Method 202 Improvement Project

- Request for participation in Project
- General Project description
- August 1, 2006 Meeting Notes
- Presentation by John Richards
- Presentation by Ray Merrill
- Draft Laboratory Plan and QAPP

To Whom it May Concern:

As you may recognize, the importance of having stationary source test methods and emissions factors to quantify emissions of condensable particulate matter with known data quality is becoming increasingly vital as a component of the management of the ambient air quality. To address concerns over these two issues, EPA has recently received resources to evaluate artifact formation of EPA Method 202, the existing condensable PM source test method, and to explore a few promising modifications to improve this method. Preliminary information indicates that there may be at least one modification that essentially eliminates artifacts which may be formed when SO_2 is absorbed in water and then converts to SO_3 and eventually to sulfuric acid.

We are also interested in using the best performing condensable test method to expand the amount of information used in developing emissions factors for use in estimating condensable PM emissions from a variety of stationary sources. Improved condensable PM emissions factors would enhance PM_{fine} emissions inventories used by State/local agencies and the U.S. EPA in developing effective control strategies.

As you may realize, conducting these two projects in a comprehensive fashion would be a highly challenging and time consuming effort for any single organization. We believe that through collaboration with several stakeholders, we can realize significant advantages and resource leverage. Therefore, we are asking you to consider partnering with EPA in this endeavor.

The attached files provide you and your members with a conceptual framework for these studies. Should you or your members wish to participate in this study, please contact me.

Ron Myers
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Sector Policy and Programs Division
Monitoring Policy Group, D243-05
RTP NC 27711
Tel. 919.541.5407
Fax 919.541.1039
E-mail myers.ron@epa.gov

Conceptual Framework to Improve Condensable PM Test Methods and Emissions Factors

Condensable PM test method issues:

1. EPA Method 202 for condensable PM has a weakness due to the formation of sulfuric acid from absorbed SO_2 that is not fully resolved with the one-hour nitrogen purge.
2. Several stakeholders believe that EPA Method 202's improperly characterizes ammonia in the presence of SO2 and NOx as particulate matter.
3. The benchmark test method for condensable PM, Conditional Test Method 39 has not been fully validated through EPA Method 301
4. The particle sizing test method for course and fine PM (Conditional Test Method 40) has not been fully validated through EPA Method 301
5. Regulatory test methods should be published in Federal Register prior to widespread use.

Background:

EPA Method 202 uses water-filled impingers to cool, condense and collect materials that are vaporous at stack conditions and become solid or liquid PM at lower temperatures. The method was promulgated as part of Appendix M of 40CFR part 51 on December 17, 1991. Although the preferred application of the method incorporates purging with nitrogen for one hour, options to exclude this purging are included in the procedures. Without the nitrogen purge, essentially all of the SO_2 forms sulfuric acid when absorbed and allowed time to react in the impinger water. The mass of sulfuric acid is then measured as particulate matter. The amount of sulfuric acid PM resulting from this SO_2/water reaction is related to the concentration of SO_2 in the stack gas, the quantity of water in the impingers, and the sampling duration.

To characterize the existing level of SO_2-related particulate matter formed in Method 202, we have performed a limited number of laboratory evaluations. The laboratory data document that a purge of the impinger solutions with nitrogen for 1 hour immediately following sample collection is more than 95 percent effective in flushing SO_2 absorbed in the impinger water before it can react. Some SO_2 will react with the water to form SO3 and then sulfuric acid before the end of the test run and the resulting sulfuric acid cannot be removed from the impinger through a purge.

For example, a typical coal-fired boiler with SO_2 emissions of 150 ppm (1.3 lb/MMBtu) and filterable PM emissions of 0.03 lb/MMBtu would produce a sample mass of about 50 mg of filterable PM and about 50 mg of condensable PM with the one-hour nitrogen purge. The condensable PM would include from less than 3 mg to over 6 mg of sulfuric acid converted from SO_2 absorbed in the water. Without the nitrogen purge, the total mass of condensable PM measured could be between 150 and 240 mg of which 100 to 200 mg would be sulfuric acid converted from SO_2.

Ammonia is increasingly being injected for the purpose of NOx reduction. In this process, some excess ammonia exists in the stack gas. Limited laboratory testing and dilution sampling system results indicates that this ammonia chemically reacts with acid gases released with the ammonia. Since Method 202 collects the sample in water and free ammonia is highly water soluble, the conditions under which ammonia is properly characterized by Method 202 requires investigation.

We have obtained additional resources to conduct limited studies to supplement the existing evaluations and to expand the evaluations exploring alternatives to reduce further the mass of SO_2 converted to sulfuric acid. Below, we have outlined an approach to such studies that would be possible with additional stakeholder involvement.

Proposed approach:

Perform additional laboratory studies in collaboration with several stakeholders to better characterize levels of SO_2/water reaction particulate mass in Method 202 and to identify potential methods to reduce further the levels.

1. Design a comprehensive laboratory study to examine the relationship between several critical source sampling parameters (SO_2 concentration, moisture concentration, sample duration, water acidity, ammonia concentration) and the quantity of artifacts formed.
   a. EPA to develop an outline for a study to be circulated to stakeholders for review and comment. (Estimated date – June 30, 2006)
   b. Hold Meeting/teleconference to resolve differences, rank order components of study and conclude study design. (Estimated date – July 14, 2006)
   c. Stakeholders select portions of those components of the study that they accept responsibility for performing.

2. Identify a limited number of modifications to Method 202 that potentially could further reduce the quantity of sulfuric acid formed from SO_2 gas and impinger water reactions.
   a. EPA circulates to stakeholders at least one methodology for consideration. (See attached AW&MA article and picture)
   b. Meeting/teleconference held to resolve differences, improve recommendations, and select not more than three alternative methodologies for further evaluation. (Estimated data July 14, 2006)
   c. Stakeholders select alternative methodologies that they accept responsibility for comparing to existing EPA Method 202 methodology.

3. Stakeholders perform limited evaluations comparing sulfuric acid formed in the modified Method 202 methodology to the existing preferred methodology.
   a. Stakeholders share the results of comparative evaluations.
   b. Stakeholders recommend to EPA preferred methodology for further evaluation.

4. For the Method 202 methodology with the least artifact formation, conduct an expanded evaluation at several SO_2 concentrations, ammonia concentrations, sampling durations and moisture concentration combinations.
   a. Stakeholders select those conditions that there will be joint responsibility for performing and for which they will be solely responsible.
   b. Stakeholders share the results of their evaluations.
   c. EPA will combine data from all evaluations, identify those conditions where there is insignificant and measurable formation sulfuric acid. For those conditions with measurable sulfuric acid formation, evaluate potential adjustment procedures to correct for erroneous particulate matter formation.
   d. EPA shares analyses with stakeholders for comment.

5. Publish the results of the laboratory study on the EMC web page. Publish the study in a widely circulated peer review journal.

6. Stakeholders develop emissions factors supporting data.
   a. Develop & coordinate general test plans, develop and coordinate general QA plans, identify test sites, obtain State/local agency collaborators, obtain test contractors. (Start January 2007)
   b. EPA OAQPS provides training for test contractors and Federal/State/local agencies on testing and analytical procedures.
   c. Develop site specific test and QA plans, submit to State/local agency for comment and approval, and coordinate with other stakeholders.
   d. Collect filterable PM10, filterable PM2.5 and condensable PM data using the best performing test method at multiple sources.
   e. Report the results of test programs to EPA for inclusion in WEBFIRE (AP-42 emissions factors repository).

7. When three supporting data are available, EPA will replace or enhance existing condensable PM emissions factors with updated data.

8. EPA will request funds for performing a collaborative validation study of the revised Method at several sources.

9. EPA will request funds to perform validation testing of CTM-039 concurrent with validation testing of revised Method 202 for course and PM_{fine}.

10. EPA will propose CTM-040 combined with the best performing version of Method 202 as a stand alone method for course and fine particulate matter.

11. EPA will propose CTM-039 as an alternative course and PM_{fine} test method for use in situations were sources consider the use of the best performing version of Method 202 would produce undependable results.

Meeting Notes:
Condensable Particulate Matter Test Methods Meeting

U.S. Environmental Protection Agency
August 1, 2006
Research Triangle Park, NC
Room C112 (919) 541-4486

Meeting Agenda

Time	Topic/Issue to be Discussed
10:00	Introductions
10:10	Ron Myers – Background
10:30	Peter Tsirigotis – Short presentation
10:45	John Richards – Modified method background and supporting information
11:00	Jorge Marson – Environment Canada’s evaluations of modified methodology
11:20	Ray Merrill – Project Plan & Quality Assurance Project Plan (QAPP) development and revisions
12:00	Lunch
1:00	Open floor for discussion on additions and revisions of protocol and QAPP
2:30	Ron Myers – Wrap up
3:00	Adjourn

Attending in person
John Richards (Air Control Techniques – Portland Cement Association, LimeManufacturing Association)
William R. Prokopy (Daimler Chrysler Corporation)
Shannon Vogel (NC Division of Air Quality)
Clifford R. Glowacki (Technicon – Iron Casting Associations)
Roger Shigehara (Emission Monitoring, Inc.)
Naomi Goodman (Electric Power Research Institute (EPRI))
Ralph Roberson (RMB Consulting – EPRI)
Marcus Cook (consultant)
Barry Rafael
Peter Tserigotis (EPA – Sector Policy and Programs Division (SPPD))
Barrett Parker (EPA – SPPD)
Peter Westlin (EPA – SPPD)
Ron Myers (EPA – SPPD)
Brenda Shine (EPA - SPPD)
Robin Segall (EPA – Emissions Measurement Center (EMC))
Tom Logan (EPA – EMC)
Gary McAlister (EPA – EMC)
Ray Merrill (Eastern Research Group – EPA Contractor)
Danny Greene (Eastern Research Group – EPA Contractor)
Randy Bower (Eastern Research Group – EPA Contractor)
Joe Fanjoy (Eastern Research Group – EPA Contractor)
Emil Stewart (MACTEC Federal Programs)
Art Warner (MACTEC Federal Programs)

Attending by teleconference
Glenn England (GE Energy – API)
Leslie Ritts (Hardison Lawson, LLP – NEDA/CAP)
Karl Loos (Shell Petroleum – API)
Krishna Row (Koch Industries)
Hannah Valmont (Koch Industries)
Mark Lutrzkowski (Delaware DNR)
Jeff Hege (Indianapolis, IN)
Gary Helm (Connective – Clean Energy Group)
Jorge Marson (Environment Canada)
Andy Sieber

Introductions: Ron Myers (EPA – SPPD)
Ron Myers began with an overview of the purpose of the meeting: To discuss improvements in the condensable particulate matter (CPM) testing methods and to get stakeholder input on EPA's plan to investigate and improve Method 202. Ron introduced Peter Tserigotis, who Ron gave credit for actively involving stakeholders in the process.

