack Ts (°F)	Orifice Pressure Differential (delta H, in.H2O)		Probe Temp. (°F)	Filter Temp. (°F)	Adsorbent Trap Temp. (°F)	Dry Gas Meter		Impinger Exit Temp. (°F)	Pump Vacuum (in.Hg)
						Desired	Actual				Inlet (Tm in)	Outlet (Tm out)		

Comments:

Figure 5-1. Method 5 Example Field Data Sheet



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MOISTURE RECOVERY FORM FOR METHOD 4

Plant	
Date	
Sampling Location	
Sample Type	
Run Number	
Impinger Box Number	
Recovery Person	
Recovery Rinses	
Sample Identification	
Filter Number	
XAD Number	

Impinger Number	Impinger Solution	Amount of Solution (g)	Impinger Tip Configuration	Impinger Weight		
				Final (g)	Initial (g)	Weight Gain (g)
1						
2						
3						
4						
5						
6						
7						
				Total Weight Gain (g)		

Figure 5-2. Method 4 Example Data Sheet

prevent leakage. A complete chain-of-custody form will be prepared for each train set and written instructions specifying the treatment of each sample will also be enclosed in the sample shipment container.

Samples will be logged into the ERG Laboratory Information Management (LIM) system. The chain-of-custody forms and sample bottle labels will be compared. Condition of the samples will be noted on the COC forms. Any discrepancies or abnormalities (leakage, etc.) will be noted. All samples will be given a unique sample identification code assigned by the LIM system. Sample fraction or container description will be entered into the LIM system and associated with the appropriate unique sample identification code. After logging samples into the ERG LIM system, the samples will be stored at 4°C to prevent decomposition and reduce further artifact formation. Once the samples are logged into the LIMS tracking and reporting system, analysts will be notified that the samples are available for further preparation and analysis.

Section 6.0
Analytical Procedures

This section describes the sample and recovery procedures that ERG will apply to both Method 202 and the dry impinger modification to Method 202. All analyses will be performed by ERG at its Morrisville laboratory. Modifications to these procedures will be documented for reference. All laboratory glassware will be washed with detergent and tap water and rinsed with organic-free water, followed by an appropriate solvent rinse (methylene chloride) prior to use.

Appendices to this document contain descriptions of the analytical procedures that stakeholders will apply in evaluation of their respective modification to Method 202.

6.1 Sample Preparation

Following a one-hour purge of the sampling train with nitrogen (N_2), the impingers and (optional) filter samples will be recovered and archived (Container M202-1A or DM-1A). The cold filter from the dry impinger modification train will be recovered from the train filter holder and placed in a glass petri dish (Container DM-1D).

6.1.1 Container Nos. 1A and 1B (Impinger Contents)

The volume of liquid in Method 202 impingers will be measured by weighing the impingers. The liquid in the first three impingers will be individually measured to the nearest 0.5 gram (g) by weighing using a top-loading balance. Impingers and connecting glassware will be rinsed at least twice and the rinses combined with the impinger sample (Container M-202-1B). The total weight of the wash plus rinse will be determined to the nearest 0.5 g.

A 20 milliliter (mL) aliquot of each aqueous impinger will be recovered for cation and anion analysis using ion chromatography (Container M-202-1C). The remainder of the impinger sample will be extracted with methylene chloride (CH_2Cl_2) container (M202-2) as described in Section 6.2.

Dry impinger train samples will be recovered immediately after sample collection and the nitrogen purge is complete. The volume of liquid in the dry impinger train impingers will be measured by weighing the impingers. The weight of the all impingers will be individually measured to the nearest 0.5 g by weighing using a top-loading balance. Impingers and connecting glassware will be rinsed at least twice and the rinses combined with the impinger sample (Container DM-1B). The total weight of the wash plus rinse will be determined to the nearest 0.5 g. A 20 mL aliquot of each aqueous impinger will be recovered for cation and anion analysis using ion chromatography (Container DM-1C). The remainder of the impinger sample will be extracted with methylene chloride (CH_2Cl_2) as described in Section 6.2 (Container DM-2).

6.1.2 Container No. 2 (Methylene Chloride Rinses)

Following the water rinses, each of the impingers and connecting glassware will be rinsed twice with methylene chloride. Rinses will be accumulated in a glass sample bottle (Containers M-202-2 and DM-2).

6.1.3 Container 3 (Water Blank)

A blank of 500 mL reagent water will be taken as the reagent blank.

6.1.4 Container 4 (Methylene Chloride Blank)

A blank of 50 mL will be taken as the methylene chloride reagent blank and evaporated to dryness identical to the methylene chloride extract sample.

6.2 Extraction

The impinger sample (Container M-202-1 or DM-1) is combined with the methylene chloride rinses (Container M-202-2 or DM-2 respectively) and serially extracted with methylene chloride (dichloromethane) using a separatory funnel. Solvents will be HPLC grade or equivalent. Once extracted, the sample will be dried using anhydrous sodium sulfate, concentrated to 10 mL with applied heat (kuderna danish apparatus) and finally evaporated to dryness at room temperature (<30°C) in a preweighed vessel. Final residue weights will be determined by allowing the organic residue to attain constant weight in a desiccator. Method 202 requires that weights are measured to the nearest 0.1 mg, which requires a standard analytical balance capable of measuring 0.0001 g. Since this project focuses on reducing artifacts to zero, residual mass will be determined to the nearest 0.00001 ±0.00005 g requiring a balance capable of measuring 0.00001 g.

6.3 Residual Inorganic CPM Preparation

The aqueous phase and rinse from the impingers (Containers M202-1B and DM-1B) of each train will be evaporated to approximately 10 mL in a glass beaker on a hot plate. The 10 mL concentration will be taken to dryness at ambient temperature not to exceed 30°C, reconstituted to approximately 10 mL with water, and neutralized with ammonium hydroxide. The aqueous inorganic material may be transferred to a preweighed vessel and allowed to dry at ambient temperature (<30°C). Residue weights will be determined by allowing samples to attain constant weight in a desiccator. Weights should be recorded to the nearest 0.00001 ±0.00005 g in an environmentally controlled room meeting filterable particulate weighing specifications.

If ammonia gas is added to the gas stream, Section 8.1 of Method 202 will be followed requiring titration of the acidity in inorganic CPM samples rather than simple neutralization. Following Section 8.1 of Method 202 allows correction for the precise amount of ammonia added during neutralization without bias to ammonium condensible particulate present in the sample.

6.4 Chromatographic Analyses

For all tests, the aliquot of impinger solution will be treated with 30 percent hydrogen peroxide to convert all unpurged SO_2 to sulfate. Sulfate concentration will be determined by ion chromatography following EPA RCRA Method 9056. For tests that include ammonia as contributor to CPM, ammonia, nitrate, sulfate, and chloride will be analyzed by ion chromatography following requirements found in EPA Method 9056 for anions and EPA Method CTM-027 for ammonia.

6.4.1 Standard Preparation

Multicomponent stock calibration standards for ion chromatographic analysis will be prepared using a primary source anion solution. Calibration standards will be prepared by diluting the primary standard to generate at least six concentrations covering the expected (linear) range for samples. Samples falling above the calibration range will be diluted appropriately with organic-free deionized water.

A check standard will be prepared at a concentration in the middle of the calibration range from a secondary multi-component source of anions. The check standard will be used to check the instrument response and the calibration curve.

6.4.2 Qualitative Identification

Analytes will be identified by retention time. The width of the retention time window that is used for identification is based on the standard deviation in retention time for multiple injections of a standard.

6.4.3 Quantitation

Calculations for Calibration Curve. A least squares linear regression analysis of the calibration standards data will be used to calculate a correlation coefficient, slope, and intercept. Concentrations will be used as the X-term and response will be used as the Y-term.

Calculation of Anion or Cation Concentration in Samples. The concentration of anion or cation in the samples will be calculated as follows:

$$\begin{array}{l}\text{Concentration}\\ \text{in Sample}\end{array} = \frac{\text{(Sample Response - Intercept)}}{\text{Slope}}$$

Calculation of Total Anion or Cation Weight in Samples. If sample dilution is required, the total weight of ion in the sample will be calculated from the concentration, the volume of water in the original sample, and the final volume of water into which the sample was diluted (as appropriate).

$$\begin{array}{l}\text{Total ion}\\ \text{in sample } (\mu\text{g})\end{array} = \begin{array}{l}\text{Concentration}\\ \text{ion in}\\ \text{sample } (\mu\text{g/mL})\end{array} \times \begin{array}{l}\text{Total volume}\\ \text{of sample (mL)}\end{array} \times \frac{\text{Dilution volume}}{\text{sample volume}}$$

Calculation of Concentration of Ion in Gas Sampled. The concentration of ion in the stack gas will be determined as follows:

$$\begin{array}{l}\text{Concentration}\\ \text{Ion in Sample}\\ (\mu\text{g/dscm})\end{array} = \frac{K\ [\text{Total Ion in Sample}]}{V_{m(std)}}$$

where:

K = 35.31 ft^3/m^3 if $V_{m(std)}$ is expressed in English units
= 1.00 m^3/m^3 if $V_{m(std)}$ is expressed in metric units

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

Section 7.0
Quality Assurance/Quality Control

This section describes the quality assurance/quality control (QA/QC) activities for the sampling and analytical procedures associated with the assessment of Method 202 and the dry impinger modification. In addition to sampling and analytical QA/QC procedures, the project staff is organized to allow review of project activities and provide QC coordination throughout the term of the program.

7.1 Sampling QA/QC Procedures

The sampling QA/QC program for this project includes manual method sampling performance criteria, equipment calibrations, consistency of gas spiking, sampling and recovery procedures, representative sampling, complete documentation of sampling data and abnormalities, and adequate sample custody procedures.

7.1.1 Train and Reagent Blanks

At least three blanks will be collected that include representative reagents and media. These blanks will be processed in the same manner as collected samples.

Reagent blanks of recovery solvents will also be collected. Reagent blanks will be archived and the need for analysis will be determined after samples and train blanks are analyzed. If train blanks show less than 1 mg of residual weight, reagent blanks will not be analyzed. Analytical results of reagent and train blanks serve as indicators of preparation and recovery contamination.

7.1.2 Sampling Calibration Procedures

Control limits and corrective actions for sampling procedures are given in Table 7-1 for the metering system, the source simulator heater, the temperature gauges, the impingers, dry gas thermocouples, the probe and stack thermocouple, and the aneroid barometer.

Table 7-1. Summary of Acceptance Criteria, Control Limits, and Corrective Action

Criteria	Control Limits[a]	Corrective Action
Final Leak Rate	#0.02 acfm or 4% of sampling rate, whichever is less	Repair or seal leak prior to starting test.
Dry Gas Meter Calibration	Post average factor agrees ±5% of pre-factor	Adjust sample volumes using the correction factor
Individual Correction Factor ( )	Agree within 2% of average factor	Redo correction factor
Average Correction Factor	1.00 ±1%	Adjust the dry gas meter and recalibrate
Intermediate Dry Gas Meter	Calibrated every six months against EPA standard	--
Analytical Balance (top loader) for Impinger Weights	0.1 g of NIST Class S Weights	Repair balance and recalibrate
Analytical Balance for residue weights.	0.00005 g of NIST Class S Weights	Repair balance and recalibrate
Barometric Pressure	Within 2.5 mm Hg of mercury-in-glass barometer	Recalibrate

[a] Control limits are established based on previous test programs conducted by the EPA.

7.2 Laboratory QA/QC Procedures

The laboratory QA program for this project includes proper handling, logging, and tracking of samples, procedure validations, including ion chromatography column efficiency, calibration curves, daily QC checks and replicate analyses, and collection and/or analysis of sample, train and reagent blanks, method spikes as well as field and laboratory spikes. A summary of ERG's laboratory QC procedures is provided in Table 7-2.

A calibration curve for ion chromatograph/conductance analysis will be determined for each anion or cation of interest using a minimum of five standards plus a blank solvent covering at least a 10-fold range in concentration. Quality control requirements in ERG SOP 85 for ion chromatography analysis will be followed as appropriate. Daily calibration check samples will be prepared from a secondary source of target analyte. All standards will be stored at 4°C and allowed to warm to room temperature prior to use. For daily calibrations, a concentration of 15 µg/mL is used for each target compound. A percent difference between the initial calibration response factor (RF_i) and the daily calibration check response factor (RF_c) is calculated using the equation below:

$$\%\ \text{difference} = \frac{RF_i - RF_c}{RF_i} * 100$$

If the percent difference for any compound is greater than 10, the laboratory will consider this as a control warning limit. If the percent difference is greater than 15 for any compound of interest, the daily calibration check will be rerun. If the condition still exists, the daily calibration check sample will be re-prepared and the instrument will be recalibrated. Possible causes for not meeting QC requirements will be evaluated including the following: poor peak integration by the data system, an improperly prepared standard, poor resolution from interfering compounds, deteriorating lamp function, etc.

Table 7-2. Summary of Quality Control Procedures

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
IC Column Efficiency	Analyze second source QC sample	At setup and 1 per sample batch	Resolution between anions should be baseline to baseline.	1) Eliminate dead volume 2) Back flush 3) Replace the column repeat analysis
Linearity Check	Run a 5-point calibration curve and daily QC sample.	At setup or when calibration check is out of acceptance criteria	Correlation coefficient $ 0.999, relative error for each level against calibration curve ± 20% or less relative error	1) Check integration 2) Reintegrate 3) Recalibrate
			Intercept acceptance should be #10,000 area counts per ion.	1) Check integration 2) Reintegrate 3) Recalibrate
Retention Time	Analyze Secondary Source sample	Once per 12 hours or less	Ions within retention time window established by determining 3F or ±2% of the mean calibration and midpoint standards, whichever is greater	1) Check system for plug 2) Regulate column temperature 3) Check gradient and solvents
Calibration Check	Analyze Secondary Source QC sample	Once per 12 hours or less	85-115% recovery	1) Check integration 2) Recalibrate or re-prepare standard 4) Reanalyze samples not bracketed by acceptable standard

Table 7-2. Summary of Quality Control Procedures (Continued)

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Calibration Accuracy	Analyze Secondary Source QC sample	Once after calibration in triplicate	85-115% recovery	1) Check integration 2) Recalibrate 3) Re-prepare standard 4) Reanalyze samples not bracketed by acceptable standard
System Blank	Analyze water	Bracket sample batch, one at beginning and one at end of batch	Measured concentration # 5 times the MDL	1) Locate contamination and document levels of contamination in file
Lot Blank Check	Analyze blank water on new lots	Every lot received	Compounds must be less than method MDLs	1) Reanalyze cartridge. 2) Notify vendor if lot blank continues to fail.
Train Blank (TB) Check	Train blank samples collected from sampling train.	#10% of the sampling schedule	Compounds must be less than detection limits.	If TB fails, schedule another TB. If no reason for failure is identified and corresponding sample has high concentration values, TB subtract that sample only and flag data in report. If sample does not have high values, do NOT blank subtract, but flag data. Additional TBs are collected until the problem is corrected and data are acceptable.

Table 7-2. Summary of Quality Control Procedures (Continued)

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Duplicate Analyses	Duplicate and replicate samples	As collected	±20% RPD	1) Check integration 2) Check instrument function 3) Reanalyze duplicate samples
Replicate Analyses	Replicate injections	Duplicate samples only	# 10% RPD for concentrations greater than 0.1 :g/mL.	1) Check integration 2) Check instrument function 3) Reanalyze duplicate samples
Method Spike/Method Spike Duplicate (MS/MSD)	Analyze MS/MSD, using calibration standard	One MS/MSD per batch of 20 samples	80-120% recovery for all compounds.	1) Check calibration 2) Check extraction procedures

7.2.1 Blanks

Reagent water (system blank) will be processed and analyzed at least once per day to ensure that the system is not contaminated. If a response is obtained that is 0.1 % of the level of the expected analyte concentration, the source of contamination will be located and eliminated before analyzing samples. Possible problem areas include improper flushing of the sample loop and sample carryover.

7.2.2 Replicate Analyses

One test sample every analysis day will be analyzed in duplicate. A minimum of 1 sample in 10 will be analyzed in duplicate. The replicate analysis should be within ±10% of the first at concentrations greater than 1 :g/mL and ±25% at concentrations less than 1 :g/mL. If the replicate analyses are outside of these limits, the following items will be checked:

- The peaks are integrated properly;
- There is no interference from other components in the sample; and
- The instrument is working properly.

Section 8.0
Data Reduction, Processing, Validation, and Reporting

Procedures for data reduction and data processing are presented in Method 202. Data validation will be performed daily by the Laboratory Studies Coordinator and the Data Analysis Task Leader. The Data Analysis Task Leader, with assistance from the QA Project Coordinator, will perform final data validation of approximately 10 percent of the final database by checking the final results against the original data sheets. Any data that are suspected to be outliers will be validated by reviewing the calculations, beginning with the original data sheets to check for transcription or calculation errors.

Initial data reduction will include correction for the amount of ammonia added to remove the waters of hydration for sulfuric acid. The procedure specified in EPA Method 202 Section 7.2 will be used to correct measured mass for neutralized sulfate. Only the correction factor for ammonia (0.354) will be used in this calculation. Following initial data reduction and calculations, the results of train samples will be compared to the expected level from the simulated stack gas stream as described in Section 13. Precision, bias (recovery), and completeness will be determined as described in Section 13. Recovery from the Method 202 and dry impinger modified trains will be compared at each of the sulfur dioxide (SO_2) spike levels. If the dry impinger modification to Method 202 shows improved performance measured by a 50 percent reduction in the artifacts from SO_2 at the 95 percent confidence interval, additional tests will be performed and a minimum of seven replicate runs will be used to calculate the method precision and artifact bias.

No system audit is planned for the laboratory tests described in this QAPP/Test Plan. A draft sampling and analytical procedure will be prepared if results of the laboratory test of the dry impinger train demonstrate statistically significant improved precision and recovery compared to the Method 202 results.

Reporting of data, results, and conclusions will be delivered to the EPA Work Assignment Manager after an internal review by senior ERG personnel.

Section 9.0
Internal QC Checks and Audits

The major quality assurance procedure that will be used in the laboratory evaluation tests of the Method 202 and dry impinger modified trains will be to follow the detailed operating procedures already available in Method 202.

Section 10
Health and Safety Plan

The purpose of this health and safety plan is to inform ERG personnel of known or potential health and safety hazards that may arise during laboratory sampling and analytical activities. This plan describes the procedures and equipment required to prevent work injury and illness. Personnel are expected to read and understand this plan and follow any additional safety procedures.

The scope of work involves a laboratory assessment of modifications to Method 202 that will reduce artifact reaction products that are not related to the primary emission of condensable particulate matter (CPM) from the source. The laboratory assessment includes using a sampling manifold to spike the suspect interfering gases into the sampling train(s) under controlled laboratory conditions, sample recovery, and sample analysis.

10.1 Responsibilities and Authorities

ERG personnel who will have the overall responsibility for the safe conduct of this project are the following:

Project Manager	Ray Merrill
Laboratory Studies Coordinator	Randy Bower
Safety Officer	Eric Goehl

10.1.1 <u>Laboratory Studies Coordinator</u>

The Laboratory Studies Coordinator is responsible for assuring that all ERG sampling and analytical activities are conducted according to this QAPP/Test Plan and ERG's Health and Safety

Manual. Prior to initiating sampling activities, the Laboratory Studies Coordinator will consult with the ERG Safety Officer or his designee to complete the review response procedures for safety issues. The Laboratory Studies Coordinator will be available at all times during the sampling phase of the project.

The Laboratory Studies Coordinator and Safety Officer have the authority to enforce the safety procedures for this project. The Laboratory Studies Coordinator may upgrade the requirements of this plan if necessary. Downgrading of this plan can occur after the review and approval by the Safety Officer. If a disagreement on downgrading the plan exists, the Laboratory Studies Coordinator may contact the ERG Corporate Health and Safety Director, Arlene Levin, who will determine what procedure will be used.

10.1.2 Project Manager

The Project Manager is responsible for communicating health and safety issues with the client and the Laboratory Studies Coordinator.

10.1.3 Sampling Personnel

Sampling personnel are responsible for complying with the requirements of this plan and notifying the Laboratory Studies Coordinator of injuries, illnesses, and unanticipated hazards.

10.2 Physical Hazard Assessment

10.2.1 Slips, Trips, and Falls

All sampling will occur in the ERG laboratory. The physical condition of the sampling area and access ways will be safe and accessible. ERG personnel will wear appropriate footware and watch for spills or other irregular hazards between the sampling area and ERG's sample receiving area.

10.2.2 Electrical

All electrical equipment and cords will be in good working condition. Electrical equipment and cords will be inspected for electrical hazards prior to use.

10.2.3 Noise

Noise levels are not expected to be excessive. However, use of sampling trains in a confined test area may elevate noise levels. The Laboratory Studies Coordinator will ensure hearing protection will be available on a daily basis to all personnel if noise levels are increased significantly.

10.2.4 Glassware Hazards

Sampling probes and manifolds may present burn hazards. Thermally insulated gloves must be worn when handling hot glassware and/or sampling probes.

All glassware must be handled with care. Laboratory technicians should not attempt to force glassware together or apart. Laboratory technicians should not attempt to clean up broken glass by using bare hands.

10.3 Chemical Hazards

This section summarizes the hazards of the chemical reagent used in the sampling method and in the spiked gas streams. Methylene chloride will be used as a reagent in sample collection. The spiked gas stream(s) will encompass the following compounds: sulfur dioxide, ammonia, nitrogen oxides (NO and NO_2), and carbon dioxide. However, the concentration of these compounds is low enough that they do not pose a hazard. The potential hazard lies in the fact that these compounds will be handled as a compressed gas.

10.3.1 Methylene Chloride

Methylene chloride ($MeCl_2$) will be used as a reagent in sample collection. Routes of potential exposure are most likely to be via short-term inhalation and skin contact. Methylene chloride is a suspected human carcinogen and it should be handled with care. Accidental contact of liquid methylene chloride with skin or eyes causes painful irritation and possible burns if not promptly removed. Exposure by way of contaminated gloves or clothing can produce these same irritant effects. Long-term exposure to mild or moderate doses of methylene chloride may cause a delayed (24 to 48 hours) onset of dizziness, headache, mental confusion, slurred speech, double vision, and sleeplessness.

Exposure by inhalation of short term, high exposures can cause respiratory tract irritation and symptoms similar to those of skin contact.

10.3.2 Compressed Gases

The spiked gas stream(s) will encompass the following compounds: sulfur dioxide, ammonia, nitrogen oxides (NO and NO_2), and carbon dioxide. Compressed gas cylinders will be fastened to solid supports (wall mounted supports or temporary laboratory bench supports/bases). Regulators appropriate for the gases will be used. Laboratory safety glasses with side shields are required during gas handling. Full face shields are available for use as required. All gases will be vented into the standard laboratory hood ventilation system.

10.4 Personal Protective Equipment

Table 10-1 specifies the conditions and requirements for personal protective equipment.

Table 10-1. Personal Protective Equipment

Item	When Used
Safety glasses	All times
Work boots or closed toe shoes	All times
Thermal insulated gloves	Hot glassware
Nitrile gloves with cotton liner	Chemical handling

10.5 Personal Grooming

Team members will keep their skin and clothing as clean as practical when working. Eating, drinking, and smoking are permitted only in areas away from the sampling area at locations designated in the ERG laboratory facility.

10.6 Training

At least one on-site employee must be certified in first aid and CPR training.

10.7 Medical Monitoring

This scope of work is not expected to present health hazards that would not be detected by ERG’s medical monitoring program for source testing personnel. Therefore, no project-specific medical monitoring is deemed to be necessary.

10.8 Emergency Response Procedure

The Laboratory Studies Coordinator will initiate ERG’s emergency response procedure if necessary.

Section 11.0
Preventive Maintenance Procedures

The major piece of equipment used for the project is a Dionex Model 600 Ion Chromatography system. ERG funds a preventative maintenance contract and follows manufacturer's recommendations for routing service of this unit. Maintenance logbooks are kept for each instrument. ERG keeps spare parts and rebuild kits for sampling trains used to perform EPA Method 202 sampling. Dry gas meters are serviced and calibrated prior to each sampling episode. Multiple spare sets of glassware including filters, impingers, condensers, and sorbent modules are readily available.

