Appendix B

NCASI, 2014. NCASI Best Practices for EPA Methods 201A and 202. Prepared by NCASI. August 29, 2014.

August 29, 2014

Electronic Submission

Re: NCASI Participation in EPA's Method 202 Best Practices Stakeholder Group

Ray Merrill Ph. D.
EPA/OAQPS/AQAD/MTG
109 T.W. Alexander Drive
Research Triangle Park, NC 27709

Dear Ray:

NCASI is pleased to be a participant in the Method 202 Best Practices Stakeholder Group. Our organization looks forward to a mutually beneficial collaboration that leads to the development of testing protocols that provide accurate estimates of PM emissions. In this spirit of collaboration, please find attached to this communication a draft of best practices that NCASI has developed and adopted with respect to EPA Methods 201A and 202.

NCASI's intent is to carry out additional train blank studies once a consensus has been arrived at with regard to what constitutes reasonable best practices for PM sampling. Let me know if you require clarification of any subjects broached within this document.

Sincerely,

Lee W. Carlson
Senior Research Associate

cc: Ron Myers, EPA/OAQPS/SPPD/MPG (D243-05)

## NCASI BEST PRACTICES FOR EPA METHODS 201A AND 202

The following protocols for EPA Methods 201A and 202 are in addition to the quality assurance procedures outlined in Methods 201A and 202, and are the result of lessons learned in carrying out

multiple studies. Following these additional quality assurance procedures will reduce the detected mass in train blank samples and provide more accurate primary $PM_{2.5}$ determinations with lower sample mass bias due to incomplete decontamination of laboratory glassware and sampling train components, reagent residue, sample storage container residue, and extraneous material introduction into particulate matter samples.

**1.0**

**MINIMIZING TRAIN BLANK BIAS IN METHOD 202**

Minimizing train blank bias is a matter of being cognizant about possible sources of contamination (decontamination of laboratory glassware, sampling train components, sample storage containers, sample retrieval equipment, etc.) and mitigating them. The sampling and sample retrieval environments, reagents used, and inadvertent contact with other objects during sample retrieval also play a part in minimizing train blank bias.

1. All laboratory glassware and Method 202 sampling train components that come into contact with the CPM sample should be cleaned per the protocols set forth in Section 8.4 of Method 202, including baking glassware at 300°C for six hours.
2. All liquid sample storage containers should be constructed of glass with Teflon lined lids. *Plastic sample containers should be avoided as leaching of plasticizers from the container may impart a positive bias in CPM sample mass determinations.*
3. All liquid sample storage containers should be pre-cleaned per the protocols used for the sampling train components and laboratory glassware. *Certified pre-cleaned sample bottles are certified for pesticide analysis, and are not certified with respect to inorganic residue.*
4. Acetone and hexane reagents should be stored in glass containers, and certified for a residue content of 1 ppm or less.
5. All reagent rinse bottles should be constructed of PTFE (Teflon®).
6. All reagent rinse bottles should be triple rinsed with the reagent they are to be dispensing prior to use.
7. Reagent rinse bottles should be filled just prior to use. Any reagent left in the rinse bottles for an extended length of time should be discarded and the bottle triple rinsed prior to reuse.
8. Only laboratory cleaned glassware should be used for each Method 202 run. No glassware should be reused in the field.
9. Every effort should be made to locate the sample retrieval area in a clean environment with minimal suspended particulate matter in the air column. *Exceedingly dusty environments will contribute extraneous material to the CPM samples. Excess ingress and egress of the sample retrieval area can also increase suspended particulate matter, contributing to extraneous material in the CPM samples.*
10. Wrapping Teflon tape around the impinger base/impinger stem joint will prevent extraneous material being deposited in the joint and being inadvertently rinsed into the sample.
11. Before recovering samples from the sampling train, clean nitrile gloves should be worn and the exterior of all components should be wiped down to remove any material deposited on the surfaces of these components. Gloves worn during decontamination of the exterior surfaces of sampling train components should be discarded after the decontamination process is completed. *Gloves should be worn to prevent any oils from the skin being deposited on the sampling train components which could be inadvertently incorporated in the CPM samples due to sloppy technique.*
12. Clean nitrile gloves should be worn just prior to collection of samples and after the exterior surfaces of the sampling train components have been decontaminated. *Nitrile gloves should be*

*used instead of latex gloves. Latex gloves are soluble in acetone and sloppy technique can result in latex being rinsed into the CPM samples. Nitrile gloves are less soluble in acetone than latex gloves.*