Background: Peter Tserigotis (EPA – SPPD)
Peter noted that CPM was not important for stationary sources until recently. Measuring fine particulate was initially focused on mobile sources. For example, the 2004 "Tier II" standards are currently being phased in for vehicles sold in the United States. Also, in March 2005, EPA issued the Clean Air Interstate Rule (CAIR), which is expected to significantly reduce sulfur dioxide (SO_2) and nitrogen oxides (NO_X). But, many areas remain as persistent nonattainment areas. On November 1, 2005, EPA proposed (70 FR 65984) requirements that States and Tribes must meet attainment status in their state implementation plans (SIPs) for fine particle (PM2.5) national ambient air quality standards (NAAQS).

The challenge for States and EPA is how to cost-effectively bring these areas into attainment. What is their relative contribution to CPM? How does EPA make the transition when measuring a "new" pollutant? How do you show consistency in measuring condensable PM and move forward? These are some of the questions EPA is addressing. Peter thanked everyone for their participation.

John Richards (Air Control Techniques – Portland Cement Association, LimeManufacturing Association) Presentation based on a paper, "Optimized Method 202 Sampling Train to Minimize the Biases Associated with Method 202 Measurement of Condensable Particulate Emissions" by John Richards, Tom Holder, David Goshaw, Air Control Techniques, P.C., presented at the Air and Waste Management Association Hazardous Waste Combustion Specialty Conference, November 2-3, 2005, St. Louis, Missouri.

John provided background on the bias of Method 202:

- Significant positive biases have been observed since the Method 202 was promulgated in 1992
- Biases are difficult to quantify
- Biases appear to vary significantly
- It is technically inappropriate to use water-filled impingers to cool a gas stream containing SO_2, NO_2, or soluble organic compounds and analyze for CPM
- Compounds such as SO_2 and NO_2 can absorb in the impinger water and then convert to form material that is counted as CPM
- Dissolution of SO_2 and NO_2 into water with subsequent oxidation to form sulfates and nitrates
    - There are a number of aqueous phase reaction mechanisms for converting SO_2 into H_2SO_4
    - Aqueous phase conversion estimated at 2-6%

  - Gases are more soluble in cold liquids, such as ice-chilled impinger solutions

John described a modified sampling train designed to achieve adequate temperature reduction of the gas stream with minimal contact between the SO_2-containing gas stream and the impinger liquid:

- Method 23 condenser
- 47 mm filter located between two dry knockout impingers
- Dry knockout impinger with short stem
- Two additional impingers similar to Method 202

Advantages:

- Positive bias is reduced to 10 – 15% of the levels of conventional Method 202 for sources having moderate-to-high SO_2 and NO_x concentrations
- Requires only off-the-shelf parts (glassware)
- No major deviations from Method 202 procedures
- Can run in conjunction with Methods 5, 17, and 201
- Reduces dissolution/oxidation of SO_2

Disadvantages:

- High moisture streams introduce more water and SO_2 conversion is increased
- Absorption of highly soluble gases can occur despite the limited water and the reduced gas-liquid contact
- High concentrations of ammonia and organic compounds can create significant bias

John's studies examined 150-500 ppm SO_2. He concluded that it is difficult to accurately measure CPM through a water solution. There are too many reactions that happen too fast (~4% per hour oxidation rate). The chilled, water-filled impinger is the perfect environment for reactions, therefore, is not appropriate. When the reactions occur, there will be artifacts formed in the impingers, plus artifacts in the filters. In addition, you cannot begin purging at the beginning of the run when the aqueous phase starts accumulating and artifacts start to form. Lab tests show the bias of the dry impinger method is 10-15% of the bias experienced with Method 202.

Summary:

- Conventional Method 202 is subject to positive biases that can result in reported CPM emissions that are 0.005 to more than 0.015 grains/DSCF higher than actual emissions.
- Modified Method 202 provides a useful interim method until dilution techniques are refined. Dissolution/oxidation related positive biases are substantially reduced.

Discussion following John Richards' presentation:

Robin Segall asked whether John tried the method in the field and compared back to lab results. John said that when compared to Method 202, the dry impinger method does not show lower bias at sources with ammonia. Other field test data on the dry impinger method is confidential client information. John will pursue release of the information with his clients. He has not compared the dry impinger modification to CTM 039 yet.

Pete Westlin asked which combustion sources would yield high CPM results in the dry impinger method. John said wet processes such as Portland cement (35-40% moisture). Ron noted that any direct contact incinerators would give high results too. Ray Merrill pointed out that sludge incinerators would too.

Ray asked John a question about reaction rate. During first 10 minutes, SO_2 is absorbed at 50% in Method 202. By 15 minutes, SO_2 has saturated the water and additional SO_2 at the spiking level is increased the train exhaust. Your data show the Method 202 adsorption of SO_2 reaches saturation quickly. With the extended sampling times, would you expect the dry impinger train to reach saturation before sampling was complete? John referred to his second slide. There was 5% moisture (35 ml in first impinger). John stated that the higher the moisture, the less useful the dry impinger method becomes because the SO_2 absorption is somewhat proportional to the water in the train.

Roger Shigehara asked if the residence time were long enough for true CPM to form. John said the time was long enough for CPM to nucleate and be captured in the filter after the third impinger. The CPM caught in the train nucleates well.

Roger asked whether John tried different sampling train flow rates. John replied yes, but budget was limited. Roger asked what quantity (mg) are the catches in the train. John said 50 or 60 mg (see the AWMA paper). There are many variables, including oxidizing gases.

Jorge Marson – Environment Canada's evaluations of modified methodology

Jorge stated that he had read John Richards' paper (cited above) and tried to find ways to complement John's research. His goal was to improve the technique and reduce CPM by using known sulfuric acid solutions.

He used 105° drying temperature for the aqueous impinger catches per Method 202. He noted that keeping the drying temperature at the Method 202 target temperature is very important. For example, at a 95° drying temperature, residues are 50% higher.

He used the following test parameters.
SO_2 concentration: 100 – 600 ppm
Moisture: 5 – 20%

Findings:
From 100 – 600 ppm, the artifact remained constant. Jorge questioned the residues and identified a systematic error: When using dry impingers, how do you purge at end? His approach is to take condensate out. He purged for 1 hour in a beaker with a glass filtered sparger. After 1 hour, 20% SO_2 remained dissolved.

Jorge learned that purging with a sparger in an open container is limited to 2 liters per minute and is insufficient to remove all dissolved SO_2. Jorge recommends careful consideration on how to do the nitrogen purge. A limiting factor for good purging is how much you can flow through.

Jorge did not store the samples long—he dried the samples overnight immediately after collection. He noted that 10 ml of air in the headspace can produce 12 mg of SO_4 artifact.

If the purge is not complete, then the artifact can increase. Nitrogen purge is a challenge if done in a separate container. Also, you cannot purge with a sparger at the rate required in Method 202.

Jorge suggested that you can control SO_2 by lowering the pH or using organic liquid to cover the aqueous condensate. Results of adding H_2SO_2 to lower the pH were inconclusive.

Amount of artifact is not affected by the following:
- SO_2 concentration (in this range)
- Moisture level (in this range)

Jorge achieved 2 mg total CPM using the dry impinger method. Standard deviation was within 1 mg. Results were 2 mg +/- 1 mg for the dry impinger method compared to 20 mg or more from Method 202.

Naomi questioned whether the 2 mg are time dependent. What about longer runs? Two to 50 mg seems to be the breaking point.

Ray Merrill – Project Plan & Quality Assurance Project Plan (QAPP) development and revisions

ERG was tasked by EPA to do the following:

- Better characterize precision and bias of EPA Method 202
- Identify and evaluate improvements to Method 202 methodologies
- Quantify Method 202 bias using existing procedures to purge SO_2
- Characterize the potential bias of ammonia in the Method 202 sampling system in the presence of SO_2

Goals:

- Keep the gas matrix mixture simple
- Keep glassware as conventional as possible
- Replicate how test would be conducted in the field

Ray stated that the source simulator can generate enough gas to run two Method 5 trains at 5 – 10% moisture. Also, the source simulator can meter multiple gases (see parameters). (Organics not part of this test plan.)

For the dry impinger train runs, ERG used Method 5 (probe, hot box), with Method 202 back half.

Parameters:

- SO_2 concentration: 25, 150 ppm
- Moisture: 5 – 10%
- Flow rate: 0.5 cfm
- Elevated temperature 160°C (320°F)
- Insert Method 23 condenser at an angle (not vertical)
- For purging, replace the short stem in first impinger with long stem to remove entrained moisture

Initial Test Plan:

- 18 test runs (9 paired test runs, 25 and 150 ppm)
- First 12 test runs are complete CO_2, O2, H_2O, NO, $NO_{2.}$ Ammonia test runs have not been performed yet.

Using the same sampling manifold and same operator allows direct comparison of Method 202 vs. the dry impinger train.

Ray noted that stakeholders would see another version of the Project Plan & Quality Assurance Project Plan (QAPP). Test plan (and the tests performed) were revised as follows based on early stakeholder comments:

- Use a 50/50 mixture of NO/NO_2
- Use Method 5 and Method 23 glassware
- Use short stem impinger insert for dry method
- Operate the heated train areas at 160 ºC
- Recover samples following Method 202
- Use reagent solvents equivalent to Method 315
- Wet impinger and dry impinger paired tests
- Purge wet and dry trains for 1 hour at ~1 cfm
- Use long stem impinger insert to purge dry method
- Collect aliquot of aqueous impinger sample prior to residue dry down
- Analyze aliquot for anions by Ion Chromatography (IC)
- Add ammonia to neutralize samples
- Dry samples and weigh residue

- Reconstitute samples in water for IC analysis

Initial results:

- Both Methods produce SO_3 and SO_4
- SO_3 is unstable during analysis
    - Converts to sulfate with time and temperature
    - Aliquot may be stabilized with glycerin
- Speculation: SO_2 retention is a function of the quantity of water (initial/Method 202 or collected/Dry Mod)

Aliquot is from both trains from the total liquid collected before drying. Total catch is 10 times higher in Method 202 compared to dry impinger method.

Ray stated that no samples have been dried because all samples showed significant sulfite and sulfate. Standards are not stable (SO_3 to SO_4 in neutral water), which was true for both trains.

Glenn noted that it is common to see sulfites when you see sulfates. But sulfites are typically not quantified. Glenn also said that sulfate and sulfite are captured quantitatively if sufficient ammonia is present.

Jorge thinks this confirms impingers are not faster or better than the sparger. Ray stated that he could not say so quantitatively. These samples are not sparged completely enough to get rid of all SO_3. ERG did not consider other sparging methods.

John Richards noted that there are procedures for stabilizing SO_2 and SO_3 in water.

Open floor for discussion on additions and revisions of protocol and QAPP

Following lunch, Ron Myers led an open discussion. Comments during the open discussion fell into essentially four categories, as follows.