Section 12.0
Precision and Accuracy

The purpose of the laboratory test program is to determine a baseline for potential artifacts in EPA Method 202 from sulfur dioxide (SO_2) stack emissions. Baseline measurements will be made under laboratory controlled conditions using simulated stack gas mixtures that approximate low level (e.g., gas-fired turbine) and elevated (e.g., coal-fired power plant) SO_2 emissions. In addition, a modification to Method 202 that cools the emission gases and collects condensible particulate in “dry” impingers will be evaluated under the same conditions as the baseline tests. ERG will collect and analyze the target compounds listed in Table 1-1.

The statistical approach compares the baseline Method 202 to the dry impinger modification of Method 202. Three replicate populations represent the absolute minimum for statistical calculations. The data evaluation described in this section will be applied as small sample statistics and reported in addition to test run means for each condition. Single group precision, confidence interval, and single group bias statistics will be determined for the seven replicate tests of the dry impinger modification to Method 202.

12.1 Single Group Precision

The objective for precision is less than 20 percent relative percent difference between each of the individual mass measurements and the average of acceptable test run measurements. A mean and standard deviation of the results of each condensable particulate matter (CPM) measurement will be estimated from three samples collected using standard, “best practice” Method 202 sampling equipment and a modified dry impinger Method 202 sampling train.

The precision, SD_s of the results are determined by measuring the mass of CPM for each test condition or train modification. The pooled standard deviation of the measured CPM values, or the precision, SD_s, is determined using the following equation:

$$SD_s = \sqrt{\frac{\sum\left(X_{im} - \overline{X}\right)^2}{n-1}}$$

Where:

n = number of sampling runs (n = 3 in this study)
X_{im} = the measured concentration for sample I
$\overline{x}$ = mean of measured concentrations

For this set of laboratory tests, an attempt will be made to collect the same sample volume and spike concentration for each of the sampling runs. It is assumed that the precision and accuracy in sample volume measurement is high and the experimentally determined mass normalizes for small precision variations.

The percent relative standard deviation of each spiked sampling run is calculated as follows:

$$RSD = \frac{SDs}{S_m} * 100$$

Where:

S_m = (normalized) measured mean recovery of a measured CPM sample.

The proposed method target for RSD is not greater than 50 percent.

12.2 Confidence Interval of the Mean Recovery

The true value of the mean cannot be determined from a finite number of measurements. Confidence intervals around the mean can be determined. For this evaluation project, the 95 percent (0.05 level of significance) confidence interval has been chosen. That is, the true mean must be within the confidence interval 95 percent of the time. The confidence interval will be determined using the following equation:

$$\overline{X} - t_{1-a/2,n-1}\frac{s}{\sqrt{n}} \le m \le \overline{X} + t_{1-a/2,n-1}\frac{s}{\sqrt{n}}$$

Where:

$\overline{X}$ = the average, or mean of the measured values

" = the level of significance = 0.05 for the 95 percent confidence level

$t_{1-"/2,n-1}$ = Student's t statistic for –1 degrees of freedom and percentage point -"/2

s = standard deviation of the measured values

n = number of data points

: = population mean

12.3 Single Group Bias

For Method 202 baseline studies, the bias, B, of the CPM measurements will be calculated from the mass of CPM, as follows:

$$B = S_m$$

Where:

B = bias at the spiking level

S_m = mean of the measured concentrations of the spiked samples

This equation assumes the only source of CPM mass is artifacts, thus, it is entirely a method bias.

The objective for bias for target compounds is less than 30 percent.

The significance of the bias will be tested using the critical *t* the number of successful sampling runs. The calculated *t* value will be determined using the following equation:

$$t_{calc} = \frac{\sum \frac{x_{mi}}{n}}{\frac{SD}{\sqrt{n}}}$$

If t_{calc} # t for n measurements, then the bias calculated in Section 12.2 is not statistically significant.

12.4 Completeness

The quality assurance objective for completeness in Phase 1 evaluation testing is at least three valid sampling runs. Invalid sampling runs will be repeated until three valid sample sets are obtained. The reasons for invalidating sampling runs will be described in the final report narrative. Results from invalid runs will not be used in the calculation of precision or bias.

12.5 Two-Group Statistical Comparison

Two-sample t-test is performed to determine if the mean value of the two test sets is statistically different. The test is used when there is a natural pairing of observations for sample sets. The two-group statistical comparison will be used to determine if results from baseline Method 202 and the dry impinger modification to Method 202 are statistically the same. The following formula is used to determine the t statistic for paired two-sample means:

$$t_{calc} = \frac{\sum \frac{(X_{M202})}{n} - \sum \frac{(X_{DryMod})}{n}}{\sqrt{\frac{(SD_{M202})^2 + (SD_{DryMOD})^2}{n-1}}}$$

For three test runs (2 degrees of freedom) with the t statistic at 95 percent, if t_{calc} is # 0.0 ± 2.92, then there is no statistical difference between the mean bias of Method 202 and the dry impinger modification to Method 202.

Where:

X_{M202} = measured concentration using Method 202
X_{DryMod} = measured concentration using dry impinger modification to Method 202
X_{si} = spiked concentration of target analyte
SD^2_{M202} = variance in differences of Method 202 measurements
SD^2_{DryMod} = variance in differences of dry impinger modification to Method 202
$n-1$ = degrees of freedom

Section 13.0
Corrective Action

This section describes the criteria and procedures for corrective action associated with the Method 202 assessment and evaluation for bias and other uses.

If the precision exceeds 50% RSD for key measurements or if key quality control parameters are exceeded, laboratory staff will determine the cause of the excessively high variability, e.g., flow control, chromatographic interference, incompatibility of the compounds with components of the sampling system or the spiking matrix, poor experimental techniques, etc. If it is not possible to determine the cause of the excess magnitude of the imprecision, the result will be reported as out of control, and experimental work will be stopped until corrective actions can be identified and implemented. Other criteria and corrective action procedures are discussed in Method 202.

Various standard performance criteria for the ion chromatograph are well established laboratory practices and corresponding corrective actions will be taken.

Notification of corrective action is documented on a corrective action report form (CAR), which is distributed to staff members and the Project Manager. Corrective action will be taken by staff members performing experimental work. If precision can not be attained through standard calibration, leak check, or analytical procedures, then the issue is raised to the Laboratory Studies Coordinator, Randy Bower. If Mr. Bower is unable to identify corrective action sufficient to bring the key measurement back into control, the issue is raised to the Project Manager, Dr. Ray Merrill, who will communicate the information to the EPA WAM. Dr. Merrill will work with ERG staff to identify alternative procedures to resolve quality control issues.

Section 14.0
QC Reports

The first QC report to management, which is required by the work assignment, is this Quality Assurance Project Plan (QAPP)/Test Plan, of which this section is a part. Regular monthly QC reports will be made to the EPA Work Assignment Manager (WAM) as part of the required written progress reports for the project. In addition, verbal QC reports will be made to the WAM when a decision may be needed to change a procedure or when a stipulation of the work plan or the QAPP/Test Plan cannot be met.

Finally, the final report will summarize all of the QC data developed during the laboratory testing and method evaluation needed to define the quality of the data from the proposed method.

Appendix Template

Section A-1. Description of Stakeholder Contribution

Stakeholders will briefly describe the experimental background and approach for their contribution to the method evaluation. Stakeholders should summarize major differences between their studies and the main body of the QAPP (e.g., challenge gas differences, sampling differences, analysis differences). Stakeholders should also provide contact information for the key person for their effort.

Section A-2. Experimental Matrix

Stakeholders should provide a table or other summary of the experiments that are planned and show the number of replicate measurements and the variables to be investigated.

Section A-3. Sampling Procedures

Stakeholders should provide a description of the sampling procedures or variation of sampling procedures and should describe the differences between the stakeholder sampling procedures and the sampling procedures in the main body of the QAPP.

Section A-4. Analytical Procedures

Stakeholders should provide a description of the analytical procedures or variation of the analytical procedures to be performed and should describe the differences between the stakeholder analytical procedures and the analytical procedures in the main body of the QAPP.

Appendix B

EPA's Best Practice Recommended Procedures for Method 202

Source: http://www.epa.gov/ttn/emc/methods/method202.html

Which of the several procedures mentioned in EPA Method 202 should be used to provide the best measurement of particulate matter emissions that would be created by dilution and cooling in the ambient air?

To obtain the best measurement of particulate matter resulting from the dilution cooling of the sampled gas stream, the following procedures should be used:
The one hour purge with dry nitrogen should be performed immediately following the final leak check of the system. Reducing purge duration, using air as a purge gas and eliminating the purge step of EPA Method 202 introduces a positive bias as a result of the conversion of SO2 to SO3 and then eventually to H2SO4. Even low concentrations of SO2 in the exhaust gas will dissolve into the impinger solution and if not removed by nitrogen purging will result in a positive bias.

Use the alternative procedure describe in section 8.1 to neutralize the H2SO4. Neutralizing the inorganic portion to a PH of 7.0 determines the un-neutralized sulfuric acid content of the sample without over correcting the amount of neutralized sulfate in the inorganic portion. These neutralized sulfates (such as (NH4)2SO4 or NH4SO4) would be created in the exhaust gas upon dilution cooling in the ambient air and result in fine particulate formation. Ion chromatography, for SO4 measures both the amount of neutralized and un-neutralized SO4 contained in the impinger solution prior to the addition of NH4OH and therefore introduces a negative bias.

Evaporate the last 1 ml of the inorganic fraction by air drying following evaporation of the bulk of the impinger water in a 105 degrees C oven as described in the first sentence of section 5.3.2.3. The presence of free ammonia and HCl in the exhaust gas will form Ammonium Chloride that produces fine particulate upon dilution and cooling in the ambient air.

While the above procedures should arrive at the best measurement of the particulate matter emissions that are created by dilution and cooling in the ambient air, many State and local agencies have established applicable limits based upon the application of other options that are included in EPA Method 202. Because of the close connection between the applicable emission limits and the method used to demonstrate compliance, the above procedures may result in different values than would be achieved using other options in Method 202. In order to measure the emissions that are specified by the State requirements, the procedures specified in the State test method should be followed.

Appendix C

Other Test Method 28 — August 11, 2008
Dry Impinger Method for Determining Condensable Particulate Emissions from Stationary Sources

OTHER TEST METHOD 28 — August 11, 2008

DRY IMPINGER METHOD FOR DETERMINING CONDENSABLE PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. Scope and Applicability

1.1 Scope. The U.S. Environmental Protection Agency (U.S. EPA or “we”) developed this method to describe the procedures that the stack tester (“you”) must follow to measure condensable particulate matter (CPM) emissions from stationary sources. This method includes procedures for measuring both organic and inorganic CPM.

1.2 Applicability. You can use this method to measure CPM from stationary source emissions after filterable particulate matter has been removed. CPM is measured in the emissions after removal from the stack and after passing through a filter. You can use Method 17 to collect condensable and filterable particulate material from sources operating at stack temperatures and/or samples collected below 30°C (85°F) if the filter is treated as described in Sections 8.5.4.4 and 11.2.1 of this method. You may use this method only for stationary source emission measurements.

1.3 Responsibility. You are responsible for obtaining the equipment and supplies you will need to use this method. You must also develop your own procedures for following this method and any additional procedures to ensure accurate sampling and analytical measurements.

1.4 Results. To obtain reliable results, you must have a thorough knowledge of the following test methods that are found in Appendices A-1 through A-3 and A-6 to Part 60, and in Appendix M to Part 51:

(a) Method 1 - Sample and Velocity Traverses for Stationary Sources.

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

(c) Method 3 - Gas Analysis for the Determination of Dry Molecular Weight.

(d) Method 4 - Determination of Moisture Content in Stack Gases.

(e) Method 5 - Determination of Particulate Matter Emissions from Stationary Sources.

(f) Method 17 – Determination of Particulate Matter Emissions from Stationary Sources (in-stack filtration method).

(g) Method 201A – Determination of PM_{10} Emissions from Stationary Sources (Constant Sampling Rate Procedure) or Other Test Method 27 – Determination of PM_{10} and $PM_{2.5}$ Emissions from Stationary Sources (Constant Sampling Rate Procedure)

1.5 Additional Methods. You will need additional test methods to measure filterable particulate matter. You may use this method to collect CPM in conjunction with Method 5 or 17 of Appendices A-1 through A-3 and A-6 to Part 60, Method 201A of Appendix M to Part 51, or Other Test Method 27. The sample train operation and front end recovery and analysis are conducted according to the filterable particulate method you choose. This method addresses the equipment, preparation, and analysis necessary to measure only CPM.

1.6 Limitations. You can use this method to measure emissions following a wet scrubber only when this method is combined with a filterable particulate method that operates at high enough temperatures to cause water droplets sampled through the probe to become gaseous.

1.7 Conditions. You must maintain isokinetic sampling conditions to meet the requirements of the filterable particulate method used in conjunction with this method. You must sample at the required number of sampling points specified in Method 5, 17, or 201A. Also, if you are using this method as an alternative to a required performance test method, you must receive approval from the appropriate authorities prior to conducting the test.

2.0 Summary of Method

2.1 Summary. The CPM is collected in dry impingers after filterable particulate material has been collected on filters maintained above 30°C (85°F) using Method 5, 17, 201A, or OTM 27. The organic and aqueous fractions of the impingers and an out-of-stack CPM filter are then taken to dryness and weighed. The total of all fractions represents the CPM. Compared to the December 17, 1991 promulgated Method 202, this method removes water from the impingers and includes the addition of a condenser followed by a water dropout impinger immediately after the final in-stack or heated filter. This method also includes the addition of one modified Greenburg Smith impinger and a CPM filter following the water dropout impinger. Figure 1 of Section 18 presents the schematic of the sampling train configured with these changes.

2.1.1 Condensable Particulate Matter. CPM is collected in the water dropout impinger, the modified Greenburg Smith impinger, and the CPM filter of the sampling train as described in this method. The impinger contents are purged with nitrogen (N_2) immediately after sample collection to remove dissolved sulfur dioxide (SO_2) gases from the impinger. The CPM filter is extracted with water and methylene chloride. The impinger solution is then extracted with methylene chloride ($MeCl_2$). The organic and aqueous fractions are dried and the residues are weighed. The total of the aqueous and organic fractions represents the CPM.

2.1.2 Dry Impinger and Additional Filter. The potential artifacts from SO_2 are reduced using a condenser and dropout impinger to separate CPM from reactive gases. No water is added to the impingers prior to the start of sampling. To improve the collection efficiency of CPM, an additional filter (the CPM filter) is placed between the second and third impingers.

3.0 Definitions

3.1 Primary PM. Primary PM (also known as direct PM) means particles that enter the atmosphere as a direct emission from a stack or an open source. Primary PM comprises two components: filterable PM and condensable PM. These two PM components have no upper particle size limit.

3.2 Filterable PM. Filterable PM means particles that are emitted directly by a source as a solid or liquid at stack or release conditions and captured on the filter of a stack test train.

3.3 Primary PM_{10}. Primary PM_{10} (also known as direct PM_{10}, total PM_{10}, PM_{10} or filterable PM_{10}, and condensable PM, individually) means particulate matter with an aerodynamic diameter equal to or less than 10 micrometers.

3.4 Primary $PM_{2.5}$. Primary $PM_{2.5}$ (also known as direct $PM_{2.5}$, total $PM_{2.5}$, $PM_{2.5}$, or filterable $PM_{2.5}$, and condensable PM, individually) means solid particles emitted directly from an air emissions source or activity, or gaseous emissions or liquid droplets from an air emissions source or activity that condense to form particulate matter at ambient temperatures. Direct $PM_{2.5}$ emissions include elemental carbon, directly emitted organic carbon, directly emitted sulfate, directly emitted nitrate, and other inorganic particles (including but not limited to crustal material, metals, and sea salt).

3.5 Condensable PM (CPM). Condensable PM means material that is vapor phase at stack conditions, but which condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack. Note that all condensable PM is assumed to be in the $PM_{2.5}$ size fraction (Reference: Part 51, Subpart Z (51.1000)).

4.0 Interferences [Reserved]

5.0 Safety

Disclaimer: You may have to use hazardous materials, operations, and equipment while performing this method. We do not provide information on appropriate safety and health practices. You are responsible for determining the applicability of regulatory limitations and establishing appropriate safety and health practices. Handle materials and equipment properly.

6.0 Equipment and Supplies

The equipment used in the filterable particulate portion of the sampling train is described in Methods 5 and 17 of Appendix

A-1 through A-3 and A-6 to Part 60, Method 201A in Appendix M to Part 51 and Other Test Method 27. The equipment used in the CPM portion of the train is described in this section.

6.1 Condensable Particulate Sampling Train Components. The sampling train for this method is consistent with the sampling train for collecting filterable particulate using Method 5, 17, 201A, or Other Test Method 27 with the following exceptions or additions:

6.1.1 Condenser and Impingers. You must add the following components to the filterable particulate sampling train: A Method 23 type condenser as described in Section 2.1.2 of Method 23 of Appendix A-8 to Part 60, followed by a dropout impinger or flask, followed by a modified Greenburg-Smith impinger with an open tube tip as described in Section 6.1.1.8 of Method 5.

6.1.2 CPM Filter Holder. The modified Greenburg-Smith impinger is followed by a filter holder that is either glass, stainless steel (316 or equivalent), or Teflon®-coated stainless steel. Commercial size filter holders are available depending on project requirements. Use a commercial filter holder capable of supporting 47 mm or greater diameter filters. Commercial size filter holders contain a Teflon® O-ring, stainless steel, ceramic or Teflon® filter support and a final Teflon® O-ring. At the exit of the CPM filter, install a Teflon®-coated or stainless steel encased thermocouple that is in contact with the gas stream.

6.1.3 Long Stem Impinger Insert. You will need a long stem modified Greenburg Smith impinger insert for the dropout impinger to perform the nitrogen purge of the sampling train.

6.2 Sample Recovery Equipment.

6.2.1 Condensable Particulate Matter Recovery.

6.2.1.1 Nitrogen Purge Line. You must use inert tubing and fittings capable of delivering at least 20 liters/min of nitrogen gas to the impinger train from a standard gas cylinder (see Figure 2 of Section 18). You may use standard 0.6 cm (1/4-in.) tubing and compression fittings in conjunction with an adjustable pressure regulator and needle valve.

6.2.1.2 Rotameter. You must use a rotameter capable of measuring gas flow up to 20 L/min. The rotameter must be accurate to 5 percent of full scale.

6.2.1.3 Ultra-high Purity (UHP) Nitrogen Gas. Compressed ultra-pure nitrogen, regulator, and filter must be capable of providing at least 20 L/min purge gas for 1 hour through the sampling train.

6.3 Analysis. The following equipment is necessary for CPM sample recovery and analysis:

6.3.1 Separatory Funnel. Glass, 1 liter.

6.3.2 Weighing Tins. 50 mL.

6.3.3 Glass Beakers. 300 to 500 mL.

6.3.4 Drying Equipment. Hot plate or oven with temperature control.

6.3.5 Pipets. 5 mL.

6.3.6 Burette. Glass, 0 to 100 mL in 0.1 mL graduations.

6.3.7 Analytical Balance. Analytical balance capable of weighing 0.0001 g (0.1 milligram). For extremely low emission sources, a balance capable of weighing 0.00001 g (0.01 milligram) may be required.

6.3.8 pH Meter. A meter capable of determining the acidity of liquid within 0.1 pH units.

7.0 Reagents and Standards

7.1 Sample Collection. To collect a sample, you will need a Teflon® filter, crushed ice, and silica gel. You must also have water and nitrogen gas to purge the sampling train. You will find additional information on each of these items in the following summaries.

7.1.1 Filter. You must use a Teflon® membrane filter that does not have an organic binder. The filter must also have an efficiency of at least 99.95 percent (<0.05 percent penetration) on 0.5 micron particles. You may use test data from the supplier's quality control program to document filter efficiency. If the source you are sampling has SO_2 or sulfur trioxide (SO_3) emissions, then you must use a filter that will not react with SO_2 or SO_3. Depending on your application and project data quality objectives (DQOs), filters are commercially available in 47 mm and larger sizes.

7.1.2 Silica Gel. Use an indicating-type silica gel of 6 to 16 mesh. We must approve other types of desiccants (equivalent or better) before you use them. Allow the silica gel to dry for 2 hours at 175°C (350°F) if it is being reused. You do not have to dry new silica gel.

7.1.3 Water. Use deionized distilled ultra-filtered water (to conform to ASTM D1193-06, Type 1 water or equivalent) (incorporated by reference) to recover material caught in the impinger, if required.

7.1.4 Crushed Ice. Obtain from the best readily available source.

7.1.5 Nitrogen Gas. Use Ultra-High Purity (UHP) compressed nitrogen or equivalent to purge the sampling train. The compressed nitrogen you use to purge the sampling train must contain no more than 1 ppm oxygen, 1 ppm total hydrocarbons as carbon, and 2 ppm moisture.

7.2 Sample Recovery and Analytical Reagents. You will need acetone, $MeCl_2$, anhydrous sodium sulfate, ammonia hydroxide (NH_4OH), and deionized water for the sample recovery and analysis. Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. If such specifications are not available, then use the best available grade. Find additional information on each of these items in the following paragraphs:

7.2.1 Acetone. Use acetone that is stored in a glass bottle. Do not use acetone from a metal container because it normally produces a high residue blank. You must use acetone with blank values < 1 ppm, by weight, residue.

7.2.2 Methylene Chloride, American Chemical Society (ACS) grade. You must use methylene chloride with a blank value < 1.5 ppm, by weight, residue.

7.2.3 Water. Use deionized distilled ultra-filtered water (to conform to ASTM D1193-06, Type 1 or equivalent) (incorporated by reference) to recover material caught in the impinger.

7.2.4 Condensable Particulate Sample Desiccant. Use indicating-type anhydrous sodium sulfate to desiccate water and organic extract residue samples.

7.2.5 Ammonium Hydroxide. Use NIST traceable or equivalent (0.1 N) NH_4OH.

7.2.6 Standard Buffer Solutions. Use one buffer with a neutral pH and a second buffer solution with an acid pH.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Qualifications. This is a complex test method. To obtain reliable results, you must be trained and experienced with in-stack filtration systems (such as, cyclones, impactors, and thimbles) and impinger and moisture train systems.

8.2 Preparations. You must clean glassware prior to field tests as described in Section 8.4, including baking glassware at 300°C for 6 hours prior to use. Cleaned, baked glassware is used at the start of each new source category tested. Analyze reagent blanks (water, acetone, and methylene chloride) before field tests to verify low blank concentrations. Follow the pretest preparation instructions in Section 8.1 of Method 5.

8.3 Site Setup. You must follow the procedures required by filterable particulate sampling method setup run in conjunction with this method including:

(a) Determining the sampling site location and traverse points.

(b) Calculating probe/cyclone blockage.

(c) Verifying the absence of cyclonic flow.

(d) Completing a preliminary velocity profile, and selecting a nozzle(s).

8.3.1 Sampling Site Location and Traverse Point. Determination. Follow the standard procedures in Method 1 of Appendix A-1 to Part 60 to select the appropriate sampling site.

Then you must do all of the following:

8.3.1.1 Sampling site. Choose a location that maximizes the distance from upstream and downstream flow disturbances.

8.3.1.2 Traverse points. Use the recommended maximum number of traverse points at any location, as found in Methods 5, 17, or 201A, whichever is applicable to your test requirements. You must prevent the disturbance and capture of any solids accumulated on the inner wall surfaces by maintaining a 1-inch distance from the stack wall (½ inch for sampling locations less than 24 inches in diameter).

8.4 Sampling Train Preparation. A schematic of the sampling train used in this method is shown in Figure 1 of Section 18. All sampling train glassware must be cleaned prior to the test with soap and water, and rinsed using tap water, deionized water, acetone, and finally, $MeCl_2$. It is important to completely remove all silicone grease from areas that will be exposed to the $MeCl_2$ rinse during sample recovery. After cleaning, you must bake glassware at 300°C for 6 hours prior to each source type sampled. Prior to each sampling run, the train glassware used to collect condensable particulate matter must be rinsed thoroughly with deionized, distilled ultra-filtered water that conforms to ASTM D1193-06, Type 1 or equivalent (incorporated by reference).

8.4.1 Condenser and Dropout Impinger. Add a Method 23 type condenser and a condensate dropout impinger without bubbler tube after the final in-stack or out-of-stack hot filter assembly. The Method 23 type stack gas condenser is described in Section 2.1.2 of Method 23. It must be capable of cooling the stack gas to less than 30°C (85°F).

8.4.2 Backup Impinger. The dropout impinger is followed by a modified Greenburg Smith impinger with no taper (see Figure 1 of Section 18). Place the dropout and other impingers in an insulated box with water at ≤ 30°C (≤ 85°F). At the start of the tests, the water dropout and backup impinger must be clean, without any water or reagent added.

