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

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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.

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

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

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

[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.

[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.

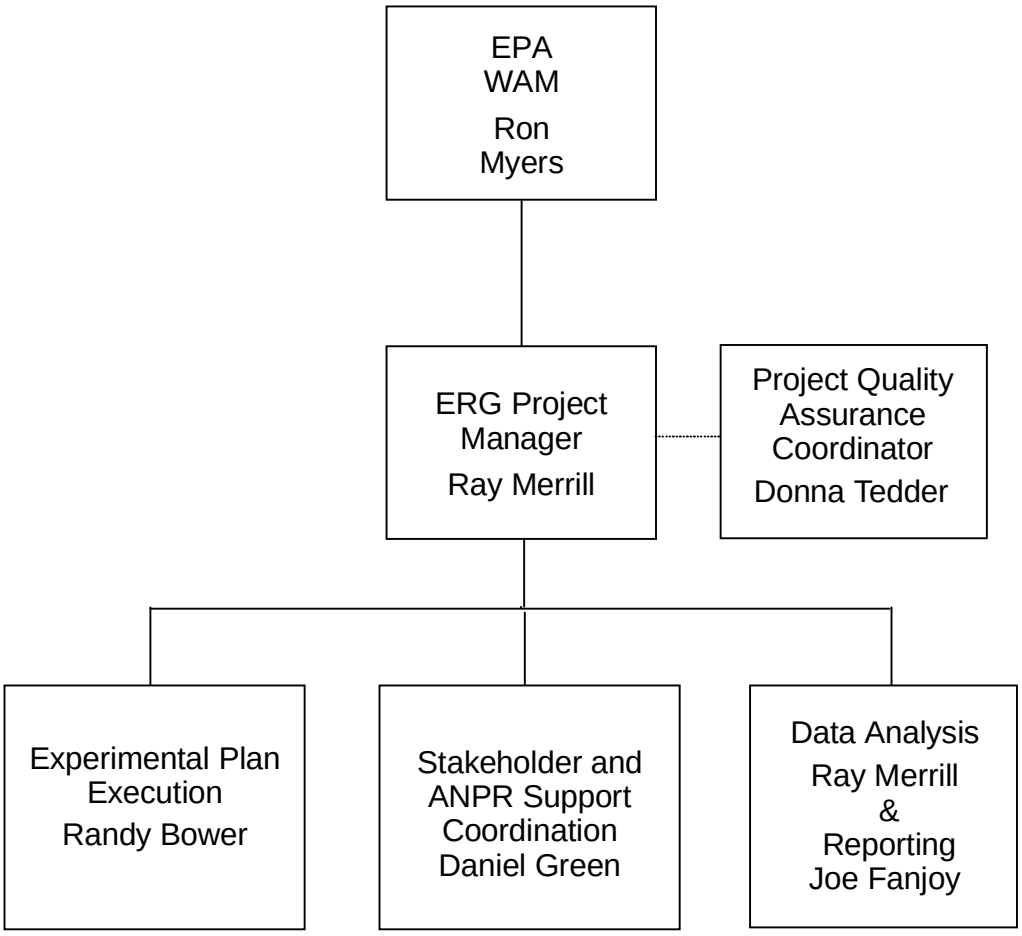

Figure 2-1. Project Organization and Responsibility

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 Laboratory Spiking Equipment and Dynamic Gaseous Spiking

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

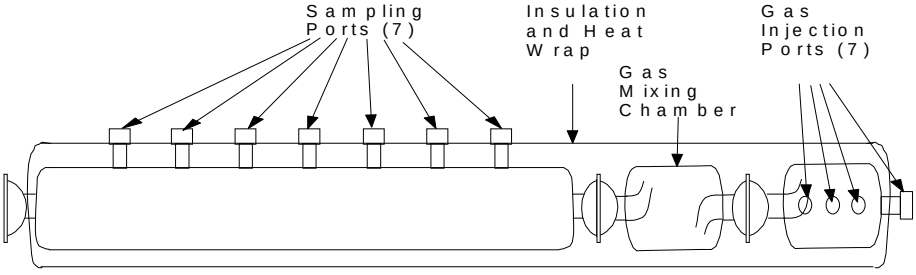

Figure 4-2. Cross Section of Simulator Manifold Mixing Chamber

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.