13. Gloved hands should be rinsed with de-ionized water just prior to collecting samples. *Residues from some gloves can form a soapy film on the surface of the glove when wetted. This residue is easily removed with rinsing.*
14. The person collecting the CPM samples must maintain awareness of the items being handled with gloved hands in order to prevent transfer of extraneous material from surrounding surfaces to the CPM samples.
15. If a rinse of the probe liner is to be included as part of the CPM sample (i.e., when Method 201A or Method 17 is used for the front-half of the sample train), this can be accomplished by sealing the inlet of the probe with an airtight fitting, introducing the rinsing reagent into the outlet of the probe, sealing the outlet of the probe with an airtight fitting, and agitating the probe by alternately rotating the probe inlet up to inlet down. The probe should be rotated a minimum of three times for each rinse. At the conclusion of each agitation cycle, the air tight fitting on the outlet of the probe can be removed and the rinsing reagent recovered into the sample storage container with the aid of a funnel.

## 3.0 COLLECTION OF THE MODIFIED FIELD TRAIN BLANK DATA

In order to accurately account for all sources of random and systematic errors in the performance of a method, the train blank collection procedure must include all operations related to obtaining the samples. This includes the operations of: 1) Decontamination of laboratory glassware, sampling equipment, sample retrieval equipment, and sample storage containers. 2) The transportation of sampling equipment to the field, assembly of the sampling equipment on the sample platform, performance of all operations associated with collection of the sample from the source, with the exception of actually collecting a sample, transport of sampling equipment to the sample recovery area, retrieval of the samples from the sampling equipment, transport of the samples to the laboratory, and analysis of the samples. The following protocols seek to capture all sources of random and systematic error when implementing EPA Methods 201A and 202.

1. A field train blank for each particulate matter method employed should be collected and processed as follows:
    a. Transport clean sampling train components to the sampling platform and assemble the sampling train.
    b. Perform a leak-check of the sampling train.
    c. Leave the sampling train on the sampling platform exposed to the sampling environment for the same amount of time expected to be required for an actual test run. (For example, collecting 3 dry-standard cubic meters using EPA Method 201A is expected to take approximately six (6) hours.)
    d. After the exposure time is complete, perform a second leak-check of the sampling train, disassemble, seal, and transport the sampling train components to the sample recovery area.
    e. Recover the samples from the sampling train as would be done for an actual test run.
    f. For EPA Method 202, charge the dropout with an amount of distilled/de-ionized water sufficient to submerge the purging stem at least one (1) centimeter below the surface of the water, and purge the water with filtered ultra high purity nitrogen prior to sample recovery, per the instructions in Section 8.5.3 of EPA Method 202.
    g. Process the samples collected from the blank train in the same manner as would be done with samples from an actual test run.

2. At least two reagent field blank samples should be collected for each reagent type (filters [front-half and CPM filters], acetone, hexane, water). Liquid reagent blank sample volumes should be a minimum of 500 ml. Liquid reagent field blanks are collected by filling a wash bottle with the reagent and transferring the reagent to the sample bottle. A small portion of the reagent should be transferred to the sample bottle by dispensing of the reagent through the spout of the wash bottle. *The 500 ml minimum reagent field blank volume improves the accuracy of the reagent residue determination. Method 202 suggests a reagent field blank volume of 200 ml. However, proving that your reagents meet the required residue concentration content of 1 ppm with a reagent field blank sample of 200 mL requires the ability to* ***accurately*** *measure a sample mass of 0.2 mg. This is beyond the capabilities of most laboratories as the gravimetric detection limit for most laboratories is frequently close to 0.2 mg or above when using a 5-place balance.*
    a. Filter blanks should be collected by loading the filter holder with a blank filter and subsequently collecting the filter into its transportation container.

## 4.0 LABORATORY PROTOCOLS

Emission estimate accuracy is dependent not only on proper implementation of field procedures, but also on analysis procedures. Most laboratories report raw gravimetric data for PM sample results. This introduces error into the mass determinations. The amount of error in gravimetric determinations for liquid samples is a function of the tare weight of the sample container, the amount of atmospheric buoyancy experienced by the sample container, extraneous material introduced into the samples during the analysis, and the potential for the sample container material to interact with the liquid sample and the atmosphere.

High tare weights for sample containers result in higher gravimetric detection limits than for sample containers with low tare weights. For example, containers with tare weights of a few grams, such as Teflon® beaker liners, would have a gravimetric detection limit of approximately 0.1 mg, while a 50 ml glass beaker with a tare weight of around 30 grams would have a gravimetric detection limit of approximately 0.2 mg. Many laboratories use 250 ml glass beakers with approximate tare weights of 130 grams to process liquid samples. Gravimetric detection limits for 250 mL glass beakers can approach 0.5 mg, depending on the capabilities of the laboratory.