1. Administrative Guidance from EPA

Test plan comments are open until August 11. Stakeholders should submit proposed changes to the test protocols or identify studies they are willing to fund/conduct.

Naomi asked how EPA sees the stakeholder process working. Ron stated that, as far as procedure and timing, EPA would propose and promulgate the new method for use in general for source categories. Estimated time: Propose within a year and approve in another year. Very hard tell time line—it depends on stakeholder participation (number/type of comments). The question to the regulated community is whether the dry method is good enough as an alternative to Method 202.

Peter Westlin stated that the process to identify an improved method will work if stakeholders fund additional studies. For example, Owens Corning will use MACTEC to evaluate CTM 039 for hot, wet, organic sources.

Ron stated that EPA can put only so many bandages on Method 202. Ultimately, sources may need to go to a dilution tunnel method. Stakeholders are becoming more involved in tests. That’s why EPA supports ASTM and dilution method development. EPA does not want to invest a lot into Method 202 since EPA eventually wants to move to dilution tunnel. Ron stated that the modified method is a transition between the Method 202 and a final National Academy dilution system.

Gary stated that EPA would judge modifications and the next work to evaluate modifications based on reduction in artifact formation. For example, 90% reduction is clearly successful. If reduction were less than 90%, we would change conditions to improve.

Gary stated that EPA will try everything it can, then go back to stakeholders.

Naomi suggested a weight-based condition as measuring success, instead of a percentage.

Ralph Roberson asked about starting work on wet stacks. He said industry needs an alternative to CTM 039 that does not require in-stack cyclone particle size capture. CTM 039 is a long way from a compliance method.

2. Purpose of the project

Roger questioned the purpose of the EPA experiment. We know Method 202 gives high artifacts. Dry impinger seems flawed with artifacts. Why proceed with this set of experiments since we know both methods generate artifacts? If SO_3 is condensable, then why not sample SO_3?

Ron and Gary stated that EPA wants to get a consistent analysis. Then, using a consistent method, data could be gathered and evaluated across sources. With a good data set, EPA can also evaluate controls. Ron stated that EPA hopes to have the improved method implemented at other sources. EPA needs a consistent database of CPM data. Then, the question is, what kind of control is appropriate?

Tom Logan noted that regarding the scope of the study, EPA is sticking to coal-fired gas concentrations. Additional matrix mixes can be added if stakeholders want to implement in their work.

Gary McAlister noted that this is Phase I. Everyone needs to agree on a procedure before a pilot study. This is part of the plan. If we are not on a path that will lead to a better method, then EPA is prepared to go in a different direction.

We need to find a procedure that provides improvements before moving ahead with a pilot. Phase I is to evaluate if John Richard's method is significantly better by getting some baseline experiments. Ray noted that Phase II could be to evaluate precision and bias on improved method.

Cliff stated that EPA must go beyond Phase I. Industries with particulate standards are now being asked to perform Method 201/202. Results are much higher and they appear to have excessive total particulate matter. We need to go beyond Phase I to evaluate these other concerns and application to other sources. Ron responded that EPA cannot guarantee the resources will be available to continue beyond Phase I.

Naomi asked whether EPA wants a generally applicable method or whether EPA expects to work sector by sector. EPA stated that it does not expect to work sector by sector, but is looking for a generally applicable method. If we went industry by industry, we would need to know the components of each source, but we don't. But, we do know the components of coal-fired utilities. Roger noted that it is easier to address some reactions in liquid with other gases. He does not recommend one method for all sources.

EPA noted that the purpose of the project is to evaluate improvements to Method 202. The 2 mg artifact generated in dry impinger method vs. 10-30 mg artifact generated in Method 202 is a big improvement. EPA does not expect to get to zero artifact with this project.

Gary stated that John Richards' observation that the source testing brings the artifact down to 5 mg is a significant improvement. The question remains: Is 80, 85, 90% reduction significant enough? We don't know the level yet.

Gary stated that implementation of alternative or modified methods, on a case-by-case basis, could be implemented quickly.

Peter discussed PM fine and NAAQS. The 2008 deadline will raise the issue and identify sources of PM fine and the need for a method to measure sources. States will have to address in their SIPs. We need a test method sooner, rather than later, to respond to the NAAQS deadline.

Many stakeholders expressed concern about how States would put the method on permits, since States tend to lump methods together. Gary noted that it's important to present the limitations of a method so it is not applied out of validation context. Glenn cautioned everyone to focus on the sources and matrices for which the method has been proven to work without making premature claims about where the method is appropriate.

Naomi Goodman asked Ron Myers at what point EPA calls a modified method a new method. Ron stated that he does not believe this is a big change. However, whether it's a big change or not depends on the stakeholders. EPA will propose the test method. If stakeholders don't believe it's a big change, then EPA does not start over. If stakeholders do believe it's a big change, then EPA may have to start over.

Tom Logan noted that Method 202 appears in thousands of permits. EPA has not determined what to do if it is determined that an improved method is essentially a new method. Ron stated that EPA is looking for 15-20 %improvement in reducing artifact formation. Ron stated that the modified method is not a solution for all sources.

Ralph questioned whether EPA had tried to determine what constitutes CPM. He noted that plants do not have a CPM control device. But he also suggested that at least that the method would measure something identifiable. Ray said the only way you would know what constitutes CPM is through dilution sampling.

3. Challenging methods with "true" condensable particulate.

Naomi expressed concern that the system has not been challenged with CPM to evaluate negative bias. After challenging the system with CPM, she would recommend going to a pilot plant. She said that EPRI can commit the resources if she thinks the study is going in the right direction. For example, EPRI would like to see other gas materials: higher SO_2; challenge with SO_3, SO_3 and ammonia; and higher moisture. Also, EPRI suggests challenging the system with CPM.

John Richards noted that generating an SO_3 and SO_4 stream that mimics a utility can be used to generate CPM and challenge both systems.

John Richards noted that there are additional modifications that could be made to the dry impinger method in addition to the basic train: warmer catch impinger, warmer filter temperatures.

The modified train will collect sulfuric acid at least as well as Method 202. As long as we are working with sources that generate SO_4, then the dry impinger method will generate CPM. Gary's concern is whether the modified dry impinger train will collect other types of CPM at other sources.

Naomi stated that there's an existing method (CTM) to deal with the SO_2 to SO_4 artifact issue.

4. Stakeholder contributions and other applicable methods

Clifford Glowacki expressed concern about examining power production sources vs. manufacturing. His sources are manufacturing. During Phase II, he would like to see a source matrix heavily loaded with organics or reactive organic material. The casting industry would put resources into the paired dry impinger method vs. standard method to generate repetitions (in the next 6 months).

Karl Loos stated that for gas-fired sources, the artifact can be 100%, which shows a major problem with Method 202. This is a problem for gas-fired turbines that are completing State tests for SIPs. Method 202 applied to low SO_2 sources does not help. Low SO_2 sources produce even more bias since CPM should be very low. NO_2 is soluble in water and no one knows if it's a problem in Method 202.

Naomi suggested that Method 202 could be corrected by taking out the artifact, and thus, the bias. She suggested "subtraction" methods. Such methods would apply to more than gas-fired sources.

John Richards acknowledged that NCASI 8A and CARB methods allow for correction of potential artifacts, if individual species (anions and cations) are measured in the samples. John stated that he tried NCASI 8A, "Determination of sulfuric acid vapor or mist and sulfur dioxide emissions from kraft recovery furnaces."

Ron noted that a Pulp and Paper Research Institute of Canada (PAPRICAN) dilution study showed 8 – 10 times as much particulate in the back half vs. filterable particulate. Sulfates and nitrites were found in the back half (condensable) fraction of the dilution train samples.

Barry Rafael asked whether fluorine would bias the method. Pulp and paper has sulfate; coal has SO_3; and other sources have reactive organics. He also noted that reactive organic substitutes in voluntary programs could pose an artifact problem.

Glenn expressed concern about applying new method to sources in general. Maybe the purpose of the study should limit and evaluate the sources the modified method should cover. Now you are just looking at SO_2 artifact and how it is affected by NH_3. State the limitations more clearly: excessive condensation and variability. Research needs to be supported by the chemical and physical means for the artifact formation.

On condensable PM: What are they; how do they convert to CPM? Very little Method 202 analysis done to evaluate what it DOES measure/accuracy/precision. There is very limited data on the organic/inorganic part of the residue. Thus, it's hard to challenge the train to figure out what it actually measures.

There's much anecdotal data that has been presented that needs to be gathered to know the conditions under which the data were collected to be able to assess what the results really mean.

Next steps:

Ray Merrill will get info from Jorge Marson on how the tests were done.
Ron Myers will get data from the coke industry on how their tests were done.
8/8/2006: EPA will share the above data with stakeholders
8/11/2006: Stakeholders submit suggestions on additional tests/matrices/funding

Modified Method 202 for The Measurement Of Condensable Particulate Matter Emissions

John Richards, Ph.D., P.E.
Tom Holder, REP, CHMM
David Goshaw, P.E.
Air Control Techniques, P.C.
Cary, NC
919-460-7811

- Presently available methods for measuring CPM
  - Method 202 (water-filled impingers)
  - CTM 039 (air dilution)
- Dilution techniques are preferable, but not yet fully demonstrated and practical.
- A modified version of Method 202 can minimize CPM measurement biases until dilution techniques are practical and economical.

Method 202 Biases

- Significant positive biases have been observed since the Method 202 was promulgated in 1992.
- Biases are difficult to quantify.
- Biases appear to vary significantly.

