September 30, 2005

Ms. Vickie Presnell
Project Officer
Office of Air Quality Planning and Standards
Emissions, Monitoring, and Analysis Division (C304-02)
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dear Ms. Presnell:

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

Please find enclosed one copy of a draft technical report entitled "Laboratory Evaluation of Method 202 to Determine Fate of SO_2 in Impinger Water." This draft report serves as a deliverable under Task 2 of the subject Work Assignment.

If you have any questions, please call me at 614/424-6538 or Jan Satola at 614/424-4251.

Sincerely,

Basil W. Coutant, Ph.D.
Principal Research Scientist
Measurement and Data Analysis Sciences

BWC:llj
Enclosure

cc:	Otelia Newsome	(EPA CO)	*(ltr only)*
	Thomas J. Logan	(EPA WAM 3-14)	

September 30, 2005

Draft Technical Report

on

LABORATORY EVALUATION OF METHOD 202 TO DETERMINE FATE OF SO_2 IN IMPINGER WATER

Contract No. 68-D-02-061
Work Assignment 3-14

for

Vickie Presnell
Project Officer

Thomas J. Logan
Work Assignment Manager

Emissions, Monitoring, and Analysis Division
Office of Air Quality Planning and Standards
U.S. ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina 27711

Prepared by

Jan R. Satola and Thomas J. Kelly

BATTELLE
505 King Avenue
Columbus, Ohio 43201-2693

DISCLAIMER

This report is a work prepared for the U.S. Environmental Protection Agency by Battelle. In no event shall either the U.S. Environmental Protection Agency or Battelle have any responsibility or liability for any consequences of any use, misuse, inability to use, or reliance upon the information contained herein, nor does either warrant or otherwise represent in any way the accuracy, adequacy, or applicability of the contents hereof.

TABLE OF CONTENTS

Page

List of Tables

List of Figures

ABBREVIATIONS AND SYMBOLS USED

APM	artifact particulate matter
cc	cubic centimeter
CO_2	carbon dioxide
CPM	Condensible Particulate Matter
DI	de-ionized (water)
Dil-corr	Dilution-corrected
IC	Ion chromatographic
L	liter
μL	microliter
LPM	liters per minute
MFC	mass flow controller
mg	milligram
min	minute
N_2	nitrogen
O_2	oxygen
pk-ht	peak height
PM	particulate matter
ppm	parts per million
SCR	selective catalytic reaction
SNCR	selective non-catalytic reaction
SO_2	sulfur dioxide
SO_3^{-2}	sulfite anion
SO_4	sulfate
SO_4^{-2}	sulfate anion
Unk 1	unknown compound #1
Unk 2	unknown compound #2
UPH	ultra high purity

Draft Technical Report
on
Laboratory Evaluation of Method 202 to Determine Fate of SO_2 in Impinger Water

Work Assignment 3-14

BACKGROUND

The U.S. Environmental Protection Agency (EPA) introduced Method 202 in 1991 as a method to quantify condensible particulate matter (CPM) in flue gas streams of elevated temperature. CPM is defined as the mass of solid residue remaining after the impinger contents are analyzed. The CPM measurement relies on gravimetric determination of the captured CPM after the impinger deionized water has been evaporated away. The method quantifies the condensibles using the impinger catch from a Method 5 type sampling train. The analysis includes dividing the catch into an organic and an inorganic portion. An important addition to Method 202 that was not in previous sampling is the nitrogen purge procedure. Due to concern of sulfur dioxide (SO_2) oxidizing to sulfates in the impingers after sampling, and then being incorrectly counted as particulate matter, the impingers are purged with nitrogen for one hour. The purge is intended to remove the sulfur dioxide, thereby preventing artifact sulfate formation. By purging the SO_2, quantifying SO_2 pseudo-particulate should not occur.

Under EPA Contract No. 68-D-02-061, Work Assignment 3-14, a literature search on CPM issues was conducted and is summarized in Appendix A. One of the literature search papers [1] succinctly summarized the sulfur dioxide chemistry taking place in the impingers during sampling observing that sulfur dioxide (SO_2) and molecular oxygen (O_2) both are soluble in water. The dissolved SO_2 can form hydrated SO_2 ($SO_2 \bullet H_2O$) and sulfite (SO_3^{-2}) and bisulfite (HSO_3^-) ions in aqueous solution. At the pH range of interest (pH 2 through 7), HSO_3^- is the preferred state. The individual dissociations are very fast, so aqueous-phase equilibria are established instantaneously. The dissociation of the dissolved species enhances its aqueous solubility so that the total amount of dissolved sulfate always exceeds that predicted by Henry's Law for SO_2 alone. There are several pathways for sulfate formation by reaction of these ions with dissolved O_2, ozone, and hydrogen peroxide (the latter two are of no importance in flue gas sampling), which can be catalyzed by many substances such as iron and manganese. Free NH_3 in the samples can increase the amount of dissolved SO_2 and, thereby, increase artifact sulfate formation, since it instantly reacts in aqueous solution forming ammonium sulfite/bisulfite ions and additional SO_2 must dissolve to maintain equilibrium.

The general consensus of the literature search regarding CPM measurement from iced impingers, as in Method 202, is that the CPM is dominated by the inorganic fraction (regardless of the type of fuel burned [2]), which turns out to be predominantly sulfate-related. It appears that a standard one hour post-sampling nitrogen purge of lower concentration impinger samples satisfactorily removes this false CPM, while higher concentrations suffer from artifact particulate that is not present in the original gas stream.

There are two main mechanisms for impinger sulfate formation:

- Gaseous SO_2 dissolves in the impinger water to form $H_2SO_3^-$, which may then oxidize by means of molecular O_2 or other compounds dissolved in the water to form H_2SO_4.
- Compared to the actual exhaust plume that cools with atmospheric dilution, condensation of vapors in the impingers is excessive, since the impingers cool the gas stream without dilution.

For example, because of the artifact particulate matter (APM), Method 202 CPM measurements from gas-fired sources may depend more on the natural gas sulfur content than on the process operating conditions, and so may not reflect the actual CPM existing in the exhaust plume. [3] Regarding the second mechanism (cooling without dilution as the source of APM), comparison of impinger sampling to dilution tunnel sampling showed that the mass of $PM_{2.5}$ measured by EPA source test methods that included the impinger fraction, was 80 to 100 times greater than that measured by a dilution sampler. Analysis of material collected in the impingers showed a dominant sulfate; much more sulfate than was collected in the dilution sampling system. This was attributable to the dissolution and oxidation of SO_2 from the stack gas in the impingers. [1, 4]

Method 202 was originally designed for use over short sampling times (i.e., one hour) at relatively high SO_2 concentrations. As SO_2 reduction measures have been applied to many sources, Method 202 has been used over much longer sampling times (e.g., up to six hours), increasing the potential for APM formation. Longer Method 202 test runs and longer sample storage after sampling allow more time for the conversion of SO_2 to solid residues, thus increasing the APM measured. This means that APM artifacts can easily dominate CPM results when the true CPM concentrations are low. A previous study [1] of SO_2 impinger concentrations, considerably lower than those for this set of tests, was performed for one-hour and six-hour sampling runs with mixtures containing 0, 1, and 10 ppm SO_2. One pair of trains was purged with nitrogen for one hour immediately following the tests, while the other was not. The samples were stored at 4 C for approximately two weeks prior to analysis. Significant amounts of SO_4^{-2}, approximately proportional to the SO_2 concentration in the gas, were present in impingers regardless of the post-test purge. While the post-test purge clearly reduced SO_4^{-2} concentration in the impingers, significant SO_4^{-2} still remained. Purging was less efficient at reducing SO_4^{-2} for the 6-hour runs than for the 1-hour runs, indicating that much of the SO_2 oxidation occurs within this period. The current study undertaken for this report not only stored samples at 4 C for approximately two weeks prior to analysis, but also it analyzed the impinger samples taken after sampling but before the nitrogen purge, as well as samples taken (but not stored) after the nitrogen purge.

Studies of oil-fired and gas-fired combustion systems [1] involving higher concentrations of approximately 2,000 ppm SO_2 report APM in spite of post-test purging, accounting for up to 42 percent of the measured CPM. Test results from a gas-fired refinery boiler using unpurged sample trains showed that approximately 50 to 100 percent of the SO_4^{-2} found in the field samples, comprising more than 80 percent of the total CPM, was attributed to the SO_2 APM artifact.

The literature search also provided some interesting information regarding impinger pH. The removal of SO_2 from the impinger through N_2 purging, according to at least one author [5], is related directly to the pH of the solution. The SO_2 is more easily removed at a pH of 2 than at pHs above 4.

This report describes a series of experiments designed to evaluate the impact of SO_2 concentration, sampling duration, and other factors on APM formation in Method 202 samples. Subsequent sections of this report summarize the experimental procedures, results, and implications of this study.

EXPERIMENTAL DESIGN

Sampling Train Setup

Two identical Method 202 sampling trains were set up to run nearly simultaneously in order to compress the total testing and sample analysis times. Figure 1 shows one of the two trains, set up such that it could be supplied by cylinders of SO_2, N_2 (nitrogen), and an O_2/CO_2 (oxygen/carbon dioxide) mixture.