Atmospheric buoyancy can also affect gravimetric determinations and is a function of the volume of air displaced by the sample container and sample, and the air density at the time of the gravimetric determination. For PM sampling, the volume of the particulate matter being weighed is a tiny fraction of the volume of air being displaced by the container and the sample, and can be ignored. When using 50 ml glass beakers for processing liquid samples, a maximum buoyancy correction of approximately 1.7 mg could be required if the air density were to change from the minimum to the maximum likely values or vice versa. By contrast, the maximum buoyancy correction for Teflon® beaker liners would be approximately 0.2 mg, with buoyancy corrections of a few hundredths of a milligram being typical under relatively stable atmospheric conditions.

Introduction of extraneous material into PM samples biases gravimetric determinations high. Those samples that require the most manipulation and/or exposure time to the laboratory atmosphere have the highest potential for extraneous material contamination. For Method 202, the inorganic water samples experience both the most manipulation and the longest exposure time to the laboratory atmosphere. One strategy to account and correct for extraneous material contamination is to use multiple blank sample containers that follow samples through the entire analysis process. A minimum of two blank sample containers follow each group of similar samples, with the sample masses being corrected by the average blank sample container weight change.

Interaction of the sample container material with the sample and the atmosphere can also significantly affect the sample mass determination. Aluminum pans will oxidize in the presence of moisture and oxygen from the atmosphere. This oxidation process incorporates oxygen from the atmosphere into the sample container substrate and causes a positive bias in sample mass determinations. Drying of acetone or hexane in aluminum pans is also subject to potential oxidation of the aluminum. This is due to the fact that as acetone and hexane evaporate they cool the sample container, which in turn can accumulate moisture on the surface due to condensation. Therefore, aluminum pans should not be used to process liquid samples of any type. The following protocols are designed to increase the accuracy of gravimetric determinations, provide a means of correcting for extraneous material contamination, and eliminate bias in gravimetric determinations due to sample container reactivity.

1. ***Under no circumstances are aluminum pans to be used to process liquid samples***. Oxidation reactions occurring on the surface of aluminum pans during sample recovery and drying will bias sample masses high. Either Teflon® beaker liners or glass beakers should be used, with Teflon® beaker liners being preferred. High volume liquid samples may be reduced in volume in large glass beakers, and samples transferred to tare weighted 50 mL glass beakers or Teflon beaker liners for final mass determinations. Reduction of aqueous sample volume should be done in an oven, rather than on a hot plate. *Heating of liquid samples on a hot plate results in deposition of PM residue on the sides of the container, and potential loss of sample if transferring to a smaller container. This deposition of material on the sides of the container is due to the temperature differential between the bottom of the container and the sides.*
2. All sampling train and laboratory glassware that come into contact with CPM samples must be cleaned as specified in Section 8.4 of EPA Method 202, including baking glassware at 300º C for six hours.
3. At least two blank sample containers (beakers, Teflon baggies, etc.) should follow each group of samples (front-half rinses, CPM water samples, CPM solvent samples) throughout the analysis process. These blank sample containers serve as indicators of any potential contamination or bias introduced during the analysis process.
4. If glass beakers are used to process liquid samples, sample masses should be corrected for buoyancy effects (Reference ASTM Standard D 6552-00). Buoyancy corrections can be ignored if Teflon beaker liners are used, and the maximum calculated buoyancy correction is less than 0.03 mg. *Buoyancy corrections can be calculated from barometric pressure, relative humidity, and ambient temperature data recorded for each mass determination, or blank sample containers (buoyancy correction blanks) can be interspersed with the sample containers, and the sample masses corrected by subtracting the mass difference of the buoyancy correction blanks from the raw sample mass determinations.* These buoyancy correction blanks are separate and distinct from the blank sample containers that follow the samples throughout the analytical process. The buoyancy correction blanks remain in the desiccator after their tare weights have been determined. *A minimum of two buoyancy correction blanks should be used for every five (5) samples (with blank sample containers considered as samples). One buoyancy correction blank should be weighed prior to every five samples, and another buoyancy correction blank weighed after the five sample containers.* Containers should be weighed in the same order for each weight determination. This applies to both tare and final weights.