8.4.3 CPM Filter. Place a filter holder with a filter meeting the requirements in Section 6.1.2 following the modified Greenburg-Smith impinger. The connection between the CPM filter and the moisture trap impinger includes a thermocouple fitting that provides a leak-free seal between the thermocouple and the stack gas. (**Note:** A thermocouple well is not sufficient for this purpose because the Teflon® or steel encased thermocouple must be in contact with the sample gas).

8.4.4 Moisture Traps. You must use a modified Greenburg-Smith impinger containing 100 mL of water or the alternative described in Method 5 followed by an impinger containing silica gel to collect moisture that passes through the CPM filter. You must maintain the gas temperature below 20°C (68 °F) at the exit of the moisture traps.

8.4.5 Silica Gel Trap. Place 200 to 300 g of silica gel in each of several air-tight containers. Weigh each container, including silica gel, to the nearest 0.5 g, and record this weight on the filterable particulate data sheet. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

8.4.6 Leak-Check (Pretest). Use the procedures outlined in Method 5, 17, 201A, or OTM 27 as appropriate to leak check the entire sampling system. Specifically, perform the following procedures:

8.4.6.1 Sampling Train. You must pretest the entire sampling train for leaks. The pretest leak-check must have a leak rate of not more than 0.02 actual cubic feet per minute (ACFM) or 4 percent of the average sample flow during the test run, whichever is less. Additionally, you must conduct the leak-check at a vacuum equal to or greater than the vacuum anticipated during the test run. Enter the leak-check results on the field test data sheet for the filterable particulate method. (**Note**: Conduct leak-checks during port changes only as allowed by the filterable particulate method used with this method).

8.4.6.2 Pitot Tube Assembly. After you leak-check the sample train, perform a leak-check of the pitot tube assembly. Follow the procedures outlined in Section 8.4.1 of Method 5.

8.5 Sampling Train Operation. Operate the sampling train as described in the filterable particulate sampling method (i.e., Method 5, 17, or 201A) with the following additions or exceptions:

8.5.1 CPM Filter Assembly. On the field data sheet for the filterable particulate method, record the CPM filter temperature readings at the beginning of each sample time increment and when sampling is halted. Maintain the CPM filter ≤30°C (≤85°F) during sample collection.

8.5.2 Leak-Check Probe/Sample Train Assembly (Post-Test). Conduct the leak rate check according to the filterable particulate sampling method used during sampling. If required, conduct the leak-check at a vacuum equal to or greater than the maximum vacuum achieved during the test run. If the leak rate of the sampling train exceeds 0.02 ACFM or 4 percent of the average sampling rate during the test run (whichever is less), then the run is invalid and you must repeat it.

8.5.3 Post-Test Nitrogen Purge. As soon as possible after the post-test leak-check, detach the probe, any cyclones, and in-stack or hot filters from the condenser and impinger train. Leave the ice in the second impinger box to prevent removal of moisture during the purge. If necessary, add more ice during the purge to maintain the gas temperature measured at the exit of the silica gel impinger below 20°C (68°F).

8.5.3.1 If no water was collected before the CPM filter, then you may skip the remaining purge steps and proceed with sample recovery (see Section 8.5.4).

8.5.3.2 Replace the short stem impinger insert with a modified Greenberg Smith impinger insert. The impinger tip length must extend below the water level in the impinger catch. If insufficient water was collected, you must add a measured amount of degassed deionized, distilled ultra-filtered ASTM D1193-06, Type 1 or equivalent) (incorporated by reference) water until the impinger tip is at least 1 cm below the surface of the water. You must record the amount of water added to the dropout impinger (see Figure 4 of Section 18) to correct the moisture content of the effluent gas. (**Note:** Prior to use, water must be degassed using a nitrogen purge bubbled through the water for at least 15 minutes to remove dissolved oxygen).

8.5.3.3 With no flow of gas through the clean purge line and fittings, attach the line to a purged inline filter. Connect the filter outlet to the input of the impinger train (see Figure 2 of Section 18). To avoid over- or underpressurizing the impinger array, slowly commence the nitrogen gas flow through the line while simultaneously opening the meter box pump valve(s). Adjust the pump bypass and nitrogen delivery rates to obtain the following conditions: (1) 20 liters/min or ΔH@, and (2) a positive overflow rate through the rotameter of less than 2 liters/min. Condition (2) guarantees that the nitrogen delivery system is operating at greater than ambient pressure and prevents the possibility of passing ambient air (rather than nitrogen) through the impingers. During the purge, continue operation of the condenser recirculation pump, and heat or cool the water surrounding the first two impingers to maintain the gas temperature measured at the exit of the CPM filter below 30°C (85°F). Continue the purge under these conditions for 1 hour, checking the rotameter and ΔH value(s) periodically. After 1 hour, simultaneously turn off the delivery and pumping systems.

8.5.3.4 Weigh the liquid, or measure the volume of the liquid collected in the dropout, impingers, and silica trap. Measure the liquid in the first impinger to within 1 mL using a clean graduated cylinder or by weighing it to within 0.5 g using a balance. Record the volume or weight of liquid present to be used to calculate the moisture content of the effluent gas in the field log notebook.

8.5.3.5 If a balance is available in the field, weigh the silica impinger to within 0.5 g. Note the color of the indicating silica gel in the last impinger to determine whether it has been completely spent, and make a notation of its condition in the field log book.

8.5.4 Sample Recovery.

8.5.4.1 Recovery of Filterable Particulate Matter. Recovery of filterable particulate matter involves the quantitative transfer of particles according to the filterable particulate sampling method (i.e., Method 5, 17 or 201A).

8.5.4.2 CPM Container #1, Aqueous Liquid Impinger Contents. Quantitatively transfer liquid from the dropout and the impinger prior to the CPM filter into a clean sample bottle (glass or plastic). Rinse the probe extension, condenser, each impinger and the connecting glassware, and the front half of the CPM filter housing twice with water. Recover the rinse water, and add it to the same sample bottle. Mark the liquid level on the bottle. CPM Container #1 holds the water soluble CPM captured in the impingers.

8.5.4.3 CPM Container #2, Organic Rinses. Follow the water rinses of the probe extension, condenser, each impinger and all of the connecting glassware and front half of the CPM filter with an acetone rinse. Then repeat the entire procedure with two rinses of $MeCl_2$, and save both solvents in a separate glass container identified as CPM Container #2. Mark the liquid level on the jar.

8.5.4.4 CPM Container #3, CPM filter Sample. Use tweezers and/or clean disposable surgical gloves to remove the filter from the CPM filter holder. Place the filter in the petri dish identified as CPM Container #3.

8.5.4.5 CPM Container #4, Cold Impinger Water. You must weigh or measure the volume of the contents of CPM Container #4 either in the field or during sample analysis (see Section 11.2.3). If the water from the cold impinger has been weighed in the field, it can be discarded. Otherwise, quantitatively transfer liquid from the cold impinger that follows the CPM filter into a clean sample bottle (glass or plastic). Mark the liquid level on the bottle. This container holds the remainder of the liquid water from the emission gases.

8.5.4.6 CPM Container #5, Silica Gel Absorbent. You must weigh the contents of CPM Container #5 in the field or during sample analysis (see Section 11.2.4). If the silica gel has been weighed in the field to measure water content, then it can be discarded. Otherwise, transfer the silica gel to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of silica gel dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel.

8.5.4.7 CPM Container #6, Acetone Rinse Blank. Take 150 mL of the acetone directly from the wash bottle you used, and place it in CPM Container #6, labeled Acetone Rinse Blank (see Section 11.2.5 for analysis). Mark the liquid level on the bottle.

8.5.4.8 CPM Container #7, Water Rinse Blank. Take 150 mL of the water directly from the wash bottle you used, and place it in CPM Container #7, labeled Water Rinse Blank (see Section 11.2.6 for analysis). Mark the liquid level on the bottle.

8.5.4.9 CPM Container #8, Methylene Chloride Rinse Blank. Take 150 mL of the $MeCl_2$ directly from the wash bottle you used, and place it in CPM Container #8, labeled Methylene Chloride Rinse Blank (see Section 11.2.7 for analysis). Mark the liquid level on the bottle.

8.5.5 Transport procedures. Containers must remain in an upright position at all times during shipping. You do not have to ship the containers under dry or blue ice. However, samples must be maintained at or below 30°C (85°F) during shipping.

9.0 Quality Control

9.1 Daily Quality Checks. You must perform daily quality checks of field log books and data entries and calculations using data quality indicators from this method and your site-specific test plan. You must review and evaluate (1) recorded and transferred raw data, (2) calculations, and (3) documentation of testing procedures. You must initial or sign log book pages and data entry forms that were reviewed.

9.2 Calculation Verification. Verify the calculations by independent, manual checks. You must flag any suspect data and identify the nature of the problem and potential effect on data quality. After you complete the test, prepare a data summary and compile all the calculations and raw data sheets.

9.3 Conditions. You must document data and information on the process unit tested, the particulate control system used to control emissions, any non-particulate control system that may affect particulate emissions, the sampling train conditions, and weather conditions. Discontinue the test if the operating conditions may cause non-representative particulate emissions.

9.4 Health and Safety Plan. Develop a health and safety plan to ensure the safety of your employees who are on-site conducting the particulate emission test. Your plan must conform with all applicable Occupational Safety and Health Administration (OSHA), Mine Safety and Health Administration (MSHA), and Department of Transportation (DOT) regulatory requirements. The procedures must also conform to the plant health and safety requirements.

9.5 Calibration Checks. Perform calibration check procedures on analytical balances each time they are used.

9.6 Glassware. Use class A volumetric glassware for titrations, or calibrate your equipment against National Institute of Standards and Technology (NIST) traceable glassware.

9.7 Analytical Balance. Check the calibration of your analytical balance each day you weigh CPM samples. You must use NIST Class S weights at a mass approximately equal to the weight of the sample plus container you will weigh.

9.8 Reagent Blanks. You must run blanks of water, acetone, and methylene chloride used for field recovery and sample analysis. Analyze at least one sample (100 mL minimum) of each reagent that you plan to use for sample recovery and analysis before you begin testing. Running blanks before field use will verify low blank concentrations, thereby reducing the potential for a high field blank on test samples.

9.9 Field Reagent Blanks. You must run at least one field blank of water, acetone, and methylene chloride you use for field recovery. Running independent reagent field blanks will verify that low blank concentrations were maintained during field solvent use and demonstrate that reagents have not been contaminated during field tests.

9.10 Field Train Blank. You must recover a minimum of one field train blank for each set of compliance tests at the facility. You must assemble the sampling train as it will be used for testing. Prior to the purge, you must add 100 mL of water to the first impinger and record this data on Figure 3. You must purge the assembled train as described in Sections 8.5.3.2. and 8.5.3.3. You must recover field train blank samples as described in Section 8.5.4. From the field sample weight, you will subtract the condensable particulate mass you determine with this blank train or 0.002 g (2.0 mg), whichever is less.

9.11 Audit Procedure. Concurrent with compliance sample analysis, and if available, analyze audit material to evaluate the technique of the analyst and the standards preparation. Use the same staff, analytical reagents, and analytical system for both compliance samples and the EPA audit sample. If this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

9.12 Audit Samples. As of the publication date of this test method, audit materials are not available. If audit materials become available, audit samples will be supplied only to enforcement agencies for compliance tests. Audit samples can be requested by a State agency. Audit materials are requested online by authorized regulatory authorities at the following internet address: http://www.sscap.net/. Authorization can be obtained by contacting an EPA Emission Measurement Center QA Team Member listed on the EPA TTN Web site at the following internet address: http://www.epa.gov/ttn/emc/email.html#qaqc. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

9.13 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency.

10.0 Calibration and Standardization

Maintain a log of all condensable particulate sampling and analysis calibrations. Include copies of the relevant portions of the calibration and field logs in the final test report.

10.1 Thermocouple Calibration. You must calibrate the thermocouples using the procedures described in Section 10.1.4.1.2 of Method 2 of Appendix A-1 to Part 60.

Calibrate each temperature sensor at a minimum of three points over the anticipated range of use against an NIST-traceable mercury-in-glass thermometer.

10.2 Ammonium Hydroxide. The 0.1 N NH_4OH used for titrations in this method is made as follows: Add 7 mL of concentrated (14.8 M) NH_4OH to l liter of water. Standardize against standardized 0.1 N H_2SO_4, and calculate the exact normality using a procedure parallel to that described in Section 5.5 of Method 6 of Appendix A-4 to 40 CFR part 60. Alternatively, purchase 0.1 N NH_4OH that has been standardized against a NIST reference material. Record the normality on the Condensable Particulate Matter Work Table (see Figure 5 of Section 18).

11.0 Analytical Procedures

11.1 Analytical Data Sheets. Record the filterable particulate field data on the appropriate (i.e., Method 5, 17, or 201A) analytical data sheets. Alternatively, data may be recorded electronically using software applications such as the Electronic Reporting Tool (ERT), available at the following internet address: http://www.epa.gov/ttn/chief/ert/ert_tool.html. Record the condensable particulate data on the Condensable Particulate Matter Work Table (see Figure 5 of Section 18).

Measure the liquid in all containers either volumetrically to ± 1 mL or gravimetrically to ± 0.5 g. Confirm on the filterable particulate analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Condensable Particulate Matter Analysis. See the flow chart in Figure 6 of Section 18 for the steps to process and combine fractions from the CPM train.

11.2.1 Container #3, CPM Filter Sample. Extract the filter recovered from the low temperature portion of the train, and combine the extracts with the organic and inorganic fractions resulting from the aqueous impinger sample recovery. If the sample was collected by Method 17 because the stack temperature was below 30°C (85°F), process the filter extracts as described in this section without combination with any other portion from the train.

11.2.1.1 Extract the water soluble (aqueous or inorganic) CPM from the CPM filter as described in this section. Fold the CPM filter in quarters, and place it into a 50 mL extraction tube. Add sufficient deionized ultra-filtered water to cover the filter (e.g., 10 mL of water). Place the extractor tube into a sonication bath and extract the water soluble material for a minimum of 2 minutes. Combine the aqueous extract with the contents of Container #1. Repeat this extraction step twice for a total of three extractions.

11.2.1.2 Extract the organic soluble CPM from the CPM filter as described in this section. Add sufficient methylene chloride to cover the filter (e.g., 10 mL of water). Place the extractor tube into a sonication bath and extract the organic soluble material for a minimum of 2 minutes. Combine the organic extract with the contents of Container #2. Repeat this extraction step twice for a total of three extractions.

11.2.2 CPM Container #1, Aqueous Liquid Impinger Contents. Analyze the water soluble CPM in Container 1 as described in this section. Place the contents of Container #1 into a separatory funnel. Add approximately 30 mL of $MeCl_2$ to the funnel, mix well, and drain off the lower organic phase. Repeat this procedure twice with 30 mL of $MeCl_2$ each time combining the organic phase from each extraction. Each time, leave a small amount of the organic/$MeCl_2$ phase in the separatory funnel, ensuring that no water is collected in the organic phase. This extraction should yield about 90 mL of organic extract.

11.2.2.1 CPM Container #2. Combine the organic extract from Container #1 with the organic train rinse in Container 2.

11.2.2.2 Organic Fraction Weight Determination. Place the organic phase in a clean glass beaker. Evaporate the organic extract at room temperature (not to exceed 30°C (85°F)) and pressure in a laboratory hood to not less than 10 mL.

Quantitatively transfer the beaker contents to a 50-mL preweighed tin, and evaporate to dryness at room temperature (not to exceed 30°C (85°F)) and pressure in a laboratory hood. Following evaporation, desiccate the organic fraction for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least 6 hours to a constant weight (i.e., ≤ 0.5 mg change from previous weighing), and report results to the nearest 0.1 mg on the Condensable Particulate Matter Work Table (see Figure 5 of Section 18).

11.2.2.3 Inorganic Fraction Weight Determination. Transfer the aqueous fraction from the extraction to a clean 500-mL or smaller beaker. Evaporate to no less than 10 mL liquid on a hot plate or in the oven at 105°C, and allow to dry at room temperature (not to exceed 30°C (85°F). You must ensure that water and volatile acids have completely evaporated before neutralizing nonvolatile acids in the sample. Redissolve the residue in 100 mL of deionized distilled ultra-filtered water (ASTM D1193-06, Type 1 water or equivalent)(incorporated by reference).

11.2.2.4 Use titration to neutralize acid in the sample and remove water of hydration. Calibrate the pH meter with the neutral and acid buffer solutions; then titrate the sample with 0.1N NH_4OH to a pH of 7.0, as indicated by the pH meter. Record the volume of titrant used on the Condensable Particulate Matter

Work Table (see Figure 5 of Section 18).

11.2.2.5 Using a hot plate or an oven at 105°C, evaporate the aqueous phase to approximately 10 mL. Quantitatively transfer the beaker contents to a 50-mL preweighed tin, and evaporate to dryness at room temperature (not to exceed 30°C (85°F)) and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least 6 hours to a constant weight (i.e., $\leq$ 0.5 mg change from previous weighing), and report results to the nearest 0.1 mg on the Condensable Particulate Matter Work Table (see Figure 5 of Section 18).

11.2.2.6 Calculate the correction factor to subtract the $NH4^{+}$ retained in the sample using Equation 1 in Section 12.

11.2.3 CPM Container #4, Cold Impinger Water. If the amount of water has not been determined in the field, note the level of liquid in the container, and confirm on the filterable particulate analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in Container #4 either volumetrically to ± 1 mL or gravimetrically to ± 0.5 g, and record the volume or weight on the filterable particulate analytical data sheet of the filterable particulate matter test method.

11.2.4 CPM Container #5, Silica Gel Absorbent. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field. Record the weight on the filterable particulate analytical data sheet of the filterable particulate matter test method.

11.2.5 Container #6, Acetone Field Rinse Blank. Use 100 mL of acetone from the blank container for this analysis. If insufficient liquid is available or if the acetone has been lost due to container breakage, either void the sample, or use methods, subject to the approval of the Administrator, to correct the final results. Transfer 100 mL of the acetone to a clean 250-mL beaker. Evaporate the acetone at room temperature (not to exceed 30°C (85°F)) and pressure in a laboratory hood to approximately 10 mL. Quantitatively transfer the beaker contents to a 50-mL preweighed tin, and evaporate to dryness at room temperature (not to exceed 30°C (85°F)) and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least 6 hours to a constant weight (i.e., ≤ 0.5 mg change from previous weighing), and report results to the nearest 0.1 mg on Figure 3.

11.2.6 Water Rinse Field Blank, Container #7. Use 100 mL of the water from the blank container for this analysis. If insufficient liquid is available, or if the water has been lost due to container breakage, either void the sample, or use methods, subject to the approval of the Administrator, to correct the final results. Transfer the water to a clean 250-mL beaker, and evaporate to approximately 10 mL liquid in the oven at 105°C. Quantitatively transfer the beaker contents to a clean preweighed 50-mL tin, and evaporate to dryness at room temperature (not to exceed 30°C (85°F)) and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least 6 hours to a constant weight (i.e., ≤ 0.5 mg change from previous weighing) and report results to the nearest 0.1 mg on Figure 3.

11.2.7 Methylene Chloride Field Reagent Blank, Container #8. Use 100 mL of $MeCl_2$ from the blank container for this analysis. Transfer 100 mL of the $MeCl_2$ to a clean 250-mL beaker. Evaporate the methylene chloride at room temperature (not to exceed 30°C (85°F)) and pressure in a laboratory hood to approximately 10 mL. Quantitatively transfer the beaker contents to a 50-mL preweighed tin, and evaporate to dryness at room temperature (not to exceed 30°C (85°F)) and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least 6 hours to a constant weight (i.e., ≤ 0.5 mg change from previous weighing), and report results to the nearest 0.1 mg on Figure 3.

12.0 Calculations and Data Analysis

12.1 Nomenclature. Report results in International System of Units (SI units) unless the regulatory authority for compliance testing specifies English units. The following nomenclature is used.

$\Delta H_{@}$ = Pressure drop across orifice at flow rate of 0.75 SCFM at standard conditions, in. W.C. [**Note:** specific to each orifice and meter box].
18.03 = mg/milliequivalents for ammonium ion.
ACFM = Actual cubic feet per minute.
C_{cpm} = Concentration of the condensable particulate matter in the stack gas, dry basis, corrected to standard conditions, milligrams/dry standard cubic foot.
m_c = Mass of the NH_4^+ added to sample to form ammonium sulfate, mg.
m_{cpm} = Mass of the total condensable particulate matter, mg.
m_{fb} = Mass of field train total CPM blank, mg
m_i = Mass of inorganic CPM matter, mg.
m_{ib} = Mass of field train inorganic CPM blank, mg.
m_o = Mass of organic CPM, mg.
m_{ob} = Mass of organic field train blank, mg.
m_r = Mass of dried sample from inorganic fraction, mg.
N = Normality of ammonium hydroxide titrant.
$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dry standard cubic meter (dscm) or dry standard cubic foot (dscf) as defined in Equation 5-1 of Method 5.

V_t = Volume of NH_4OH titrant, mL.
V_p = Volume of water added during train purge.

12.2 Calculations. Use the following equations to complete the calculations required in this test method. Enter the appropriate results from these calculations on the Condensable Particulate Matter Work Table (see Figure 5 of Section 18).

12.2.1 Mass of ammonia correction. Correction for ammonia added during titration of 100 mL aqueous CPM sample. This calculation assumes no waters of hydration.

$$m_c = 17.03 \text{ x } V_t \text{ x } N \qquad \text{Eq. 1}$$

12.2.2 Mass of the Field Blank (mg). Per Section 9.9, the mass of the field blank, m_{fb}, shall not exceed 2.0 mg.

$$m_{fb} = m_{ib} + m_{ob} \qquad \text{Eq. 2}$$

12.2.3 Mass of Inorganic CPM (mg).

$$m_i = m_r + m_c \qquad \text{Eq. 3}$$

12.2.4 Total Mass of CPM (mg).

$$m_{cpm} = m_i + m_o - m_{fb} \qquad \text{Eq. 4}$$

12.2.5 Concentration of CPM (mg/dscf).

$$C_{cpm} = \frac{m_{cpm}}{V_{m(std)}} \qquad \text{Eq. 5}$$

12.3 Emissions Test Report. Include the following list of conventional elements in the emissions test report.

(a) Emission test description including any deviations from this protocol.

(b) Summary data tables on a run-by-run basis that include the condensable particulate mass.

(c) Flowchart of the process or processes tested.

(d) Sketch of the sampling location.

(e) Preliminary traverse data sheets including cyclonic flow checks.

(f) Raw field data sheets and copies of field log pages.

(g) Laboratory analytical sheets and case narratives.

(h) Pretest and post test reagent blank results.

(i) Sample calculations.

(j) Pretest and post-test calibration data.

(k) Chain of custody forms.

(l) Documentation of process and air pollution control system data.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management

Solvent and water are evaporated in a laboratory hood during analysis. No liquid waste is generated in the performance of this method. Organic solvents used to clean sampling equipment should be managed as RCRA organic waste.

16.0 Alternative Procedures [Reserved]

17.0 References

1. U.S. Environmental Protection Agency, Federal Reference Methods 1 through 5 and Method 17, 40 CFR 60, Appendix A-1 through A-3 and A-6.

2. Richards, J., T. Holder, and D. Goshaw. "Optimized Method 202 Sampling Train to Minimize the Biases Associated with Method 202 Measurement of Condensable Particulate Matter Emissions." Paper presented at Air & Waste Management Association Hazardous Waste Combustion Specialty Conference. St. Louis, Missouri. November 2-3, 2005.

3. DeWees, W.D., S.C. Steinsberger, G.M. Plummer, L.T. Lay, G.D. McAlister, and R.T. Shigehara. "Laboratory and Field Evaluation of the EPA Method 5 Impinger Catch for Measuring Condensable Matter from Stationary Sources." Paper presented at the 1989 EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants. Raleigh, North Carolina. May 1-5, 1989.

4. DeWees, W.D. and K.C. Steinsberger. "Method Development and Evaluation of Draft Protocol for Measurement of Condensable Particulate Emissions." Draft Report. November 17, 1989.

5. Texas Air Control Board, Laboratory Division. "Determination of Particulate in Stack Gases Containing Sulfuric Acid and/or Sulfur Dioxide." Laboratory Methods for

Determination of Air Pollutants. Modified December 3, 1976.

