Optimized Method 202 Sampling Train to Minimize the Biases Associated with Method 202 Measurement of Condensable Particulate Matter Emissions

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ABSTRACT

Numerous papers have addressed the significant positive biases associated with the use of EPA Method 202 for the measurement of condensable particulate matter ("CPM") emissions. These biases are due, in part, to the oxidation of soluble gases inadvertently captured in the cold impinger solutions used in Method 202 sampling trains. In some cases, the artifact CPM formed from gases in the impingers can be up to ten times the concentration of filterable particulate matter in the sample gas stream. The CPM emissions measured by Method 202 can significantly over-state the actual emissions of CPM to the atmosphere.

In response to the bias problems, the U.S. Environmental Protection Agency ("U.S. EPA") has been actively developing an air dilution sampling train that can be used to measure CPM without the use of water-filled impingers. This air dilution method is available as EPA Conditional Test Method 039 ("CTM 039"). Unfortunately, this method requires extremely large bulky sampling equipment, is expensive to operate, cannot distinguish between filterable and condensable $PM_{2.5}$ emissions, and is vulnerable to significant wall losses of CPM. The authors are not aware of any uses of CTM 039 outside of limited EPA research test programs.

Until CTM 039 or alterative air dilution techniques are available for practical commercial use, there is a need to minimize the Method 202 biases associated with the measurement of CPM. Air Control Techniques, P.C. has developed an optimized Method 202 sampling train that utilizes off-the-shelf components and operates without the need for water filled impingers. The only water present in the impingers is sample gas stream moisture condensing on the cold surfaces of the dry impingers. The absorption and subsequent aqueous phase reactions of dissolved gases are substantially reduced in this optimized Method 202 sampling train. A filter is used after the dry impingers to achieve high efficiency capture the condensed CPM particles formed in the optimized sampling train. This paper provides data comparing the sulfate artifact levels in a conventional Method 202 sampling train with the optimized Method 202 sampling train. The results of tests indicate that the optimized Method 202 sampling train reduces sulfate artifact levels to 15% of the levels in an un-purged conventional train and to 33% of the levels in a purged conventional train. The results of these laboratory tests are very similar to artifact formation rates calculated based on sulfur dioxide solubility and a 4% per hour oxidation rate in solution.

1. INTRODUCTION

The primary emissions of CPM from stationary sources are of increasing concern because the U.S. EPA believes that these emissions could be significant contributors to ambient $PM_{2.5}$ particulate matter in some geographical areas. U.S. EPA regional offices have been encouraging state and local agencies to request that stationary sources conduct CPM emission tests to compile the data necessary to evaluate future control strategies for the $PM_{2.5}$ National Ambient Air Quality Standards. At the present time, U.S. EPA Method 202 is the only promulgated method available to measure primary CPM emissions. This method is usually conducted with U.S. EPA method 5 for the determination of filterable particulate matter ("FPM") emissions. The combined sampling train is termed Method 5/202.

FPM are defined as particulate matter that exists at a temperature set by the air emission testing procedures which for Method 5 is 248ºF ± 25ºF. Vapor phase materials (e.g. high molecular weight organic compounds and sulfuric acid) sometimes present in the sample gas streams of combustion sources passes through the sampling train filters and are not collected. EPA has argued that the condensable vapors not collected in a filterable particulate matter test method can form particles once the stack emissions cool in the atmosphere. Accordingly, in 1991 EPA promulgated Method 202 to be used as a stand alone method or in combination with a FPM measurement method such as Method 5. Method 202 involves the analyses of the total organic and total inorganic material trapped in the water filled impingers in the "back half" of the Method 5 sampling train. The impingers capture all vapor phase materials that condense at a temperature below the Method 5 filter temperature and above the impinger exit temperature (<68ºF).

