September 27, 2006 e-mail from Ron Myers to:

Method 202 improvement stakeholders:

As I promised, here are some of the data with the IC and dry down results for everyone to start looking at. I've attached two spreadsheets in PDF format. One contains just the dry impinger sulfate data, the other contains the M-202 and the dry impinger sulfate results. These data are from the first set of test runs plus the two additional dry impinger mod runs.

Our contractor has finished and QC's the Ion Chromatography Data for Sulfate analysis on reconstituted samples. After taking them to dryness according to what we believe is the most commonly used options source testers use from M-202. While the initial IC analyses before dry down created what we thought was unusual high artifact when SO2 was higher, the dry down data changes our perspective a bit. Our observation is that the Dry Impinger Method shows less sulfate in the samples taken to dryness and reconstituted. These same samples were taken to dryness and weighted. The residual sulfate results are also more consistent between the 25 ppm and 150 ppm SO2 tests. Note that we found no sulfate in any of the blanks. The dry impinger modification sulfate results seem to settle at about 0.8 mg regardless of the SO2 concentration.

The Method 202 (wet impinger) tests are between 9 and 13 mg. If we base our conclusions on the post dry-down sulfate analysis, we're are exceeding our expectations for reducing the sulfate artifact of the CPM method with about a 91% reduction. That's the good news. We have seen additional nonsulfate residual mass numbers and we are determining the source of a potential contaminant that adds mass to our samples. The gravimetric weights from the first set of tests are biased by this high blank. We won't start the replicate analysis until we isolate the source of the blank contamination. That's the not-so-good news. We have confirmed that ERG is using Ultra High Purity nitrogen and doubly deionized ASTM type 1 water. Speaking with Jorge Marson I also confirmed he is using the same quality materials for his nitrogen and water reagent.

I am also attaching a document that Jorge Marson of Environment Canada prepared summarizing the work that he has done. I hope to forward everyone our final plan and QAPP soon. This will include those additional experiments that several of the stakeholders have recommended to add to the evaluation. At this time, I will request that those stakeholders that volunteer to perform some of these additional experiments to provide addendums to our plan so we have a more unified coordinated plan. I expect that stakeholders can use the core of EPA's plan and QAPP and only provide the necessary additions to the plan.

EPA Method 202
and
Modified Method 202
results

M202 (Wet) Preliminary Test Results

	Condensate Vol (mL)	Total Wash recovery Vol (mL)	Sulfate before Drying (Total ug)	Sulfate after Drying (Total ug)
Condition 1				
Run 1	27	397	6946	13050
Run 2	41	406	11568	17088
Run 3	44	391	9120	10349
Average	*38*	*398*	*9211*	*13496*
Condition 2				
Run 1	38	384	9878	9563
Run 2	31	376	8564	9454
Run 3	31	373	8407	10344
Average	*33*	*378*	*8949*	*9787*

M202 Dry Impinger Modification Preliminary Test Results

	Condensate Vol (mL)	Total Wash recovery Vol (mL)	Sulfate before Drying (Total ug)	Sulfate after Drying (Total ug)
Condition 1				
Run 1	31	112	1418	445
Run 2	41	168	1886	846
Run 3	47	150	2482	878
Average	*40*	*143*	*1928*	*723*
Condition 2				
Run 1	40.9	141.4	4496.52	930.412
Run 2	34.9	122.3	4733.01	1399.112
Run 3	35.1	97.9	3583.14	496.353
Run 4	37.8	255.8	1266.21	787.864
Run 5	36.3	219.7	3163.68	478.946
Average	*37*	*167*	*3449*	*819*
Blanks				
Reagent Blk	NA	500	ND	ND
Wet Method FB	NA	414.6	ND	ND
Dry Method FB	NA	113.2	ND	ND

Test Conditions	**Oxygen**	**Carbon Dioxide**	**NO**	**Sulfur Dioxide**
Condition 1	8%	12%	50 ppm	25 ppm
Condition 2	8%	12%	50 ppm	150 ppm

ND = Not Detected

Dry Impinger results

provided by

Jorge Marson

Environment Canada

PRELIMINARY RESULTS WITH "DRY IMPINGER" METHOD 202

1.0 Sampling

Fifteen (15) Method 202 laboratory runs were performed with conventional stack testing equipment. Ambient air was aspirated trough a 3" glass fiber filter and then humidified by bubbling through a water impinger housed within the oven of a Method 5 sampling train. This impinger was fitted with a 250 w heating tape which was powered from an adjustable rheostat. Moisture levels were varied by altering the oven temperature as well as the power to the heating tape.