Method 202 Biases

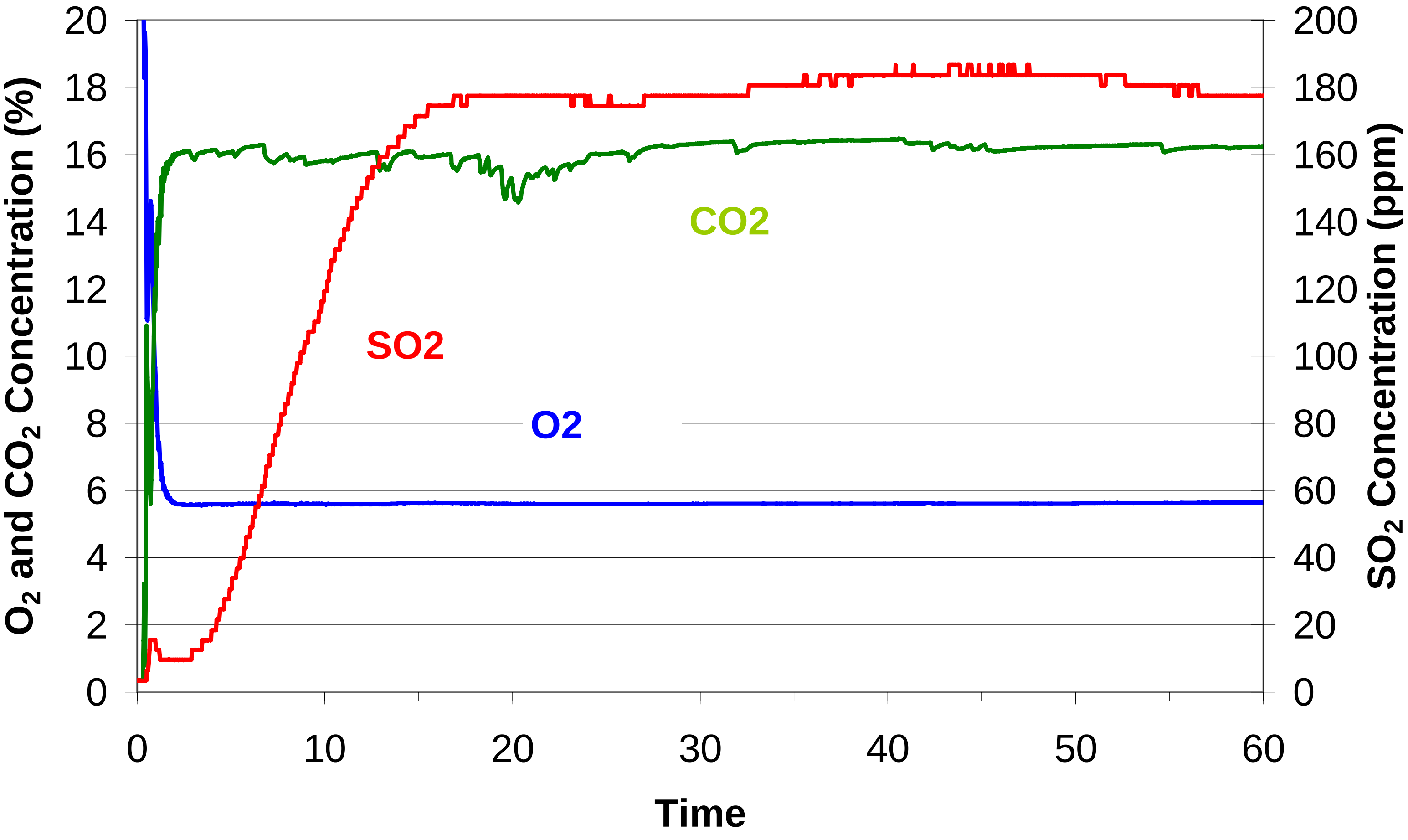
- Technically inappropriate to use water-filled impingers to cool a gas stream containing SO_2, NO_2, or soluble organic compounds and analyze for CPM
- Compounds such as SO_2 and NO_2 can absorb in the impingers and then convert to form material counted as CPM.

Method 202 Biases

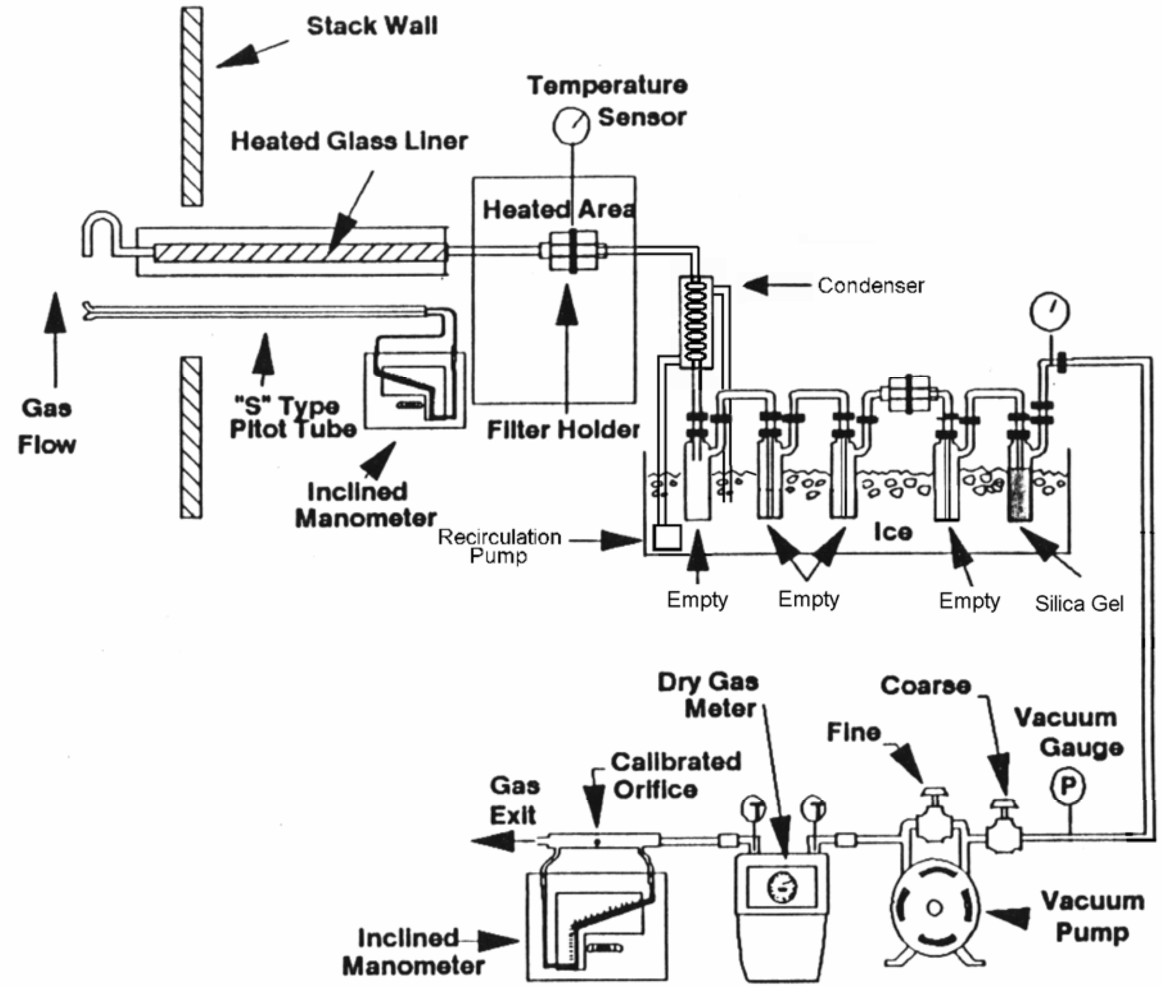
- Dissolution of SO_2 and NO_2 into water with subsequent oxidation to form sulfates and nitrates
    - There are a number of aqueous phase reaction mechanisms for converting SO_2 into H_2SO_4.
    - Aqueous phase conversion estimated at 2-6%
    - Gases are more soluble in cold liquids, such as ice-chilled impinger solutions.

Method 202 Biases

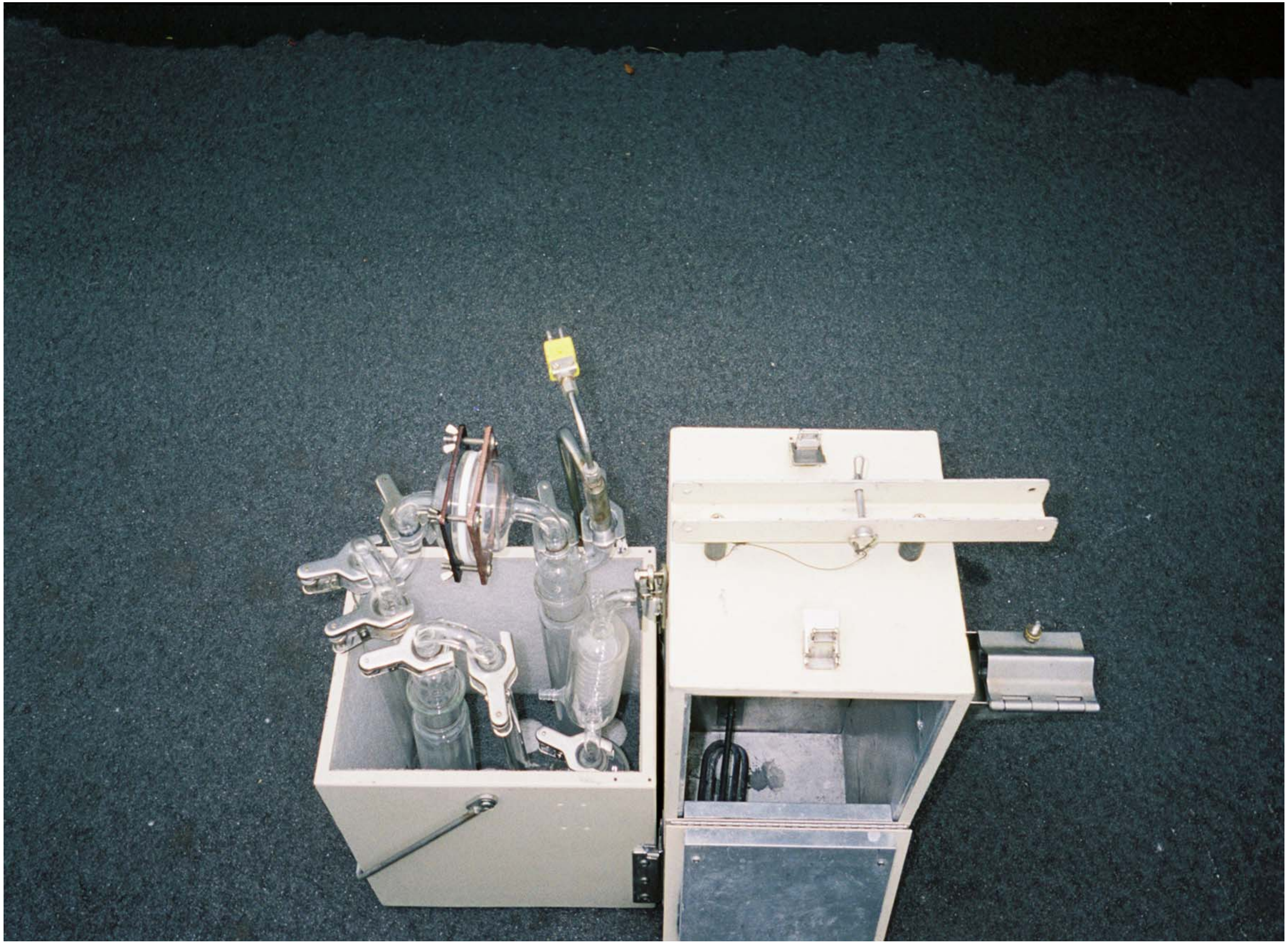
- Incomplete Purging of Dissolved SO_2
  - Method 202 recommends impinger solution be purged with clean N_2 to remove dissolved SO_2.
  - The aqueous phase reactions; however, start immediately.
  - Purge efficiencies of 80%-90% are common.
  - The remaining 10%-20% becomes “CPM.”