2. METHOD 202 MEASUREMENT BIAS

Air emission testing experience since the promulgation of Method 202 in 1991 has demonstrated that it is inappropriate to use water-filled impingers to cool the sample gas stream for CPM combustion sources having SO_2, NO_2[1], and/or soluble organic compound[2] emissions. These gaseous contaminants can partially absorb in the impingers 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. Dissolution of sulfur dioxide and nitrogen oxides into water with subsequent oxidation to form sulfates and nitrates in the impingers
2. Dissolution of soluble organic compounds into water
3. Penetration of submicrometer sized condensed particles through the impingers of the Method 202 sampling train
4. Gas phase homogeneous reactions between ammonia and hydrogen chloride and/or between ammonia and sulfur dioxide in the cold, water-filled impingers

Of these four sources of bias, the absorption and reaction of sulfur dioxide is most common. Since Method 202 was promulgated, there has been considerable concern that absorption of soluble sulfur dioxide and nitrogen dioxide and subsequent reactions of these dissolved gases occur within the aqueous phase in the impingers (references 1, 2, 3, 4 and 8). These reactions are

[1] NO_2 is one of the two oxidized nitrogen oxides included as NOx. NO_2 is usually present at levels of 2% to 10% of the total NOx concentration.
[2] Soluble organic compounds include alcohols, aldehydes, ketones, and organic acids.

important because these gases are considerably more soluble in cold liquids than in warm liquids. The 32°F to 68°F temperatures of the liquid in the impingers provide an ideal environment for the collection of soluble inorganic gases.

Atmospheric reactivity studies summarized in the final edition of the Particulate Matter Air Quality Criteria Document (reference 5) indicate that there are a number of reaction mechanisms for converting dissolved sulfur dioxide (sulfite ion) to sulfuric acid. These studies indicate that the conversion rate of sulfur dioxide in water droplets can be "several times" higher than the 1% to 3% per hour conversion rate observed for dry, gas phase reactions. Based on this general relationship, the aqueous phase conversion rates relevant to water filled impingers are estimated to be 2% to 6% per hour.

> "Chemical reactions of SO_2 and NOx within plumes are an important source of H^+, SO_4^{-2}, and NO_3^{-1}. These conversions can occur by gas-phase and aqueous-phase mechanisms. For the conversion of SO_2 to H_2SO_4, the gas-phase rate in such plumes during summer midday conditions in the eastern United Stated typically varies between 1 and 3% per hour, but in the cleaner western United States rarely exceeds 1% hr^{-1}."
>
> U.S. EPA, Particulate Matter Criteria Document (October 2004), Page 3-63. (Concerning dry, gas phase reactions)

> "The contribution of aqueous-phase chemistry to particle formation in point-source plumes is highly variable, depending on the availability of the aqueous phase (wetted aerosols, clouds, fog, and light rain)... The in-cloud conversions of SO_2 to SO_4^{-2} can be several times larger than the gas-phase rates give above."
>
> U.S. EPA, Particulate Matter Criteria Document (October 2004), Page 3-63. (Concerning aqueous phase reactions similar to those that could occur in Method 202 impingers)

The 2% to 6% per hour secondary particulate (sulfate) formation rates suggested by EPA (reference 5) are very high. Similar SO_2 oxidation rates in the impingers of Method 202 can create significant quantities of sulfate material.

Method 202 includes provisions to address the SO_2 absorption and reaction issue. EPA recommends that the impinger solutions from the Method 202 sampling train be purged with clean nitrogen to strip out the dissolved SO_2 from the solution. Unfortunately, there are two factors that limit the effectiveness of this approach: (1) SO_2 oxidation reactions begin immediately during the test run and prior to the start of the purge step and (2) purging is often not complete.

Obviously, a post test run nitrogen purge has no impact on the quantity of SO_2 that reacts to form sulfates in solution during the one hour Method 202 test run and the one to two hours after the test run that are often needed before purging is started. At a reaction rate of 2% to 6% per hour, there is considerable time prior to purging for the dissolved SO_2 to react to form sulfates that are subsequently falsely counted as "condensable particulate matter" emissions from the source.