**Density of Air**

$\rho_{air} = (0.348444 \times P_{air} - [(0.00252 \times t_{air} - 0.020582) \times \%R.H.])/(273.15 + t_{air})$

$\rho_{air}$ = density of air in $Kg/m^3$

$P_{air}$ = absolute pressure of air in milli-bars

$t_{air}$ = temperature of air in degrees Celsius

%R.H. = relative humidity in percent

**Mass Buoyancy Correction**

| | |
|---|---|
| $m_{corrected}$ = mass corrected for buoyancy | $m_{corrected} = R \times \frac{\left(1 - \frac{\rho_{air}}{\rho_W}\right)}{\left(1 - \frac{\rho_{air}}{\rho_S}\right)}$ |
| R = balance reading | |
| $\rho_{air}$ = current air density | |
| $\rho_W$ = density of calibration weight | |
| $\rho_S$ = density of sample substrate | |

1. It is recommended that a balance with a resolution of 0.00001 grams (0.01 mg) be used for the gravimetric analysis. The extra resolution is necessary to get accurate results for reagent blanks, sample container blanks, and buoyancy correction blanks.
2. Weighing room temperature should be maintained in the range of 68ºF ± 10º, and relative humidity should be maintained in the range of 35 to 50 percent. Wide swings in temperature and humidity should be avoided to prevent calibration errors with the balance.
3. Balance performance should be checked against NIST traceable weigh standards and results logged in a permanent record.
4. Balances exhibiting a weighing error in excess of 0.05 percent should not be used for gravimetric analysis of PM samples.
5. An anti-static device should be employed to ensure that static charges on the samples and sample processing containers do not adversely affect the gravimetric analysis.
6. The two CPM filter blanks collected in the field should be extracted in the same manner as CPM samples from an actual sample run, per Section 11.2.1 of EPA Method 202. Water and hexane extracts from the CPM filter blanks should be analyzed separately for extract residues.
7. CPM filters should be processed as follows:
    a. CPM filters should be placed in a pre-cleaned Petri dish bottom of sufficient volume to easily contain 10 to 15 mL of extraction reagent. The Petri dish bottom should be large enough to accommodate the CPM filter without folding of the filter. Filters should be handled with clean plastic forceps. *Method 202 instructs the analyst to fold the CPM filter into quarters and place same in an extraction tube. However, preliminary NCASI study data indicate that unnecessary manipulation of the filter can result in either loss of sample due to material being retained in the folds of the filter or introduction of CPM filter material into the sample because of disruption of the filter substrate. This procedure minimizes the manipulation of the filter and reduces the possibility of either sample loss or extraneous material introduction.*
    b. Introduce enough extraction reagent into the Petri dish bottom to cover the filter.
    c. Place Petri dish bottom in a bath type sonicator and sonicate for a minimum of two minutes per Section 11.2.1 of Method 202.
    d. Pour extract into an appropriate sample container.
    e. Complete three extractions with water followed by three extractions with hexane.

## 4.1 Data Analysis

1. Gravimetric data should be corrected for buoyancy effects (if applicable) and sample container blank corrected.
    a. The buoyancy adjustment to the raw sample masses involves either correcting the sample mass based on barometric pressure, relative humidity, and temperature, or by subtracting the average mass difference for the two buoyancy correction blanks that bracket a given set of samples from the raw sample mass determinations.
    b. The final correction to the sample masses is to subtract the average *buoyancy corrected* blank sample container masses from the *buoyancy corrected* sample masses.

**Example Buoyancy and Container Blank Corrections**

| Run ID | Description | Raw Weight (mg) | Buoyancy Corrected Weight (mg) | Container Blank Corrected Weight (mg) |
|---|---|---|---|---|
| PB4R1 | CPM Organic Run 1 | 0.60 | 0.73 | 0.63 |
| PB4R2 | CPM Organic Run 2 | 0.72 | 0.85 | 0.75 |
| PB4R3 | CPM Organic Run3 | 0.68 | 0.81 | 0.71 |
| CB 1 | Container Blank 1 | -0.10 | 0.03 | |
| CB 2 | Container Blank 2 | 0.04 | 0.17 | |

2. The residue content for liquid reagent field blanks should be reported in parts per million (ppm) on a mass basis.
3. The extract residues for the CPM filter blanks should be reported in milligrams for both water and hexane extracts.
4. Field Train Blank gravimetric data should be reported in milligrams for each sample collected from the blank sampling train.
    a. Method 5 (probe rinse, filter)
    b. Method 201A (Cyclone I rinse, Cyclone IV rinse, Cyclone IV exit/Filter Holder front-half, filter)
    c. Method 202 (Organic, Inorganic)
5. For PSD determinations and NSR permitting, Method 202 CPM emission estimates should be reported with a full train blank correction applied to the gravimetric data, up to a maximum of 5.1 mg per the EPA interim guidance document published April 8, 2014.