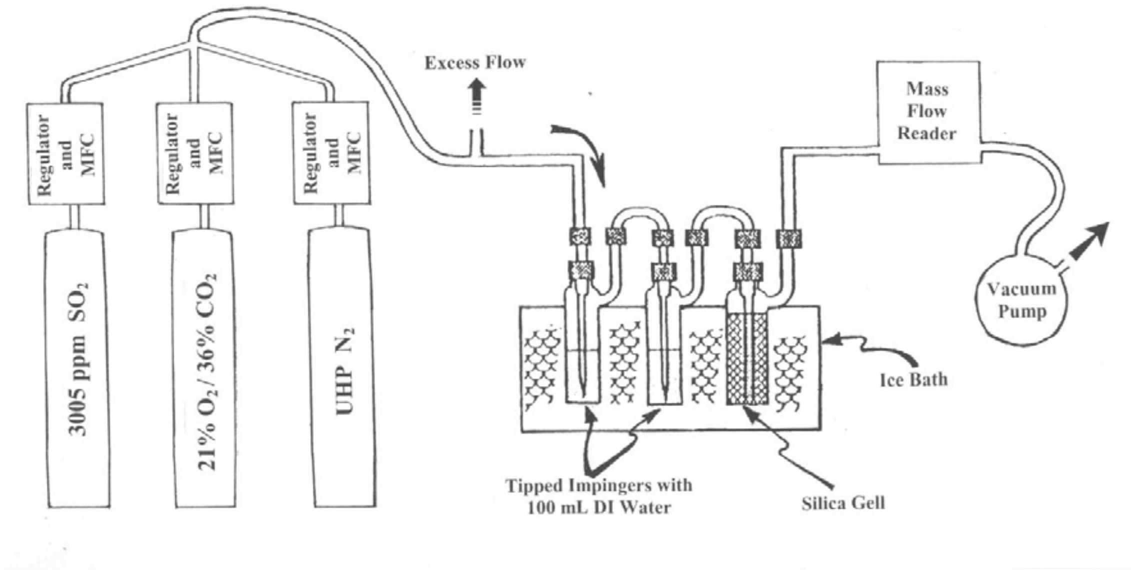


Figure 1. **Sampling Train Setup Schematic.**

Each cylinder was equipped with a regulator and its own mass flow controller to supply the target gas flows. The O_2/CO_2 cylinder mixture of 21 percent/36 percent was diluted with nitrogen for all runs by a factor of 3 to simulate actual stack concentrations of 7 percent oxygen and 12 percent carbon dioxide. The second sampling train was simultaneously supplied from these same three cylinders by inserting a "T" connector and a second mass flow controller at each cylinder regulator. A vacuum pump was connected to the train exhausts and the exit flows were monitored to determine total system flows (approximately 20 liters per minute, LPM) through each train. During the test runs, an excess flow (<1 LPM) was maintained through the "Excess Flow" line leading off the manifold just before the gases entered into the impingers, as shown in Figure 1. The constant flow through this excess line insured that outside air was not pulled into the system by the vacuum pump and, thus, the exit flow measured by the mass flow reader consisted entirely of the input gases. The gas flow from each of the three cylinders passing through each sampling train was set before each run and monitored during the runs. In addition, the total flow from each train exhaust was monitored throughout the runs. Table 1 shows the originally intended test matrix with gas flows totaling 20 LPM; however, this matrix was modified during the actual testing.

Table 1. Planned Concentration/Sampling Time Test Matrix.

SO_2 Concentration, ppm	Impinger Flow Time, Hours	3005 ppm SO_2, cc/min.	O_2/CO_2 Mix 21% / 36%, Liters/min.	Nitrogen Diluting Flow, Liters/min.	Total Sample Flow, Liters/min.
300	1	1997	6.67	11.33	20.00
100	3	666	6.67	12.66	20.00
50	6	333	6.67	13.00	20.00

Sample Collection

The twin sampling trains (**a** and **b**) were run with an offset of about an hour in order to minimize the time required to collect impinger samples, measure impinger pHs, and begin the nitrogen purge. The pH measurements were taken on the contents of each impinger prior to each test, before beginning an immediate post-sampling nitrogen purge, and after the nitrogen purge. To measure the pH of the front and back impingers, pH paper as opposed to a pH meter was selected because of the paper's speed and small sample requirement.

A pipet was employed to collect four impinger samples of 2 mL each for each test. For each sample, 1 mL was collected from the front impinger and added to 1 mL from the back impinger of each train. For each test, the first pair of samples was collected after the test run but immediately before the nitrogen purge, and the second pair was collected immediately after the nitrogen purge. Samples were placed in 2 mL IC vials and capped for later analysis. The entire process of collecting the impinger samples, measuring the impinger pHs, and starting the nitrogen purge was accomplished in 5 minutes or less for each run. With almost 200 mL of impinger solution for each sample run, the samples removed before the purge negligibly decreased the total impinger volume.

Quality of Cylinder Gases Used

The cylinders of SO_2 (3005 ppm) and O_2/CO_2 mix (21 percent/36 percent) were Master Class grade gases obtained from Scott Specialty Gases (Troy, Michigan) with a tolerance of ±2 percent. The dilution nitrogen was ultra high purity grade.

Sulfate and Sulfite Detection

A Shimadzu Ion Chromatographic (IC) system with a CDD-6A conductivity detector was chosen to analyze samples simultaneously for both sulfate and sulfite anions. A sulfate calibration curve was set up for this instrument using a NIST sulfate standard (using the convention that 1 ppm SO_4^{-2} = [1 mg SO_4^{-2}]/L); however, the rapid oxidation of any sulfite standard into sulfate made the use of a sulfite calibration curve impractical. To overcome this difficulty, some samples were divided in two portions: the first portion underwent regular analysis, while 20 or 50 µL of 30 percent H_2O_2 was added to the second portion, rapidly oxidizing all of the sulfite to sulfate. By comparing these oxidized samples with their original sulfite/sulfate counterparts, a linear sulfite calibration curve (Appendix B) was generated by subtraction, and this curve was then used with the sulfite peak heights to calculate the sulfite content of all the samples.

Sample Designation

The 49 samples analyzed in this study were each given a sample ID starting with A, B, C … AU, plus YA and YB. Following the sample ID, there is a 5-slot code in brackets that tells how the sample was created and handled, including the matrix run time, sample source (Train **a**, Train **b**, or other source), nitrogen purged/non-purged status, hydrogen peroxide addition/non-addition status, the hold time before analysis, and, finally, the sample dilution factor. This sample coding system is shown more clearly in Figure 2 below:

►Matrix run-time in hours (1, 1.3, 3, or 6)
| ►Sampling Train (**a** or **b**), or special sample type (S_i, i = 1, 2, or 3)
| | ►Sample N_2 purged (N for 1 hour and N/2 for 0.6 hours) or non-purged, 0
| | | ►H_2O_2 added to sample, H; or not added, 0
| | | | ►Holding time in hours before analysis
| | | | |
R [3 b N H (4.7)] 10.02
| |
| ►Dilution Factor if different from 1.00
►Sample ID: the 49 sample IDs run from A to AU, plus YA and YB

Figure 2. Sample Identification Code.

The code in Figure 2 indicates this particular sample is "Sample R," which came from a 3-hour run using Train **b**, and was purged with nitrogen for 1 hour. This sample was diluted by a factor of 10 (100 µL sample + 900 µL DI water), and then 20 µL of hydrogen peroxide was added for a total dilution factor of 10.02. The time between the end of the 3-hour sampling run and analysis by IC was 4.7 hours. The chromatograms for all the test runs (Appendix B) are also labeled according to this coding system. Some samples were run more than once, with the different holding times indicated by the sample code.

RESULTS AND DISCUSSION

Six experiments were performed with the available cylinder gas resources in order to determine the formation of sulfate APM as a function of SO_2 concentration and duration of the sampling. Initially, it was expected from the literature that the impinger concentrations generated would be a fraction of the concentration of SO_2 bubbled through the sample train, and so the calibration curve was set up to span from 0 to 100 ppm. However, when the first sample of the first run (one hour at 300 ppm SO_2) was analyzed, it yielded a total sulfate concentration of over 400 ppm. At this point, the IC operator's recommendation was to keep the initial 0 - 100 ppm calibration curve to maintain sensitivity to lower sample concentrations, and at the same time simply dilute the higher concentration samples to fit within this same curve. Although the first high value of 400 ppm was outside of the calibration curve, subsequent 1:10 dilutions (samples G and H) of this test run demonstrated the accuracy of the original high value.

Actual Test Matrix

The actual tests performed are designated by the sampling duration (1, 1.3, 3, or 6 hours) followed by the impinger train (**a** or **b**), and the SO_2 concentration in ppm in parenthesis; the test designations are listed in the first column of Table 2. The actual test matrix differs from the planned pre-test Table 1 matrix in three ways. First, the amount of cylinder gas resources did not allow an anticipated repeat of the 1a test (although Test 1.3a was run with a 38-minute nitrogen purge). Secondly, test flows were not always 20 LPM, but, in fact, varied between about 17.7 - 18.8 LPM, as shown in the fourth column of Table 2; and nitrogen purge flows (Table 2, fifth column) were between 0.1 and 0.5 L higher than the corresponding test flows. Lastly, the SO_2 flow was not changed between the first (1a) and second tests (3a and 3b), resulting in an SO_2 concentration of 300 ppm for both the 1 hour and 3-hour tests; that is, the 3-hour tests originally planned as 100 ppm runs are actually 3-hour extensions of Test 1a. In spite of the higher concentrations for the 3-hour tests, interesting insights into APM formation were nevertheless gathered.

Table 2. Actual Test Matrix and Test Conditions.

Test	SO_2 Flow, LPM	Purge Time, hours	Total Average Gas Flow, LPM	Total Average Purge Flow, LPM	SO_2 Concen., ppm	Total SO_2 Impinger Exposure, ppm-hour	Relative Humidity, %	Temp., F	Barometric Pressure, Inches Hg
1a (300)	1.77	1.0	17.81	18.11	299	299	45	69	29.15
3a (300)	1.76	1.0	17.67	17.90	300	900	51	69	29.18
3b (300)	1.82	1.0	18.20	18.64	301	902	51	69	29.18
6a (50)	0.299	1.0	17.95	18.03	50.0	300	42-43	70-71	29.18-29.21
6b (50)	0.296	1.0	18.75	19.28	47.5	285	42-43	70-71	29.18-29.21
1.3a (50)	0.316	0.63	17.74	0	50.0	65.1	40	70	29.21

Chromatographic Data

The raw chromatographic data are compiled in two tables in this report:

- Table 3a: Raw Test Data, and
- Table 3b: Two Week Post-Test Raw Data.

The raw data in the first two tables were processed and are presented in two additional tables:

- Table 3c: Processed Test Data, and
- Table 3d: Two Week Post-Test Processed Data.

The patterns in the data comprising these four tables are more readily recognized if all the tables are combined into one single table (photocopies pasted together), which, unfortunately, makes too large a table to place in this report.