It is also apparent that purging is more difficult than anticipated in Method 202. Tests conducted by Corio (reference 3) indicated that, in many cases, the one-hour purge time listed in Method

202 is not adequate to eliminate the gaseous material (e.g. sulfur dioxide) that has absorbed into solution. Similar problems have been observed by McCain and Williamson (references 2, 6, and 7). Purge efficiencies in the mid-80% to low 90%s have been measured in these tests. The remaining 10% to 20% of the dissolved sulfur dioxide (and other dissolved gases) is converted to condensable particulate matter in the samples in the hours to days that pass until the samples are analyzed. This can significantly affect the accuracy the Method 202 test results.

To evaluate the extent of the error in Method 202 caused by SO_2 absorption and reaction, the quantity of SO_2 absorbed in the Method 202 impingers has been calculated based on Henry's Law constants for a pure water - SO_2 solution. The results are summarized in Table 1 for a typical Method 202 sampling run involving the capture of 30 DSCF of sample gas and a 3 hour period after the test run before the initiation of the Method 202 allowed purge step. The results are also based on a SO_2 oxidation rate of 4% per hour.

The hourly and annual artifact CPM "emissions" are based on a total stack gas flow rate of 50,000 DSCFM and 7,500 operating hours per year. The stack gas flow rate is representative of a small-fossil fuel-fired boiler, a moderately sized kiln, or a moderately sized furnace.

Table 1. Calculated Absorption and Oxidation of Sulfur Dioxide in the Impinger Solutions (pure water-sulfur dioxide solution)

SO_2, ppm	N_2 Purge Efficiency, %	Sulfate Artifact @ 4% per hour formation rate, grains/DSCF	Sulfate Artifact, Equivalent @ 50,000 DSCFM, lbs/hour	Sulfate Artifact, Equivalent @ 7,500 hours per year, tons per year
200	No Purge	0.0157	6.7	25.2
	80	0.0055	2.3	8.8
	90	0.0039	1.7	6.2
	100	0.0023	1.0	3.7
500	No Purge	0.0449	19.3	72.2
	80	0.0136	5.8	21.9
	90	0.0097	4.2	15.6
	100	0.0058	2.5	9.3

In laboratory tests conducted by Air Control Techniques, P.C. in 2001 using clean impinger water, condensable particulate matter levels exceeding 0.014 grains/DSCF were found even though the Method 202 laboratory tests were conducted with a sample gas stream blended with Protocol 1 high quality particulate-free gaseous sulfur dioxide, nitrogen oxides, and ammonia (reference 4). There was no condensable particulate matter in the blended gas stream entering the Method 202 sampling train. These measured "CPM" levels observed in these tests confirmed that significant positive biases that can exist with Method 202 techniques when used on stationary sources with sulfur dioxide concentrations in the range of 200 to 500 ppm.

The laboratory tests conducted in 2001 did not include carbon dioxide or water vapor in the sample gas stream. Furthermore, the previous tests did not include any modifications to the conventional Method 202 sampling train to minimize the positive bias related to sulfur dioxide absorption and oxidation. To further evaluate means to minimize the positive bias in Method 202, additional tests were conducted in 2005. The experimental techniques and the characteristics of the optimized Method 202 sampling train are summarized in Section 3. The results of the evaluation program are summarized in Section 4.

3. EVALUATION PROCEDURES

3.1 Conventional Method 202 Sampling Train.

A conventional Method 202 sampling train was set-up in the Air Control Techniques, P.C. laboratory. A sample gas stream was blended from (1) oxygen in nitrogen and carbon dioxide in nitrogen gas cylinders, and (2) a sulfur dioxide in nitrogen gas cylinder. The oxygen and carbon dioxide carrier gases were bubbled through a set of impingers operating at 160ºF to 180ºF to provide water vapor levels of 1.45% to 3.36% in the blended sample gas stream. This gas stream was then heated to 290ºF to 310ºF. The concentrations of sulfur dioxide, carbon dioxide, and oxygen were monitored continuously at the outlet of the Method 202 impingers using EPA Methods 3A and 6C. The concentrations were also measured at the inlet to the Method 202 sampling train prior to the test run. The water vapor concentrations were measured using EPA Method 4.