6. Nothstein, Greg. Masters Thesis. University of Washington. Department of Environmental Health. Seattle, Washington.

7. "Particulate Source Test Procedures Adopted by Puget Sound Air Pollution Control Agency Board of Directors." Puget Sound Air Pollution Control Agency, Engineering Division. Seattle, Washington. August 11, 1983.

8. Commonwealth of Pennsylvania, Department of Environmental Resources. Chapter 139, Sampling and Testing (Title 25, Rules and Regulations, Part I, Department of Environmental Resources, Subpart C, Protection of Natural Resources, Article III, Air Resources). January 8, 1960.

9. Wisconsin Department of Natural Resources. Air Management Operations Handbook, Revision 3. January 11, 1988.

10. U.S. Environmental Protection Agency, "Laboratory Evaluation of Method 202 to Determine Fate of SO2 in Impinger Water," EPA Contract No. 68-D-02-061, Work Assignment 3-14, September 30, 2005.

11. U.S. Environmental Protection Agency, "Evaluation and Improvement of Condensable Particulate Matter Measurement," EPA Contract No. EP-D-07-097, Work Assignment 2-03, October 2008.

12. Electric Power Research Institute (EPRI), "Laboratory Comparison of Methods to Sample and Analyze Condensable

Particulate Matter," EPRI Agreement EP-P24373/C11811 Condensable Particulate Methods: EPRI Collaboration with EPA, October 2008.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

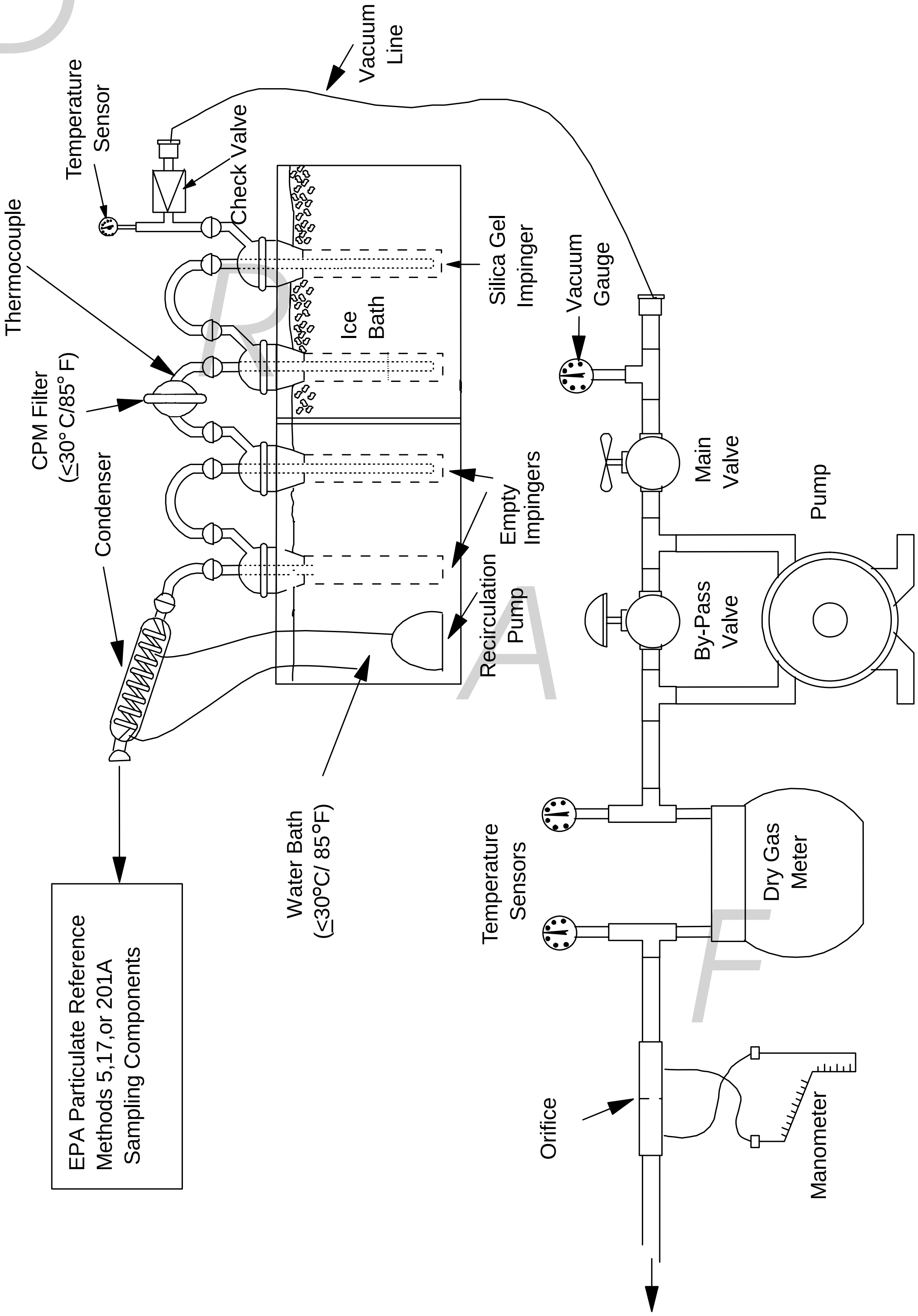

Figure 1. Schematic of Condensable Particulate Sampling Train

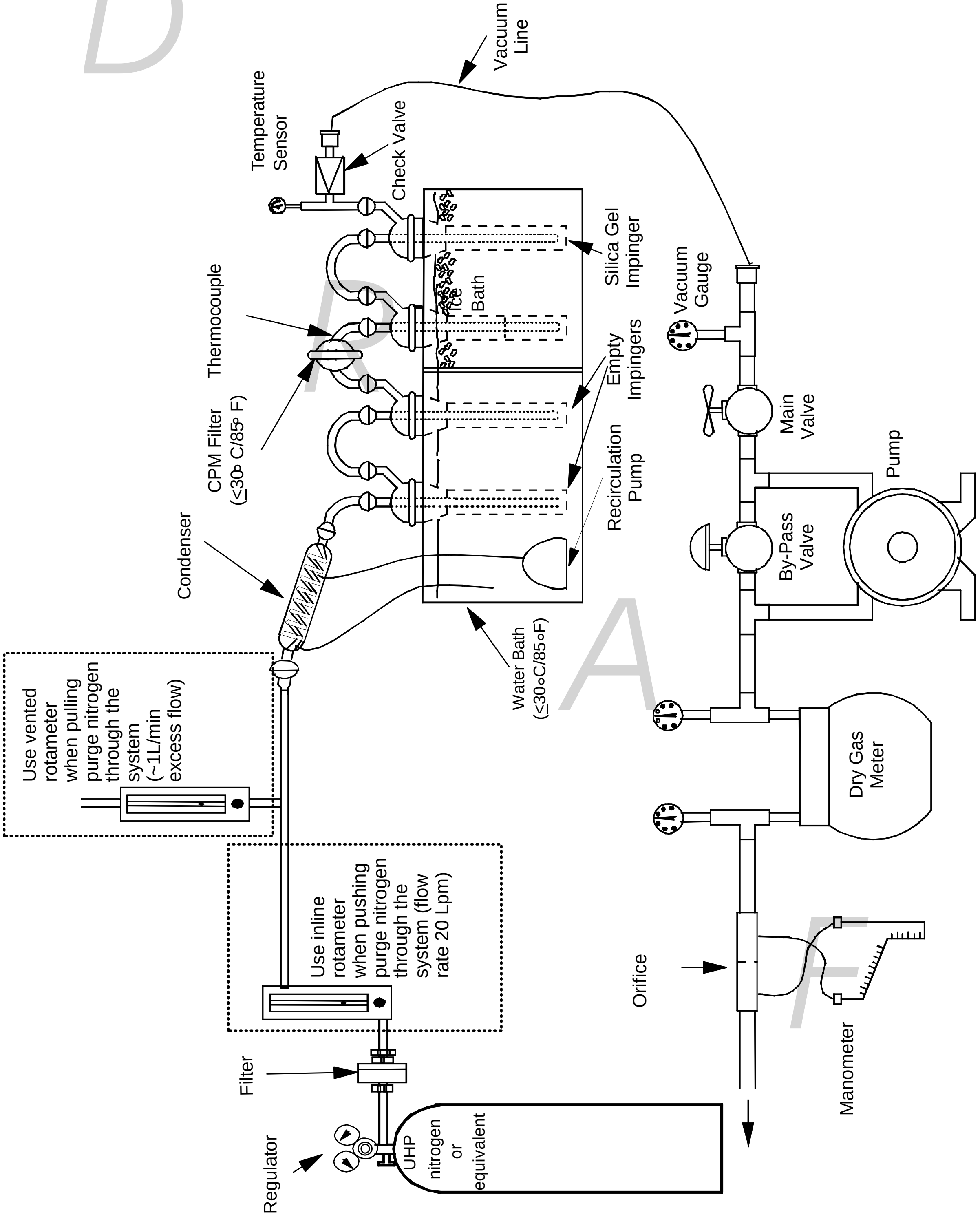

Figure 2. Nitrogen Purge Train Configuration

Field Train Blank Condensable Particulate Calculations	
Plant	
Date	
Blank No.	
CPM Filter No.	
Water volume added to purge train (V_p)	ml
Field Reagent Blank Mass	
Water (Section 11.2.6)	mg
Acetone (Section 11.2.5)	mg
Methylene Chloride (Section 11.2.7)	mg
Field Train Reagent Blank Mass	
Mass of Organic CPM (m_{ob}) (Section 11.2.2.2)	mg
Mass of Inorganic CPM (m_{ib}) (Equation 3)	mg
Mass of the Field Train Blank (not to exceed 2.0 mg) (Equation 2)	mg

Figure 3. Field Train Blank Condensable Particulate Calculations

Other Field Train Sample Condensable Particulate Data	
Plant	
Date	
Run No.	
CPM Filter No.	
Water volume added to purge train [max 50 mL] (V_p)	ml
Date	
Run No.	
CPM Filter No.	
Water volume added to purge train [max 50 mL] (V_p)	ml
Date	
Run No.	
CPM Filter No.	
Water volume added to purge train [max 50 mL] (V_p)	ml

Figure 4. Other Field Train Sample Condensable Particulate Data

Calculations for Recovery of Condensable Particulate Matter (CPM)

Plant ____

Date ____

Run No.____

Sample Preparation - CPM Containers No. 1 and 2 (Section 11.1)

Was significant volume of water lost during transport? Yes or No ______________________

If Yes, measure the volume received. ______________________

Estimate the volume lost during transport. ______________________ mL

Was significant volume of organic rinse lost during transport? Yes or No ______________________

If Yes, measure the volume received. ______________________

Estimate the volume lost during transport. ______________________ mL

For Titration

Normality of NH_4OH (N) (Section 10.2) ______________________ N

Volume of titrant (V_t) (Section 11.2.2.4) ______________________ mL

Mass of NH_4 added (m_c) (Equation 1) ______________________ Mg

For CPM Blank Weights

Inorganic Train Field Blank Mass (m_{ib}) (Section 9.9) ______________________ Mg

Organic Train Field blank Mass (m_{ob}) (Section 9.9) ______________________ Mg

Mass of Train Field Blank (M_{fb}) (max. 2 mg) (Equation 2) ______________________ Mg

For CPM Train Weights

Mass of Organic CPM (m_o) (Section 11.2.2.2) ______________________ mg

Mass of Inorganic CPM (m_i) (Equation 3) ______________________ Mg

Total CPM Mass (m_{cpm}) (Equation 4) ______________________ Mg

Figure 5. Condensable Particulate Matter Work Table

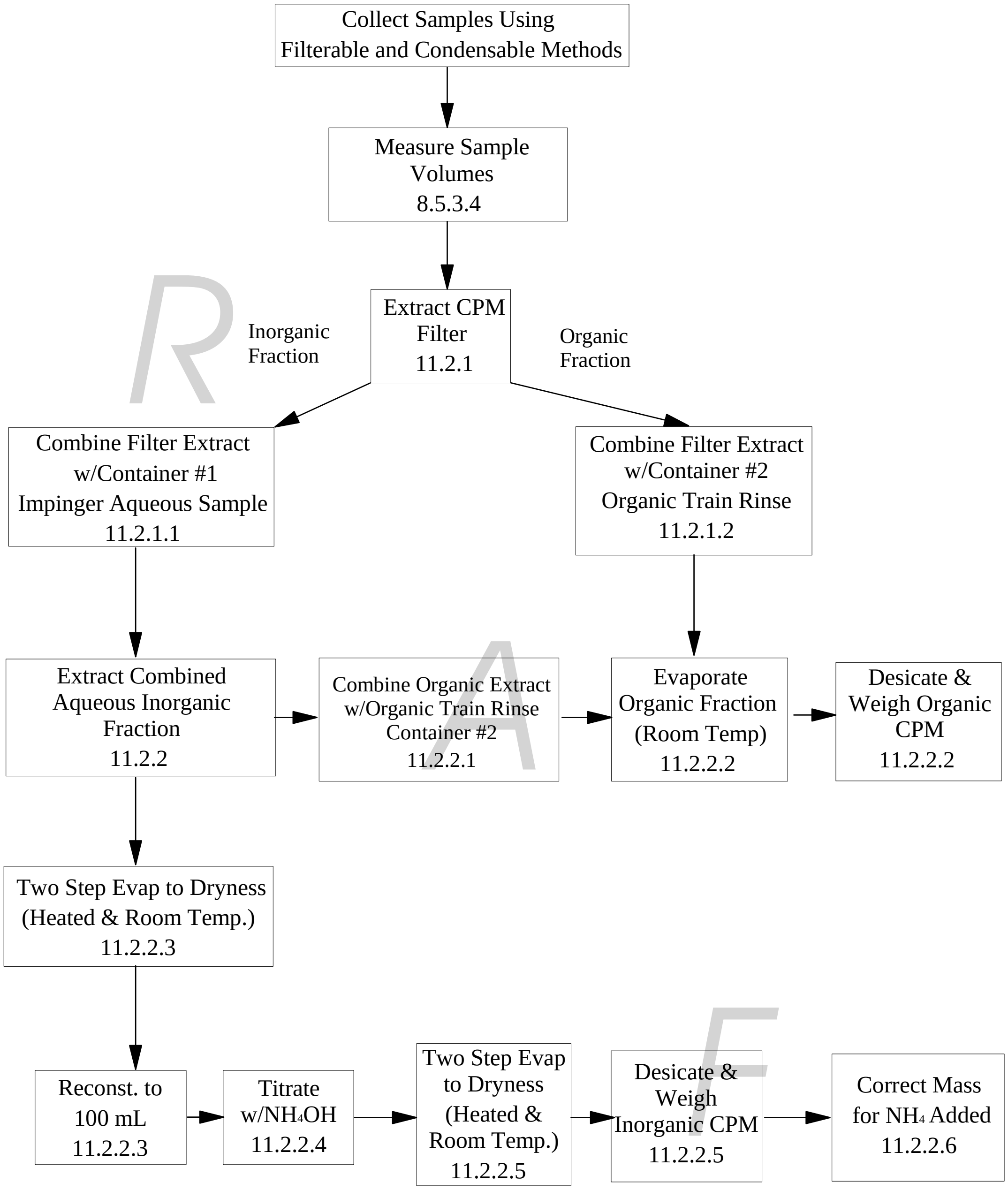

Figure 6. CPM Sample Processing Flow Chart

Appendix D

EPRI Supplement to EPA Laboratory Test Plan and Quality Assurance Project Plan Method 202 Assessment and Evaluation for Bias and Other Uses

Table A-1 [Revised 8-14-08]
EPRI Test Matrix Addendum for CPM Method Evaluation

Test	Methods*	SO_2 (ppmv)	NH_3 (ppmv)	CO_2 (%)	O_2 (%)	H_2O (%)	Nitrogen Oxide Mix (ppmv)	SO_3/ Sulfuric Acid (ppmv)	Inlet Gas Temperature, (°F)
1	A, B	500	0	12	8	10	50	0	300
2	A, B	500	0	12	8	10	50	0	300
3	A, B	500	0	12	8	10	50	0	300
4	A, B	25	0	12	8	15	50	0	140
5	A, B	25	0	12	8	15	50	0	140
6	A, B	25	0	12	8	15	50	0	140
7	A, B	150	0	12	8	15	50	0	140
8	A, B	150	0	12	8	15	50	0	140
9	A, B	150	0	12	8	15	50	0	140
10	A, B	500	0	12	8	15	50	0	300
11	A, B	500	0	12	8	15	50	0	300
12	A, B	500	0	12	8	15	50	0	300
19	B, C	150	0	12	8	10	50	2	300
20	B, C	150	0	12	8	10	50	2	300
21	B, C	150	0	12	8	10	50	2	300
22	B, C	150	0	12	8	15	50	10	300
23	B, C	150	0	12	8	15	50	10	300
24	B, C	150	0	12	8	15	50	10	300
31	B, C	0	0	12	8	10	50	2	300
32	B, C	0	0	12	8	10	50	2	300
33	B, C	0	0	12	8	10	50	2	300
34	B, C	0	0	12	8	15	50	10	300
35	B, C	0	0	12	8	15	50	10	300
36	B, C	0	0	12	8	15	50	10	300
25	B, D	0	0	12	8	10	50	2	300
26	B, D	0	0	12	8	10	50	2	300
27	B, D	0	0	12	8	10	50	2	300
13	B, D	150	0	12	8	10	50	2	300
14	B, D	150	0	12	8	10	50	2	300
15	B, D	150	0	12	8	10	50	2	300
28	B, D	0	0	12	8	15	50	10	300
29	B, D	0	0	12	8	15	50	10	300
30	B, D	0	0	12	8	15	50	10	300
16	B, D	150	0	12	8	15	50	10	300
17	B, D	150	0	12	8	15	50	10	300
18	B, D	150	0	12	8	15	50	10	300

*Methods:

A = Method 202
B = Dry Impinger Modification to M-202
C = Controlled Condensation
D = EPRI Low-temperature Filter Modification to M-202

Gray shaded matrix runs have not been completed.

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EPRI Supplement to EPA Laboratory Test Plan and Quality Assurance Project Plan Method 202 Assessment and Evaluation for Bias and other Uses

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Draft: February 27, 2007

Table of Contents

Section A-1
Description of Stakeholder Contribution

EPRI is participating as a stakeholder and funder in a collaborative research project conducted by the U.S. EPA to develop an alternative to EPA Method 202 for measurement of condensible particulate matter (CPM). The intent of EPA's research is to test methods that could potentially reduce or eliminate the known artifacts produced by Method 202, particularly the conversion of sulfur dioxide (SO_2) to sulfuric acid (H_2SO_4) in the Method 202 impingers. EPRI's objective as a stakeholder is to aid EPA in developing a method that will produce accurate results in coal-fired power plants with state-of-the-art particulate controls, on both scrubbed and unscrubbed units, and on coals with a wide range of sulfur content.

This appendix presents a Supplemental Work Plan describing procedures to be followed by EPA's contractor, Eastern Research Group (ERG), in conducting supplemental tests funded by EPRI. Procedures in the Supplemental Work Plan include:

- Generation and testing of additional flue gas mixtures that represent a broader range of potential coal flue gas conditions, including wet and dry stacks.
- Generating inorganic CPM components (vapor-phase H_2SO_4) to add to the synthetic flue gas tested.
- Tests of methods other than the dry impinger method currently under investigation, including the Controlled Condensation Method and EPRI's Low-temperature Filter modification to correct for SO_2 bias.

Details of this Supplemental Work Plan are presented in Sections A-2 through A-4 below.

The EPRI contact for these supplemental tests is Naomi Goodman, Senior Project Manager (ngoodman@epri.com, 650-855-2193). An alternate contact for technical details in this Supplemental Work Plan is Gary Blythe at URS Corporation (gary_blythe@urscorp.com, 512-419-5321).

Section A-2
Experimental Matrix for EPRI Tests

The current Laboratory Test Plan for the Method 202 Assessment and Evaluation for Bias and Other Uses[1] proposes to test synthetic gas mixtures that are intended to approximate low level (e.g., gas-fired turbine) and elevated (e.g., coal-fired power plant) SO_2 emissions. However, the proposed gas mixtures do not represent the full range of composition of flue gases from coal-fired power plants, particularly in two areas. First, the range of SO_2 concentrations being tested (25 ppmv and 150 ppmv) does not adequately represent power plants that fire low-sulfur coals and are unscrubbed (i.e., no wet or dry flue gas desulfurization (FGD) system to control SO_2 emissions).

The second observation is that the planned flue gas moisture content (5% for all runs) is low for most coals fired in the U.S., and does not include the even higher moisture content that would be encountered in the flue gas from scrubbed units. Based on EPRI's review of the proposed "dry impinger" method, it appears that the amount of flue gas moisture and the amount of SO_2 in the flue gas could each influence the magnitude of any SO_2 bias in the method, so it is important that the full range of both of these variables be tested in the evaluation.

Consequently, EPRI proposes to add two additional synthetic gas moisture levels (10% and 15%) and one additional SO_2 concentration (500 ppmv) to the Method 202 Baseline Evaluation Experimental Matrix shown in Table 4-1 of the current plan.[1] Note that ERG reports that they have conducted some experiments with 8 to 10% moisture in the simulation gas rather than the 5% value shown in Table 4-1. The EPRI proposed experimental matrix has been adjusted to account for test conditions already tested by ERG at 8 to 10% moisture.

Furthermore, EPRI proposes that a measurable amount of SO_3/sulfuric acid (the relative proportions of SO_3 and sulfuric acid in the gas depends on the gas temperature and moisture content) be added to the synthetic gas mixture for selected tests, to determine the ability of each candidate method to quantify inorganic CPM that is actually present in the gas sampled. As an example of the need for such testing, EPRI research shows that under some conditions, SO_3 is not fully retained in the Method 202 impingers, possibly due to incomplete capture of sub-micron sulfuric acid mist that forms at the wet/dry interface in the first water impinger. Any new method that is proposed for measuring CPM needs to demonstrate not only the lack of positive bias, but the ability to quantitatively capture the target constituents.

ERG has stated that they currently are not set up to generate SO_3/sulfuric acid in their laboratory. EPRI is aware of three methods that have been used to inject SO_3/sulfuric acid into synthetic flue gas mixtures in the laboratory, and will work with ERG to identify the one that is most practical to implement for this test series. These methods are:

1) Pass a small amount of bottled gas containing SO_2, nitrogen and oxygen across a vanadium catalyst at high temperature (>1000°F) in a tube furnace, to convert essentially 100% of the SO_2 to SO_3, then adding this stream to the synthetic gas mixture.

2) Use a syringe pump to inject vaporized, dilute sulfuric acid into the heated synthetic gas mixture, and

3) Pass a small amount of nitrogen over a reservoir of oleum. This allows a near equilibrium amount of SO_3 to evaporate into the nitrogen stream, which is then added to the synthetic gas mixture.

These three methods vary in complexity and precision, with the first two being more complex to set up but able to achieve more precise injection rates, while the last is relatively simple to implement but is less precise in injection rate. After discussions with ERG, it was determined that the first method described above would be most straightforward for them to implement. This method is further described in Appendix A to this document.

EPRI's proposed test matrix shown in Table A-1. The matrix includes testing at higher synthetic gas moisture concentrations of 10% and 15%, a higher SO_2 concentration of 500 ppmv, and tests that include SO_3 in the synthetic gas matrix. The matrix also includes testing of two alternative methods to correct for the SO_2 to SO_3 conversion artifact. [Note: Table A-1 was revised on 8-14-08.]

The matrix consists of 36 tests, each employing two sampling trains in parallel. These tests can be grouped into four sets by their primary objective:

- Tests 1 through 12 expand the ERG experimental matrix to challenge the dry impinger method with two higher moisture concentrations and include a higher SO_2 concentration. The dry impinger method is run in parallel with unmodified Method 202.

- Tests 13 through 24 add two alternative measurement techniques to be compared to Method 202 and the Dry Impinger modification: 1) the Controlled Condensate System (CCS) method of correcting the SO_2 conversion bias, and 2) the EPRI low-temperature filter method of correcting the SO_2 bias. In these runs, the test gas contains both SO_2 and SO_3/sulfuric acid. These runs are intended to demonstrate the use of the correction approach and compare that approach to Method 202 and the dry impinger method.

- Tests 25 through 36 are run with the same flue gas conditions as tests 13 through 24, but with no SO_2 in the synthetic gas mixture. These tests are intended to verify the adequacy of capture of sulfuric acid by each of the four CPM measurement techniques.