O$_2$ and CO$_2$ Concentration (%)
SO$_2$ Concentration (ppm)
Time
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
120
140
160
180
200
0
10
20
30
40
50
60
CO2
SO2
O2

Modified Method 202

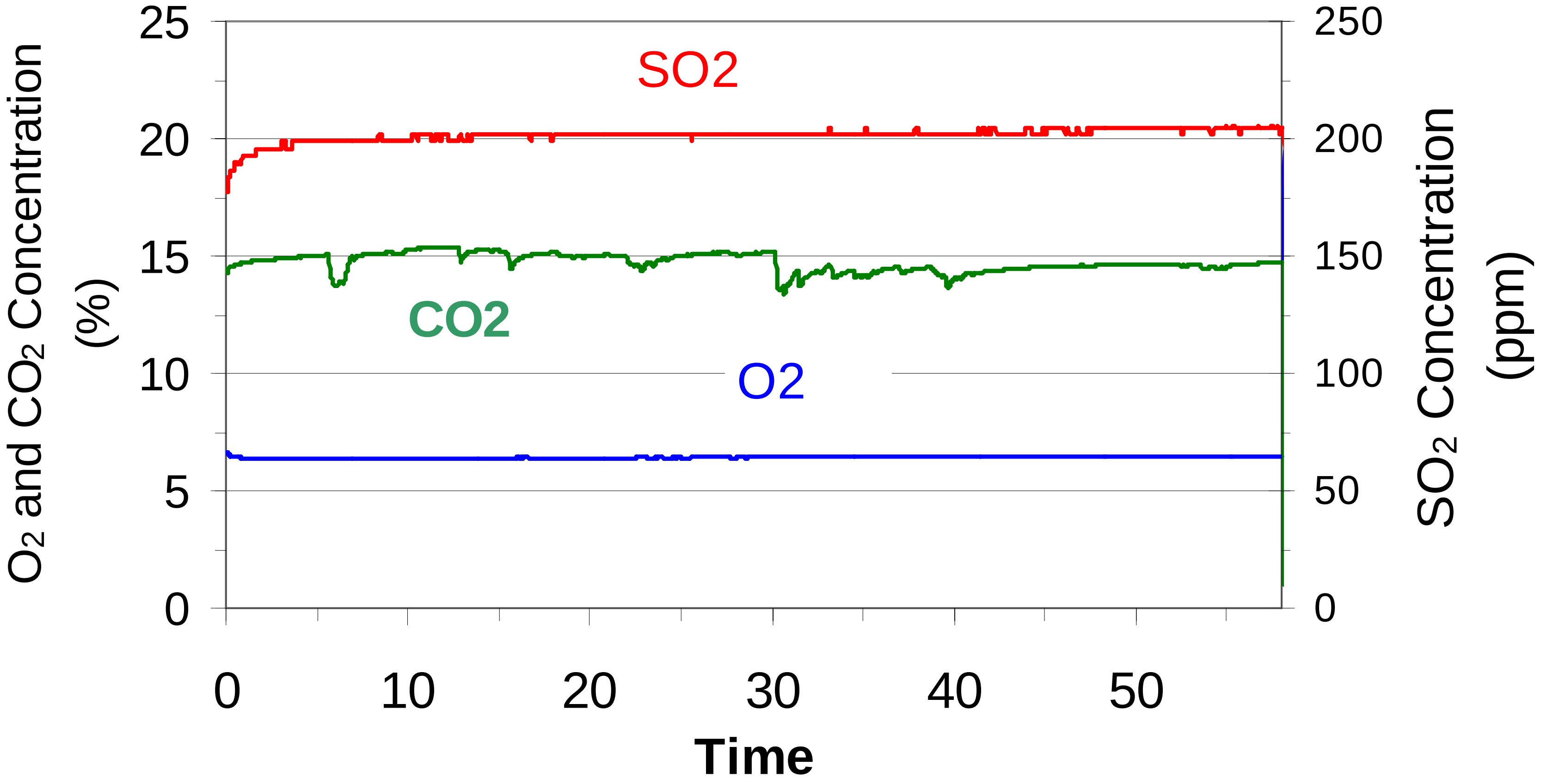


Modified Method 202



Modified Method 202 (cont)

- Glassware Modification
  - Method 23 condenser
  - Drop out impinger
  - Modified Greenberg Smith impinger
  - Back-up filter
  - Silica Gel Impingers


SO2
CO2
O2
25
20
15
10
5
0
250
200
150
100
50
0
0
10
20
30
40
50
Time
O$_2$ and CO$_2$ Concentration (%)
SO$_2$ Concentration (ppm)

Advantages, Modified 202

- Positive bias is reduced to 10% to 15% of the levels of conventional Method 202 for sources having moderate-to-high SO_2 and NOx concentrations.
- Method is economical and requires only off-the-shelf components.
- There are no major deviations from Method 202 procedures.

Limits to Modified Method 202

- High moisture sample gas streams will re-introduce water to the “dry” impingers.
- Absorption of highly soluble gases can occur despite the limited water and the reduced gas-liquid contact. High concentrations of ammonia and organic compounds can create significant bias.

Method 202 Biases

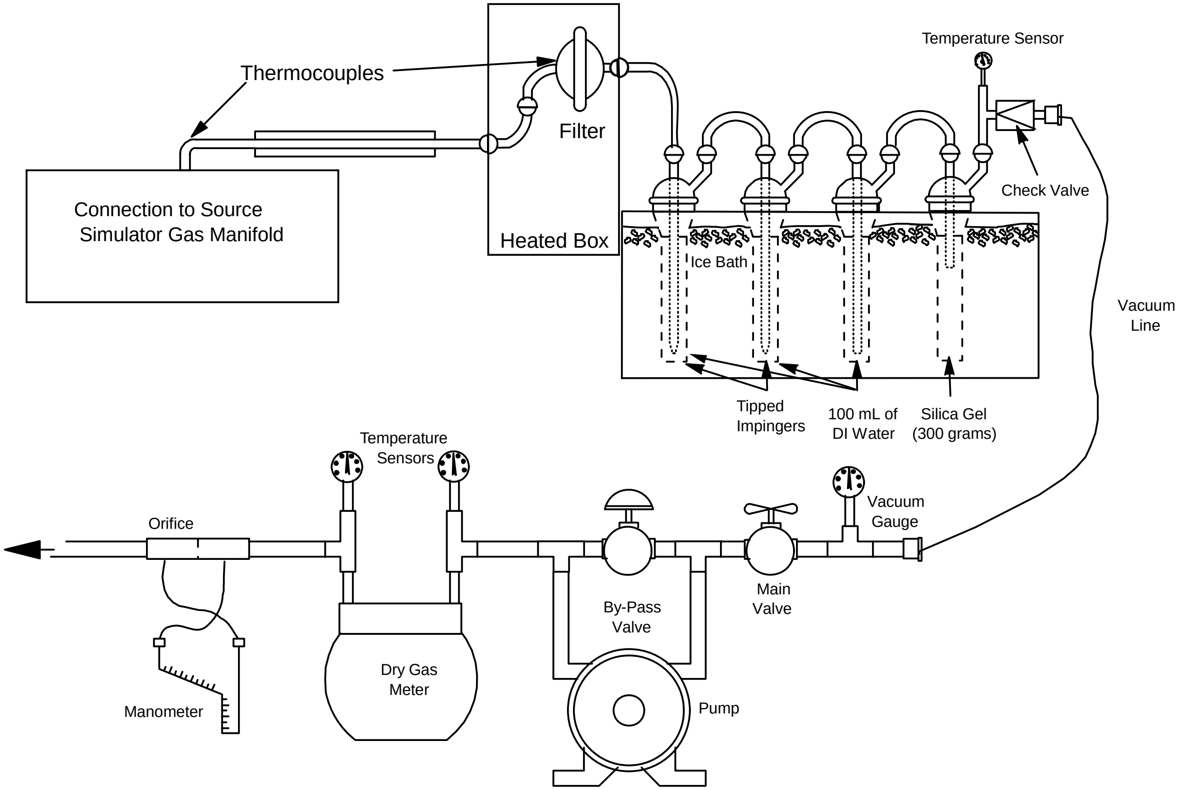
- Summary
    - Conventional Method 202 is subject to positive biases that can result in reported CPM emissions that are 0.005 to more than 0.015 grains/DSCF higher than true.
    - Modified Method 202 provides a useful interim method until dilution techniques are refined. Dissolution/oxidation related positive biases are substantially reduced.

M-202 Assessment and Evaluation Project Plan and QAPP

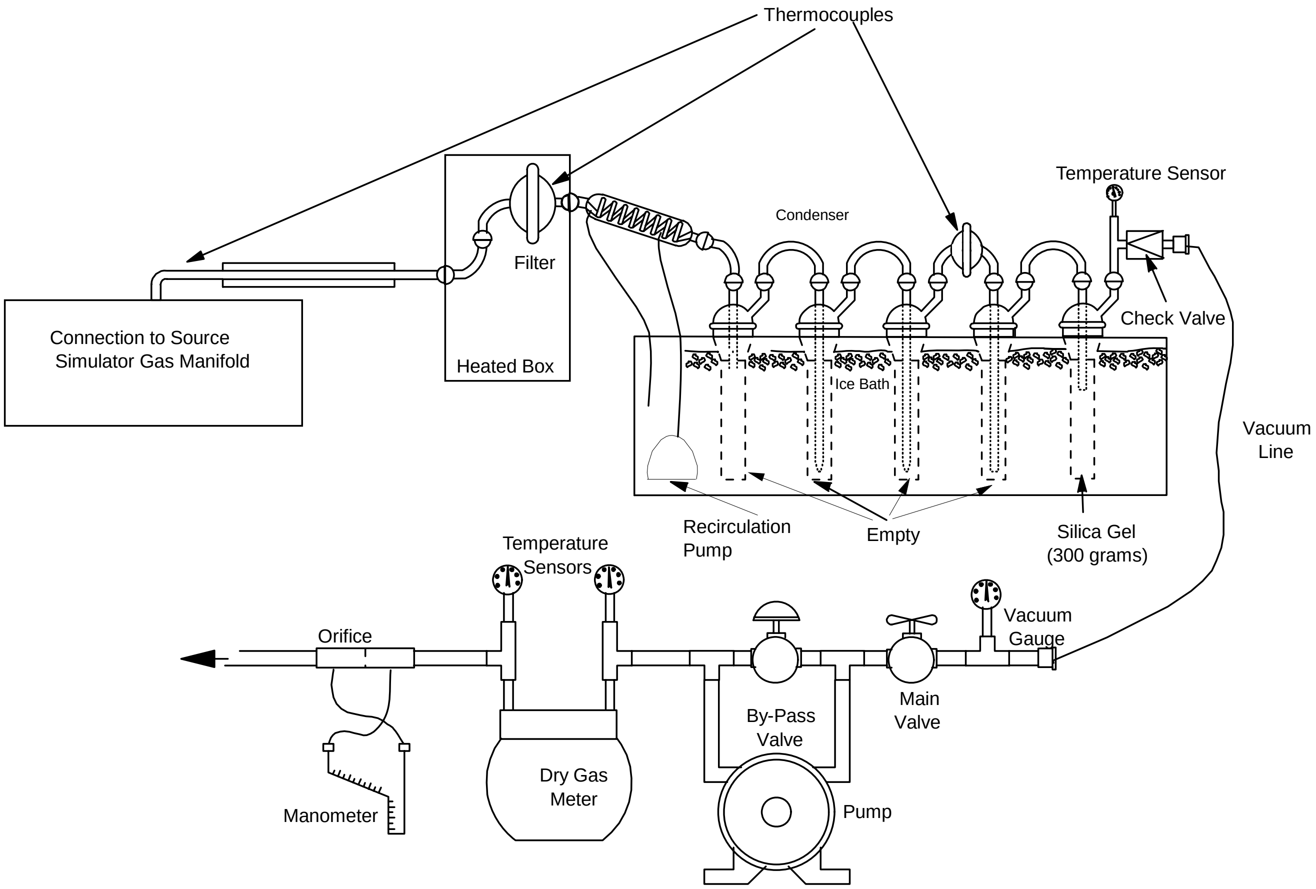
- Initial Test Plan
  - Revisions
  - Early Results
- Test Plan Revisions
- Test Plan Additions (Stakeholders)