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

The sampling train consisted of a water-cooled coil, a condensate reservoir ("dry impinger"), a strait stem impinger, and a silica gel impinger. All these components were kept at ice bath temperature, except the condensate reservoir which was external to the ice box.

The sampling train was linked to the corresponding control module and operated at a rate of approximately 0.6 scfm. Approximately 94% of the moisture gain was collected in the "dry impinger", 1% in the second impinger and the balance in the silica gel impinger.

2.0 Nitrogen purging

At the completion of each run, the condensate was transferred to a Greenburg-Smith impinger and it was purged at room temperature with a total of 1.2 Sm^3 of nitrogen (Praxair, ultra high purity) over 1 hour. Black CPM residue was observed on some preliminary runs, so a 47 mm glass fiber filter was installed in the low pressure nitrogen line and in the SO_2 mixture line. Black CPM residue was not encountered on subsequent test runs.

3.0 Evaporation and Weighing of Inorganic CPM

Method 202 requires the evaporation of considerable amounts of water and the gravimetric determination of the evaporation residue. Even in the case of the proposed "dry impingers" version of Method 202, it is necessary to evaporate approximately 200 ml for a 1hr test run on a 20% moisture source. The samples are placed in glass containers and dried in an oven set at 105 deg. C.

The determination of residue may follow two main alternatives:

a) Direct residue determination in the same glass container where evaporation was carried out
b) Drying in large glass containers followed by wet transfer to a weighing pan and a second drying step

Alternative a) is simple from the point of view of residue manipulation, but it is quite demanding regarding the precision weighing of bulky glass containers. In our investigation, the evaporation/drying jars were pre-cleaned 120 ml and 250 ml clear wide mouth jars (EP Scientific Products) which weighed approximately 114 g and 204 g, respectively. The jars had a glass volume of 44 ml and 78 ml, assuming 2.6 g/l glass density. The scale had 210 g capacity, 0.0001 g readability and 2.5ppm/^{o}C sensitivity drift (Mettler-Toledo AL204).

Taring of the empty glass containers is required two or more days prior to the weighing of the evaporation residues. Weighing room pressure and temperature may not be exactly the same. The effect of common environmental differences on the apparent weight of the 250 ml jars was estimated as follows:

Effect of 1 kPa lab pressure change:

1 kPa/101.3 kPa*0.0012 g/ml *78 ml = 0.9 mg, due to air buoyancy

Effect of 1 ^{o}C lab temperature change:

1^{o}C*2.5ppm per ^{o}C/1,000,000 *204 g = 0.6 mg, due to scale thermal sensitivity drift

Several weighing experiments were carried out to confirm the shortcomings of conventional “weight-before-and-after” approach for the determination of inorganic CPM in glass jars.

Four (4) sets of 24 jars each were weighed in a given order 6 times over a 4 day period. The average weight of each jar had a standard deviation of 0.5 mg. However, the average weight differences of consecutive jars had a standard deviation of 0.2 mg. This appears due to the fact that the environmental conditions during the weighing of consecutive jars were more consistent than the conditions from weighing the same jar on different days.

It was also observed that the 0.5 mg consistency criterion for acceptance of consecutive weightings was often exceeded, even though the weight was stable with respect to the preceding glass jar. This criterion may be suitable for filters but it is inadequate for bulky glass jars.

Based on these observations, an alternate weighing scheme was adopted for the condensable particulate matter (CPM) samples. Prior to running Method 202 experiments a set of weighing jars were tared by multiple weightings >=6 hours apart, which were < 0.5 mg from each other. Each time the jars were weighted in the same order. Every other jar in the set was used to contain and evaporate the samples. The remaining jars stayed empty and served as reference for the jar that in the set was weighted immediately before or after. In this manner the above mentioned effects were compensated for, at least in what is associated to the bulky weighing containers.