The chromatograms themselves are available in Appendix C.

Compounds Detected

There were five main compounds of interest detected in the samples analyzed from the impinger trains. Three of these compounds are identified in the three special sample chromatograms; that is, sample IDs A, B, and C in Table 3a.

The **Sample A** chromatogram was a test sulfite preparation in which a small portion of the sulfite had already been oxidized into sulfate. The sulfite eluted at about 3.96 minutes

(Figure 3) while the sulfate peak's elution time was about 4.10 minutes. **Sample B** shows the same sulfite solution, to which 20 µL of 30 percent hydrogen peroxide had been added. Note that the Sample B sulfite was completely oxidized into sulfate; the excess peroxide had a peak at about 3.50 minutes (Figure 3). **Sample C** consisted of hydrogen peroxide in DI water, and the peroxide peak again eluted at about 3.5 minutes. For the samples analyzed, the sulfite peak heights are found in column G of Table 3a and the corresponding concentration in ppm in column M of Table 3b. The corresponding sulfate data are found in columns H and L of the respective tables.

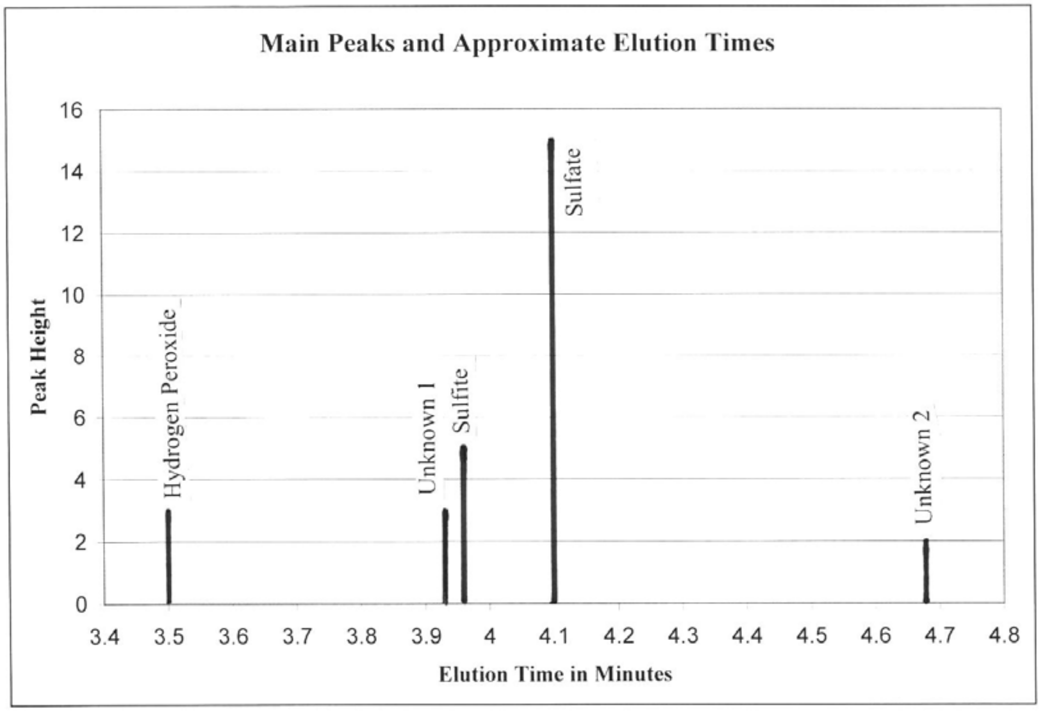


Figure 3. Typical IC Chromatogram Locations of Main Sample Components.

Sample O shows the other two compounds of interest. The sulfate and hydrogen peroxide are readily identifiable in this chromatogram, but there are two additional compounds that show up not only here, but also with most of the other runs. The more prevalent compound can be seen eluting at around 3.93 minutes (referred to as "Unknown 1"), and the second compound elutes at about 4.68 minutes (referred to as "Unknown 2"). The peak heights of these unknown compounds are found in the raw data tables in columns I and J, respectively. The peak height of Unknown 1 is sometimes given as "?", meaning that the peak may be zero; however, it may also be non-zero but still small enough to be masked by a larger nearby peak. Note that the Sulfite and Unknown 1 elute at almost the same time. It should also be noted that elution times can vary slightly from chromatogram to chromatogram, and the closeness of peaks together tends to shift peak elution times slightly, as can be often observed with the three closest peaks: Unknown 1, Sulfite, and Sulfate.

Table 3a. Raw Test Data.

A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*	*K*
Sample ID	**Sample creation/handling**					**SO_3^{-2} pk-ht**	**SO_4^{-2} pk-ht**	**Unk 1 pk-ht**	**Unk 2 pk-ht**	**Run Date/Time**
	Run Time	**a, b, or S**	**Purge**	**H_2O_2**	**Hold Hours**					
A	0	S_1	0	0	***0.0***	20.3	3	**?**	**0.2**	6/21/16:18
B	0	S_2	0	H	***0.0***	0	43	**0.1**	**0.3**	6/21/16:23
C	0	S_3	0	H	***0.0***	0	0	**0.1**	**0.6**	6/23/15:15
300 ppm										
D	1	a	0	0	***1.4***	98	35	**?**	**0.5**	6/21/17:51
E	1	a	0	0	***1.6***	87	47	**?**	**0.5**	6/21/18:04
F	1	a	0	H	***1.8***	0	210	**5**	**1**	6/21/18:16
G	1	a	0	0	***2.3***	1.5	23	**0.5**	**0.25**	6/21/18:47
H	1	a	0	H	***2.5***	0	26	**1**	**0.5**	6/21/19:00
I	1	a	N	0	***2.8***	0.1	13	**4**	**0.1**	6/21/19:14
J	1	a	N	H	***3.0***	0	14	**5**	**0.5**	6/21/19:27
K	1	a	0	0	***16.7***	75	66	**?**	**0.5**	6/22/10:11
L	1	a	N	0	***18.2***	0.5	13	**4**	**0.1**	6/22/11:39
M	1	a	N	0	***18.4***	0.1	12	**4**	**0.1**	6/22/11:52
N	1	a	N	H	***18.7***	0	14	**4**	**0.5**	6/22/12:08
O	1	a	N	H	***18.9***	0	13	**5**	**0.5**	6/22/12:21
300 ppm										
P	3	b	0	0	***3.3***	0.7	26	**0.2**	**0.1**	6/22/14:30
Q	3	b	0	H	***3.5***	0	28	**0.2**	**0.3**	6/22/14:42
R	3	b	N	0	***3.8***	0.1	1.5	**0.4**	**0.2**	6/22/14:55
S	3	b	N	H	***4.0***	0	1.6	**0.4**	**0.5**	6/22/15:08
T	3	b	N	0	***4.5***	0.2	15	**4**	**0.2**	6/22/15:41
U	3	b	N	H	***4.7***	0	13	**4**	**0.6**	6/22/15:53
V	3	a	0	0	***3.7***	6	33	**?**	**0.2**	6/22/16:06
W	3	a	0	H	***3.9***	0	48	**0.1**	**0.3**	6/22/16:18
X	3	a	N	0	***4.1***	0.02	1.9	**0.3**	**0.2**	6/22/16:31
Y	3	a	N	H	***4.3***	0	2	**0.3**	**0.6**	6/22/16:43
50 ppm										
YA	1.3	a	0	0	***0.9***	15	47	**15**	**0.1**	6/22/17:48
YB	1.3	a	0	0	***1.1***	18	43	**16**	**0.1**	6/22/18:00
Z	6	b	0	0	***0.9***	20	37	**?**	**0.2**	6/22/21:07
AA	6	b	0	H	***1.1***	0	75	**4**	**1**	6/22/21:20
AB	6	b	0	0	***1.3***	0.37	7	**0.4**	**0.2**	6/22/21:32
AC	6	b	0	H	***1.5***	0	8	**0.4**	**0.6**	6/22/21:45
AD	6	b	0	0	***1.7***	0.4	7	**0.4**	**0.2**	6/22/21:57
AE	6	b	0	0	***1.9***	19.4	39	**?**	**0.2**	6/22/22:10
AF	6	b	N/2	0	***15.4***	2.7	35	**5**	**0.2**	6/23/11:39
AG	6	b	N/2	H	***15.6***	0	42	**5**	**0.4**	6/23/11:52
AH	6	a	0	0	***12.3***	25.1	32	**?**	**0.2**	6/23/12:05
AI	6	a	0	H	***12.5***	0	81	**0.5**	**0.5**	6/22/21:07
AJ	6	a	N	0	***12.7***	0.5	7	**1.5**	**0.3**	6/22/21:20
AK	6	a	N	H	***12.9***	0	8	**2**	**0.5**	6/22/21:32

a: Dil-corr means corrected for sample dilution.
b: Total $SO_4^{-2} = SO_3^{-2} + SO_4^{-2}$

Table 3b. Two Week Post-Test Raw Data.

A	B	C	D	E	F	G	H	I	J	K
Sample ID	**Sample creation/handling**					**SO_3^{-2} pk-ht**	**SO_4^{-2} pk-ht**	**Unk 1 pk-ht**	**Unk 2 pk-ht**	**Run Date/Time**
	Run Time	**a, b, or S**	**Purge**	**H_2O_2**	**Hold hours**					
Hold for 2 Weeks										
AL	1	a	0	0	***384***	57	130	**?**	**0.1**	7/7/17:42
AM	1	a	N	0	***385***	0.1	15	**0.2**	**0.1**	7/7/18:45
AN	3	a	0	0	***366***	75	98	**?**	**0.2**	7/7/18:32
AO	3	a	N	0	***366***	0.4	10	**1.5**	**0.25**	7/7/18:07
AP	3	b	0	0	***366***	76	108	**?**	**0.5**	7/7/17:55
AQ	3	b	N	0	***366***	0.1	16	**4**	**0.2**	7/7/18:20
AR	6	a	0	0	***356***	18	46	**?**	**0.2**	7/7/19:23
AS	6	a	N	0	***356***	1.5	7	**0.7**	**0.2**	7/7/19:35
AT	6	b	0	0	***359***	3	78	**4**	**0.2**	7/7/18:58
AU	6	b	N/2	0	***359***	0.1	44	**5**	**0.2**	7/7/19:10

Sample Normalization

Sample dilutions were corrected by multiplying the diluted concentration by the inverse of the dilution factor (Table 3c, column N) for the sample. In addition, since the sample flows in the test runs varied as much as 5 percent from each other, a final normalization factor was applied to the total sample sulfate (column Q) by adjusting all flows to 19 LPM. These normalized sulfate values are shown in column S of Tables 3c and 3d. This was accomplished by multiplying the column Q sulfate value by the factor of: 19 LPM / (Run Flow). The "Run Flow" is the number of liters per minute for a particular test, and is found in the fourth column of Table 2.