Each Method 202 test run in the lab was conducted for one hour at a sample gas flow rate of approximately 0.62 DSCFM. The oxygen concentrations ranged from 6.4% to 17.0% by volume and the carbon dioxide concentrations ranged from 0% to 16.7%. The sulfur dioxide concentrations at the inlet to the Method 202 sampling train ranged from 130 ppm to 210 ppm. The probe and the filter in the Method 5 “front half” was operated at 250ºF to 270ºF, within the required Method 5 temperature range. The impinger outlet temperatures ranged from 42ºF to 55ºF, well within the required Method 202 operating range.

Following each test run, the sampling train was recovered using Method 202 procedures. However, since this test program was limited to the absorption and oxidation of sulfur dioxide, the methylene chloride rinse step was omitted.

3.2 Optimized Method 202 Sampling Train

The optimized Method 202 sampling train shown in Figure 1 has been designed to achieve adequate temperature reduction with minimal contact between the SO_2 containing gas stream and the liquid. A filter located after two “dry” knockout impingers is the primary location for the capture of condensed particulate matter. The optimized Method 202 sampling train is rinsed using water and methylene chloride to collect any condensed material on glassware surfaces.

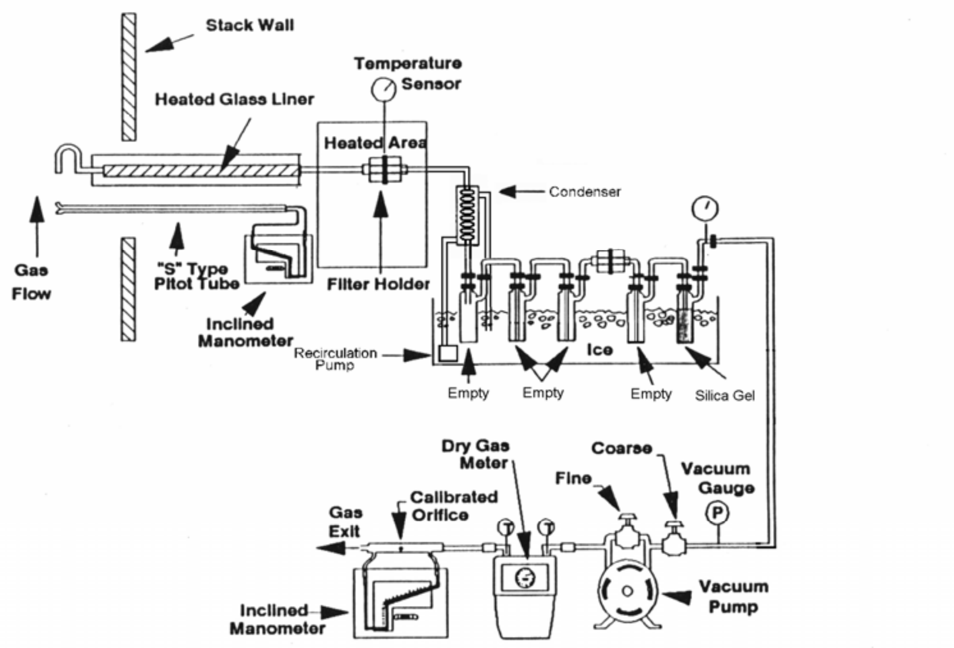

Figure 1. Optimized Method 202 sampling train

The gas stream entering the optimized Method 202 sampling train is first contacted using an indirect condenser that uses cold water recirculated from the impinger case. This decreases the gas temperature to below 68ºF. The only contact between gaseous SO_2 and condensed water is with the sample gas stream moisture that condenses on the surfaces of the indirect heater exchanger.

A large knockout impinger is used following the indirect heat exchanger to quickly separate the sample gas stream from the condensed water. The sample gas stream then passes through two empty Greenberg-Smith impingers to ensure complete droplet knockout and CPM formation prior to the filter. A 47mm filter is used to filter out the condensed particulate matter. The filter is combined with the knockout impinger solution and the rinses of the entire sampling train. All of the condensed material is extracted from this combined sample and is analyzed in accordance with standard Method 202 analytical procedures.