The rationale for the test conditions chosen for this test matrix addendum is further discussed in the following paragraphs.

As mentioned above, the first 12 tests in the EPRI matrix expand the original ERG experimental matrix to include the two higher moisture concentrations and the higher SO_2 concentration value. These tests are proposed with no SO_3 in the flue gas. The objective of these runs is to quantify the SO_2 bias in Method 202 and the extent to which the dry impinger method mitigates this bias. It is more straightforward to quantify the bias if there is no inorganic CPM (SO_3/sulfuric acid) in the synthetic flue gas.

Table A-1
EPRI Test Matrix Addendum for CPM Method Evaluation

Test	**Methods***	**SO_2 (ppmv)**	**NH_3 (ppmv)**	**CO_2 (%)**	**O_2 (%)**	**H_2O (%)**	**Nitrogen Oxide Mix (ppmv)**	**SO_3/ Sulfuric Acid (ppmv)**	**Inlet Gas Temperature, (°F)**
1	A, B	500	0	12	8	10	50	0	300
2	A, B	500	0	12	8	10	50	0	300
3	A, B	500	0	12	8	10	50	0	300
4	A, B	25	0	12	8	15	50	0	140
5	A, B	25	0	12	8	15	50	0	140
6	A, B	25	0	12	8	15	50	0	140
7	A, B	150	0	12	8	15	50	0	140
8	A, B	150	0	12	8	15	50	0	140
9	A, B	150	0	12	8	15	50	0	140
10	A, B	500	0	12	8	15	50	0	300
11	A, B	500	0	12	8	15	50	0	300
12	A, B	500	0	12	8	15	50	0	300
13	A, C	150	0	12	8	10	50	2	300
14	A, C	150	0	12	8	10	50	2	300
15	A, C	150	0	12	8	10	50	2	300
16	A, C	150	0	12	8	15	50	10	300
17	A, C	150	0	12	8	15	50	10	300
18	A, C	150	0	12	8	15	50	10	300
19	B, D	150	0	12	8	10	50	2	300
20	B, D	150	0	12	8	10	50	2	300
21	B, D	150	0	12	8	10	50	2	300
22	B, D	150	0	12	8	15	50	10	300
23	B, D	150	0	12	8	15	50	10	300
24	B, D	150	0	12	8	15	50	10	300
25	A, C	0	0	12	8	10	50	2	300
26	A, C	0	0	12	8	10	50	2	300
27	A, C	0	0	12	8	10	50	2	300
28	A, C	0	0	12	8	15	50	10	300
29	A, C	0	0	12	8	15	50	10	300
30	A, C	0	0	12	8	15	50	10	300
31	B, D	0	0	12	8	10	50	2	300
32	B, D	0	0	12	8	10	50	2	300
33	B, D	0	0	12	8	10	50	2	300
34	B, D	0	0	12	8	15	50	10	300
35	B, D	0	0	12	8	15	50	10	300
36	B, D	0	0	12	8	15	50	10	300

*Methods:

A = Method 202
B = Dry Impinger Modification to M-202
C = Controlled Condensation
D = EPRI Low-temperature Filter Modification to M-202

Two inlet gas temperatures are proposed, 300°F and 140°F. The inlet sample gas temperature may be important because it could impact where in the dry impinger train the flue gas moisture condenses, and correspondingly how much SO_2 from the flue gas is absorbed. The 10% moisture runs all represent unscrubbed flue gas, which would most likely be sampled at air heater outlet temperatures in the range of about 270°F to 320°F. These runs are proposed at 300°F as a mid-point for this range.

The 15% moisture runs are primarily intended to represent scrubbed flue gas, which would be nearly or completely saturated with moisture. These flue gases would typically be sampled at temperatures ranging from 120°F (saturated) to about 160°F (with significant reheat or when sampling a semi-dry scrubber). The 140°F temperature was chosen to represent a mid-point for this range. Also, it is difficult to mix and deliver a synthetic flue gas that contains acid gas species and that is completely saturated with moisture; the 140°F temperature allows for mixing and delivering a flue gas that is about 15-20°F above saturation. The exception for the 15% moisture runs is the high SO_2 (500 ppmv) condition. This is high for a scrubbed flue gas, even for high-sulfur coal. Consequently, it does not make sense to conduct this test at 140°F inlet temperature. However, it is worthwhile to conduct this test with a 300°F inlet temperature, as this condition is representative of unscrubbed flue gas from high-moisture solid fuels such as North Dakota lignite.

As will be discussed in the following subsection, EPRI is proposing two other sampling procedures as potential alternatives to the dry impinger modification. These alternatives eliminate the SO_2 bias in Method 202 by providing a separate measurement of the amount of SO_3/sulfuric acid in the flue gas; any sulfate species captured in the Method 202 water impinger recoveries are disregarded. Consequently, it is not necessary or informative to test these methods without SO_3/sulfuric acid in the synthetic gas matrix. Therefore, for the first 12 tests in the matrix, only Method 202 and the Dry Impinger modification will be tested on the synthetic gas mixtures.

The next 24 tests included in the proposed matrix include SO_3 in the synthetic gas mixture. Half of the tests (Tests 13 through 24) are proposed at the 150 ppmv mid-point SO_2 concentration. Of these, the first six are proposed at low-sulfur-coal, unscrubbed flue gas conditions (10% moisture, 300°F), and a relatively low inlet SO_3/sulfuric acid concentration of 2 ppmv. While this is higher than the SO_3 concentration typically measured in most low-sulfur-coal flue gas, it is proposed at 2 ppmv to ensure that a readily measurable SO_3 concentration is present. Also, some low-sulfur-coal applications include SO_3 conditioning, which can result in SO_3 concentrations in this range in the electrostatic precipitator outlet flue gas. Six tests are required at each condition because it is assumed the ERG gas mixing apparatus can generate only enough gas to conduct two measurements at the same time. Since all four measurement types are to be tested (unmodified Method 202, Dry Impinger modification, Controlled Condensation, and the EPRI Low-Temperature Filter modification), it will require six tests with two parallel trains to get triplicate measurements at each condition by all four methods.

The remaining six of the twelve150-ppmv tests are proposed at scrubbed flue gas moisture conditions (15%), but at 300°F gas temperature. The reason for the elevated temperature is that the acid dew point of this gas mixture is estimated to be 287°F. At the scrubber outlet temperature condition (140^{o}F) virtually all of the sulfuric acid in the synthetic gas mixture would be condensed. While this is the situation encountered when sampling scrubber outlet flue gas (all of the sulfuric acid is present as sub-micron-diameter acid mist), it is difficult to simulate this situation at the bench scale. Issues include ensuring that the acid mist is present in the appropriate size range and that all of the acid mist is delivered to the sampling system rather than collecting on sample delivery tubing walls. Consequently, the proposed gas conditions of 15% moisture and 300^{o}F inlet temperature represent a compromise intended to minimize these issues. The 10 ppmv SO_3/sulfuric acid concentration is in the typical range for high-sulfur-coal, scrubbed flue gas.

By conducting these twelve tests at 2 ppmv and 10 ppmv inlet SO_3/sulfuric acid concentrations, the ability of each method to quantitatively capture and report flue gas SO_3/sulfuric acid concentrations will be measured at relatively high and low concentrations. The actual range of SO_3/sulfuric acid in coal flue gases can vary from undetectable (less than 0.1 ppmv) to upwards of 60 ppmv.

The next twelve tests in the matrix (Tests 25 through 36) repeat the conditions of Tests 13 through 24, but without SO_2 in the synthetic flue gas matrix. The purpose of these runs is to determine the accuracy of each method in quantifying sulfuric acid actually present in the sample gas, without any potential SO_2-related bias. That is, in the runs with SO_2 in the gas matrix, it is likely that some of the sulfate-related CPM reported by one or more methods could be due to SO_2 artifacts. Repeating these runs with no SO_2 in the synthetic gas matrix will allow any such bias to be measured by difference, and will allow a direct measurement of the efficiency of the methods to retain SO_3/sulfuric acid.

All of these 36 tests will be conducted over a run duration of two hours, which is double the duration specified in the ERG plan. EPRI believes that the longer run duration will allow the potential effects of SO_2-related biases in CPM measurements to be more precisely quantified. Two-hour run times are typically required when trying to quantify low-level concentrations of CPM by Method 202. Given the time dependency of SO_2 to SO_3 oxidation in water impingers, it is more realistic to conduct these tests over the longest period of testing that may be encountered in the field.

None of the EPRI tests include ammonia in the synthetic gas matrix, as ammonia is an additional variable that should ideally be tested at several levels. Given limited resources, EPRI has chosen to defer the evaluation of ammonia effects to future studies, after the potential biases of each method have been quantified in an ammonia-free gas matrix. This decision may be revisited based on the results of the preliminary ERG test runs.

EPRI concurs with ERG that the method that provides the greatest reduction in the method bias should be tested with a minimum of eight runs at a selected set of conditions, to evaluate bias and precision of the selected measurement method(s). Final test conditions will be selected after the original ERG test matrix and the proposed EPRI test matrix are completed. EPRI, EPA, ERG and URS will hold a conference call after these results have been distributed to select the test conditions and measurement method(s) for evaluation.

Section A-3
Sampling Procedures

Based on EPRI's review of the proposed Dry Impinger modification to Method 202, it is expected that this modification will reduce but not eliminate the SO_2 bias in Method 202. Depending on the bias that remains, the reduction may not be sufficient for facilities that have stringent fine particulate limits in their permits. It would be advantageous to have an alternative available if this turns out to be the case.

EPRI recommends two additional methods for consideration as alternatives. Both of these methods have the potential to completely eliminate the SO_2 bias, by correcting the CPM total to remove pseudoparticulate sulfuric acid. These alternatives include the Controlled Condensation method and the EPRI Low-temperature Filter modification to Method 202. A summary of each method is given below. Appendices B and C to this document provide more detailed descriptions of these methods.

Controlled Condensation Method. This method was originally developed for EPA in the mid- to late-1970s as an improvement over Method 8 for quantifying flue gas SO_3/sulfuric acid concentrations.[3] However, it was never promulgated as a Reference Method. It has been practiced by a number of flue gas sampling organizations for nearly 30 years. The Controlled Condensation method is widely regarded as the most accurate manual method for measuring SO_3/sulfuric acid in stationary combustion source flue gases.

EPRI proposes the use of the Controlled Condensation method in parallel with the current version of Method 202 to provide a more accurate measure of flue gas CPM. The Controlled Condensation result will be used to provide a direct measurement of the amount of SO_3/sulfuric acid in the flue gas. The sulfate content of the Method 202 impingers will be measured and subtracted from the inorganic CPM measured with Method 202. The total CPM will be the sum of the SO_3/sulfuric acid from the Controlled Condensation Method and the non-sulfate inorganic and organic CPM from Method 202.

Figure A-1 illustrates the Controlled Condensation method sampling train. The basic approach employed by this method is to collect a particulate-free sample in a heated (600^{o}F), quartz-lined probe. The sample is filtered across a heated (550^{o}F) quartz thimble, then the particulate-free sample passes through a water-cooled, glass condenser. The condenser is controlled by water bath at a temperature about 20^{o}F above the flue gas moisture dew point, typically 140^{o}F to 160^{o}F. At this temperature, virtually all of the SO_3/sulfuric acid in the flue gas condenses. The large surface area of the glass condenser ensures that most of the sulfuric acid condenses on the glass surface rather than nucleating as sub-micron droplets and remaining in the sample gas. A quartz wool plug at the outlet of the condenser further ensures that droplets do not leave the condenser. From the condenser, the sample gas flows through chilled impingers (usually a Method 6 train) to condense moisture and remove other acid gases, then to a dry gas meter.

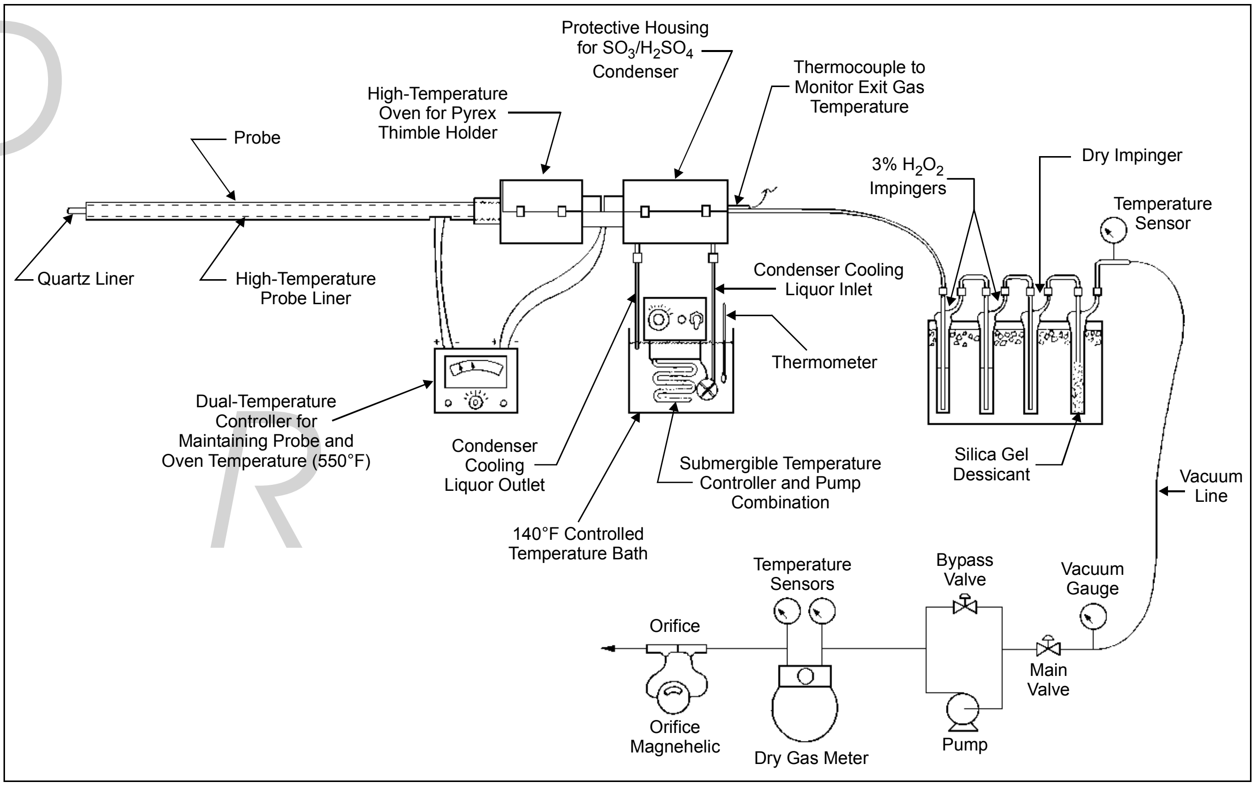

Figure A-1
Controlled Condensation Sampling Train

At the end of the run, the condensed acid is rinsed from the condenser coil, collected and analyzed for sulfate content. This content is compared to the gas volume sampled to calculate the SO_3/sulfuric acid concentration (the relative proportions of SO_3 and sulfuric acid in the sample gas depends on the gas temperature and moisture content).

The downstream impingers are typically recovered for weight gain to provide a measure of the sample gas moisture content, and analyzed for sulfate content (if a Method 6 train is used) to provide a measure of the sample gas SO_2 content. These moisture and SO_2 analyses provide a level of QC on the integrity of the sample gas, by determining whether representative values were measured for the sample gas.

The analysis of the condenser catch can be conducted by titration or by ion chromatography. The titration method has the advantage that it can be conducted in the field to provide rapid turnaround of results, but the ion chromatography results are typically regarded as being more accurate as the titration method end point is difficult to see. Some organizations do both, analyzing aliquots of the condenser catch by both methods to allow field determination of results but later refine those results using ion chromatography values. For these tests, we recommend that only ion chromatography results be used to calculate measured SO_3/sulfuric acid concentrations.

The biggest variation in how the Controlled Condensation method is practiced has to do with how particulate matter is removed from the sample gas. Some accomplish this by placing a quartz wool plug at the entrance of the sample probe, to prevent particulate matter from entering the probe. Others use a heated (550°F) quartz thimble, located in a hot box between the probe and condenser, to remove particulate matter. The quartz thimble can more quantitatively remove particulate matter than the gas wool plug, but has some capacity to adsorb SO_3 from the sample gas. This adsorption is avoided by conducting a "conditioning" run on a fresh thimble to allow it to reach adsorption equilibrium with the sample gas. Typically several runs can be completed without changing the thimble once it is conditioned. Since the proposed EPRI synthetic gas matrix will not include any particulate matter, neither the quartz wool plug nor the heated thimble will be required.

There are some drawbacks to employing the Controlled Condensation method for measuring stack flue gas SO_3/sulfuric acid concentrations. One is that the method is not well suited to traversing the duct or stack. This is due to the use of a heated, quartz-lined sampling tube that limits the probe length that can be used, and due to the thimble and condenser typically being rigidly connected to the end of the probe. Originally it was felt that the method would not need to traverse the stack since SO_3/sulfuric acid should be in the gas phase in hot flue gases. It has since been determined that significant stratification of SO_3/sulfuric acid concentrations can occur due to effects such as temperature variations across a duct downstream of a Ljungstrom-type air heater. Also, downstream of wet scrubbers, all of the SO_3 is present as sub-micron particles which may be stratified in the scrubber outlet flue gas. Furthermore, the method as developed does not sample isokinetically. The end of the quartz sampling tube is inserted perpendicular to gas flow to limit the amount of particulate matter in the sample gas, and no isokinetic nozzle is used.

It is also widely regarded that the Controlled Condensation method is not suitable for sampling scrubbed gas. However, EPRI has conducted heat transfer calculations and field tests that indicate the method is suitable for sampling scrubber outlet flue gas if a relatively long sampling probe is used (e.g., 10-ft length) and the probe and thimble temperatures are maintained at least 550°F.

Finally, the Controlled Condensation method requires experienced samplers to ensure good results. For example, run times are not of set duration, but sampler judgment is used to stop each run when a sufficient quantity of sulfuric acid is seen on condenser surfaces.

EPRI Low-temperature Filter Modification to Method 202. Figure A-2 illustrates the proposed sampling train. The front end of the sampling train is similar to that of a conventional Method 202 run, with either a Method 17 in-stack filter (for dry stacks) or a Method 5b out-of-stack filter (for wet stacks). The back end of the sampling train is a standard Method 202 impinger set. Between these components, a second, fiberglass particulate filter in a temperature-controlled hot box is inserted. This filter operates at 160°F, which should be well below the sample gas acid dew point. Virtually all of the SO_3/sulfuric acid in the sample gas should condense on the filter (160°F corresponds with only 0.01 ppmv of SO_3 remaining in a flue gas with 5% moisture, and less than 0.004 ppmv of SO_3 in a flue gas with 10% moisture).

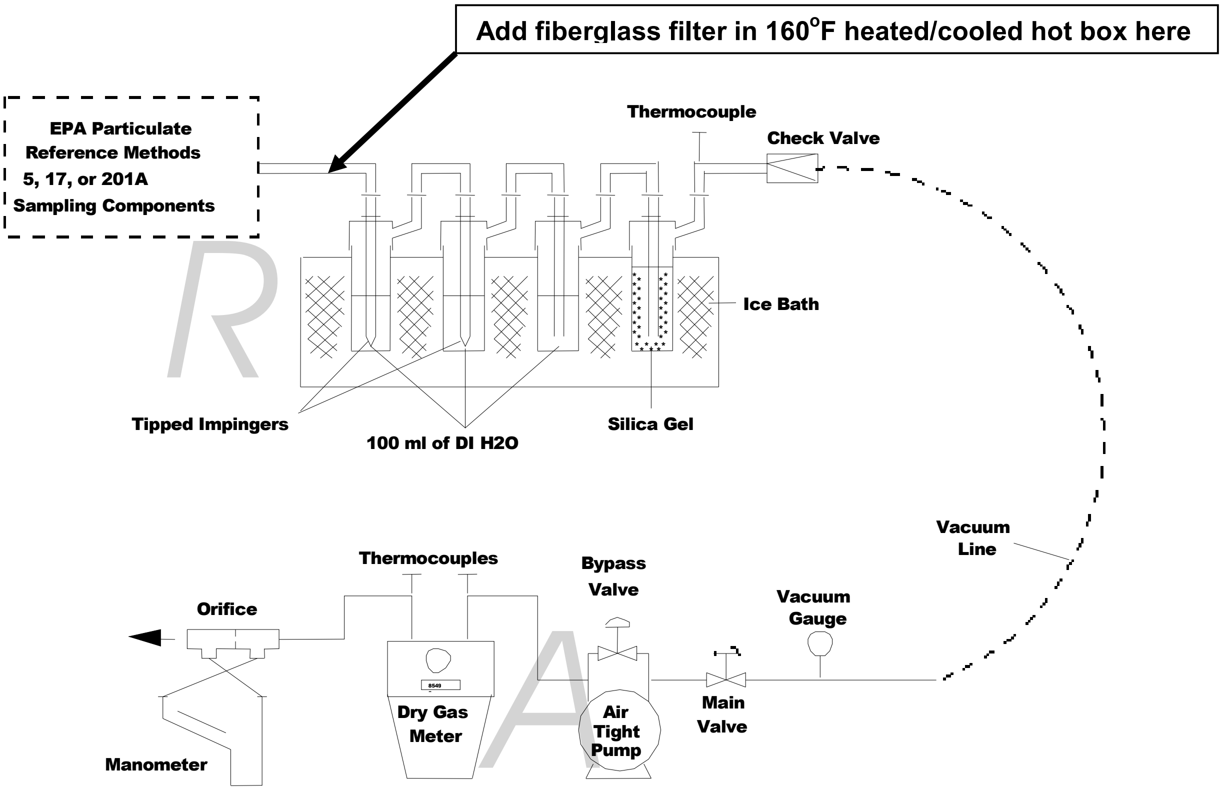

Figure A-2
Schematic of EPRI Low-Temperature Filter Modification

For the current EPRI test matrix, the synthetic gas matrix will not include any particulate matter, so the upstream Method 17 or Method 5b filter will not be required. Only the low-temperature filter assembly and Method 202 impingers will be needed for these tests. EPRI owns a prototype low-temperature filter housing and temperature control box, which can be made available to ERG for these tests.

At the end of the run, the low-temperature filter is recovered, weighed, digested in deionized water, and analyzed for sulfate content by titration or ion chromatography. All of the sulfate recovered is reported as condensible sulfuric acid. The Method 202 impingers are recovered and analyzed as per the method. The sulfate content of the Method 202 impingers is then measured and subtracted from the inorganic CPM. Any sulfate found in the impingers is ignored as a SO_2-related measurement artifact; all of the SO_3/sulfuric acid should be removed by the upstream 160°F filter.

The EPRI low-temperature method has some advantages over the controlled condensate correction method: traversing is more practical, and the procedures will be familiar to stack testers that perform Method 202. The low temperature filter holder and oven are simple and inexpensive to construct. Like the CCS correction method, the EPRI method greatly reduces the importance of the post-sampling nitrogen purge of the Method 202 impingers, as the pseudoparticulate sulfuric acid that is formed does not count towards the total CPM.

There are a few potential drawbacks to the Low-temperature Filter modification. One is that EPRI has only tested the Low-temperature Filter modification on a hot (300°F) stack using a Method 17 filter as the upstream particulate filter. While it should be possible to use a Method 5b filter setup as the particulate filter when sampling downstream of a wet scrubber, this configuration has not been tested. Again, this is a potential issue for future field testing, but not for the proposed laboratory test program.

A second potential drawback is that the low-temperature filter could capture lower vapor-pressure organics that condense between the upstream filter temperature and 160°F. This organic CPM would not be collected by the downstream water impingers and recovered by Method 202. This is not expected to be an issue for coal-fired sources, as very little condensible organic material is typically found in the flue gas. However, it could be an issue for other stationary sources. One possible solution is to include a methylene chloride rinse and extraction of the low-temperature filter to recover any such organic matter, but this step has not been tested by EPRI.