Sample Oxidation

Examination of the chromatograms (Appendix C) yielded three major sources of sample sulfite oxidation, which transformed the sulfite into sulfate:

- The addition of peroxide.
- Dilution/mixing of high concentration samples to fit the calibration curve, which converted most of the sample sulfite into sulfate.
- Sample holding time before analysis; i.e., the longer the holding time, the more sulfite was oxidized into sulfate.

Note that for those samples that received the addition of peroxide, there was no detectable sulfite peak, and there was always the additional peroxide peak indicating an excess of peroxide present. These three points are elaborated upon in the next paragraphs.

Table 3c: Process Test Data.

A	L	M	N	O	P	Q	R	S
Sample ID	**SO_4^{-2} IC, ppm**	**SO_3^{-2} calc, ppm**	**Dilute Factor**	**Dil-corr[a] SO_4^{-2}, ppm**	**Dil-corr[a] SO_3^{-2}, ppm**	**Dil-corr[a] Total[b] SO_4^{-2}, ppm**	**SO_3^{-2}/ SO_4^{-2}, P/O**	**Total SO_4^{-2}, Flow Adj To 19 LPM**
A	5.1	72.2	1.00	5.1	72.2	77.3	14.1	
B	73.5	0.0	1.02	75.0	0.0	75.0		
C	0.2	0.0	1.02	0.2	0.0	0.2		
300 ppm								
D	67.8	348.5	1.00	67.8	348.5	416.3	5.14	444.1
E	93.0	309.4	1.00	93.0	309.4	402.4	3.33	429.3
F	409.9	0.0	1.02	418.1	0.0	418.1		446.0
G	40.2	5.3	10.00	402.0	5.3	407.3	0.01	434.6
H	43.8	0.0	10.00	437.5	0.0	437.5		466.8
I	22.1	0.4	1.00	22.1	0.4	22.4	0.02	23.9
J	23.0	0.0	1.02	23.4	0.0	23.4		25.0
K	127.4	266.7	1.00	127.4	266.7	394.1	2.09	420.4
L	21.7	1.8	1.00	21.7	1.8	23.5	0.08	25.1
M	20.9	0.4	1.00	20.9	0.4	21.3	0.02	22.7
N	23.1	0.0	1.02	23.5	0.0	23.5		25.1
O	21.4	0.0	1.02	21.8	0.0	21.8		23.3
300 ppm								
P	44.6	2.5	10.00	445.5	24.9	470.4	0.06	491.1
Q	46.7	0.0	10.02	467.8	0.0	467.8		488.4
R	2.7	0.4	10.00	27.2	3.6	30.8	0.13	32.1
S	2.7	0.0	10.02	27.0	0.0	27.0		28.2
T	24.8	0.7	1.00	24.8	0.7	25.5	0.03	26.6
U	25.6	0.0	1.02	26.1	0.0	26.1		27.2
V	59.0	21.3	5.00	295.1	106.7	401.7	0.36	432.0
W	80.1	0.0	5.02	402.1	0.0	402.1		432.4
X	3.4	0.1	5.00	17.2	0.4	17.6	0.02	18.9
Y	3.3	0.0	5.02	16.5	0.0	16.5		17.7
50 ppm								
YA	87.7	53.7	1.00	87.7	53.7	141.3	0.61	151.3
YB	80.7	64.4	1.00	80.7	64.4	145.1	0.80	155.4
Z	67.5	71.1	1.00	67.5	71.1	138.6	1.05	140.4
AA	132.2	0.0	1.02	134.8	0.0	134.8		136.6
AB	10.9	1.3	11.00	120.4	14.5	134.9	0.12	136.6
AC	12.8	0.0	11.05	141.9	0.0	141.9		143.7
AD	11.8	1.4	11.00	129.5	15.6	145.1	0.12	147.0
AE	70.7	69.0	1.00	70.7	69.0	139.7	0.98	141.5
AF	61.2	9.6	1.00	61.2	9.6	70.8	0.157	71.7
AG	68.8	0.0	1.02	70.2	0.0	70.2		71.1
AH	59.1	89.3	1.00	59.1	89.3	148.4	1.51	157.1
AI	138.8	0.0	1.02	141.6	0.0	141.6		149.9
AJ	10.5	1.8	1.00	10.5	1.8	12.3	0.17	13.0
AK	12.0	0.0	1.02	12.3	0.0	12.3		13.0

a: Dil-corr means corrected for sample dilution.
b: Total SO_4^{-2} = SO_3^{-2} + SO_4^{-2}

Table 3d. **Two-Week Post-Test Process Data.**

A	L	M	N	O	P	Q	R	S
Sample ID	**SO_4^{-2} IC, ppm**	**SO_3^{-2} calc, ppm**	**Dilute Factor**	**Dil-corr[a] SO_4^{-2}, ppm**	**Dil-corr[a] SO_3^{-2}, ppm**	**Dil-corr Total[b] SO_4^{-2}, ppm**	**SO_3^{-2}/ SO_4^{-2}, P/O**	**Flow Adjust of Total SO_4^{-2} To 19 LPM**
Hold for 2 Weeks								
AL	247.1	202.7	1.00	247.1	202.7	449.8	0.82	479.9
AM	23.7	0.4	1.00	23.7	0.4	24.0	0.02	25.6
AN	181.8	266.7	1.00	181.8	266.7	448.5	1.47	482.3
AO	15.1	1.4	1.00	15.1	1.4	16.5	0.09	17.8
AP	204.0	270.3	1.00	204.0	270.3	474.2	1.33	495.1
AQ	24.2	0.4	1.00	24.2	0.4	24.2	0.02	26.0
AR	78.9	64.0	1.00	78.9	64.0	142.9	0.81	151.2
AS	11.3	5.3	1.00	11.3	5.3	16.7	0.47	17.6
AT	125.0	10.7	1.00	125.0	10.7	135.7	0.09	137.4
AU	70.9	0.4	1.00	70.5	0.4	70.9	0.01	70.9

a: Dil-corr means corrected for sample dilution.
b: Total $SO_4^{-2} = SO_3^{-2} + SO_4^{-2}$

Time Evolution of Non-Purged Sulfate/Sulfite Sample Concentrations

In this series of tests, as the trains began sampling, the sulfite anions quickly built up in the impingers and more slowly began converting into sulfate anions. Thus, for the same input SO_2 concentration, longer sampling/storage periods will produce more sulfate than shorter periods. This trend of an initially dominant sulfite concentration transforming into sulfate over time can be clearly seen by tracking one of the non-purged samples over time. To quantify this trend, the 1 hour non-purged sample sulfite and sulfate levels are tracked through time in Table 4.

Table 4. **Test 1 Sulfate/Sulfite Time Evolution.**

Hours Since Test Completion	SO_3^{-2} Concentration, ppm	SO_4^{-2} Concentration, ppm
1.5	329	80.4
16.7	267	127
384	203	247

At 1.5 hours samples D and E averaged, at16.7 hours sample K averaged, and, finally, at 384 hours sample AL averaged. Examination of the table time-concentrations suggests an exponential rise of the sulfate concentration and a corresponding exponential decay of the sulfite. This is indeed the case, as can be seen in a graph of the Table 4 data shown in Figure 4. Each curve was fit with an exponential curve, which is placed next to each curve.

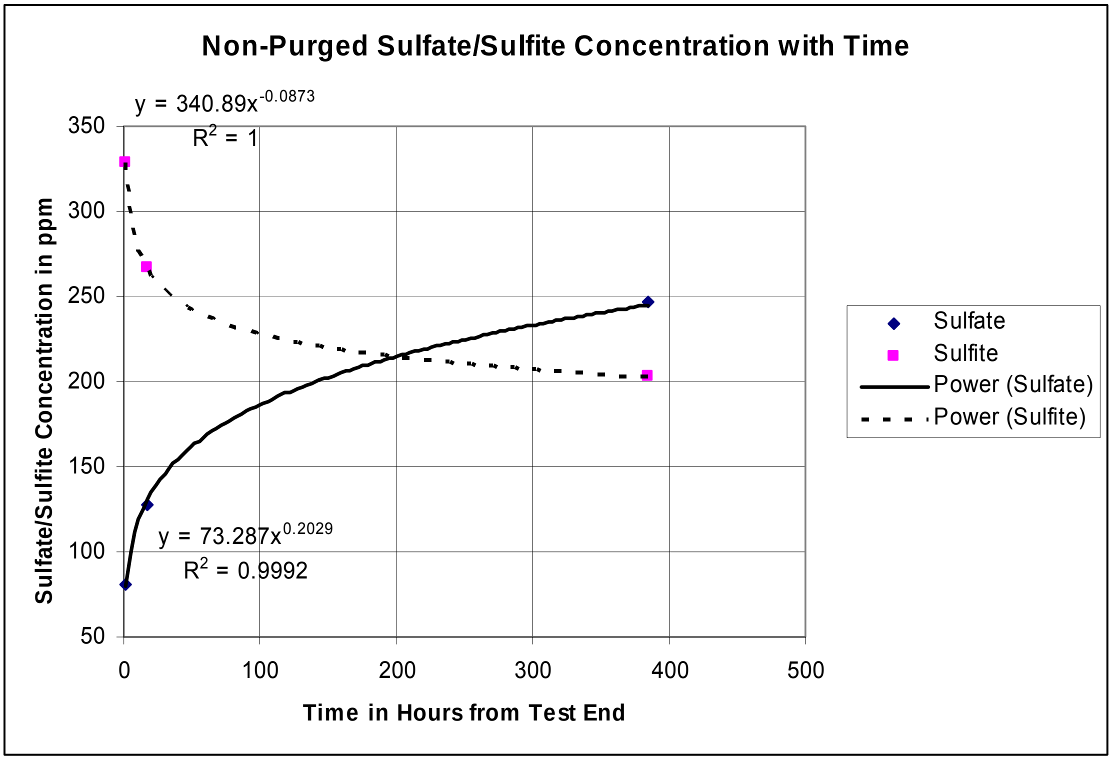


Figure 4. Transformation of Sulfite to Sulfate Over Time.

