

# CHESTER LabNet

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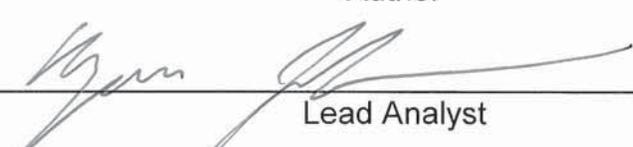
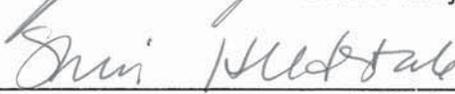
## Standard Operating Procedure ME-008.03

Subsectioning of Exposed 8x10" Quartz or Glass Fiber Filters  
Chester LabNet Proprietary Method

Modified 40CFR50 Appendix G

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### Approvals:

 _____ Author	<u>3.18.14</u> _____ Date
 _____ Lead Analyst	<u>3.13.14</u> _____ Date
 _____ QA/QC	<u>3.18.14</u> _____ Date

Effective from: 3.18.14  
Effective until: present



## Subsectioning of Exposed 8x10" Quartz or Glass Fiber Filters Chester LabNet Proprietary Method

### Modified 40CFR50 Appendix G

#### 1.0 Introduction

1.1 Test Method Reference ID: Chester LabNet proprietary method, modified 40CFR50 Appendix G.

1.2 Applicability: This method applies to the subsectioning of 8x10" Quartz or Glass Fiber filters. Note that other matrices of 8"x10" filters may present problems in subsectioning due to the physical properties of the matrices. Quartz coated Teflon weave filters do not cut well due to the fibrous nature of the Teflon weave. Carbon impregnated cellulose filters are very dense and do not cut easily or cleanly, with a punch or with a blade such as an X-acto knife.

1.3 Detection Limit: N/A

1.4 Method Performance: N/A

#### 2.0 Summary

2.1 Scope and Application: The intended use of this method is for the subsectioning of exposed 8x10" Quartz or Glass Fiber filters for subsequent chemical analysis.

2.2 Summary of Method: Filters are placed in the laminar flow hood. Representative sections of sample deposit are removed from the filters using a circular, stainless steel punch. The number of punches taken per sample depends upon the detection limits required for the subsequent chemical analysis. This procedure describes the taking of four punches per sample. Fewer punches may be taken following the procedure below.

Generally, for ICP or GFAA analysis, 4 punches are taken. For IC, XRF or OC/EC analysis, 1 punch is taken. For CVAA, 1 or 2 punches are taken depending on required detection limit. The majority of subsectioning is performed for subsequent digestion and analysis by ICP.

There is no detection limit associate with this method. Detection Limits are dependent upon the analytical technique employed during chemical analysis.

Specificity is determined visually by inspecting the filter deposit. Filter deposit that appears to have transferred on or off of the filter or has miscellaneous debris such as insects or water spots is avoided during subsectioning.

2.3 Interferences: While not technically an interferent, homogenous subsectioning may be hampered by irregular or loose deposits on the filter, improper loading of the filter in the filter holder during sampling, or by improper storage of the filter such that the deposit is physically transferred to the container in which the filter was stored/shipped or to non-deposit areas of the filter. See Appendix B.

2.4 Sample collection/preservation/shipment/storage: Collection, field preservation and shipment of samples is performed by the client. Chester LabNet has no control over the actions of the client in the field. Upon receipt, store samples at room temperature, or as required by the client and/or contract.

### **3.0 Safety**

3.1 Follow the Chester LabNet Chemical Hygiene plan. Always treat samples of unknown origin and/or constitution as hazardous.

3.2 This method presents no safety risk beyond typical laboratory safety hazards.

3.3 No carcinogenic reagents are used in this method.

### **4.0 Pollution Prevention and Waste Management**

4.1 The smallest quantity of chemical feasible is removed from its primary container for use.

4.2 Chemicals are used in amounts needed by the method.

4.3 Chester LabNet is a conditionally exempt small quantity generator and as such does not require formal chemical waste processing. Filters are generally not considered hazardous

and are disposed of in the normal solid waste containers.

5.0 Apparati, Equipment and Supplies

- 5.1 Laminar flow hood
- 5.2 Stainless Steel Forceps
- 5.3 Kimwipes
- 5.4 16.6 cm<sup>2</sup> circular, stainless steel punch
- 5.5 Lexan or other white hard plastic cutting board
- 5.6 1" nylon bristled paint brush

6.0 Reagents and Standards

- 6.1 Reagent grade 95% ethanol

7.0 Preparation, Calibration and Standardization

7.1 Prior to performing any punching, clean all areas of the laminar flow hood using ethanol and Kimwipes:

- 7.1.1 Wipe down the entire countertop area in the laminar hood.
- 7.1.2 Wipe off the lexan cutting board
- 7.1.3 Carefully wipe off the cutting edge, inside and outside of the punch
- 7.1.4 Clean the forceps and the bristles of the paint brush

7.2 Where possible, obtain a blank filter of the same lot as the sample filters for use in the method blank and LCS. This may not be possible if the client has provided their own filters and has not sent the laboratory any blank filters.

8.0 Procedure

8.1 Take four punches for the Method Blank and LCS as follows:

*Metals an appropriate # of*

*8.1 Punching of filters may be performed for several different analyses. The typical # of punches is as follows:*

*as follows:*

- ⊙ Metals by ICP: 4*
- " " XRF: 1*
- Anions/Cations by IC: 1*
- OC/EC: 1*
- Mercury by CVAA: 1*

8.1.1 Lay a blank filter flat on the cutting board. Do not fold the filter

8.1.2 Method blank: <sup>Take an appropriate number of punches equivalent to that used for the samples</sup> Punch a series of four filters in a line down the 8" side of the filter.