Table A-2 shows a comparison of how the sample trains are configured for the baseline Method 202 train and the two alternate sampling configurations proposed by EPRI

Table A-2
Configuration of Sample Trains

Sample Train	**Method 17/202 Baseline**	**Mod 17/5/202 Low-temperature Filter Modification**	**Controlled Condensation (in addition to baseline Method 17/202)**
In-stack filter (not needed for laboratory tests)	Fiberglass thimble	Fiberglass thimble	Quartz wool plug or external quartz thimble
Probe (not needed for laboratory tests)	Unheated Teflon	Heated glass	Heated quartz
Connector line	Teflon	None	None
SO_3 Collection Media	Impingers	160°F fiberglass filter	Condensing coil
Impingers	Water	Water	Method 6 train

Section A-4
Analytical Procedures

EPRI proposes no changes to the analytical procedures presented in the ERG QAPP for the dry impinger method. Analytical methods for the two EPRI-proposed alternate procedures – the Controlled Condensation method and the Low-temperature Filter modification to Method 17/5b/202 – are presented in the attached descriptions of these methods.

EPRI is specifying additional quality control (QC) measures to be implemented for the supplemental tests, and recommends that ERG follow a similar QC regimen when conducting the baseline test matrix. Because the results of this investigation are focused on low-level weight and sulfate concentration gains, the QC measures include field blanks, frequent balance calibration checks, and rigorous QC for sulfate analyses by ion chromatography. These QC measures are outlined below in Table A-3 for the laboratory sampling effort and Table A-4 for the recovery/analytical effort.

Table A-3
Laboratory Test QC Samples

QC Check	Frequency	Action
Reagent Blanks	Three for every lot of reagent or solvent	Hold portion for possible investigation of contamination issues
Field (Laboratory) Blank Trains	Recover 1 blank train for every 5 sampling trains run. Blanks should include all steps for the accompanying test, including recovery of the appropriate sampling glassware and/or filter, sample preparation, and analysis. Alternate blank collection times (some morning runs and some afternoon runs)	Analyze these trains with the measurement run samples. Compare magnitude of blank values to measured values*

*Report all blank values greater than 10% of measured values in data tables

Table A-4
Laboratory Test QC Activities

Parameter	QC Check	Frequency	Acceptance Criteria	Corrective Action
Particulate Mass Gain	Balance Calibration Check	Daily	Within ±0.1% of true value	Remove balance from service until repaired
	Mass Increase Check. For 20, 50 and 100 gram weights, check reading with increase of 0.1 mg and 0.5 mg.	Daily	0.1 mg addition must be within ±0.01 mg. 0.5 mg addition must be within ±0.03 mg.	Remove balance from service until repaired
Sulfate by Ion Chromatography	Calibration Curve – Five Point	Daily	Correlation Coefficient of 0.999 or greater	Recalibrate, if necessary repair instrument and recalibrate
	Analyze second source standard	Initially, and after every ten samples	90-110% recovery	Reanalyze any samples not bracketed by acceptable second source standards
	Duplicate analysis	Every 10th sample	10% RPD	1. Reanalyze sample and duplicate 2. Reanalyze batch of 10 3. Recalibrate and reanalyze all samples from the day
	Matrix Spike and Matrix Spike Duplicate (MS/MSD)	Every 10 samples	85-115% recovery 15% RPD	1. Reanalyze MS and MSD 2. Dilute all samples of a similar concentration, re-prepare MS/MSD, analyze diluted samples 3. Flag data

RPD = relative percent difference

Section A-5
References

1. *Laboratory Test Plan and Quality Assurance Project Plan for Method 202 Assessment & Evaluation for Bias and Other Uses*, EPA No. 68-D-02-079, Eastern Research Group, Morrisville, NC, November 2, 2006.

2. *Alternative Methods for Measurement of Condensible Particulate Matter: Field Test Report,* EPRI, Palo Alto, CA, Carolina Power and Light, New Hill, NC, and Duke Energy, Huntersville, NC: 2000. 1000749.

3. Cheney, J. and J. Homolya. "Characterization of Combustion Source Sulfate Emissions with a Selective Condensation Sampling System", in *Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources*, Vol. 1, Measurements Technology, EPA 600/9-78-020a. NTIS PB287-436.

Appendix A
Methods of Spiking SO_3/Sulfuric Acid into a Synthetic Gas Matrix

Three methods were originally proposed by EPRI as options for spiking SO_3/sulfuric acid into the synthetic gas matrix. These three methods include:

1) Pass a small amount of bottled gas containing SO_2, nitrogen and oxygen across a vanadium catalyst at high temperature ($>1000^{o}$F) in a tube furnace to convert essentially 100% of the SO_2 to SO_3, then adding this stream to the synthetic gas mixture.

2) Use a syringe pump to inject vaporized, dilute sulfuric acid into the heated synthetic gas mixture, and

3) Pass a small amount of nitrogen over a reservoir of oleum, which allows a near equilibrium amount of SO_3 to evaporate into the nitrogen stream, which is then added to the synthetic gas mixture.

After discussions with ERG, it was decided the first method would be most straightforward to implement for the proposed test matrix addendum. This method is further described below.

This method was used by the University of North Dakota Energy and Environmental Research Center (UNDEERC) to add SO_3/sulfuric acid to synthetic flue gas used to evaluate the draft Ontario Hydro method of mercury measurement. In the UNDEERC setup, they flow SO_2 across a vanadium catalyst (similar to that used in SCR) at high temperature ($>1000^{o}$F). Small amounts of catalyst can be bought from SO_3 injection system suppliers such as Chemithon, Wilhelm, or Wahlco, or directly from catalyst manufacturers such as Applied Ceramics or Sud-Chemie Prototech. UNDEERC typically observes 100% conversion of SO_2 to SO_3 across the catalyst.

UNDEERC calibrates the SO_2 gas flow rate using an SO_2 monitor. An alternate approach would be to use a certified SO_2 calibration gas as the source of SO_2 to the catalyst. The flow rate of this stream could be measured with a calibrated rotameter to get a precise SO_3 injection rate. An air or oxygen stream would also have to be metered in upstream of the catalyst to provide the oxidizing species. Figure A.1 is an illustration of this proposed setup.

The vanadium catalyst method should be precise in the amount of SO_3/sulfuric acid injected, but is relatively complex to set up. It requires the use of a high-temperature tube furnace and the acquisition of a vanadium catalyst. Some technical input from the catalyst supplier or trial and error is required to size the catalyst to ensure complete SO_2 to SO_3 oxidation at the desired spiking rates. Some measurements will be required (presumably by the Controlled Condensation method) to ensure complete conversion of SO_2 to SO_3 across the catalyst.

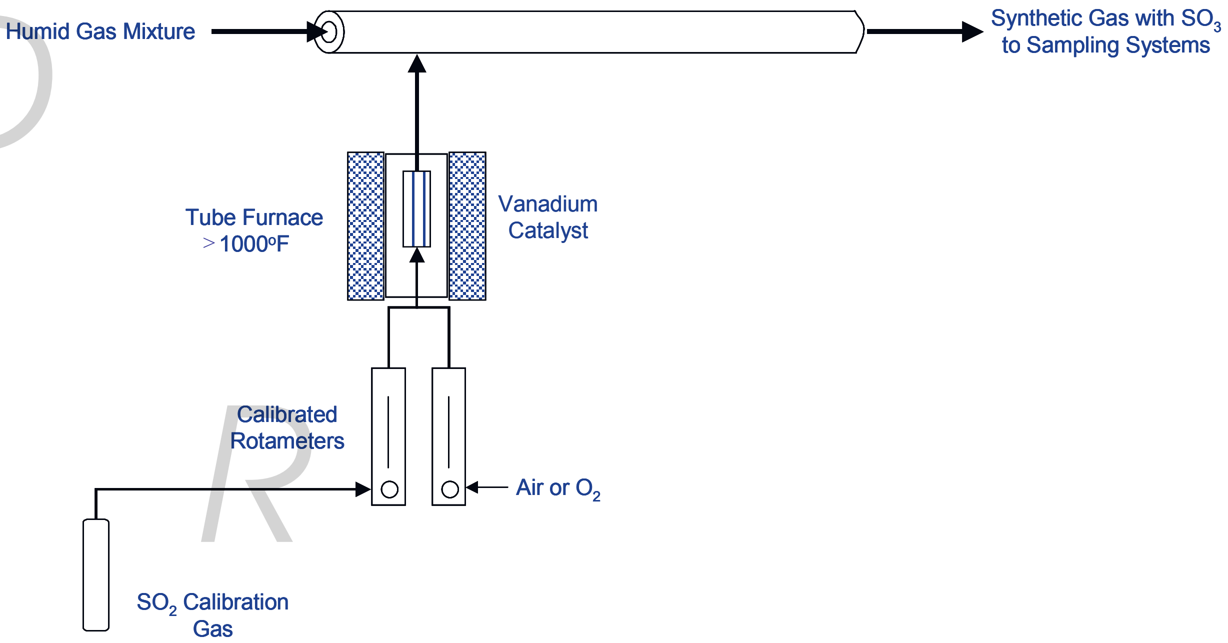

Figure A.1
Schematic of Catalyst-based SO_3 Injection Setup

Appendix B

Measurement Of SO_3/H2SO_4 Using The Controlled Condensation System[1]

B.1 Introduction

In the past few years, it has become increasingly important to characterize sulfuric acid concentrations in the flue gas from coal-fired plants. The measurement of SO_2 has become a well-developed art. However, the characterization of sulfuric acid concentrations has remained fairly difficult. A measurement method is desirable which can differentiate between gaseous H_2SO_4 and particulate sulfate.

Over the past 20 years, the controlled condensation system (CCS) technique has been established as one of the better methods to measure SO_3/H_2SO_4 in flue gas streams. This technique has the ability to provide measurements of metal sulfate, SO_3/H_2SO_4 and SO_2 in the gas stream simultaneously.

This technical note describes the system, equipment requirements, operation of the system, and sample recovery.

B.2 System Description

Gas is introduced into the controlled condensation system (CCS) via a heated (600°F) quartz-lined probe. The gas exits the probe and impacts on a quartz thimble filter maintained at 550°F. Metal sulfates are retained by the quartz thimble filter. The high temperatures in the probe and filter holder maintains SO_3/H_2SO_4 in the gaseous phase and thereby allows it to pass through the filter. The filtered gas stream then passes into a modified Graham condenser which is cooled by circulating 140°F water around the coils. At this temperature, SO_3/H_2SO_4 condenses on the inside walls of the coil. Water vapor and SO_2, and other acid gas species (HCl, HF, and NO_x) are not affected and continue through the coil. At the outlet of the coil is a glass wool plug to remove any acid aerosols that may have been reentrained in the gas stream. The gas exits the condensation coil, flows through an umbilical line, and bubbles through two impingers. The impingers contain 6% H_2O_2 to absorb SO_2. The SO_2 free gas then passes through an empty knockout impinger, a silica gel impinger to remove residual moisture, a dry gas meter, and a pump. This technique thus allows measuring metal sulfate, gaseous SO_3/H_2SO_4, and SO_2 simultaneously.

B.3 System Requirements

The SO_3/H_2SO_4 controlled condensation system (CCS) consists of a heated quartz-lined probe, quartz thimble filter holder, a modified Graham condenser, impingers, and sampling console.

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[1] *Published as Appendix A in *Flue Gas Sulfuric Acid Measurement Method Improvements,* EPRI, Palo Alto, CA: 2001. 1004027. Adapted from Radian Corporation Technical Note “Measurement of SO_3/H_2SO_4 in Stack Gas Using the Controlled Condensation System,” Radian DCN 80-290-403-07-04-01, prepared by J.L. Martinez and W.D. Balfour, Austin, Texas, April 14, 1980.

The following specialized equipment is necessary to perform SO_3/H_2SO_4 measurements by the CCS:

- High-temperature probes;
- Quartz probe liners;
- Quartz thimble holders;
- Controlled condensation coils with provisions for a glass wool plug;
- Combination high-temperature ovens and condenser protective housing; and
- Sample recovery glassware.

Electrical requirements for operating the system require a minimum of one 20-amp circuit. This will allow operating a dual temperature controller, a submergible temperature controller, a submergible pump, a sampling console or pump, and one temperature readout. Experience has shown that operating any additional equipment overloads the circuit. Therefore, it is preferable that two 20-amp circuits be available at the sampling point.

B.4 Site Equipment Setup and Operation

Train Setup

There are two types of controlled condensation coils (CCC), one employs a glass frit to trap entrained acid aerosols and the second uses a glass wool plug. Both CCC's perform the same function, however, the one with the glass wool plug has several advantages. The pressure drop is considerably lower through the plug than through the frit. This provides for greater ease of operation during sampling. The glass wool plug provides the opportunity to measure the amount of acid aerosols that penetrated the coil. Figure B.1 illustrates the preferred coil with provisions for a glass wool plug.

Prior to use, be sure the CCC is clean and dry. Carry the CCC to the sampling location with each end stoppered. If any condensation appears because of temperature changes, connect the CCC to the water bath and start the circulation of the 60ºC (140ºF) water. This should evaporate any premature condensate.

Figure B.2 details the quartz thimble holder. An extension to the male joint acts as a pressure seal when the quartz fiber thimble is in place. If there is not a tight seal, carefully cut a washer out of a spare filter to make a seal. With the probe still out of the stack, the train is assembled as shown in Figure B.3. The probe is connected to the thimble holder, and the thimble holder to the controlled condensation coil. Ball and socket (18/9) joints are used to make these connections.

Be sure that each ball joint is completely clean and free of dust. Because of the possibility that the greases will melt at the temperature employed, it is not recommended that any grease be used. Proper care of the ground glass fittings will ensure that vacuum seals are maintained. Should any ground glass fitting not seal vacuum-tight, a small amount of Apiezon H grease may be used for emergency repair. As soon as it is possible, the joint in question should be returned to the glass shop for regrinding.

Leak Check

Close off the end of the probe with a stopper, turn on the sample pump, and adjust the vacuum to read at least 10 in Hg. Begin measuring the flow rate with the dry gas meter and a watch. If the leak rate is less than 80 ml/min (0.003 cfm), then the system is ready for use. If a leak rate greater than 80 ml/min is found, the system should be checked for loose joints and connections.

Once the leak test is completed, close off the main valve at the console and slowly bleed air into the system by carefully removing the stopper in the probe.

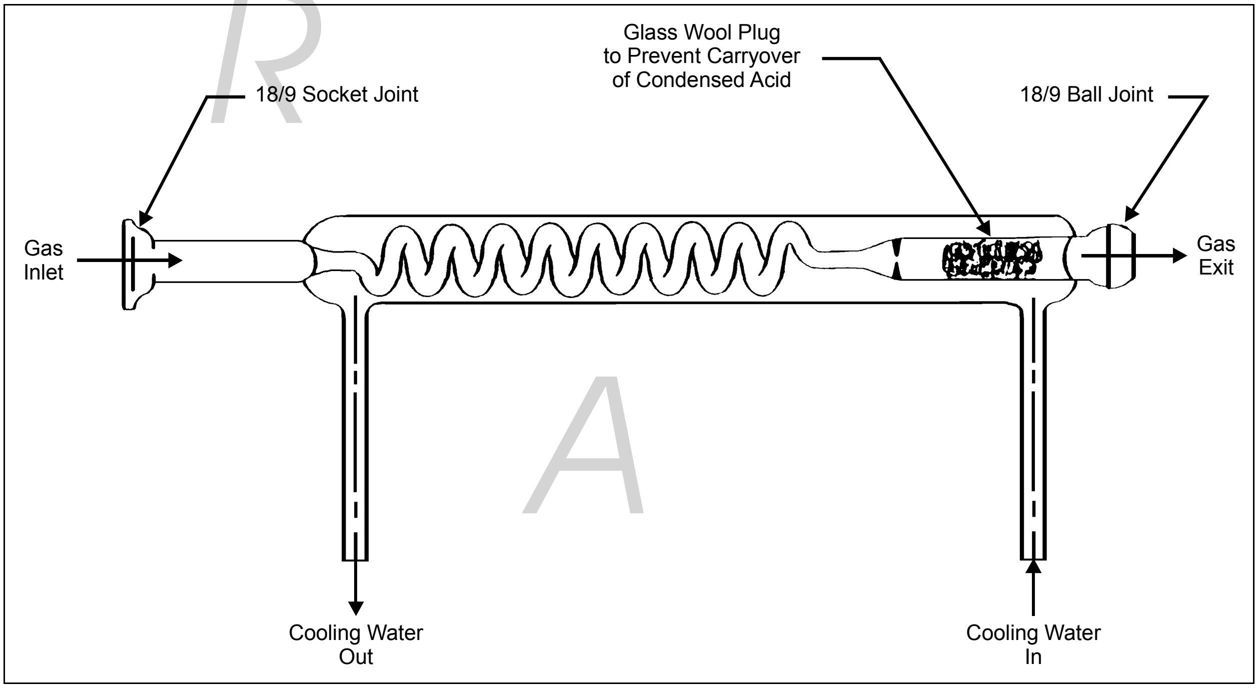

Figure B.1
Controlled Condensation Coil with Glass Wool Plug

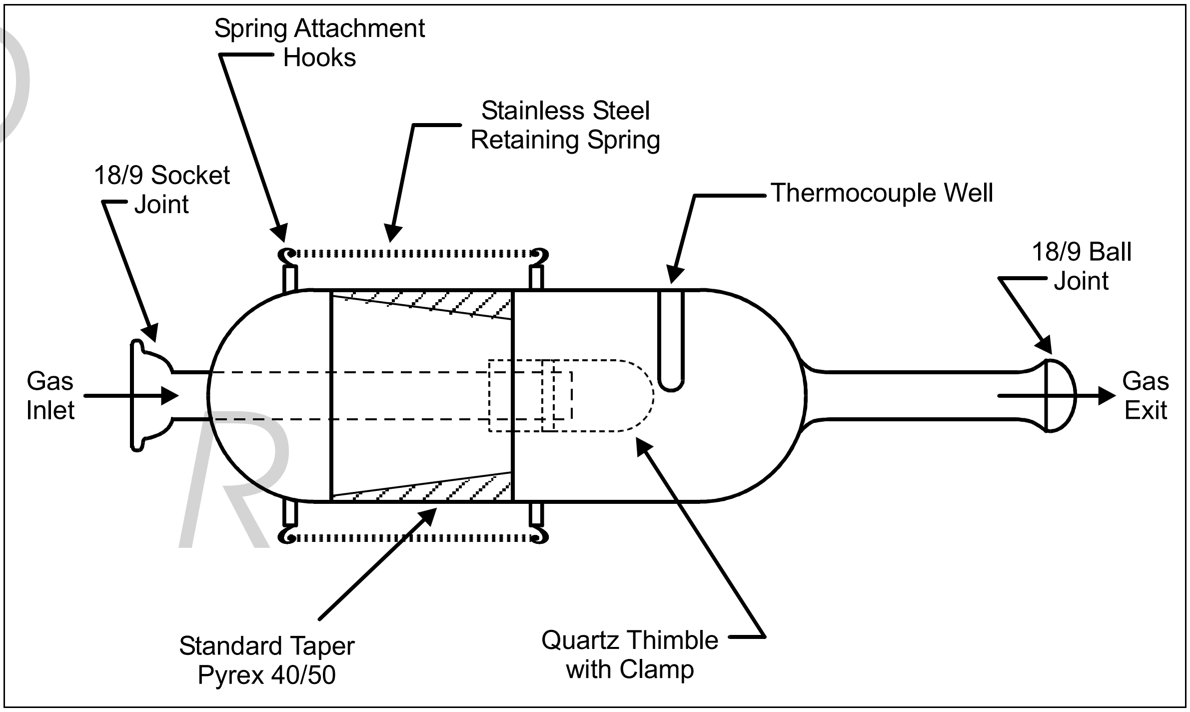

Figure B.2
Quartz Filter Holder

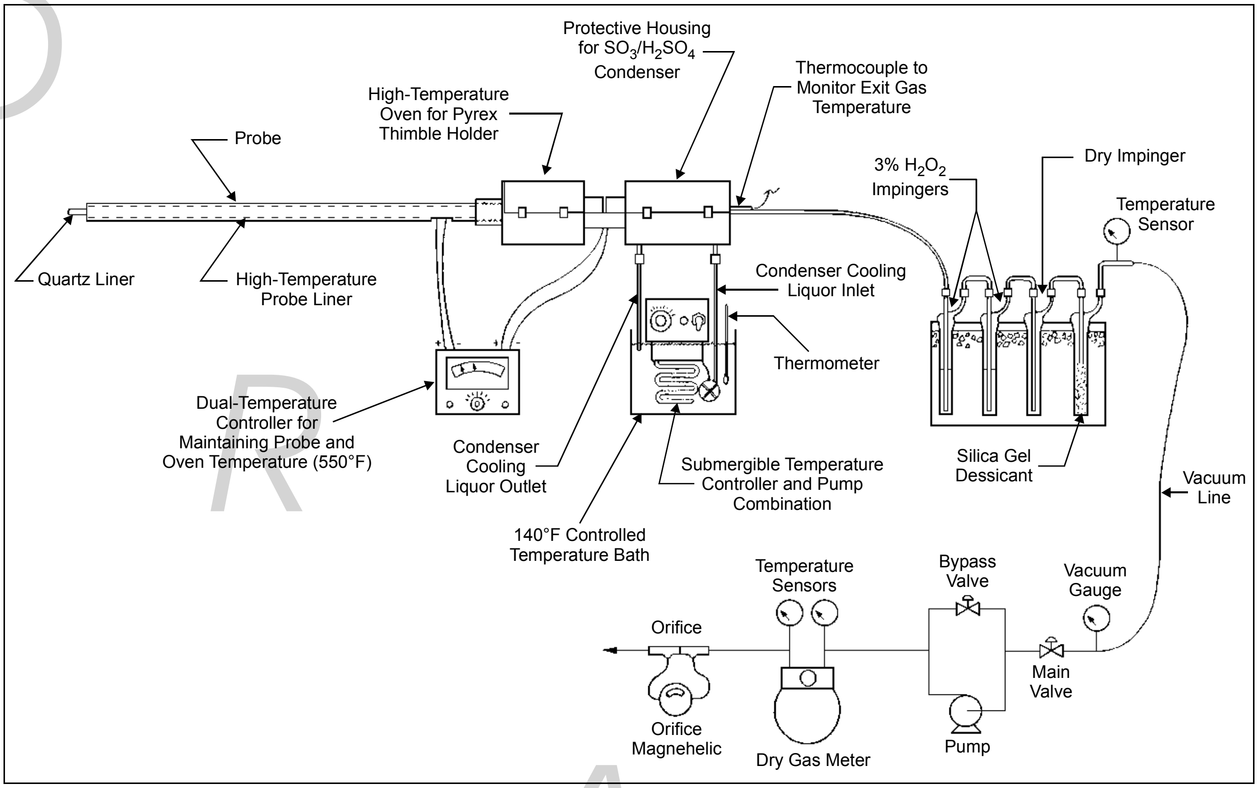

Figure B.3
SO_3/H_2SO_4 Sampling System

Gas-Phase Sampling

Break the seal between the two sections of the thimble holder to avoid breakage during expansion. Begin heating the probe and the thimble holder to 316ºC (600ºF) and 288ºC (550ºF), respectively. The heating bath should already be at 60ºC (140ºF). Once the skin temperatures reach these values, the thimble holder can be sealed and the run can commence.

After leak testing, the pump is again turned on and the flow rate adjusted to 0.3 cfm using the calibrated orifice or the dry gas meter and a stopwatch. The pump is turned off without readjusting the valve setting. Due to its fragility, remove the condenser and insert the heated probe into the duct. Place the condenser back in-line, obtain an initial dry gas meter reading, and turn on the pump. Throughout the run, collect the data required on the Source Sampling Field Data Sheet. Record the quartz thimble holder and recirculating water temperature in the hot box and last impinger temperature column.

Sample for one hour or until 1/2 to 2/3 of the length of the coils are frosted with H_2SO_4. If the coil is operated properly, the H_2SO_4 will cover the inside of the coils as a thin gray-white film. If large drops of a clear liquid form and begin to block the coil, then moisture is being condensed. Either the percentage moisture has exceeded 16% or the temperature of the water bath has dropped below 60ºC. Abort the run, and check the water bath temperature with a thermometer and confirm the percentage moisture in the gas stream. If the water bath is below 60ºC, recalibrate the temperature bath control. For every percent above 16% H_2O, adjust the CCC temperature 2ºC upward (see table below). Clean and dry the CCC, and replace the reagents in the impingers prior to restarting the run.