The general trend of conversion of $SO_3^{-2} \rightarrow SO_4^{-2}$ over time for non-purged/non-diluted samples can also be seen in the aging of the Test 1 samples, but cannot be seen in the Test 3 samples since, as previously noted, the process of diluting the Test 3 samples converted most of the sulfite into sulfate almost immediately. For Test 1, the ratio of sulfite/sulfate (samples D and E, Tables 3c and 3d, column R) starts out between about 3 and 5, about 1.5 hours after Test 1 ends. The same sample's (K) ratio reduces to 2.1 after 16.7 hours, reaches a ratio of 1 around 200 hours (Figure 4), and, finally, after 384 hours, the sample's (sample AL) ratio is only 0.82.

For the lower concentration of Test 6, the ratio of sulfite/sulfate (non-purged and non-diluted samples Z and AE) starts out at an average of 1.0, about 1.5 hours after the test ended, while the impinger sample (AH) is still elevated at a ratio of 1.5 12 hours after sampling has ended, showing some unexpected variability in the two sample trains.

After two weeks of storage, mostly at 4 C, the non-purged 6–hour samples (AT and AR) have an average sulfite/sulfate ratio of 0.45; i.e., having less sulfite than sulfate. (All samples were refrigerated at 4 C beginning 1740 hours on 6/24/2005; column K in Tables 3a and 3b shows the sample run times and dates.) Note that sample AT's ratio is about one-tenth that of the corresponding sample AR. This lower ratio was first observed in the short-term comparison of Z and AE to AH, but, after two weeks, the trend has become significantly magnified. This anomalous example shows that samples may be sensitive to small changes in the initial conditions during or shortly after sampling.

Overall, however, the basic trend in sulfite to sulfate ratios in the non-purged/non-diluted samples is clear, as summarized in Table 5. In the short-term, the higher concentration SO_2 gas (300 ppm) bubbled for the shorter time (1 hour, Test 1) results in the much larger ratio of sulfite to sulfate of 4.2, as compared to the lower concentration SO_2 (50 ppm) bubbled for the longer time (6 hours, Test 6).

Table 5. Time-Concentration Trend in Ratio of Sample Sulfite/Sulfate and Total Sulfate.

Test	Pre-Purge Avg. Ratio, (total SO_4^{-2} ppm)	Two-Week Storage Avg. Ratio, (total SO_4^{-2} ppm)	SO_2 Exposure, ppm-hours
1	4.2 (440)	0.8 (480)	300
3	* (461)	1.4 (489)	901
6	1.0 (144)	0.45 (144)	292

* Not available

In this short-term case, the sulfite forms rapidly because of the high SO_2 concentration; however, the transformation of sulfite into sulfate is a slower process than the conversion of SO_2 into sulfite, hence, the large ratio of sulfite to sulfate. The 6-hour test at the lower concentration does not put SO_2 into solution as quickly as the shorter test; however, this test allows more time for the conversion of sulfite into sulfate, hence, the resulting ratio is much closer to unity.

In the long-term, the highest exposure level (900 ppm-hours) generates the most sulfite and, hence, requires the longest time to transform its sulfite into sulfate, as reflected in the long-term by the sulfite to sulfate ratio of 1.4 (compared to 0.8 and 0.45).

Total Sample Sulfate

As Table 5 shows, the amounts of total SO_4^{-2} (Table 3c, column S) for the 3-hour tests are only slightly higher than for the 1-hour test, despite the fact that both 3-hour tests consisted of an exposure level three times higher than the 1-hour test. This comparison points to what appears to be an impinger SO_2 saturation, so that exposures higher than 900 ppm-hours would probably show very little, if any, additional sample sulfate increases in either the purged or non-purged samples under these test conditions.

Without refrigeration, the conversion of sulfite to sulfate should be accelerated and the last data points at 380 hours on each curve of Figure 4 would be further separated than they are. On the other hand, if the samples were refrigerated immediately after generation and in between the analyses, the last points should be closer together.

Test 1.3 (un-purged samples YA and YB in Tables 3a and 3c) was run at 50 ppm SO_2 (see Table 2). In these chromatograms (see Appendix C), nearly equal amounts of Unknown 1 and sulfite can be seen next to the sulfate peak. It is significant that these samples were analyzed only one hour after the test ended (or about two hours earlier than Z and AE were analyzed), at which time the sulfite/sulfate ratio for the two samples from this single Test 1.3 are about 0.7. It seems likely that, in order to have a sulfite/sulfate ratio around 1 (for Z and AE), most of the intermediate Unknown 1 may rapidly convert to sulfite and sulfate in under one and one-half hours.

Two samples from Test 6 (Table 2, 6 hours at 50 ppm SO_2), AF and AG were purged for only 0.63 hours, and then analyzed after about 15.5 hours. These are identical samples except AG was treated with hydrogen peroxide. Comparing the two chromatograms (Appendix C), it is easy to see that the peroxide oxidized the sulfite entirely into sulfate, and also affected the level of Unknown 2. In fact, whenever a sample has had hydrogen peroxide added, the sulfite is always totally transformed, and the Unknown 2 peak increases moderately (for example, the following pairs of samples: E, F; G, H; I, J; L, N; M, O; P, Q; R, S; V, W; X, Y; Z, AA; AB, AC; AF, AG; AH, AI; AJ, AK). Also, as the concentration of the SO_2 increases (as with Test 1, samples D and E) and as the time increases (as with Test 6, sample AH, Unknown 1), peak is overtaken and covered by the sulfite peak.

Sulfite/Sulfate Formation in the Nitrogen-Purged Samples

As indicated by the letter N in column D of Tables 3a and 3b, the nitrogen-purged samples are:

- I, J, L, M, N, O (1 hour, 300 ppm)
- R, S, T, U, X, Y (3 hour, 300 ppm)
- AF (0.63 hours), AG (0.63 hours), AJ, AK (6 hour, 50 ppm)
- AM, AO, AQ, AS, AU (2 Week Hold of 1, 3 and 6 hour samples).

The following is the subset of the nitrogen-purged samples that includes only those that had the full 60-minute purge and without a subsequent addition of hydrogen peroxide:

- I, L, M (1 hour, 300 ppm)
- R, T, X (3 hour, 300 ppm)
- AJ (6 hour, 50 ppm)
- AM, AO, AQ, AS (2 Week Hold of 1, 3 and 6 hour samples).

The dilution-corrected sulfite concentrations from these purged samples are given in column P of Tables 3c and 3d, and that for sulfate in column O. Overall, the sulfite concentrations are very small or nearly zero, and the sulfate concentrations are all small. It is interesting to note that the 1-hour (300 ppb) purged samples (I and J) show almost zero sulfite when analyzed about three hours after sampling, but the next day (L and M, 18 hours after sampling) they show a slight increase in sulfite content with a high value of 1.8 ppm. The 3-hour (300 ppb) purged samples show essentially zero sulfite about four hours after sampling, but it should be noted that all purged 3-hour samples were diluted with water before analysis, which, as noted earlier, oxidizes most of the sulfite. Indeed, all run samples diluted before analysis (nitrogen purged and non-purged) have considerably less sulfite (except V) than their non-diluted counterparts. Still, there is a high value of 3.6 ppm sulfite (column P) for the purged 3-hour samples. The 6-hour samples have a slightly higher short-term sulfite level than the other tests, and five times or more higher level for the long-term samples, in spite of the lower SO_2 concentration of only 50 ppm. These results are summarized in Table 6 below.

Table 6. SO_3^{-2} and SO_4^{-2} Results, 1-Hour Purge with No Peroxide Addition.

Test	SO_3^{-2} Average for Short Hold, ppm	SO_3^{-2} for 2-Week Hold, ppm	SO_4^{-2} Average for Short Hold, ppm	SO_4^{-2} for 2-Week Hold, ppm
1	0.4	0.4	21.6	23.7
3	1.6	0.9	23.2	19.7
6	1.8	5.3	10.5	11.3

Nevertheless, overall, the nitrogen purge was very successful in removing all or almost all of the sample sulfites. Removing the sulfite effectively prevented the formation of APM in the form of sulfate in the samples, as can be seen in Table 7 when comparing the flow-adjusted (Tables 3c and 3d, column S) total sulfate values to their corresponding non-purged samples. Table 7 also shows that, for both the rapidly analyzed samples as well as for the long-term samples stored for two weeks, a 1-hour post-sampling purge reduced sulfate formation by 95 percent for the 1- and 3-hour runs, and by about 90 percent for the 6-hour runs.

Table 7. Purge Efficiency at Reducing Sulfate from Samples.

Test	% SO_4^{-2} Reduction By Purge (2- to 5-Hour Hold)	% SO_4^{-2} Reduction By Purge (2-Week Hold)
1	94.6	94.7
3	94.5	95.5
6	91.0	88.3

Measurements of Impinger pH

Six pH measurements were taken for each run using a few drops of impinger solution for each measurement and pH paper:

- pre-test front and back impingers,
- post-test pre-purge front and back impingers, and
- post purge front and back impingers.

These measurements are given in Table 8.

Table 8. Measurements of Impinger pH at Different Stages.