ERG Combustion Source Simulator

Wet Impinger Train (M-202)



Dry Impinger Train (Richards)



M 202 Project Plan and QAPP

- Initial Test Plan

Test	Method	Effective SO_2 (ppm)	Effective Ammonia (ppm)	Carbon Dioxide (%)	Oxygen (%)	Water (%)	Nitrogen Monoxide (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
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
Optional Tests							
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

Test Plan Revisions

- Use a 50/50 mixture of NO/NO_2
- Use Method 5 and Method 23 Glassware
  - Use short stem impinger insert for dry method
- Operate the Heated Train Areas at 160 ºC
- Recover samples following Method 202
- Use reagent solvents equivalent to Method 315
- Wet Impinger and Dry Impinger Paired Tests

Test Plan Revisions

- Purge Wet and Dry Trains for 1 Hour at ~1 cfm
    - Use long stem impinger insert to purge dry method
- Collect aliquot of Aqueous Impinger Sample
    - Prior to residue dry down
    - Analyze for anions by Ion Chromatography
- Add ammonia to neutralize samples
- Dry samples and Weigh Residue
- Reconstitute Samples in Water for IC Analysis

Initial Results

Baseline Experiments Performed

Test	**Method**	**SO2 (ppm)**	**Ammonia (ppm)**	**Carbon Dioxide (%)**	**Oxygen (%)**	**Water (%)**	**Nitrogen oxides (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

Initial Observations

- Both Methods produce SO_3 and SO_4
- Sulfite is unstable during analysis
  - Converts to Sulfate with time and temperature
  - Aliquot may be stabilized with glycerin
- Speculation
  - SO_2 retention is a function of the quantity of water (initial/M202 or collected/Dry Mod)

Test Plan Additions (Stakeholders)

- Replicate Tests to Evaluate Best Method
- Additional Tests to Evaluate Other Conditions
- Additional Tests to Evaluate Related Methods

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

DRAFT

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

Prepared by:

Eastern Research Group
900 Perimeter Park
Morrisville, NC 27560

Prepared for:

Mr. Ron Myers
Office of Air Quality Planning and Standards
Emissions, Monitoring, and Analysis Division
Source Measurement Technology Group
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

ERG: Project Manager____

ERG QA Project Coordinator: ____

U.S. EPA Work Assignment Manager: ____________________________________

U.S. EPA QA Manager: ____

July 14, 2006

Table of Contents

Table of Contents

Table of Contents

Table of Contents

List of Tables

List of Figures

Table of Contents

Table of Contents

Table of Contents

Table of Contents

List of Tables

List of Figures

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 SO_2, NO_2, and/or soluble organic compound emissions.[1] These gaseous contaminants can be partially absorbed in

---

[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

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 carbonate 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 in biases in the emissions factors. The use of biased emissions factors in

---

David Goshaw, Air Control Techniques, P.C., Cary, North Carolina.

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

The objective of this work assignment is to identify and 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. This Quality Assurance and Laboratory Test Plan describes the approach and quality control procedures that will be used to evaluate modifications to Method 202. Laboratory tests are planned to determine method precision and bias of the modified EPA Method 202 train with the compounds of interest.

For this work assignment, ERG will establish a baseline for Method 202 performance under the “best” EPA recommended conditions. ERG will also test a dry impinger modification to Method 202 sampling trains. Testing will include collection of spiked samples from a simulated stack gas generation system as described in Section 4.2.

An EPA Method 202 sampling train will form the basis of the sampling hardware. The suspect interfering gases will be spiked into a sampling manifold 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 will be spiked at concentrations described in the experimental matrix in Section 4.1. A minimum of three valid sampling runs will be collected for each of the conditions. If the dry impinger modification to Method 202 shows statistically significant reduced interference from SO_2 compared to the baseline Method 202, then additional replicate tests will be conducted to establish the bias and precision of the method modification under laboratory test conditions.

In this sampling method, the EPA Method 202 sampling train will collect gaseous and particulate pollutants from a simulated emission source. The Method 202 sampling train is described in Section 4.3. Samples are recovered and analyzed according to the procedures in Method 202 described in Sections 4 and 6.

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.

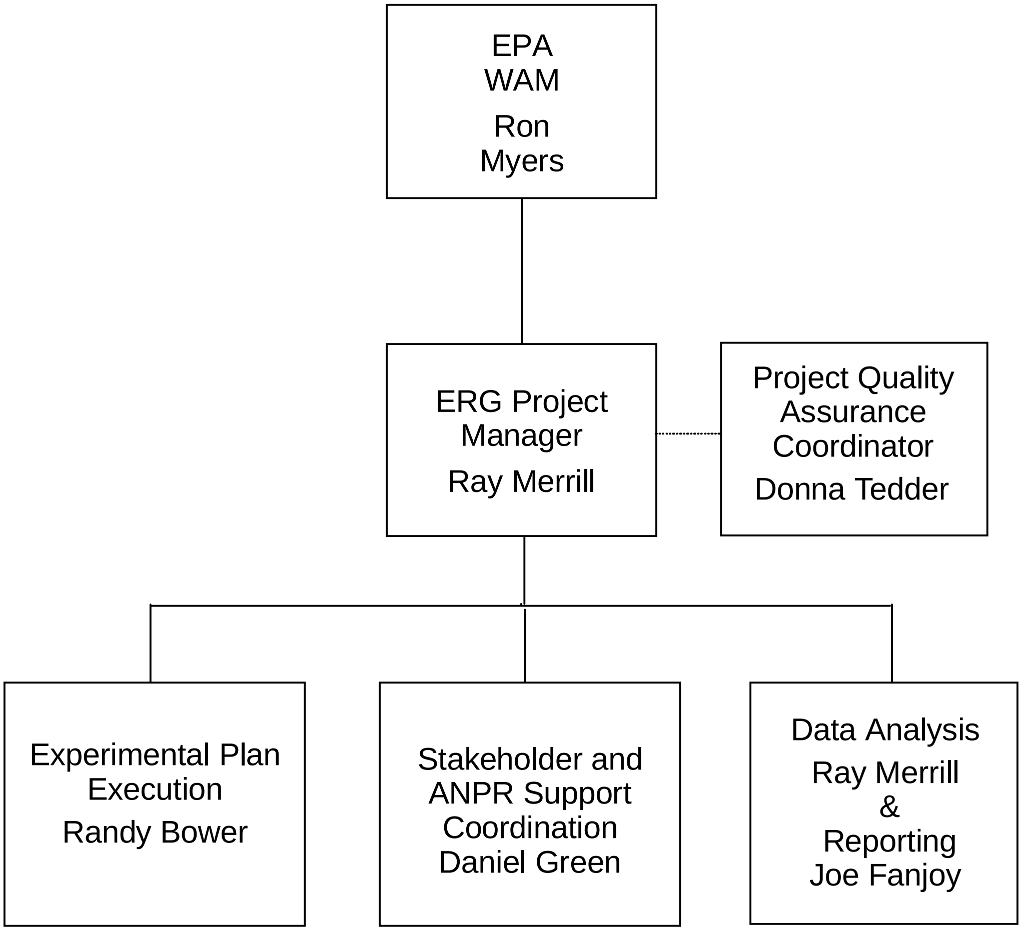


Figure 2-1. Project Organization and Responsibility

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 all activities with stakeholders, including conference calls, information gathering, and responding to public comments.

The Project Secretary, Jody Tisano, is responsible for all permanent records and correspondence for the project. Ms. Tisano will prepare all 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.

3.1 Work Assignment DQO

The work assignment DQO is to establish a baseline measurement of condensed PM by following the procedures in Method 202 at three different simulated stack gas conditions. For these baseline Method 202 measurements, three single sampling runs will be performed at each of the three different simulated stack gas conditions (nine baseline runs). For the modified Method 202 (dry impinger) tests, three single sampling runs will also be performed at each of the three simulated stack gas conditions used to establish the baseline Method 202 performance (nine dry impinger runs).

The number of replicate spiked analyses planned during the baseline and dry impinger stage of this project will not be sufficient for an exhaustive statistical verification. However, if the dry impinger test runs show an improvement of 50% at the 95% confidence level reducing the artifact CPM, then additional test runs will be performed to characterize the dry impinger modification precision and bias. A minimum of seven valid additional dry impinger modified method tests will be performed and evaluated to determine if the improvement is statistically significant. The precision and bias from the seven replicate tests of the dry impinger modification to Method 202 will form the basis of the methods probable performance.

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. MQOs for EPA Method 202 are shown in Table 3-1. Since this project focuses on reducing artifacts to zero residual weight, the method evaluation performed in this test will be performed to recorded to the nearest 0.00001 ±0.00005 g requiring a balance capable of measuring 0.00001g. The need to require balance sensitivity ten times lower than Method 202 will be assessed at the end of the experimental effort. Bias is established by comparing the method's recovery against a reference value. Precision is determined, at the minimum, using paired test results under identical conditions. The precision of the method at the level of the standard shall 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.

Table 3-1. Method 202 Data Quality Objectives

Method	Accuracy (Percent Recovery)	Precision
Method 202	70-130%[1]	<50% RSD <20% RD

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

---

[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.

Section 4.0
Laboratory Spiking Equipment and Sampling Procedures

4.1 Experimental Design

The laboratory test program will determine a baseline for potential artifacts in EPA Method 202 from 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.