Percent Moisture	CCC Temperature (ºC)
≤ 16	60
17	62
18	64
19	66
20	68

The quartz thimble material used in the thimble holder maintained at 550ºF has been determined to have an appreciable capacity for adsorbing sulfuric acid from the flue gas sampled. This adsorption capacity becomes saturated during the first CCS run, but the adsorption results in a low bias for the results of the first run. Consequently, the first run on a new quartz thimble should be considered a "conditioning" run and the results should not be reported. The thimble is considered "conditioned" after either an hour of sampling or when H_2SO_4 is apparent in the condenser. A conditioned quartz thimble should be used for subsequent runs, until the pressure drop across the thimble becomes excessive or the thimble tears.

Recovering the Sample

At the end of the sampling period, remove the probe from the duct and slowly shut off the pump. After the pressure drops, disconnect the CCC from the thimble holder and umbilical line. Remove the water bath hoses and seal both ends of the CCC with Teflon tape. Take the CCC to the lab and recover the condensate into an Erlenmeyer flask or nalgene bottle by rinsing it in 10 ml increments (up to 50 ml), using DI water (Figure B.4). Be careful not to spill any of the condensate and to avoid introducing any dust or grease into the rinse solution. Multiple rinses are recommended to ensure a quantitative wash of the coil. Analysis of these solutions will provide a concentration of SO_3/H_2SO_4 mist.

Rinse the probe with 30 to 40 ml of DI H_2O after it has cooled. Take this solution back to the laboratory, and filter it through a Whatman Number 1 filter into a 50 ml volumetric. Dilute this solution to 50 ml with DI water.

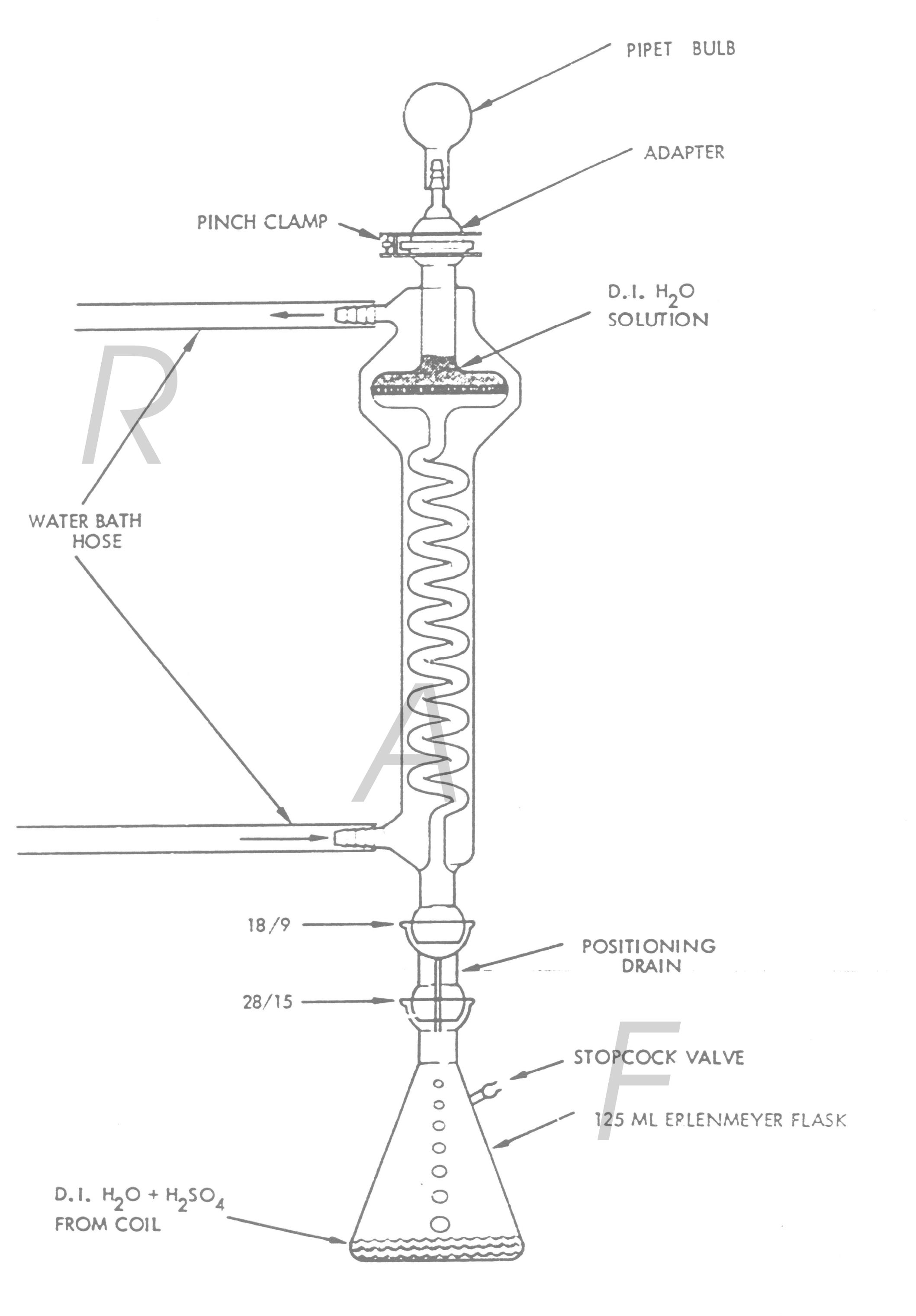

Figure B.4
Controlled Condensation Coil Rinsing Apparatus

After multiple runs have been completed with a thimble, the thimble can be recovered and leached to determine the total particulate sulfate in the flue gas stream during the runs over which the thimble was used.

After the thimble holder has cooled, remove the thimble and any debris from the filter holder and place it into a beaker. Add 30 ml of leaching solution (0.003 M $NaHCO_3$ and 0.0024 M Na_2CO_3) and swirl the beaker. Filter the solution through a Whatman Number 1 filter into a 50 ml volumetric. Repeat with 10 ml portions of leaching solution until the volumetric is filled to the mark. The total sulfate value obtained by adding the results from the probe wash and filter leachate gives a value for particulate sulfate in the flue gas stream.

The umbilical line is rinsed with DI water and saved. The sulfate concentration in the rinse and in the impinger catches is the value of SO_2 in the flue gas stream.

All the sample solutions are then analyzed for sulfate by ion chromatography. Alternatively, a $BaCl_2$ (thorin) titration may be used to measure sulfate. An acid/base titration may be used to measure the H_3O^+ concentration of the CCC rinse. This value is not specific for H_2SO_4, however, and has been shown to provide a total acid aerosol value.

B.5 Calculations

For measuring SO_3/H_2SO_4 mist, the calculations are:

C = total mmoles $SO_4^{=}$ reported from ion chromatography (condenser rinse)

$$C \times 10^{-3} \quad \frac{\text{moles}}{\text{mmole}} \times \frac{24.0\ \ell}{\text{mole}} = \ell \text{ of } SO_3 / H_2SO_4 \text{ at STP}$$

Volume of gas sampled = DSCF

$$\text{DSCF} \times \frac{28.3\ \ell}{\text{SCF}} = \text{Volume of gas sampled } (\ell)$$

$$\frac{(\ell)\ SO_3 / H_2SO_4}{(\ell)\ \text{gas}} \times 10^6 = \text{ppm } SO_3/H_2SO_4 \text{ (v/v)}$$

If the concentration of H_2SO_4 aerosol is desired in μg/m³, then the calculations are:

$$C \times 10^{-3} \ \frac{\text{mole}}{\text{mmole}} \ \text{x } 98 \text{ g/mole} \times 10^6 \mu\text{g/g} = \mu\text{g } H_2SO_4$$

$$\text{DSCF} \times 0.283 \text{ m}^3/\text{CF} = \text{m}^3$$

$$\frac{\mu g H_2SO_4}{\text{m}^3 \text{ sampled}} = \frac{\mu g\ H_2SO_4}{\text{m}^3}$$

Similar calculations can be performed to determine particulate sulfate and SO_2 in the flue gas stream.

B.6 Equipment

Following is a detailed list of equipment needed to set up and operate the CCS:

Heated probe with quartz liner

Quartz thimble holder

Quartz thimbles

Springs to keep thimble holder halves together

Modified Graham condenser

High-temperature oven for quartz thimble holder

Protective housing for condenser

Dual temperature controller for maintaining probe and oven temperature

Thermocouples and digital readouts for monitoring temperatures

Submersible temperature controller and pump combination

EPA 5 cold box to be used as 140°F temperature bath thermometer for cooling bath

Plastic tubing with 18/9 socket joints on each end to connect condenser to impinger inlet

EPA Method 5 cold box

4 impingers

3 impinger crossover connectors

8 impinger clamps

3 spring-loaded clamps

1 umbilical line

Sampling console

3% H_2O_2

Silica gel

Silicone grease

B.7 Bibliography

More information about the CCS method can be found in the following documents:

1. Cheney, J. and J. Homolya. “Characterization of Combustion Source Sulfate Emissions with a Selective Condensation Sampling System”, in *Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources*, Vol. 1, Measurements Technology, EPA 600/9-78-020a. NTIS PB287-436.
2. Maddalone, R. and N. Garner. “Process Measurement Procedures–H_2SO_4 Emissions.” EPA 600/7-79-156.

Appendix C
Low-temperature Filter Modification to Method 202

C.1 Description of Method

This sample train includes a reduced temperature (160°F) filter downstream of the Method 17 (dry stack) or Method 5b (wet stack) filter to collect condensible H_2SO_4. The purpose of the reduced temperature filter is to condense any H_2SO_4 upstream of the Method 202 impingers. Any sulfates found in the impingers can then be clearly identified as pseudo-particulate (SO_2 bias), and not included in the CPM total. This method is based on California's South Coast Air Quality Management District (SCAQMD) Method 5.2. Method 5.2 contains an option that if the filter temperature is maintained at 170ºF or below, it can be assumed that H_2SO_4 is collected on the filter and thus all sulfuric acid in the impingers can be subtracted as pseudo-particulate. For the EPRI method a target filter temperature of 160°F was chosen to be conservative and to better ensure complete condensation of the sulfuric acid in the sample gas.

C.2 Equipment

The sample train includes the following components:

- A stainless steel nozzle, sized to provide isokinetic sampling.
- A tared fiberglass thimble filter in a stainless steel holder.
- A glass probe heated to 160°F.
- A Method 5 filter heated to 160°F. The modified filter holder is shown in Figure C.1. Modifications to a standard Method 5 filter holder include:
    - A thermocouple in the sample gas stream downstream of the filter to directly measure gas temperature. This is in addition to the standard Method 5 thermocouple place in the oven.
    - A thermocouple in the gas stream at the sample probe exit. This is in addition to the standard Method 5 thermocouple positioned between the probe shell and inner liner.
    - A variable speed fan located on the bottom of the oven to provide outside air for cooling.
- Slotted vents in the side of the oven, near the top. These vents allow cooling air from the blower to pass through the oven. The opening of the vents is adjustable.
- Three impingers containing 100 ml of distilled and deionized water.
- A control box containing a sample pump, a calibrated gas meter, and all necessary instrumentation to measure stack gas velocity, establish isokinetic flow rate, and control oven and probe temperatures.

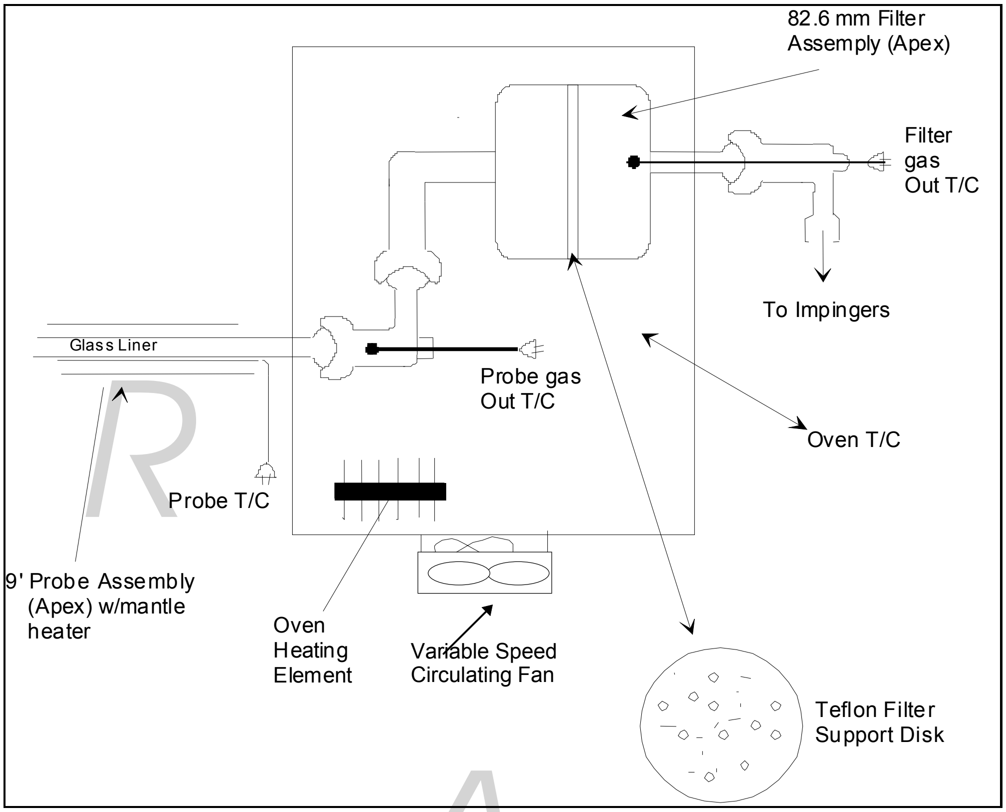

Figure C.1
Instrumented Oven Assembly for EPRI Low-temperature Filter Modification

Initial probe and oven heating are achieved by setting the heater controls to the target temperature and monitoring the probe shell and oven temperatures. When sampling is started, the filter exit gas temperature is monitored. With the oven heater still controlling to the oven temperature, the blower speed is manually adjusted to control the exit gas temperature. From past experience using this train, the heating element is typically on and outside air is used to keep the filter exit gas from overheating.

C.3 Sampling and Analysis Procedures

Sample recovery procedures are the same as for the Method 17/202 train, with two changes: (1) the probe and all other surfaces between the Method 17 and Method 5 filters are rinsed with water, and (2) the Method 5 filter is recovered and stored. The Method 202 nitrogen purge is still performed.

Table C.1 lists analyses to be performed for the reduced filter temperature tests. The analysis of solid particulate is identical to that for Method 17 tests. There are two major differences between these analyses and those for baseline Method 17/202 tests:

1. Condensible sulfate is quantified as the mass collected in the probe downstream of the Method 17 filter, and on the low-temperature Method 5 filter.

2. Because any H_2SO_4 is assumed to be collected on the low-temperature Method 5 filter, any sulfate collected in the impingers (measured by ion chromatography of the reconstitututed impinger residue) is assumed to be pseudoparticulate and is subtracted out.

Table C.1
Analytical Methods and Sample Fractions for Low-temperature Filter Modification Tests*

Sample Fraction	Media	Analysis	Result
1. In-Stack Nozzle Wash*	Acetone Rinse	Evaporate, weigh residue	Solid particulate deposited in nozzle.
2. In-Stack Filter*	Fiberglass Filter	Desiccate, weigh	Solid particulate collected on in-stack filter.
3. Probe wash	Water	Evaporate, add NH_4OH to convert H_2SO_4 to $(NH_4)_2SO_4$, evaporate, weigh, correct final weights	Condensible inorganics, corrected for sulfuric acid content.
4. Reduced temperature filter	Fiberglass Filter	a. Bake, weigh b. Extract with water, analyze for sulfate	a. Inorganic condensible H_2SO_4 b. Inorganic condensible H_2SO_4
5. Impinger Water Fraction	Water	Evaporate, add NH_4OH to convert H_2SO_4 to $(NH_4)_2SO_4$, evaporate, weigh, correct final weights	Condensible inorganics, corrected for sulfuric acid content.
6. Impinger Organic Fraction	$MeCl_2$ Rinse and extraction	Evaporate at room temperature, weigh	Organic CPM.
7. Pseudo-particulate Sulfate Correction	Residue from water impinger fraction	Determined by ion chromatography	Represents H_2SO_4 residue formed by conversion of SO_2 in impingers.
Total PM = 1+2+3+4+5+6-7 Solid PM = 1+2 Condensible PM = 3+4+5+6-7			

* Not collected during laboratory testing

The resulting particulate fractions measured by this method are as follows:

Solid particulate. Solid particulate is the sum of the residues from the nozzle wash (Fraction 1) and the in-stack filter (Fraction 2).

Condensible inorganic particulate. Condensible inorganic particulate is the sum of Fractions 3, 4, and 5, minus a correction for pseudoparticulate sulfate collected in the impingers. These fractions are further defined in the following paragraphs.

Fraction 3: probe rinse. The probe rinse (or rinse of lines between Method 5b filter and low-temperature filter) is evaporated and handled using the same procedures as for a Method 202 impinger sample water fraction. Material collected is expected to include any H_2SO_4 deposited in the probe.

Fraction 4: reduced temperature filter. This filter is expected to hold any H_2SO_4 in the sample that was not already deposited in the probe. The filter is analyzed two ways. First, it is baked, desiccated, and weighed. Second, it is extracted with water, and the extract is analyzed for H_2SO_4. It is expected that the two techniques will result in the same mass of H_2SO_4 being measured. Both are done to (a) compare the two results and gain insight into the modified method, and (b) gain experience in the practicality of each technique.

Fractions 5 and 7: impinger residue and pseudo-particulate correction. Since any H_2SO_4 in the sample gas should be collected on the low temperature filter, sulfuric acid collected in the impingers can then be assumed to be pseudo-particulate formed by conversion of SO_2 to sulfate in the impingers.

Ion chromatography is used to quantitatively determine H_2SO_4 in the impinger water. Since the H_2SO_4 in the impingers will represent pseudo-particulate, it will be subtracted from the weighed residue. For the EPRI lab experiments, there will be no inorganic CPM other than sulfuric acid in the system; thus, the subtraction should produce zero inorganic CPM in the impinger content.

The total inorganic condensible catch is the sum of the probe wash residue, the low temperature filter weight gain, and the impinger residue, minus the measured sulfuric acid calculated as $H_2SO_4 \cdot 2H_2O$.

Organic condensible particulate. Organic condensible particulate is determined from Fraction 6 as in Method 202, with no changes.

Appendix E

Phase I EPA Test Runs 1 through 8 – Sulfate Results by IC Analysis and CPM Results by Gravimetric Analysis

TEST MATRIX

Test	Sulfur Dioxide (ppm)	Carbon Dioxide (%)	Oxygen (%)	Water (%)	Nitrogen Oxides (ppm)
1	25	12	8	5	50
2	25	12	8	5	50
3	25	12	8	5	50
4	150	12	8	5	50
5	150	12	8	5	50
6	150	12	8	5	50
7	150	12	8	5	50
8	150	12	8	5	50

Initial EPA Tests 1 through 9: Sulfate Analysis by Ion Chromatorgraphy

M202 (Wet) train

Condition 1	Condensate Vol (mL)	Total recovery Vol (mL)	Sulfate (ug/mL)	Sulfate (Total ug)	Residual Mass (ug)	Sulfate (ug/mL)
Run 1	27.4	396.9	17.5	6945.75	39440	32.88
Run 2	41	405.9	28.5	11568.15	76910	42.1
Run 3	44.2	391.4	23.3	9119.62	61925	26.44
Condition 2						
Run 1	37.8	383.6	25.75	9877.7	71925	24.93
Run 2	30.6	375.6	22.8	8563.68	48865	25.17
Run 3	30.6	373.3	22.52	8406.716	65800	27.71

M202 (Dry) train

Condition 1	Condensate Vol (mL)	Total recovery Vol (mL)	Sulfate (ug/mL)	Sulfate (Total ug)	Residual Mass (ug)	Residual Sulfate (ug/mL)
Run 1	31	112.2	12.64	1418.208	40095	3.97
Run 2	41.3	167.6	11.25	1885.5	41885	5.05
Run 3	47	150.4	16.5	2481.6	37365	5.84
Condition 2						
Run 1	40.9	141.4	31.8	4496.52	44715	6.58
Run 2	34.9	122.3	38.7	4733.01	41100	11.44
Run 3	35.1	97.9	36.6	3583.14	41270	5.07
Run 4	37.8	255.8	4.95	1266.21	25250	3.08
Run 5	36.3	219.7	14.4	3163.68	39555	2.18

Blank Results

	Condensate Vol (mL)	Total recovery Vol (mL)	Sulfate (ug/mL)	Sulfate (Total ug)	Residual Mass (ug)	Residual Sulfate (ug/mL)
Reagent Blk	NA	500	0	0	10580	0
Wet Method FB	NA	414.6	0	0	19515	0
Dry Method FB	NA	113.2	0	0	10725	0

	Oxygen	Carbon Dioxide	NO	Sulfur Dioxide
Condition 1	8%	12%	50 ppm	25 ppm
Condition 2	8%	12%	50 ppm	150 ppm

Initial EPA Tests 1 through 9: CPM Gravimetric Analysis Summary

Method 202 Wet Train Conditions	**Moisture Collected (g)**	**Total Water (g)**	**Residual Sulfate CPM (mg)**
25 ppm SO_2 Run 1	27.4	397	13
25 ppm SO_2 Run 2	41	406	17
25 ppm SO_2 Run 3	44	391	10
150 ppm SO_2 Run 1	38	384	9.6
150 ppm SO_2 Run 2	31	376	9.5
150 ppm SO_2 Run 3	31	373	10.3

Method 202 Dry Train Conditions	**Moisture Collected (g)**	**Total Water (g)**	**Residual Sulfate CPM (mg)**
25 ppm SO_2 Run 1	31	11	0.45
25 ppm SO_2 Run 2	41	168	0.85
25 ppm SO_2 Run 3	47	150	0.88
150 ppm SO_2 Run 1	41	141	0.93
150 ppm SO_2 Run 2	35	122	1.4
150 ppm SO_2 Run 3	58	98	0.5
150 ppm SO_2 Run 4	38	256	0.79
150 ppm SO_2 Run 5	36	220	0.48

Appendix F

Phase I EPA Test Runs 1 through 9 – Method 202 and Dry Impinger Moisture Calculations

Method 202 Moisture Calculations
Test Runs 1 through 7

Test Run 1		**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Barometric Pressure	30			0		
Y	0.98			5	75	71
Vm	35.15	664.45	629.3	10	78	71
Delta Ha	0.71			15	83	72
Tm (°F)	84.5			20	86	72
				25	88	72
Vm (std)	33.53733			30	90	73
				35	91	73
VLc (g)	9.1			40	91	74
Vw (std)	0.428337			45	92	75
				50	92	75
% water	1.261088			55	93	72
				60	93	76
				65	93	76
				70	93	76
				Average	88.42857	73.42857

Test Run 2		**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Barometric Pressure	30			0		
Y	0.98			5	73	72
Vm	35.255	737.68	702.425	10	80	72
Delta Ha	0.71			15	84	72
Tm (°F)	82.39286			20	88	73
				25	90	74
Vm (std)	33.76819			30	91	75
				35	92	75
VLc (g)	27.4			40	93	76
Vw (std)	1.289718			45	93	76
				50	94	77
% water	3.678822			55	94	77
				60	94	78
				65	94	78
				70	94	78
				Average	89.57143	75.21429

Test Run 3		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	29.92			0		
Y	0.98			5	82	71
Vm	35.45	805.45	770	10	86	72
Delta Ha	0.71		387	15	91	72
Tm (°F)	82.53571			20	91	73
				25	92	74
Vm (std)	33.85566			30	92	74
				35	92	75
VLc (g)	41			40	92	75
Vw (std)	1.92987			45	92	75
				50	92	76
% water	5.392878			55	92	76
				60	92	76
				65	92	76
				70	92	76
				Average	90.71429	74.35714

Test Run 4		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	29.92			0		
Y	0.98			5	78	71
Vm	35.269	861.51	826.241	10	87	72
Delta Ha	0.71			15	88	72
Tm (°F)	81.64286			20	88	73
				25	88	73
Vm (std)	33.73832			30	90	74
				35	90	75
VLc (g)	44.2			40	90	75
Vw (std)	2.080494			45	91	75
				50	91	76
% water	5.808383			55	91	76
				60	91	76
				65	91	76
				70	92	76
				Average	89	74.28571

Test Run 5		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	30.15			0		
Y	0.98			5	77	70
Vm	35.26	928.68	893.42	10	85	71
Delta Ha	0.71			15	88	72
Tm (°F)	81.46429			20	89	72
				25	90	73
Vm (std)	33.99976			30	90	74
				35	90	74
VLc (g)	37.8			40	91	75
Vw (std)	1.779246			45	91	75
				50	91	75
% water	4.972878			55	91	76
				60	91	76
				65	91	76
				70	91	76
				Average	89	73.92857