Test	Pre-Test		Post Test, Pre-purge		Post-Purge	
	Front	Back	Front	Back	Front	Back
1a	5.3	5.3	2.5	2.5	4	4.5
3a	5.3	5.3	1.9	2.5	3.9	4.2
3b	5.3	5.3	2.5	2.5	3.9	3.9
6a	5.3	5.3	2.5	2.5	3.4	3.4
6b*	5.3	5.3	2.5	2.5	2.5	2.5

* purged for only 38 minutes.

All tests showed a decrease in the impinger water pH as well as an increase in sulfate compounds as a result of sampling, indicating the creation of sulfuric acid, as expected. The Post-Test, Pre-Purge impinger pH was nearly the same for all runs, about 2.5. However, the Post-Purge pH was more acidic for the longer runs, indicating that the longer runs allowed more time for the transformation of gaseous SO_2 into H_2SO_4. The Post-Purge pH was generally higher than the Pre-Purge pH, indicating the effectiveness of the nitrogen purge, except for the last test, Test 6b, which was purged for only 63 percent of the stand purge time. Test 6b demonstrates the effectiveness of the last portion of the 60-minute purge in removing the sulfuric acid formed.

SUMMARY

APM Formed

Significant amounts of APM were captured by the impinger trains in these simulated Method 202 stack sampling tests. Nitrogen purging did reduce the APM by 90 to 95 percent; however, it is significant that the 5 to 10 percent APM that remained was never genuine CPM present in the gas stream, since no CPM was ever introduced into the gas stream. In general, higher concentrations and longer sampling times tended to produce higher impinger APM concentrations; however, the APM levels in purged samples (Table 6) were found to be almost gas stream concentration-independent for the exposure levels used in this series of tests.

Purged Samples Relatively Independent of Gas Stream Concentration

The highest levels of APM were, not surprisingly, found in unpurged samples from the highest concentration-time exposure test (see Table 9; note that total SO_4^{-2} is from Table 3c, column S). That is, the 3-hour, 300 ppm tests (900 ppm-hours) had the highest sample sulfate levels.

Table 9. SO_2 Exposure Level and Normalized Sample Concentrations.

Test	Exposure Level, ppm-hours	Unpurged Average Total SO_4^{-2} Concentration, ppm	Samples Averaged for Total SO_4^{-2}	Purged Total SO_4^{-2} Concentration, ppm
1a	299	440	DEFGHK	24.4
3a, 3b	901	461	PQVW	25.1
6a, 6b	292	144	Z,AA,AB,AC, AD,AE,AH,AI	13.0

What is surprising, though, is when comparing Tests 1 and 3, the unpurged sulfate levels in the Test 3 samples are only 5 percent higher than in the Test 1 samples, in spite of the fact that the Test 3 exposure level is three times as high as the Test 1 exposure level. The slight difference in these values may show that the impinger solution was nearly saturated in the 1-hour test at 300 ppm SO_2, and that even tripling the exposure did not significantly raise the solution concentration. This comparison shows that near this saturation level, the impinger catch does not linearly reflect the actual gas SO_2 levels under the test conditions used. Thus, for higher gas stream exposure levels than those investigated in these experiments, the impinger capture might be an even smaller portion of the actual SO_2 level in the gas stream.

This means that with proper sample purging, Method 202 particulate results are not disproportionately affected by APM from high SO_2 gas stream concentrations. That is, SO_4^{-2} levels in properly purged samples are typically below 25 ppm for the exposure levels investigated in these experiments. Purging reduces artifact sulfate formation by about 90 to 95 percent for all conditions tested.

These data indicate that the highest sulfate APM would be expected from high concentration gas streams sampled for long time periods, such as 6 hours. A 6-hour, 900 ppm-hour test would likely produce much higher levels of sulfate in the purged samples than were found in this set of lower exposure tests. It has been reported that studies of systems with SO_2 levels around 2,000 ppm had significant sulfate APM in spite of nitrogen purging, accounting for up to 42 percent of the measured CPM. [1]

Finally, the full 60 minutes of a nitrogen purge insures the maximum reduction of APM for the concentration-times investigated here. This is evidenced by Test 6b, in which the samples were purged for only 38 minutes, resulting in purged samples that contained sulfate levels that were 50 percent of the non-purged samples. It may be the case that additional purging past the 60 minutes may further reduce the APM found in these experiments.

Parameters Affecting APM Formation

The main factors affecting APM formation in these experiments are: nitrogen purging, oxidation, and dilution/mixing. The parameters affecting the APM formation are summarized in Table 10. The mixing and introduction of oxygen that occurs during dilution promoted significant oxidation of samples analyzed in these tests, as is evident in the small sulfite peaks for all the diluted Test 3 samples.

Table 10. Summary of Parameters Affecting Observed Compounds.

Affecting Agent ↓	**SO_4^{-2}**	**SO_3^{-2}**
Nitrogen Purging	Decreases 90-95 percent	Greatly Decreases
Hydrogen Peroxide	No Effect	Oxidizes to SO_4^{-2}
Dilution/Mixing	No Effect	Oxidizes to SO_4^{-2}
Holding Time	Promotes Formation	Decreases

As the holding time of a non-purged impinger sample increases, even for refrigerated samples, oxidation of the sulfite to sulfate continues. The ratio of sulfite to sulfate changes from a larger whole number, such as 5 close to the end of the test run, to a value close to unity after several days. If the samples are stored long enough, ultimately all of the sulfite would be expected to become oxidized into sulfate. At least two other compounds, though unidentified, were detected among the sulfite and sulfate compounds. Unknown 1 was prominent during and shortly after sampling was completed, but after only a few hours, Unknown 1 decreased rapidly in concentration.

If samples are properly purged immediately after sampling, about 90 to 95 percent of the APM formation will be prevented. About 20 ppm of APM in the form of SO_4^{-2} remained in all of the purged samples. Samples not purged immediately after sampling would be expected to contain higher levels of sulfate than if had they been purged sooner, since more of the sulfite oxidizes into sulfate. Samples purged later would have proportionately larger sulfate residues than those purged immediately after sampling.

REFERENCES

1. Chang, M.C., and England, G.C. (2004). "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil-and Gas-Fired Combustion Systems, Other Report: Pilot-Scale Dilution Sampler Design and Validation Tests (Laboratory Study)." GE Energy and Environmental Research Corporation, Irvine, California. Prepared for National Petroleum Technology Office, National Energy Technology Laboratory, and U.S. Department of Energy (DOE Contract No. DE-FC26-00BC15327); Gas Research Institute, California Energy Commission-PIER, and New York State Energy R&D Authority (GRI Contract No. 8362); and American Petroleum Institute (Contract No. 00-0000-4303), July 28.

2. Corio, L.A., and Sherwell, J. (2000). "In-stack Condensible Particulate Matter Measurements and Issues." *Air Waste Management Association*, February, 50(2): 207-18.

3. England, G.C. (2004). "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil-and Gas-Fired Combustion Systems, Topical Report: Impact of Operating Parameters on Fine Particulate Emissions from Natural Gas-Fired Combined Cycle and Cogeneration Power Plants." GE Energy and Environmental Research Corporation, Irvine, California. Prepared for National Petroleum Technology Office, National Energy Technology Laboratory, and U.S. Department of Energy (DOE Contract No. DE-FC26-00BC15327); Gas Research Institute, California Energy Commission-PIER, and New York State Energy R&D Authority (GRI Contract No. 8362); and American Petroleum Institute (Contract No. 00-0000-4304), November 5.

4. Canadian Chemical Producers' Association (CCPA) (2001). Source Characterization Guidelines: Primary Particulate Matter and Particulate Precursor Emission Estimation Methodologies for Chemical Production Facilities. CCPA, 805-350 Sparks Street, Ottawa, Ontario, Canada, March.

5. DeWees, W.G., and Steinsberger, K.C. (1990). "Test Report: Method Development and Evaluation of Draft Protocol for Measurement of Condensible Particulate Emissions." CEM/Engineering Division, Entropy Environmentalists, Inc., Research Triangle Park, North Carolina, May 16.

6. Pathak, R.K., Louie, P.K., and Chan, C.K. (2004). "Characteristics of Aerosol Acidity in Hong Kong." *Atmospheric Environment*, 38(2004) 2965-2974.

7. U. S. Environmental Protection Agency (US EPA) (2005). Method 202: Determination of Condensible Particulate Emissions from Stationary Sources. Technical Support Division, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

8. Pjetraj, J. (1998). "Condensable Particulate Matter: Regulatory History and Proposed Policy." North Carolina Department of Air Quality, Stationary Source Compliance Branch, January 27.

9. Farber, P.S., and Marmer, D.L. (2005). "Condensible Particulate Matter Emission Sources and Control in Coal-Fired Power Plants." Environmental Consulting Group, Sargent and Lundy LLC, 55 East Monroe Street, Chicago, Illinois 60603. Presented at Electric Power 2005, April 5-7.

APPENDIX A:

LITERATURE SEARCH SUMMARY

Appendix A: Literature Search Summary

(1) Chang, M.C., and England, G.C. (2004). "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil-and Gas-Fired Combustion Systems, Other Report: Pilot-Scale Dilution Sampler Design and Validation Tests (Laboratory Study)." GE Energy and Environmental Research Corporation, Irvine, California. Prepared for National Petroleum Technology Office, National Energy Technology Laboratory, and U.S. Department of Energy (DOE Contract No. DE-FC26-00BC15327); Gas Research Institute, California Energy Commission-PIER, and New York State Energy R&D Authority (GRI Contract No. 8362); and American Petroleum Institute (Contract No. 00-0000-4303), July 28.

Previous experiments have demonstrated that the iced impinger test methods can artificially produce inorganic condensable matter. SO_2 and molecular oxygen (O_2) both are soluble in water. The dissolved SO_2 can form hydrated SO_2 ($SO_2 \bullet H_2O$) and sulfite ions (SO_3^{-}) in aqueous solution. At the potential of hydrogen (pH) range of interest (pH between 2 and 7), HSO_3^{-} is the preferred state. The individual dissociations are very fast, so aqueous-phase equilibria are established instantaneously. The dissociation of the dissolved SO_2 enhances its aqueous solubility so that the total amount of dissolved sulfate always exceeds that predicted by Henry's Law for SO_2 alone. There are several pathways for sulfate formation by reaction of these ions with dissolved O_2, zone, and hydrogen peroxide, which can be catalyzed by many substances such as iron and manganese. Free NH_3 in the samples can increase the amount of dissolved SO_2, and, thereby, increase artifact sulfate formation since it instantly reacts in aqueous solution forming ammonium sulfite/bisulfite ions and the additional SO_2 must dissolve to maintain equilibrium.