The average standard deviation resulting from weighing multiple inorganic CPM samples in this manner was estimated to be 0.2 mg.

The multiple weighing experiment was also performed on aluminum weighing pans, using the same equipment.

The effect of common environmental differences on the apparent weight of the weighing pans was estimated as follows:

Effect of 1 kPa lab pressure change
1 kPa/101.3 kPa*0.0012 g/ml *0.44 ml = 0.005 mg, due to air buoyancy

Effect of 1 ^{o}C lab temperature change
1^{o}C*2.5ppm per ^{o}C/1,000,000 *1.2 g = 0.003 mg, due to scale thermal sensitivity drift

The effects are much lower than the readability of the scale used (0.1 mg). In this respect, weighing alternative b) appears to be more favorable than alternative a). It remains to be determined, however, that: 1) the CPM can be transferred quantitatively from the drying jars, and 2) that no artifact results from the interaction of the transferred liquid with the aluminum foil.

The residues of 15 Method 202 laboratory runs were transferred into 1.2 g aluminum pans by 3 successive rinses, each with 2 ml DI water. In some runs (1 to 10), the condensate was evenly split into 2 jars, therefore the total water volume loaded into the weighing pans was approximately 12 ml. The tared weighing pans were dried overnight. Tare and final weighing was the average of 3 consecutive determinations >=6 hours apart, which were < 0.5 mg from each other.

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

The results from 15 Method 202 laboratory runs (inorganic CPM determinations) are summarized in Table 1.

Table 1
Results Summary

Test run No.	1	2	3	4	5	**Avg.**	Std. dev.	Notes
CPM, mg/Dm3	2.8	1.0	1.0	1.1	2.5	**1.7**	0.9	pan weighing
CPM, mg/Dm3	4.1	1.5	1.4	1.4	2.0	**2.1**	1.2	jar weighing
Moisture, %	12.7%	11.1%	11.2%	11.3%	11.2%	**11.5%**	0.7%	
SO2, ppmd	253	252	255	258	258	**255**	2.9	
Test run No.	6	7	8	9	10			
CPM, mg/Dm3	1.9	0.9	1.0	0.8	0.8	**1.1**	0.4	pan weighing
CPM, mg/Dm3	3.1	0.5	1.3	1.5	1.0	**1.5**	1.0	jar weighing
Moisture, %	12.3%	11.8%	11.7%	11.6%	10.8%	**11.7%**	0.5%	
SO2, ppmd	25	25	25	25	25	**25**	0.2	
Test run No.	11	12	13	14	15			
CPM, mg/Dm3	2.4	0.9	0.7	0.9	2.0	**1.1**	0.7	pan weighing
Moisture, %	20.8%	19.7%	19.5%	19.8%	21.0%	**11.7%**	0.7%	
SO2, ppmd	123	121	121	121	122	**121**	1.1	

5.0 Sample Storage

In this scouting test program the liquid samples were dried a few hours after the test runs. It is acknowledged that sulfites remaining in the condensate after the nitrogen purge may oxidize during longer storage and hence produce additional inorganic CPM. To investigate this potential contribution to inorganic CPM formation, the condensate from test runs 1 to 10 was split in two halves, one of which was spiked with 3 drops of 30% H_2O_2 (approximately 0.15 ml). The peroxide spike would oxidize instantaneously any residual sulfite. Subsequent evaporation and jar weighing determined that the spiked jars contained on average 0.4 mg higher CPM than the unspiked jars. This rather modest increase provides an upper bound indication of potential CPM formation upon extended sample storage.

6.0 Observations and Comments

- The inorganic CPM artifact caused by SO2 may be reduced to approximately 2 mg or less by the proposed “dry impinger” version of Method 202.
- A ten fold increase in SO_2 level caused only a modest increase in inorganic CPM artifact.
- Nitrogen gas volume is similar to the sample volume, and should be filtered to the same extent.
- The drying and weighing of condensate on the same glass jars requires special consideration to the effects of changes in atmospheric pressure and weighing room temperature
- The quantitative transfer of redissolved condensate to weighing pans should be described in the method
- Nitrogen purge at ambient temperature is likely to be more effective than the prescribed purge at ice bath temperature