The optimized Method 202 sampling train was used with the same simulated stack gas stream used with the conventional Method 202 sampling train. The sulfur dioxide, carbon dioxide, and oxygen concentrations were monitored continuously at the outlet of the last impinger prior to the silica gel. The performance of the optimized Method 202 sampling train was compared with the test results with the conventional Method 202 sampling train.

4. TEST RESULTS

The sulfur dioxide, carbon dioxide, and oxygen concentration trends during the test run with the conventional Method 202 train is illustrated in Figure 2. It is apparent that high efficiency removal of sulfur dioxide occurs in the impinger solutions for the first ten to fifteen minutes of the test run. After saturation of the impinger solutions, the SO_2 concentrations at the outlet of the Method 202 sampling train (prior to the silica gel) reached the inlet concentration level of 180 ppm.

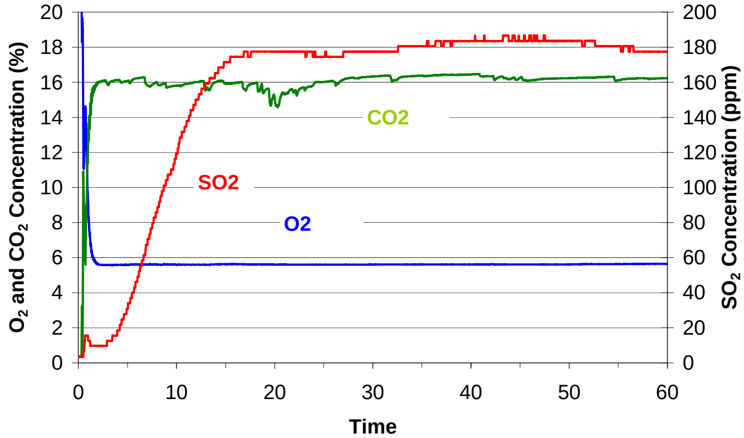

Figure 2. Concentration trends in a conventional Method 202 sampling train

The impact of carbon dioxide on the absorption and reaction of sulfur dioxide in the sampling train was evaluated by eliminating the carbon dioxide source. The concentration trends in Figure 3 for a conventional Method 202 sampling train without the presence of carbon dioxide are very similar to the results with carbon dioxide. In this test run, the inlet sulfur dioxide concentration was 130 ppm.

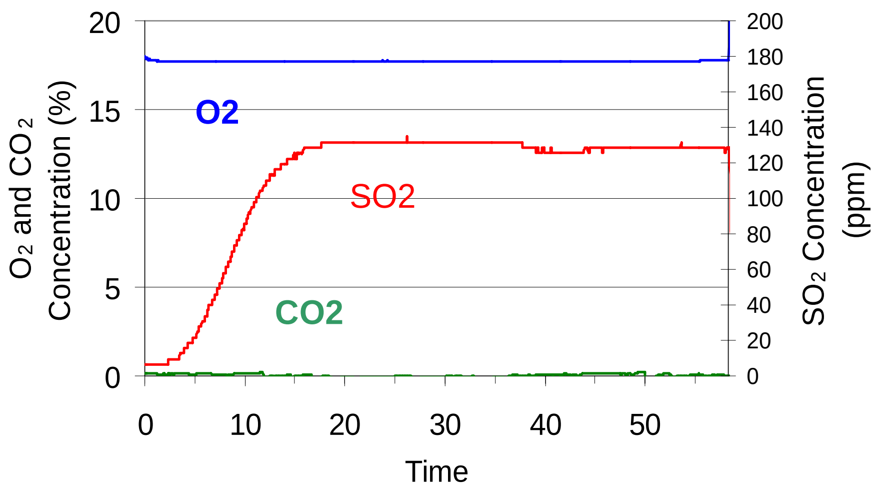

Figure 3. Concentration trends in a conventional Method 202 sampling train without carbon dioxide in the sample gas stream

It is apparent that the elimination of carbon dioxide did not strongly affect the rate at which the sampling train outlet SO_2 concentration ramped back to the inlet concentration level.