The EPA Methods 202 and 8 implicitly acknowledge the potential for conversion of SO_2 to sulfate ion (SO_4^{-2}) by requiring a post-test purge of the impingers immediately following the test to purge impinger solutions of dissolved SO_2. Studies of systems having SO_2 levels of approximately 2000 ppm showed that the SO_2–to- SO_4^{-2} artifact occurs in spite of post-test purging and that it can account for up to 42 percent of the measured CPM.

Wien et al. (2001) evaluated the SO_2–to-SO_4^{-2} artifact in the laboratory at low SO_2 concentrations typical of gas combustions by passing pure compressed gas mixtures with representative amounts of oxygen, carbon dioxide, nitrogen gas, nitric oxide (NO) and SO_2 through two sets of paired Method 202 impinger trains. No particulate or condensable substances were added. Tests were performed for 1-hour and 6-hour sampling runs with mixtures containing 0, 1, and 10 ppm SO_2. One pair of trains was purged with nitrogen for one hour immediately following the tests, while the other was not. The samples were stored at 4 C for approximately 2 weeks prior to analysis. Significant amounts of SO_4^{-2}, approximately proportional to the SO_2 concentration in the gas, were present in impingers regardless of the post-test purge. While the post-test purge clearly reduced SO_4^{-2} concentration in the impingers, significant SO_4^{-2} still remained. Purging was less efficient at reducing SO_4^{-2} for the 6-hour runs than for the 1-hour runs, indicating that much of the SO_2 oxidation occurs within this period. Wien compared the laboratory data to field result from a gas-fired refinery boiler using unpurged sample trains and concluded that approximately 50 to 100 percent of the SO_4^{-2} in the field samples, which comprised more than 80 percent of the CPM in that field test, could be attributed to the SO_2–to- SO_4^{-2} artifact.

As the flue gases rapidly cool beyond the injection point, moisture in the flue gas reacts with SO_3 and H_2SO_4 forms. The vapor becomes supersaturated, favoring aerosol formation by nucleation followed by condensational growth.

Samples that are analyzed without the optional NaOH titration procedure for preservation of H_2SO_4 in the sample would be expected to contribute significantly to the condensable PM catch for sulfur-bearing fuels. Therefore, the condensable PM catch is uncharacteristically small compared to other test results. This probably accounts for most of the difference between the EPA method and dilution sampler results.

(2) Corio, L.A., and Sherwell, J. (2000). "In-stack Condensible Particulate Matter Measurements and Issues." ***Air Waste Management Association,*** **February, 50(2): 207-18.**

Methods 202 and 201/201A results for several coal-burning boilers showed that the condensible PM, on average, comprises approximately three-fourths (76 percent) of the total PM10 stack emissions. The results for oil- and natural gas-fired boilers showed that the condensible PM, on average, comprises 50 percent of the total PM10 stack emissions. Results for oil-, natural gas-, and kerosene-fired combustion turbines showed that the condensible PM, on average, comprises 69 percent of the total PM10 emissions. A positive bias in CPM may exist due to the conversion of dissolved sulfur dioxide to sulfate compounds in the sampling procedure. These Method 202 results confirm that CPM, on average, is composed mostly of inorganic matter, regardless of the type of fuel burned.

(3) England, G.C. (2004). "Development of Fine Particulate Emission Factors and Speciation Profiles for Oil-and Gas-Fired Combustion Systems, Topical Report: Impact of Operating Parameters on Fine Particulate Emissions from Natural Gas-Fired Combined Cycle and Cogeneration Power Plants." GE Energy and Environmental Research Corporation, Irvine, California. Prepared for National Petroleum Technology Office, National Energy Technology Laboratory, and U.S. Department of Energy (DOE Contract No. DE-FC26-00BC15327); Gas Research Institute, California Energy Commission-PIER, and New York State Energy R&D Authority (GRI Contract No. 8362); and American Petroleum Institute (Contract No. 00-0000-4304), November 5.

In 1997, the EPA promulaged new National Ambient Air Quality Standards (NAAQS) for particulate matter, including for the first time particles smaller than 2.5 microns ($PM_{2.5}$). $PM_{2.5}$ contributes to reduced atmospheric visibility.

Traditional stationary source air emission sampling methods tend to under or overestimate the contributions of the source to ambient aerosols because they do not properly account for primary aerosol formation, which occurs after the gases leave the stack.

CPM is defined as the mass of solid residue remaining after the impinger contents are analyzed.

The EPA Method 202 sample collection and analysis include optional procedures to minimize SO_2 interference (by purging the impingers with N2 for one hour immediately following sample collection), and loss of sulfuric acid (by titrating the inorganic sample fraction with ammonium hydroxide prior to final evaporation and weighing). CPM results are dominated by the inorganic fraction, which chemical analysis shows to be predominantly sulfate related. The net weight of the residues is well above the analytical resolution (5.6 to 9.9 mg sample net weights compared to analytical resolution of 0.1 mg). The standard deviation of the CPM results suggests an in-stack LQL (lower quantitation limits) of approximately 5 mg/dscm (dry standard cubic meters), which is greater than all of the CPM test results. It should be noted that the CPM results are probably biased high due to aqueous phase oxidation of dissolved SO_2 gas to sulfites/sulfates in the impingers during sample collection and storage. Furthermore, condensation of vapors in the impingers is excessive compared to the actual exhaust plume because the sample cools without dilution. Thus, it is likely that CPM measurement results from iced impinger methods applied to gas-fired sources depend more on the natural gas sulfur content than on the process operating conditions and do not represent actual CPM that exists in the exhaust plume.

Based on the iced impinger methods (Methods 202 and 8) with post-test nitrogen purge and optional procedures to minimize H_2SO_4 loss during analysis, the majority of the condensable PM mass is inorganic (sulfate/sulfuric acid), with lesser amounts of other substances. Other tests indicated that most of the sulfate/sulfuric acid in the condensable PM majority of the CMP mass is likely “pseudo-particulate matter” (which is defined in this report as APM) caused by a measurement artifact (aqueous phase oxidation of the dissolved gaseous SO_2 to sulfite/sulfate in the impingers during sampling and sample storage prior to analysis. Thus, the biggest factors determining measured condensable PM emissions from gas-fired sources are believed to be sulfur content of the fuel and the specific methods, procedures, techniques, and reporting protocols used for determining CPM emissions using iced impinger methods. Because these measurement artifacts dominate the results, the biggest factors governing true condensable emissions cannot be determined from results using this method.

Lab results showed that bias in CPM results might increase with longer test runs due to increased aqueous-phase conversion of SO_2 to solid residues.

Post-test impinger purge: The impingers should be purged for one hour immediately following sample collection to reduce uncontrolled bias and variation due to aqueous phase SO_2 oxidation.

This research showed that sulfate-related substances dominate CPM measurements. Previous studies indicated that artifact conversion of gaseous SO_2 to solid residues during sample collection and storage can dominate results at low concentrations. Since conditions affecting this artifact are rarely controlled, it remains a source of considerable random uncertainty in the measurements. If the sulfate-related substances include sulfuric acid, random variation can be introduced when drying the samples since sulfuric acid is relatively volatile and can be lost during analysis unless measures are taken to stabilize it.

(4) Canadian Chemical Producers' Association (CCPA) (2001). Source Characterization Guidelines: Primary Particulate Matter and Particulate Precursor Emission Estimation Methodologies for Chemical Production Facilities. CCPA, 805-350 Sparks Street, Ottawa, Ontario, Canada, March.

"Method 202 … [is] subject to substantial artifacts that do not occur in atmospheric processes, especially when ammonia, sulfates and/or chlorides are present in the exhaust, and, thus, may not provide an accurate measure of primary condensible particles. For example in comparison tests … it was shown that the mass of $PM_{2.5}$ measured by EPA source test methods that included the impinger fraction, was 80-100 times greater than that measured by a dilution sampler. Analysis of material collected in the impingers showed a dominant sulfate; much more sulfate than was collected in the dilution sampling system … attributable to the dissolution and oxidation of SO_2 from the stack gas in the impingers. While the SO_2 artifact is well known for coal- and oil-fired systems, this is the first time it was shown to be significant for very low SO_2 concentrations (0.3 to 3 ppm)".

(5) DeWees, W.G., and Steinsberger, K.C. (1990). "Test Report: Method Development and Evaluation of Draft Protocol for Measurement of Condensible Particulate Emissions." CEM/Engineering Division, Entropy Environmentalists, Inc., Research Triangle Park, North Carolina, May 16.

Method 202 allows the determination of both the filterable PM and CPM simultaneously.

Formation of false CPM: Since gases are bubbled through the impinger water, noncondensable gases may react with other gases or condensables to form CPM that would not have otherwise formed. The most notable case of this is the oxidation of SO_2 to form SO_4^{-2}. The SO_2 dissolves in water to form H_2SO_3, which may oxidize to form H_2SO_4. This SO_4^{-2} would then be counted as CPM. Purging the impinger solution immediately after sampling with air effectively removes the SO_2, but may lead to the possible conversion of SO_2 to SO_3.

If the pH of the sample is less than 4.5, then NH_4OH should be added to the sample to stabilize H_2SO_4 and provide for accurate weighing of the residue.

Remove 4 mL from each impinger, combine, and determine SO_3^- and SO_4^{-2} by IC.

The removal of SO_2 from the impinger through N_2 purging is related directly to the pH of the solution. The SO_2 is more easily removed at a pH of 2 than at above 4 (typical impinger pH was about 2).

After samples were saturated with SO_2, they were purged with air. The results were very much pH dependent. At pHs greater than about 4, SO_2 was not effectively removed. At the low pHs, there was much more scatter than with the nitrogen purge.