Replicate gas samples will be collected from an atmosphere generator to determine potential bias and precision. The test will consist of at least three test runs for 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 for bias and precision. 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 “best practice” application of Method 202. The experimental matrix with key emission gas concentrations is shown in Table 4-1.

Additional dry impinger modified Method 202 tests will be conducted if this modification demonstrates at least 50% reduction in artifact formation during baseline tests. A minimum of seven 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.

4.2 Special Equipment

A single M5/M202 train will be assembled following requirements in Method 202 as shown in Figure 4-1. Several stack gas simulants will be spiked into the stack gas simulator described in section 4.2.1. Three interfering target compounds will be spiked into the stack gas simulator: sulfur dioxide, ammonia, and nitrogen monoxide (NO).

Table 4-1. Method 202 Baseline Evaluation Experimental Matrix

Test	Method	Effective SO_2 (ppm)	Effective Ammonia (ppm)	Carbon Dioxide (%)	Oxygen (%)	Water (%)	Nitrogen Monoxide (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
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
Optional Tests							
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

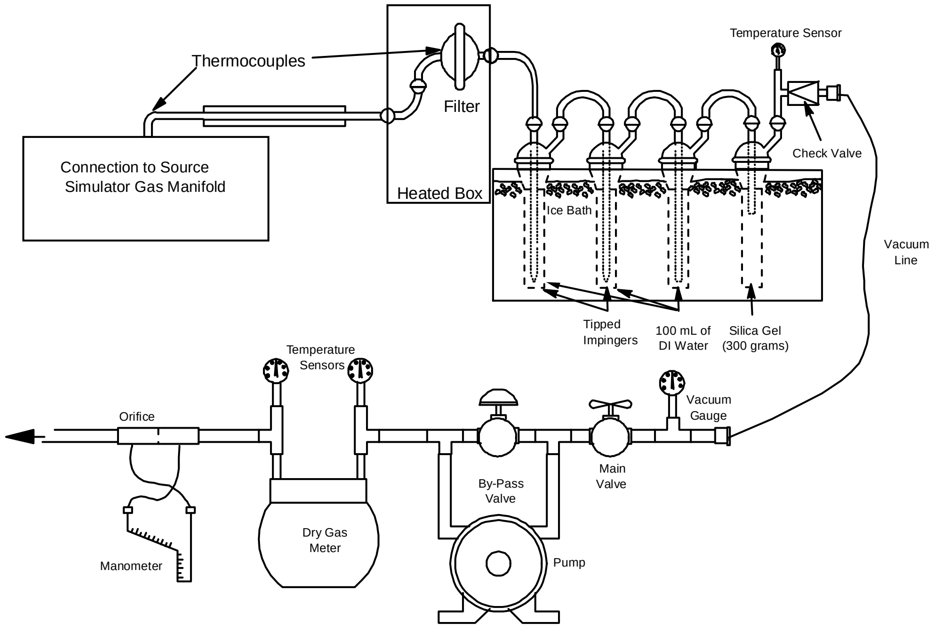


Figure 4-1. Schematic of Condensible Particulate Sampling Train (Method 202)

The 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 4-3). At the start of the tests, impingers in the modified train will be clean without any water or reagent added.

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. The sampling train will be connected to the end of the heated manifold on the laboratory source gas simulator. Sufficient flow from the combination of cylinders and humidified zero air will be generated to produce excess gas. Sampling trains will be operated between 14.5 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 gas generation system shown in Figure 4-2. The manifold delivery system will generate synthetic stack gas at a flow rate in excess of 21 L/min (0.75 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 phase. The Method 202 and modified Method 202 sampling train will collect gas from the manifold at approximately 14 L/min for approximately 1 hour. The resulting gas volume will be approximately 1 dry standard cubic meter (dscm).

4.3 Sampling Preparation

4.3.1 Glassware Preparation

All glassware used for sampling will be thoroughly cleaned prior to use. This includes the probe, 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.

Figure 4-2. Source Gas Simulator Manifold

4.3.2 Method 202 Equipment Preparation

The remaining preparation includes leak checking all the train equipment. This includes meter boxes, nozzles, and umbilicals. Reference calibration procedures will be followed when available, and the results will be properly documented and retained. A discussion of the techniques used to calibrate this equipment is presented below.

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% 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 which were used during the actual test.

Dry gas meter calibrations will be performed by Apex Environmental, Inc.

4.3.3 Dry Impinger Equipment Preparation

Preparation of 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 train is shown in Figure 4-3.

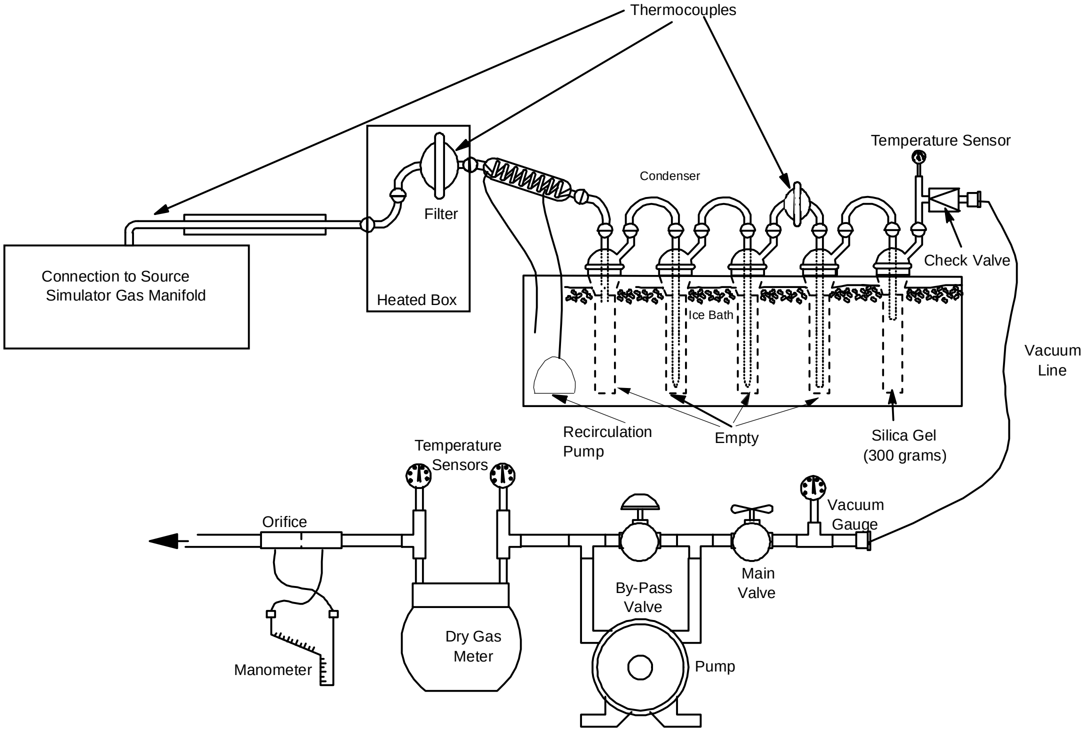


Figure 4-3. Dry Impinger Modification to Method 202

4.3.4 Sampling Operations

Preparation of Sample Train

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.

The sampling train will be leak checked after sampling is complete as required in EPA Method 5/202. Leak checks will also be performed prior to sampling as a precautionary measure. 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% 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% 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 checklist for sampling is included in Figure 4-4. Sampling train data will be recorded every five minutes on standard data forms.

4.3.5 Sample Recovery

The sample bottles containing the probe and nozzle washes and each of the sampling trains will be prepared in an adjacent hood to the sampling system to avoid contamination. Each train component will be carefully removed from the train assembly, sealed and moved to ERG's sample preparation laboratory. 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.

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

Figure 4-4. Sampling Checklist

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 as necessary to maintain a temperature of <68°F at the silica gel outlet.

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

4. 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.

5 Check the ice in the 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 68°F.

Figure 4-4. Continued

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.

4.4 Blank(s)

4.4.1 Train Blanks

At least one set of train blanks will be prepared. A sampling train will be assembled in the staging area, and leak-checked before and after the test period. The sampling train will be recovered in the same manner previously described.

4.4.2 Laboratory Method Blanks

Analysis of the laboratory blank will indicate any sulfur dioxide contributions attributable to laboratory procedures.

4.4.3 Reagent Blanks

Aliquots of each lot of methylene chloride and water will be collected for analysis as reagent blanks.

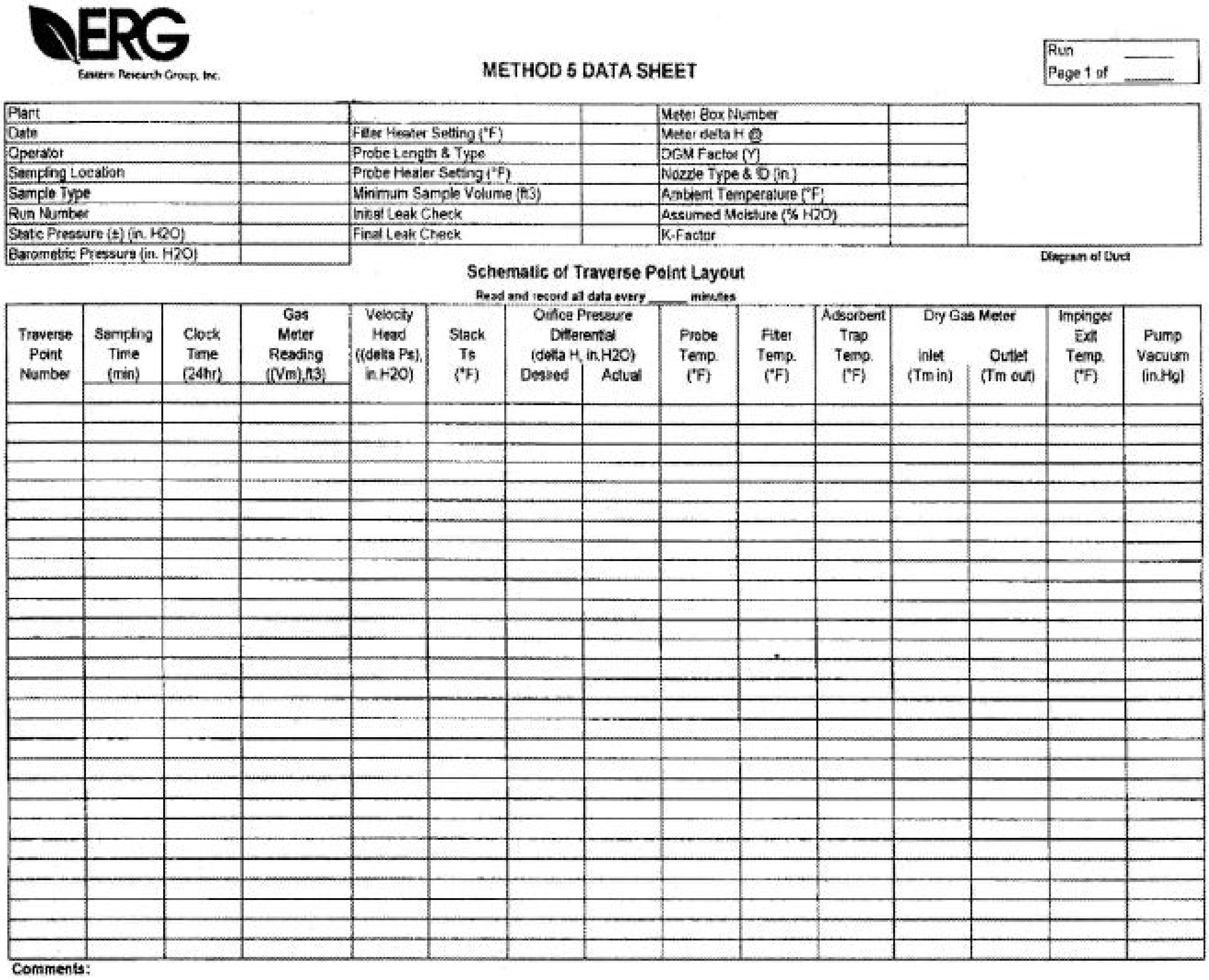
Section 5.0
Sample/Data Custody

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; and
- Initials of the person taking the sample.