The results of the test on the optimized Method 202 sampling train are illustrated in Figure 4. It is apparent that SO_2 absorption is significantly reduced with this optimized arrangement. The SO_2 outlet concentration almost immediately increases to the inlet concentration value of 210 ppm.

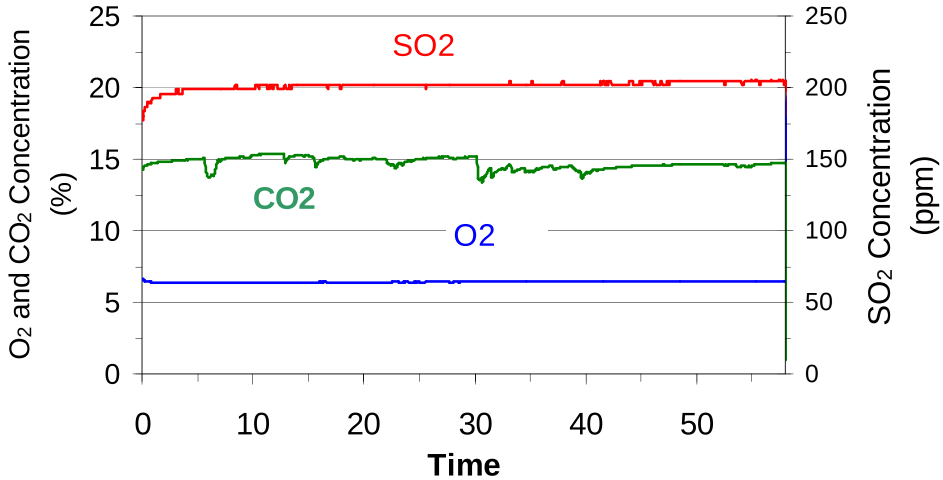

Figure 4. Concentration trends in an optimized Method 202 sampling train

Due to the substantial reduction in the capture of sulfur dioxide, the vulnerability to positive bias related to aqueous phase oxidation reactions is minimized. The differences in the sulfate concentration levels in the Method 202 samples confirm that the positive bias with the optimized train is reduced well below the levels observed in the conventional Method 202 sampling train.

Table 2. Method 202 Test Results

Run	Sampling Train	Test Conditions	Artifact Sulfate, milligrams	Artifact Sulfate, grains/DSCF
1	Conventional	No purge	38.0	0.016
2	Conventional	Purge	15.0	0.006
3	Conventional	Purge, No CO_2	13.8	0.006
4	Optimized	No purge	5.2	0.002

The results with the optimized Method 202 sampling train indicate the artifact levels are 15% of the levels in the conventional Method 202 sampling train with no purge. The optimized Method 202 sampling train had artifact levels that were only 33% of the levels measured in a conventional Method 202 train with a 1-hour nitrogen purge.

5. CONCLUSIONS

Laboratory tests conducted using a conventional Method 202 sampling train on a simulated combustion source gas stream confirmed that this method is subject to a substantial positive bias due to sulfur dioxide absorption and aqueous phase oxidation. This bias can be substantially reduced by modifying the conventional sampling train. Instead of water-filled impingers, Air Control Techniques, P.C. recommends that the sample gas stream first pass through a water-cooled indirect condenser, a "dry" knock-out impinger, and two empty impingers in an ice-bath. This provides sufficient heat exchange to cool the sample gas stream below 68ºF and to condense all vapor phase material to form CPM. The condensed particulate matter is captured on a high efficiency filter following the third impinger.

A comparison of the performance of the conventional and optimized Method 202 sampling trains indicates that the optimized unit has artifact formation levels of approximately 15% of an un-purged conventional train and 33% of a purged conventional train. The beneficial impact of the optimized sampling train will be even greater in actual gas streams that have additional gaseous species that can increase sulfur dioxide aqueous phase reaction rates.

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