Test Run 6		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	30.15			0		
Y	0.98			5	79	71
Vm	34.895	994.49	959.595	10	84	72
Delta Ha	0.71			15	89	72
Tm (°F)	82.17857			20	90	73
				25	90	74
Vm (std)	33.60347			30	90	75
				35	90	75
VLc (g)	30.6			40	91	75
Vw (std)	1.440342			45	92	75
				50	92	76
% water	4.110117			55	92	77
				60	92	77
				65	92	77
				70	92	77
				Average	89.64286	74.71429

Test Run 7		**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Barometric Pressure	30.09			0		
Y	0.98			5	85	71
Vm	35.218	59.8	24.582	10	89	71
Delta Ha	0.71			15	89	72
Tm (°F)	82.07143			20	90	73
				25	90	74
Vm (std)	33.85383			30	90	74
				35	90	74
VLc (g)	30.6			40	91	75
Vw (std)	1.440342			45	91	75
				50	91	75
% water	4.080962			55	91	75
				60	91	76
				65	91	76
				70	92	76
				Average	90.07143	74.07143

Dry Impinger Moisture Calculations
Test Runs 1 through 9

Test Run 1		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	30			0		
Y	0.98			5	72	70
Vm	34.356	869.421	835.065	10	79	70
Delta Ha	0.72			15	82	71
Tm (°F)	79			20	84	71
				25	86	72
Vm (std)	33.11505			30	87	72
				35	87	72
VLc (g)	10.6			40	88	73
Vw (std)	0.498942			45	88	73
				50	89	74
% water	1.484328			55	89	74
				60	89	74
				65	89	74
				70	89	74
				Average	85.57143	72.42857

Test Run 2		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	30			0		
Y	0.98			5	75	71
Vm	34.429	941.372	906.943	10	81	71
Delta Ha	0.72			15	84	72
Tm (°F)	80.53571			20	86	73
				25	87	73
Vm (std)	33.09113			30	88	74
				35	89	74
VLc (g)	31			40	89	75
Vw (std)	1.45917			45	89	75
				50	90	75
% water	4.22332			55	90	76
				60	90	76
				65	90	76
				70	90	76
				Average	87	74.07143

Test Run 3		**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Barometric Pressure	29.92			0		
Y	0.98			5	85	71
Vm	34.392	1008.23	973.838	10	83	71
Delta Ha	0.72			15	85	72
Tm (°F)	79.71429			20	87	72
				25	87	72
Vm (std)	33.01775			30	88	72
				35	87	73
VLc (g)	41.3			40	87	73
Vw (std)	1.943991			45	88	73
				50	88	73
% water	5.560337			55	88	73
				60	88	74
				65	88	73
				70	88	73
				Average	86.92857	72.5

Test Run 4		**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Barometric Pressure	29.92			0		
Y	0.98			5	73	69
Vm	34.482	63.182	28.7	10	79	70
Delta Ha	0.72			15	82	70
Tm (°F)	78.53571			20	84	71
				25	84	71
Vm (std)	33.17661			30	86	72
				35	87	73
VLc (g)	47			40	87	73
Vw (std)	2.21229			45	87	73
				50	87	73
% water	6.251368			55	88	74
				60	88	74
				65	88	74
				70	88	74
				Average	84.85714	72.21429

Test Run 5		**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Barometric Pressure	30.15			0		
Y	0.98			5	73	69
Vm	34.227	128.02	93.793	10	83	70
Delta Ha	0.71			15	85	71
Tm (°F)	78.96429			20	86	71
				25	86	72
Vm (std)	33.15677			30	87	72
				35	87	73
VLc (g)	40.9			40	87	73
Vw (std)	1.925163			45	87	73
				50	88	73
% water	5.48762			55	88	73
				60	88	74
				65	88	73
				70	88	73
				Average	85.78571	72.14286

Test Run 6		**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Barometric Pressure	30.15			0		
Y	0.98			5	73	69
Vm	34.344	192.394	158.05	10	78	70
Delta Ha	0.71			15	82	70
Tm (°F)	78.60714			20	82	70
				25	86	72
Vm (std)	33.29217			30	86	72
				35	86	73
VLc (g)	34.9			40	88	73
Vw (std)	1.642743			45	88	73
				50	88	74
% water	4.702296			55	88	74
				60	88	74
				65	88	74
				70	88	74
				Average	84.92857	72.28571

Test Run 7		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	30.09			0		
Y	0.98			5	71	69
Vm	34.502	256.415	221.913	10	77	69
Delta Ha	0.71			15	81	70
Tm (°F)	77.89286			20	83	70
				25	84	71
Vm (std)	33.42321			30	85	72
				35	85	72
VLc (g)	35.1			40	87	72
Vw (std)	1.652157			45	87	73
				50	87	73
% water	4.710305			55	87	73
				60	88	73
				65	88	73
				70	88	73
				Average	84.14286	71.64286

Test Run 8		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	29.94			0		
Y	0.984			5	81	72
Vm	33.554	322.35	288.796	10	89	72
Delta Ha	0.72			15	87	73
Tm (°F)	80.78571			20	88	73
				25	89	73
Vm (std)	32.30218			30	89	73
				35	89	73
VLc (g)	37.8			40	89	73
Vw (std)	1.779246			45	89	74
				50	89	75
% water	5.220574			55	89	75
				60	89	75
				65	88	74
				70	88	74
				Average	88.07143	73.5

Test Run 9		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	29.94			0		
Y	0.979			5	75	74
Vm	34.185	127.34	93.155	10	81	75
Delta Ha	0.71			15	86	75
Tm (°F)	82.85714			20	91	75
				25	92	76
Vm (std)	32.61668			30	92	76
				35	92	77
VLc (g)	36.3			40	91	77
Vw (std)	1.708641			45	92	77
				50	92	77
% water	4.977786			55	92	77
				60	92	78
				65	91	78
				70	91	78
				Average	89.28571	76.42857

Appendix G

Phase I EPA Eight Replicate Tests – Sulfate Results by IC Analysis and CPM Results by Gravimetric Analysis

Dry Impinger Train Replicate Run Results

Run	% Water	Water Captured g	Aqueous Residue mg	Organic Residue mg	Filter Capture mg	Ammonium Correction Mass mg	Aqueous Residue Corrected mg	Total CPM (mg)
1	10.3	81.6	2.44	0.11	-0.34	0.208	2.232	2.3
2	10.3	82.6	3.10	0.145	-0.055	0.211	2.884	3.0
3	8.65	67.5	1.54	0.095	16.125	0.172	1.368	1.5
4	8.47	66.8	2.09	0.305	-16.285	0.170	1.915	2.2
5	9.05	69.7	1.71	0.165	0.07	0.178	1.537	1.7
6	9.86	69.5	2.43	0.33	-0.175	0.236	2.189	2.5
7	6.58	50.4	1.27	0.08	0.3	0.086	1.179	1.3
8	5.99	46	1.99	0.02	0.165	0.117	1.873	1.9
Train Blank 1	NA	NA	0.455	-0.11	-0.04	NA	NA	0.5
Train Blank 2	NA	NA	1.02	0.135	-0.125	NA	NA	1.2
Train Blank 3	NA	NA	0.56	-0.075	-0.115	NA	NA	0.6
Reagent Blank	NA	NA	0.205	-0.29	0	NA	NA	0.2

Sulfate Titration EPA Dry Impinger Modification Replicate Runs 1-8

Run	Titrant Normality (meq/mL)	Volume used (mL)	Conc Sulfate (mg)	Impinger Catch Volume (g)	K	Ammonium mass correction (mg)
1	0.1	0.15	0.00720	81.6	0.354	0.208
2	0.1	0.15	0.00720	82.6	0.354	0.211
3	0.1	0.15	0.00720	67.5	0.354	0.172
4	0.1	0.15	0.00720	66.8	0.354	0.170
5	0.1	0.15	0.00720	69.7	0.354	0.178
6	0.1	0.2	0.00961	69.5	0.354	0.236
7	0.1	0.1	0.00480	50.4	0.354	0.086
8	0.1	0.15	0.00720	46	0.354	0.117
Train Blank 1	0.1	0.05	0.00240			
Train Blank 2	0.1	0.05	0.00240			
Train Blank 3	0.1	0.1	0.00480			
Reagent Blank	0.1	0.4	0.01921			

EPA Dry Impinger Modification Replicate Runs 1-8 Gravimetric Analysis

Pan	Description	Tare wt 1 (g)	Tare wt 2 (g)	Tare Wt (g)	Final wt 1 (g)	Final wt 2 (g)	Final Wt (g)	Residual Mass (g)	Residual Mass (ug)	Pass QC? (<0.5 mg)
AQ1	Run 1 Aqueous	6.17452	6.17448	6.1745	6.17699	6.17689	6.17694	0.00244	2440	0.05
AQ2	Run 2 Aqueous	6.22326	6.22333	6.223295	6.22652	6.22626	6.22639	0.003095	3095	0.13
AQ3	Run 3 Aqueous	6.24903	6.24903	6.24903	6.25062	6.25052	6.25057	0.00154	1540	0.05
AQ4	Run 4 Aqueous	6.19475	6.19474	6.194745	6.19688	6.19678	6.19683	0.002085	2085	0.05
AQ5	Run 5 Aqueous	6.30541	6.30538	6.305395	6.30721	6.30701	6.30711	0.001715	1715	0.10
AQ6	Run 6 Aqueous	6.28984	6.28974	6.28979	6.29225	6.29218	6.292215	0.002425	2425	0.04
AQ7	Run 7 Aqueous	6.27697	6.27689	6.27693	6.27825	6.27814	6.278195	0.001265	1265	0.06
AQ8	Run 8 Aqueous	6.24109	6.24098	6.241035	6.24308	6.24297	6.243025	0.00199	1990	0.05
AQ9	Train Blank 1 Aqueous	6.20359	6.2036	6.203595	6.2041	6.204	6.20405	0.000455	455	0.05
AQ10	Train Blank 2 Aqueous	6.28054	6.2805	6.28052	6.28159	6.28149	6.28154	0.00102	1020	0.05
AQ11	Train Blank 3 Aqueous	6.2351	6.23502	6.23506	6.23567	6.23557	6.23562	0.00056	560	0.05
AQ12	Reagent Blank Aqueous	6.32148	6.32149	6.321485	6.32169	6.32169	6.32169	0.000205	205	0.00
OR1	Run 1 Organic	6.1674	6.1674	6.1674	6.16755	6.16747	6.16751	0.00011	110	0.04
OR2	Run 2 Organic	6.2505	6.2505	6.2505	6.25069	6.2506	6.250645	0.000145	145	0.05
OR3	Run 3 Organic	6.2194	6.2194	6.2194	6.21951	6.21948	6.219495	9.5E-05	95	0.02
OR4	Run 4 Organic	6.21	6.2102	6.2101	6.21043	6.21038	6.210405	0.000305	305	0.02
OR5	Run 5 Organic	6.1456	6.1457	6.14565	6.14582	6.14581	6.145815	0.000165	165	0.00
OR6	Run 6 Organic	6.2164	6.2165	6.21645	6.21677	6.21679	6.21678	0.00033	330	-0.01
OR7	Run 7 Organic	6.1984	6.1984	6.1984	6.19851	6.19845	6.19848	8E-05	80	0.03
OR8	Run 8 Organic	6.2584	6.2585	6.25845	6.25851	6.25843	6.25847	2E-05	20	0.04
OR9	Train Blank 1 Organic	6.2377	6.238	6.23785	6.23781	6.23767	6.23774	-0.00011	-110	0.07
OR10	Train Blank 2 Organic	6.2311	6.2311	6.2311	6.2313	6.23117	6.231235	0.000135	135	0.07
OR11	Train Blank 3 Organic	6.2065	6.2066	6.20655	6.20652	6.20643	6.206475	-7.5E-05	-75	0.05
OR12	Reagent Blank Organic	6.2433	6.2432	6.24325	6.2431	6.24282	6.24296	-0.00029	-290	0.14
F5	Run 1 Filter	0.57489	0.57487	0.57488	0.57452	0.57456	0.57454	-0.00034	-340	-0.02
F6	Run 2 Filter	0.58053	0.58049	0.58051	0.58049	0.58042	0.580455	-5.5E-05	-55	0.03
F13	Run 3 Filter	0.57247	0.5725	0.572485	0.57244	0.57236	0.5724	-8.5E-05	-85	0.04
F14	Run 4 Filter	0.58866	0.58871	0.588685	0.58866	0.58856	0.58861	-7.5E-05	-75	0.05
F15	Run 5 Filter	0.58321	0.58321	0.58321	0.58333	0.58323	0.58328	7E-05	70	0.05
F16	Run 6 Filter	0.58863	0.58868	0.588655	0.58853	0.58843	0.58848	-0.00017	-175	0.05
F17	Run 7 Filter	0.59592	0.59595	0.595935	0.59628	0.59619	0.596235	0.0003	300	0.05
F18	Run 8 Filter	0.58173	0.58168	0.581705	0.58192	0.58182	0.58187	0.000165	165	0.05
F19	Train Blank 1 Filter	0.58555	0.58559	0.58557	0.58554	0.58552	0.58553	-4E-05	-40	0.01
F20	Train Blank 2 Filter	0.58703	0.5869	0.586965	0.58689	0.58679	0.58684	-0.00012	-125	0.05
F21	Train Blank 3 Filter	0.58777	0.58772	0.587745	0.58767	0.58759	0.58763	-0.00011	-115	0.04

Appendix H

Phase I EPA Eight Replicate Tests – Moisture Calculations

Test Run 1

Barometric Pressure	30.23	**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Y	0.984			0		
Vm	34.205	458.55	424.345	5	72	69
Delta Ha	0.73			10	76	70
Tm (°F)	78.5			15	81	70
				20	83	71
Vm (std)	33.38921			25	85	72
				30	86	72
VLc (g)	81.6			35	86	73
Vw (std)	3.840912			40	87	73
				45	87	73
% water	10.31668			50	88	74
				55	88	74
				60	88	74
				65	88	75
				70	88	75
				Average	84.5	72.5

Test Run 2

Barometric Pressure	30.23	**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Y	0.979			0		
Vm	35.323	192.575	157.252	5	85	72
Delta Ha	0.71			10	89	73
Tm (°F)	83.39286			15	88	74
				20	90	75
Vm (std)	33.9948			25	91	75
				30	92	76
VLc (g)	82.6			35	92	76
Vw (std)	3.887982			40	92	77
				45	92	77
% water	10.26319			50	93	76
				55	93	77
				60	92	78
				65	92	78
				70	92	78
				Average	90.92857	75.85714

Test Run 3

Barometric Pressure	30.15	Meter Start	Meter End	Time	Temp in	Temp Out
Y	0.984			0		
Vm	34.387	523.876	489.489	5	70	68
Delta Ha	0.73			10	74	68
Tm (°F)	77.28571			15	77	68
				20	82	70
Vm (std)	33.55386			25	83	70
				30	85	71
VLc (g)	67.5			35	85	71
Vw (std)	3.177225			40	85	73
				45	85	73
% water	8.649962			50	87	73
				55	88	73
				60	88	73
				65	88	74
				70	88	74
				Average	83.21429	71.35714

Test Run 4

Barometric Pressure	30.15	Meter Start	Meter End	Time	Temp in	Temp Out
Y	0.979			0		
Vm	35.173	259.743	224.57	5	69	69
Delta Ha	0.71			10	76	69
Tm (°F)	79.85714			15	80	70
				20	85	71
Vm (std)	33.98212			25	87	72
				30	89	73
VLc (g)	66.8			35	89	73
Vw (std)	3.144276			40	90	74
				45	90	74
% water	8.469111			50	91	75
				55	92	75
				60	92	75
				65	92	76
				70	92	76
				Average	86.71429	73

Test Run 5

Barometric Pressure	29.93	**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Y	0.984			0		
Vm	34.141	588.351	554.21	5	81	69
Delta Ha	0.73			10	85	70
Tm (°F)	78.67857			15	85	70
				20	85	72
Vm (std)	32.98565			25	86	71
				30	86	72
VLc (g)	69.7			35	86	72
Vw (std)	3.280779			40	86	72
				45	86	72
% water	9.046324			50	86	73
				55	86	73
				60	87	73
				65	86	73
				70	87	73
				Average	85.57143	71.78571

Test Run 6

Barometric Pressure	29.93	**Meter Start**	**Meter End**	**Time**	**Temp in**	**Temp Out**
Y	0.979			0		
Vm	31.325	322.91	291.585	5	84	70
Delta Ha	0.71			10	89	71
Tm (°F)	82.03571			15	90	72
				20	90	73
Vm (std)	29.9232			25	90	74
				30	90	74
VLc (g)	69.5			35	90	74
Vw (std)	3.271365			40	90	75
				45	91	75
% water	9.855122			50	91	75
				55	91	76
				60	91	76
				65	91	76
				70	92	76
				Average	90	74.07143

Test Run 7

		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	30.24					
Y	0.984			0		
Vm	34.535	653	618.465	5	73	71
Delta Ha	0.73			10	87	72
Tm (°F)	79.39286			15	87	73
				20	87	73
Vm (std)	33.66665			25	87	73
				30	87	73
VLc (g)	50.4			35	87	73
Vw (std)	2.372328			40	87	73
				45	87	73
% water	6.582672			50	87	73
				55	87	73
				60	87	73
				65	87	73
				70	87	73
				Average	86	72.78571

Test Run 8

		Meter Start	Meter End	Time	Temp in	Temp Out
Barometric Pressure	30.24					
Y	0.979			0		
Vm	35.287	393.5	358.213	5	73	72
Delta Ha	0.71			10	91	73
Tm (°F)	82.96429			15	92	74
				20	92	75
Vm (std)	33.99818			25	92	75
				30	92	76
VLc (g)	46			35	92	76
Vw (std)	2.16522			40	92	76
				45	92	76
% water	5.987325			50	92	76
				55	92	76
				60	92	76
				65	92	77
				70	92	77
				Average	90.57143	75.35714

Appendix I

Phase I EPA Tests 16-18 – Raw Results by Fraction

Method	Experimental Matrix #	Fraction	Sample #	Tare	Final	Net Wt (g)	Net Wt (mg)
160M202	M16	160Filter	EPA Filter #7	0.25122	0.25114	-0.00008	-0.08
160M202	M16	320Filter	EPA Filter #6	0.25277	0.25246	-0.00031	-0.31
160M202	M16	Acetone/DCM	70	6.18086	6.18139	0.00053	0.53
160M202	M16	AmbFilter	EPA Filter #8	0.25093	0.25143	0.00050	0.50
160M202	M16	Aq	84	6.30322	6.30947	0.00625	6.25
DIM-202	M16	320Filter	EPA Filter #9	0.25249	0.25243	-0.00006	-0.06
DIM-202	M16	Acetone/DCM	71	6.39416	6.39491	0.00075	0.75
DIM-202	M16	AmbFilter	EPA Filter #10	0.25417	0.25464	0.00047	0.47
DIM-202	M16	Aq	80	6.32593	6.33071	0.00478	4.78
160M202	M17	160Filter	EPA Filter #12	0.25267	0.25258	-0.00009	-0.09
160M202	M17	320Filter	EPA Filter #11	0.25381	0.25353	-0.00028	-0.28
160M202	M17	Acetone/DCM	78	6.27774	6.27876	0.00102	1.02
160M202	M17	AmbFilter	EPA Filter #13	0.25447	0.25488	0.00041	0.41
160M202	M17	Aq	89	6.11727	6.12445	0.00718	7.18
DIM202	M17	Acetone/DCM	77	6.19651	6.19748	0.00097	0.97
DIM-202	M17	320Filter	EPA Filter #14	0.25472	0.25480	0.00008	0.08
DIM-202	M17	AmbFilter	EPA Filter #15	0.25542	0.25577	0.00035	0.35
DIM-202	M17	Aq	87	6.24113	6.24632	0.00519	5.19
160M202	M18	160Filter	EPA Filter #22	0.24992	0.24984	-0.00008	-0.08
160M202	M18	320Filter	EPA Filter #21	0.25151	0.25131	-0.00020	-0.20
160M202	M18	Acetone/DCM	76	6.30251	6.3047	0.00219	2.19
160M202	M18	AmbFilter	EPA Filter #23	0.25157	0.25194	0.00037	0.37
160M202	M18	Aq	88	6.12178	6.13149	0.00971	9.71
DIM-202	M18	320Filter	EPA Filter #24	0.25146	0.25143	-0.00003	-0.03
DIM-202	M18	Acetone/DCM	75	6.30812	6.30989	0.00177	1.77
DIM-202	M18	AmbFilter	EPA Filter #25	0.25400	0.25443	0.00043	0.43
DIM-202	M18	Aq	90	6.21088	6.21518	0.0043	4.30
Acetone	Reagent Blk	Acetone/DCM	64	6.33682	6.33679	-3E-05	-0.03
DCM	Reagent Blk	Acetone/DCM	65	6.31007	6.3102	0.00013	0.13
DI Water	Reagent Blk	Aq	74	6.23591	6.23626	0.00035	0.35
160M202	TB-1	160Filter	EPA Filter #2	0.25019	0.25010	-0.00009	-0.09
160M202	TB-1	320Filter	EPA Filter #1	0.25369	0.25354	-0.00015	-0.15
160M202	TB-1	Acetone/DCM	67	6.34277	6.34384	0.00107	1.07
160M202	TB-1	AmbFilter	EPA Filter #3	0.24933	0.24927	-0.00006	-0.06
160M202	TB-1	Aq	79	6.28671	6.29513	0.00842	8.42
DIM-202	TB-1	320Filter	EPA Filter #4	0.25324	0.25314	-0.00010	-0.10
DIM-202	TB-1	Acetone/DCM	69	6.33881	6.33942	0.00061	0.61
DIM-202	TB-1	AmbFilter	EPA Filter #5	0.25235	0.25221	-0.00014	-0.14
DIM-202	TB-1	Aq	83	6.39261	6.39873	0.00612	6.12
160M202	TB-2	320Filter	EPA Filter #18	0.25233	0.25224	-0.00009	-0.09
160M202	TB-2	160Filter	EPA Filter #19	0.25118	0.25114	-0.00004	-0.04
160M202	TB2	Acetone/DCM	66	6.26001	6.2613	0.00129	1.29
160M202	TB-2	AmbFilter	EPA Filter #20	0.25236	0.25235	-0.00001	-0.01
160M202	TB-2	Aq	82	6.33480	6.33947	0.00467	4.67
DIM-202	TB-2	320Filter	EPA Filter #17	0.25321	0.25322	0.00001	0.01
DIM-202	TB-2	AmbFilter	EPA Filter #16	0.25152	0.25142	-0.00010	-0.10
DIM-202	TB-2	Acetone/DCM	68	6.22363	6.22469	0.00106	1.06
DIM-202	TB-2	Aq	81	6.38442	6.38857	0.00415	4.15

Method	Experimental Matrix #	Fraction	Sample #	Tare	Final	Net Wt (g)	Net Wt (mg)
DIM202	TB3	320Filter	EPA Filter #29	0.25186	0.25191	0.00005	0.05
DIM 202	TB3	AmbFilter	EPA Filter #30	0.25352	0.25356	0.00004	0.04
DIM-202	TB-3	Acetone/DCM	72	6.18648	6.1892	0.00272	2.72
DIM-202	TB-3	Aq	86	6.35202	6.35407	0.00205	2.05
160M202	TB-3	320Filter	EPA Filter #26	0.25044	0.25025	-0.00019	-0.19
160M202	TB-3	160Filter	EPA Filter #27	0.25319	0.24826	-0.00493	-4.93
160M202	TB3	AmbFilter	EPA Filter #28	0.25052	0.24631	-0.00421	-4.21
160M202	TB-3	Acetone/DCM	73	6.27323	6.27375	0.00052	0.52
160M202	TB-3	Aq	85	6.30020	6.3041	0.0039	3.90
Extra Aqueous Blanks	Aqueous Reagent Blank	DI-BLK-1	91	6.20095	6.20116	0.00021	0.21
Extra Aqueous Blanks	Aqueous Reagent Blank	DI-BLK-2	92	6.34145	6.34616	0.00471	4.71
Extra Aqueous Blanks	Aqueous Reagent Blank	B-3	50 mL Glass Beaker Evaporation	29.94312	29.94344	0.00032	0.32