If the sample pH is greater than 4.5, indicating low concentrations of H_2SO_4 and SO_2 in the sample, then the ammonia addition is no longer required to stabilize the SO_4^{-2}. Thus, when sources of SO_2 are low, the post-test purge and addition of the ammonium hydroxide can be eliminated; i. e., when the sample pH is greater than 4.5.

(6) Pathak, R.K., Louie, P.K., and Chan, C.K. (2004). "Characteristics of Aerosol Acidity in Hong Kong." ***Atmospheric Environment*****, 38(2004) 2965-2974.**

The acidity characteristics of fine particles are a function mainly of the relative humidity and the ammonium-to-sulfate ratio ($[NH_4^+]/[SO_4^{-2}]$). The ammonium-to-sulfate ratio has been used to describe the acidic nature of atmospheric aerosols. The in-situ free acid concentration, the normalized water content ($[H_2O]AIM2/[SO_4^{-2}]$), and the dissociation of bisulfate to free acid in the aerosols decrease as the ammonium-to-sulfate ratio increases and the relative humidity decreases. It was found that a ratio a ratio of 1.5 is a critical condition to the sampling artifact characteristics of $PM_{2.5}$. AR (ammonia-rich) is defined as the ratio $[NH_4^+]/[SO_4^{-2}] > 1.5$, while AP (ammonia-poor) has a ratio 1.5 or less.

(7) U. S. Environmental Protection Agency (US EPA) (2005). Method 202: Determination of Condensible Particulate Emissions from Stationary Sources. Technical Support Division, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

This method was referenced for the Experimental Design portion of this report.

(8) Pjetraj, J. (1998). "Condensable Particulate Matter: Regulatory History and Proposed Policy." North Carolina Department of Air Quality, Stationary Source Compliance Branch, January 27.

Particulate matter exists in the solid and liquid physical states, and gases or vapors may also condense to form PM. The latter, CPM, is of great concern due to the inherently small size of condensation products; overwhelmingly, CP can be classified as $PM_{2.5}$.

Thus, whenever the effluent is at an elevated temperature, there is the potential for condensation of some particulate matter when the effluent temperature decreases.

Analyses by EPA show that the material collected in the impingers of the sampling train is usually, although not in every case, a consistent fraction of the total particulate loading.

Condensable PM_{10}: CPM can be broadly defined as material that is not particulate matter at stack conditions but which condenses and/or reacts (upon cooling and dilution in the ambient air) to form particulate matter immediately after discharge from the stack. CPM is usually quite fine and, thus, falls primarily within the PM_{10} fraction.

Secondary PM_{10} (PM Precursors): Secondary particulate matter can be broadly defined as particles that form through chemical reactions in the ambient air well after dilution and condensation have occurred (i.e., usually at some distance downwind from the emission point). An example of this phenomenon is the formation of sulfate particles in a plume from the oxidation of sulfur dioxide by one of several atmospheric transformation mechanisms. Generally, SPM can be distinguished from CPM by the time and/or distance downwind from the stack required for formation.

Particulate matter is dependent on the temperature of a given effluent. As the effluent temperature changes, the physical state of the particulate constituents may change as well. Therefore, it is difficult to define particulate matter without a reference temperature. The current Method 5 particulate matter test defines particulate as a material that condenses at or above 248 F.

The EPA has designed Method 202 to prevent the formation of reaction materials from dissolved gases. The EPA believes that any remaining material collected and measured by Method 202 represents the material that would condense in the ambient air.

The method may collect some portion of the SO_2 as condensable. The dissolution of SO_2 in water does not lead immediately to the formation of sulfuric acid, but tends to lower the solution pH, which further inhibits sulfate or sulfuric acid formation. The method includes a purging procedure that effectively removes SO_2 before significant oxidation occurs.

Method 202 and M5'71 are virtually the same with respect to the condensable portion of the sampling train. Ultimately, the methods can be described as functionally equivalent when the nitrogen purge is applied to both methods.

(9) Farber, P.S., and Marmer, D.L. (2005). "Condensible Particulate Matter Emission Sources and Control in Coal-Fired Power Plants." Environmental Consulting Group, Sargent and Lundy LLC, 55 East Monroe Street, Chicago, Illinois 60603. Presented at Electric Power 2005, April 5-7.

Coal-fired power plants produce emissions that must be controlled for compliance with State and Federal regulations.

"… testing has shown that a portion of the SO_2 in the gas stream may convert to a "pseudoparticulate" in the impingers of the sampling train. Furthermore, the ammonia (NH_4) use to control NO_x in SCR and SNCR systems can also react in the impingers to form salts that are falsely measured as condensable particulate matter (CPM) in the impingers".

Organic CPM from coal boilers comes mainly from the incomplete combustion of the organic constituents in the coal. Inorganic CPM from coal fired boilers includes salts, acid mists, and trace metals. As an example, sulfur trioxide (SO_3) in the flue gas can react with water or ammonia to produce CLPM in the following reactions:

(Eq. 1) $SO_3\text{ (gas)} + H_2O\text{ (gas)} \rightarrow H_2SO_4\text{ (gas)} \rightarrow H_2SO_4\text{ (liquid)}$
(Eq. 2) $SO_3\text{ (gas)} + H_2O\text{ (gas)} \rightarrow 2NH_3\text{ (gas)} \rightarrow (NH_4)_2SO_4\text{ (solid)}$

There are a few reactions that take place in the impinger solutions that do not normally occur when the flue gas cools to ambient temperatures as it exits the stack into the atmosphere. Such reactions can form “pseudoparticulates” that are measured as CPM by Method 202 and as sulfuric acid by Method 8, but are not truly reflective of actual emissions. Sulfur dioxide in the flue gas, which would normally exit the stack unaffected, can undergo the following pseudoparticulate reaction in the impinger solutions:

(Eq. 3) SO_2 (gas) + H_2O (liquid) → SO_2 (dissolved gas) + time, O_2 → H_2SO_4 (liquid)

During a flue gas emissions test, a portion of the SO_2 in the flue gas dissolves in the impinger water. Throughout the test run, some of the dissolved SO_2 will oxidize to sulfate ions and sulfuric acid. Unlike the formation of SO_3 into sulfuric acid (equation 1), the formation of SO_2 into H_2SO_4 (equation 3) does not reflect what actually happens at the stack exit as the flue gas stream begins to cool.

Staff from the EPA’s Environmental Measurements Branch conducted simultaneous testing of Method 5/202 sampling trains at a coal-fired boiler (1.5 percent sulfur content) in order to determine the adequacy of the nitrogen purge under field conditions. The total CPM measured in the purge impingers averaged 4.7 mg, while the CPM measured in the unpurged impingers averaged 51.4 mg. The 10-fold difference between the two suggests that the 1-hour nitrogen purge is effective in removing a good portion of the dissolved SO_2. Comparison of the purged and unpurged trains also indicates that the nitrogen purge has little effect on organic condensibles, as the two measurements had a 95 percent confidence level. Based on these pair-trained tests, the EPA concluded that the 1-hour nitrogen purge was appropriate for Method 202.

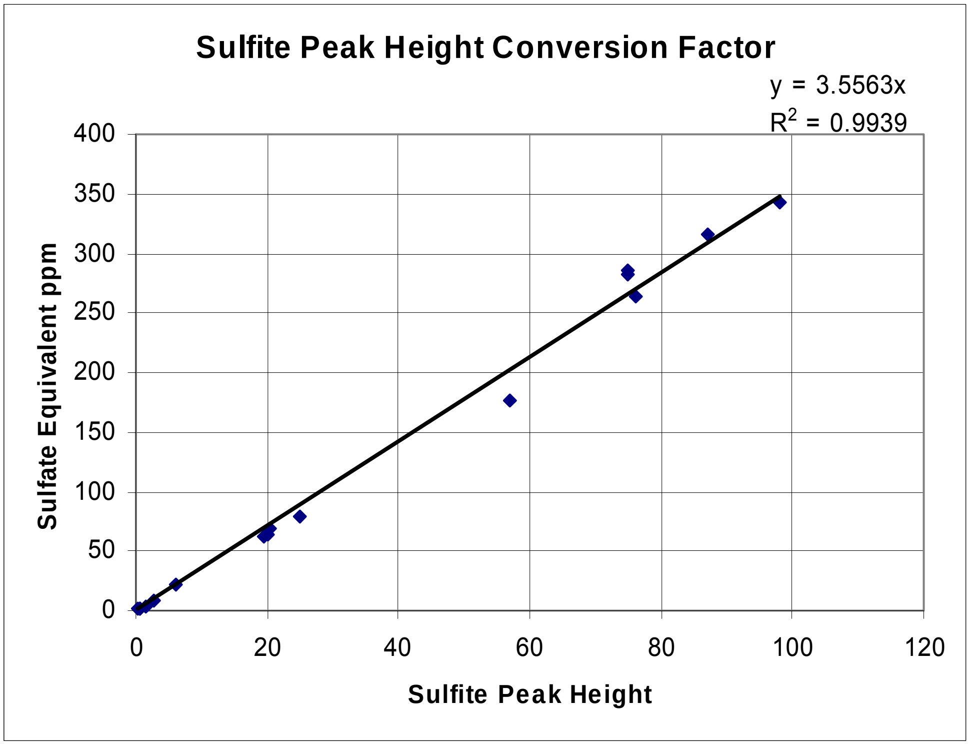
“Another potential pseudoparticulate reaction in the Method 202 impingers occurs when ammonia slip form an SCR or SNCR reacts with SO_2 and SO_3 to form ammonium sulfate and ammonium bisulfate… . Even with the small amounts of ammonia slip sound at modern coal-fired power plants (2 to 10 ppm), the production of ammonia salts can be significant. A nitrogen purge will have no effect in removing the ammonia salts”.

“The bulk of the CPM emissions appear to be related to SO_3”.

APPENDIX B:

SULFITE PEAK HEIGHT CALIBRATION CURVE

Appendix B: Sulfite Peak Height Calibration Curve



APPENDIX C:

CHROMATOGRAMS OF SULFATE/SULFITE ANALYSES

Appendix C: Chromatograms of Sulfate/Sulfite Analyses