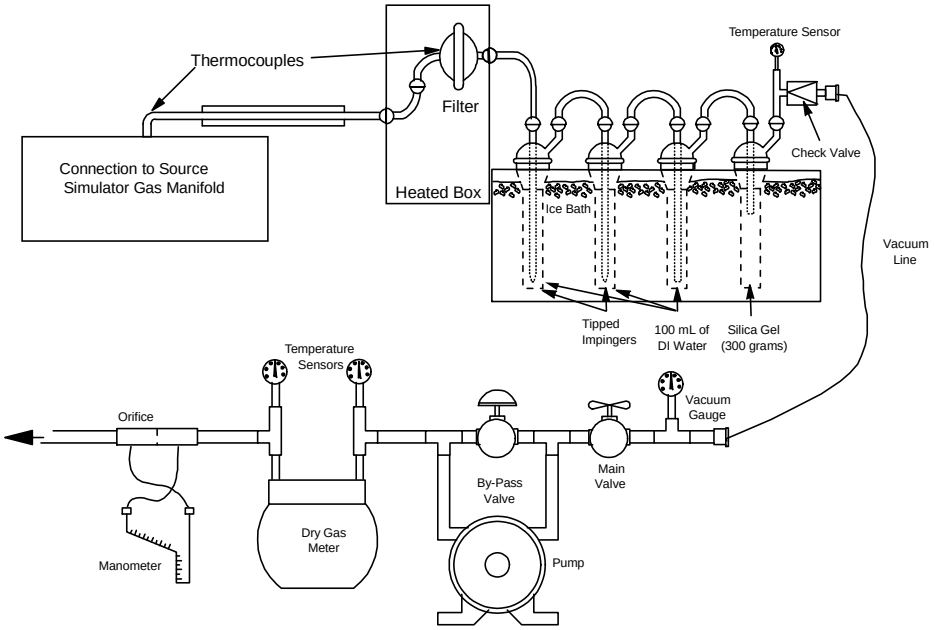

Figure 4-3. Schematic of Condensible Particulate Sampling Train (Method 202)

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 (ΔH) 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 (γ_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.

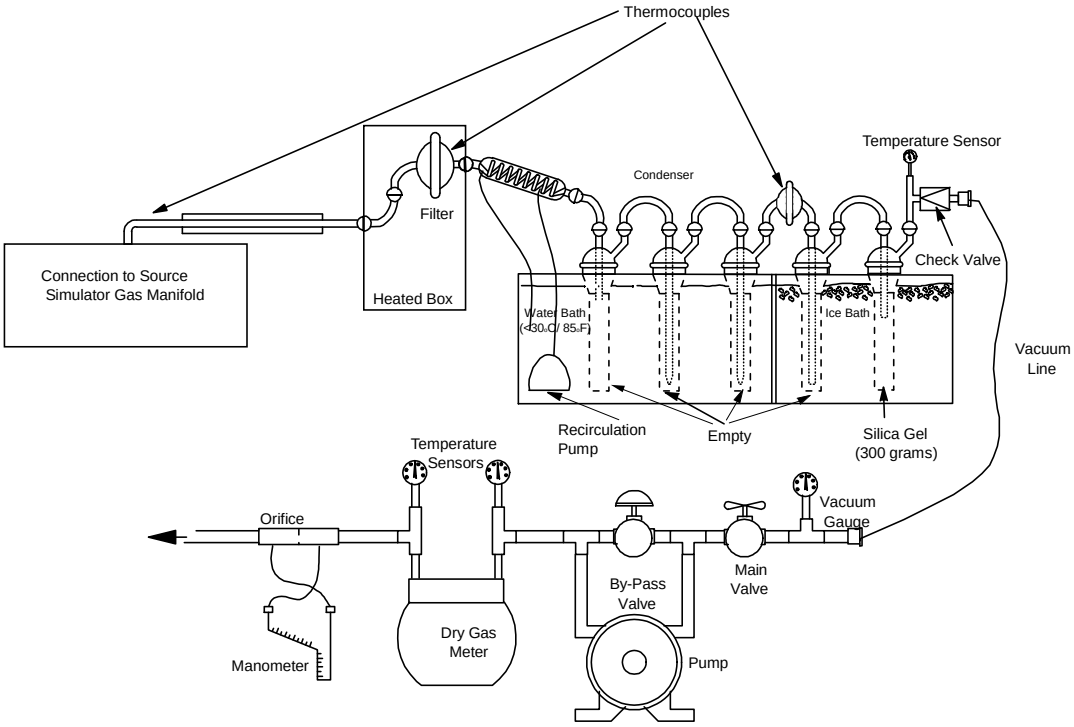

Figure 4-4. Dry Impinger Modification to Method 202

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) Desired	Actual	Probe Temp. (°F)	Filter Temp. (°F)	Adsorbent Trap Temp. (°F)	Dry Gas Meter Inlet (Tm in)	Dry Gas Meter Outlet (Tm out)	Impinger Exit Temp. (°F)	Pump Vacuum (in.Hg)

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:

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

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).

$$\text{Total ion in sample (µg)} = \text{Concentration ion in sample (µg/mL)} \times \text{Total volume of sample (mL)} \times \frac{\text{Dilution volume}}{\text{sample volume}}$$

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

$$\text{Concentration Ion in Sample (µg/dscm)} = \frac{K\,[\text{Total Ion in Sample}]}{V_{m(std)}}$$

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 Laboratory Studies Coordinator

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

$\bar{\times}$ = 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:

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

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.