The data sheet 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 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 by the Recovery Task Leader to provide a hard copy of all sample collection activities. Manual flue gas sampling data will also be maintained by the Recovery Task Leader. The Sampling Task Leader will place the original field data sheets in the project master file at the ERG laboratory. 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



ERG
Eastern Research Group, Inc.

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

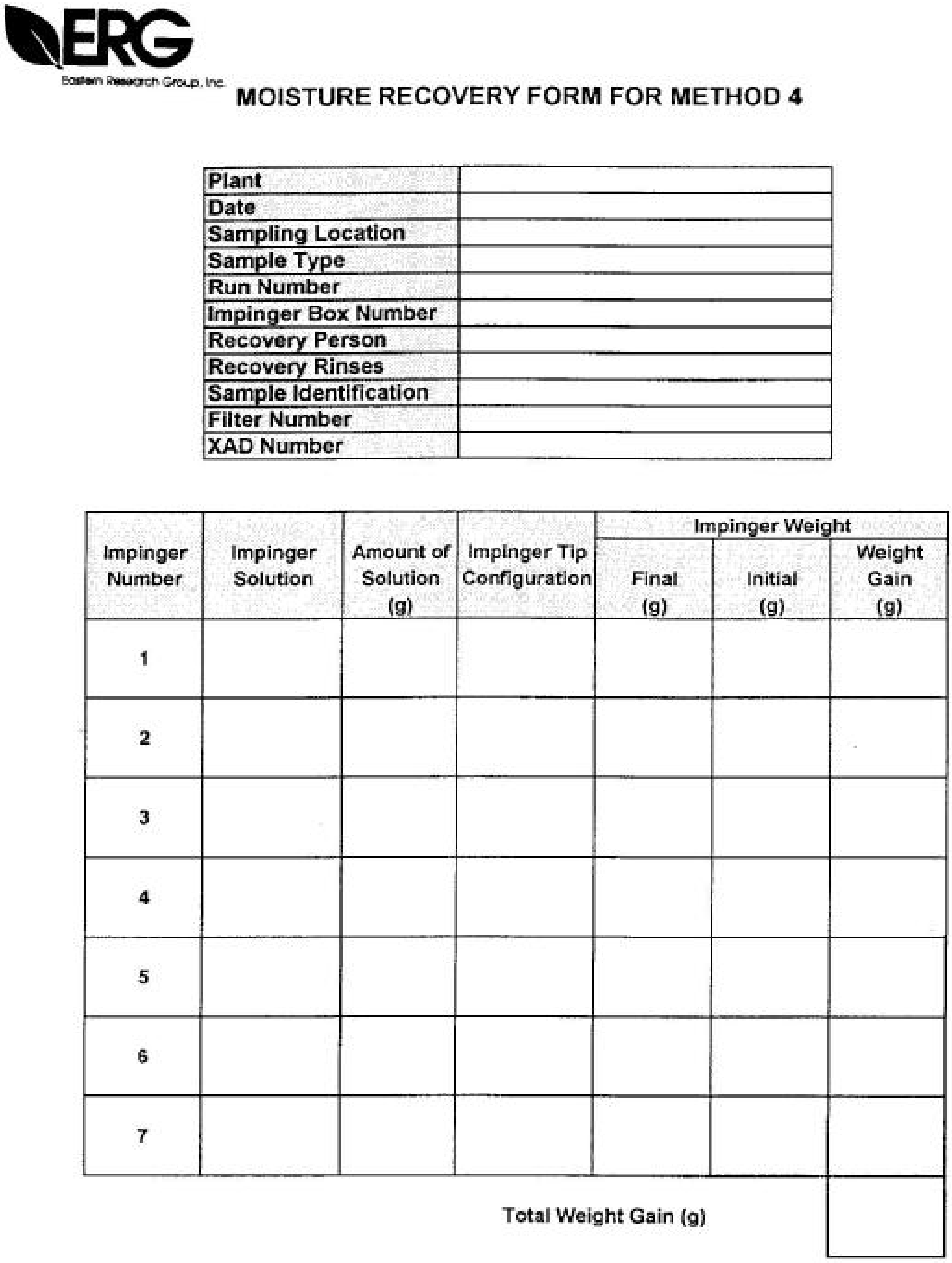
Schematic of Traverse Point Layout

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



Eastern Research Group, Inc.

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.

The Sample Custodian will verify the condition of the samples and log the samples into the ERG Laboratory Information Management (LIM) system. The chain-of-custody forms and sample bottle labels will be compared. 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 of derivatives. The train samples will be transferred to the Laboratory Studies Coordinator who will review the project documentation and notify the analysts that the samples are available for preparation and analysis.

Section 6.0
Analytical Procedures

All analyses will be performed by ERG at the 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 (acetone and methylene chloride) prior to use.

6.1 Sample Preparation

Following a one-hour purge of the sampling train with nitrogen (N_2), impinger, and (optional) filter samples will be recovered (Container 1A).

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

Samples will be recovered immediately after collection. The volume of liquid in Method 202 impingers will be measured. The liquid in the first three impingers will be measured to the nearest 0.5 g by weighing using a top-loading balance. Impingers and connecting glassware will be rinsed twice and the rinses combined with the impinger sample. 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 1B). The remainder of the impinger sample will be extracted with methylene chloride (CH_2Cl_2) concentrated to 10 mL at elevated temperature and evaporated dryness at ambient temperature to prevent vaporization of condensible particulate matter (CPM).

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.

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 1) is combined with the methylene chloride rinses (Container 2) 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 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 0.0001g. 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 0.00001g.

6.3 Residual Inorganic CPM Preparation

Assume NH_4Cl is counted as CPM. The aqueous impinger fluid remaining after organic extraction of Containers 1 and 2 will be taken to approximately 1 mL on a hot plate or in an oven at 105 °C. The concentrated inorganic material may be transferred to a smaller, preweighed beaker and then allowed to come to dryness at room temperature. Final residue weights will be determined by allowing the residue to attain constant weight in a desiccator. Weights should be recorded to the nearest 0.00001 ±0.00005 g.

6.4 Chromatographic Analyses

For all tests, sulfite and sulfate recovered from impinger samples will be analyzed by ion chromatography. For tests that include ammonia as contributor to CPM, ammonia, sulfite, sulfate, and chloride will be analyzed by ion chromatography following requirements found in EPA Method 26/26A 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 from a secondary multicomponent 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 solvent exchange is used, the total weight of cation 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 dissolved (as appropriate).

$$\text{Total ion in Sample } (\mu g) = \text{Concentration ion in Sample } (\mu g/mL) \times \text{Total Volume of sample } (mL) \times$$

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

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

where:

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

= 1.00 n^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 Method 202 assessment and evaluation for bias and other uses. 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 evaluation 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 one blank will be collected that includes representative reagents and media. This blank will be collected on the first day of sampling and 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 within 30 days of train sample analysis. Field and reagent blank analytical results 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 8-1 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 ( ) agree ±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:

Equation

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 reprepared 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 reprepared 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) Reprepared standard 4) Reanalyze samples not bracketed by acceptable standard
System Blank	Analyze-water	Bracket sample batch, 1 at beginning and 1 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.
Field Blank (FB) Check	Field blank samples collected from sampling train.	#10% of the sampling schedule	Compounds must be less than detection limits.	If FB fails, schedule another FB. If no reason for failure is identified and corresponding sample has high concentration values, FB subtract that sample only and flag data in report. If sample does not have high values, do NOT blank subtract, but flag data. Additional FBs 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

One matrix spike/matrix spike duplicate will be prepared by spiking an aliquot of one sample with the appropriate anions or cation.

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 µg/mL and ±25% at concentrations less than 1 µg/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% 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.

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 trains will be compared at each of the SO_2 spike levels. If the dry impinger modification to Method 202 shows improved performance measured by a 50% reduction in the artifacts from SO_2 at the 95% confidence interval, additional test 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 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% 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.

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 trains will be compared at each of the SO_2 spike levels. If the dry impinger modification to Method 202 shows improved performance measured by a 50% reduction in the artifacts from SO_2 at the 95% confidence interval, additional test 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 baseline and modified Method 202 sampling 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 modification(s) to Method 202 that will reduce artifact reaction products that are not related to the primary emission of 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:

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 <u>Project Manager</u>

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

10.1.3 <u>Sampling Personnel</u>

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 <u>Slips, Trips, and Falls</u>

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 manufacturers 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 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 taken here is a comparison of the baseline Method 202 to dry impinger modification(s) of Method 202. Three replicate populations represent the absolute minimum for statistical calculations. The data evaluation proposed 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% 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 CPM measurement will be estimated from three samples collected using both standard, "best practice" Method 202 sampling equipment and a modified "dry impinger" Method 202 sampling train.

The precision, SD_s of the measurement 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:

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

Where:

n = number of sampling runs (n = 3 in this study) and

x_{im} = the measured concentration for sample I.

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:

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

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% (0.05 level of significance) confidence interval has been chosen. That is, the true mean must be within the confidence interval 95% of the time. The confidence interval will be determined using the following equation:

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

Where:

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

" = the level of significance = 0.05 for the 95% confidence level;

$t_{n-1"/2}$ = 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; and

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

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; and

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

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

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 M-202 and the dry glass modification to M-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) the t statistic at 95%, if t_{calc} is # 0.0 ± 2.92 there is no statistical difference between the mean bias of the Reference Method 202 and the Dry Glass 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.

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.