8.1.3 LCS: <sup>Take # punches etc. SM 3.17-16</sup> Punch a series of four filters in a line immediately next to the punches taken for the Method Blank.

8.1.4 Place the punches in a clean container (digestion vessel, petri dish, petri slide).

8.1.5 Remove the parts of the filter between the holes where the punches were taken and place the blank filter back into its container.

8.1.6 Use the paint brush to brush any filter fibers off of the cutting board.

<sup>an appropriate # SM 3.17-16</sup>  
8.2 Take four punches of each sample as follows:

8.2.1 Remove the folded filter from its container and place on the cutting board.

8.2.2 Unfold the filter and examine the deposit area for uniformity and miscellaneous imperfections (e.g. insects, tears, wrinkles, water spots etc). Attempt to avoid imperfections where possible.

8.2.3 Note the deposit margins to ensure that no punches are taken in any location where the deposit has been compromised (see Appendix B).

8.2.4 Refold the filter.

8.2.5 Perform a single punching action through both layers of the filter, approximately 0.5 cm from outer edge of the deposit area, and approximately 0.5 cm from either the top or the bottom of the deposit edge.

8.2.6 <sup>if 4 punches are needed, SM 3.17-16</sup> Perform a <sup>second</sup> single punching action through both layers of the filter, approximately 0.5 cm from fold line of the filter, and approximately 0.5 cm from either the top or the bottom of the deposit edge, whichever was not used in section 8.2.5.

8.2.7 Place the <sup>SH 3-17-16</sup> four punches in a labeled container (digestion vessel, Petri slide, Petri dish).

X SH 2-15-15

→ Return the 8x10 filter to its original container (folder, bag etc) <sup>SH 2-15-15</sup>

8.2.8 After punching each filter, use the paint brush to brush any filter fibers off of the cutting board.

8.2.9 Duplicates and Spikes:

X SH 2-15-15

8.2.9.1 Due to the limited amount of filter available, duplicate and spike subsections must be taken from separate filters.

may need to SH 3-17-16

8.2.9.2 One filter will have a duplicate subsection taken, while a different filter will have a spike subsection taken. Duplicate and spike subsections are punched as above.

8.2.9.3 Ensure that punching of duplicate or spike filters is performed such that enough available deposit remains to obtain a third set of ~~X~~ <sup>SH 3-17-16</sup> punches should redigestion be necessary.

8.3 For certain clients, a different punching scheme is required by contract. RMA is one such client. The following details the punching scheme for RMA filters (refer to diagram 1).

8.3.1 Place the filter on the cutting board and unfold it.

8.3.2 Prior to punching, examine the deposit area for uniformity and miscellaneous debris (e.g. insects, tears, water spots etc). Note any debris or non-uniformity of deposit area on the digestion log, however, at the requirement of RMA, do not attempt to avoid any such variations or debris.

8.3.3 A single punching action is performed through the filter for each of the four individual punches needed (see diagram 1).

8.3.3.1 Take the first punch at the top left most corner of the deposit area, no closer than ¼ inch away from the deposit edge (black circle 1).

- 8.3.3.2 Take the second punch at the top left side of the folding crease (black circle 2), again no closer than  $\frac{1}{4}$  inch away from the deposit edge.
  - 8.3.3.3 Take the third punch halfway down the filter, on the right side of the crease (black circle 3), no closer than  $\frac{1}{4}$  inch away from the crease.
  - 8.3.3.4 Take the fourth punch in the lower right hand corner of the deposit area (black circle 4), no closer than  $\frac{1}{4}$  inch away from the deposit edge.
  - 8.3.4 Place the four punches in a labeled container (Petri slide, Petri dish, or clean digestion flask).
  - 8.3.5 Due to the limited amount of filter available, duplicate and spike subsections must be taken from separate filters. One filter will have a duplicate aliquot taken, while a different filter will have a spike subsection taken.
  - 8.3.6 Duplicate and spike aliquots are punched in mirror image to the punching scheme for the sample aliquots, and correspond to the gray circles in Diagram 1 below.
  - 8.3.7 The remainder of the filter can be used for redigestion if necessary (white circles in Diagram 1 below)
- 8.4 In all cases, purposeful care shall be taken to avoid taking any punch that lies on the crease of the filter, or near the deposit edge.

## 9.0 QA/QC

- 9.1 Method Blank: where possible, punch an equal number of punches from the same lot number of filter as done for the samples.
- 9.2 LCS: where possible, punch an equal number of punches from the same lot number of filter as done for the samples.

9.3 Field Blank: treat this filter as a sample. If the filter arrives flat (not folded), fold the filter prior to punching.

## **10.0 Calculations**

10.1 Refer to analytical SOPs for area conversion calculations.

## **11.0 References**

11.1 40 CFR 50, Appendix G. Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air. July 3, 2013.

## **12.0 Definitions**

12.1 Analyst: the designated individual who performs the "hands-on" method and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.

12.2 Analysts' Notes: non-essential aspects of a method, which may help the analyst during some phase of the method. Notes may include, but not be limited to, historical aspects of the method, "tricks" of the method, unexpected issues to be aware of, or other facts or opinions related to the method, but not directly part of the procedure.

12.3 Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

12.3.1 Preparation Batch: a group of one to 20 samples of the same matrix which are prepared together as a group, and which share common QC samples.

12.4 Blank: a clean aliquot of the same matrix as the digested samples. A blank is subjected to the usual analytical and measurement processes.

12.4.1 Method Blank: an unspiked clean sampling media aliquot, taken through the entire preparation and analytical processes associated with a method. This blank determines if the sampling media may be contributing any analyte of interest in the samples.

12.4.2 Field Blank: a blank prepared by the client in the field. This blank is treated as a sample by the laboratory.

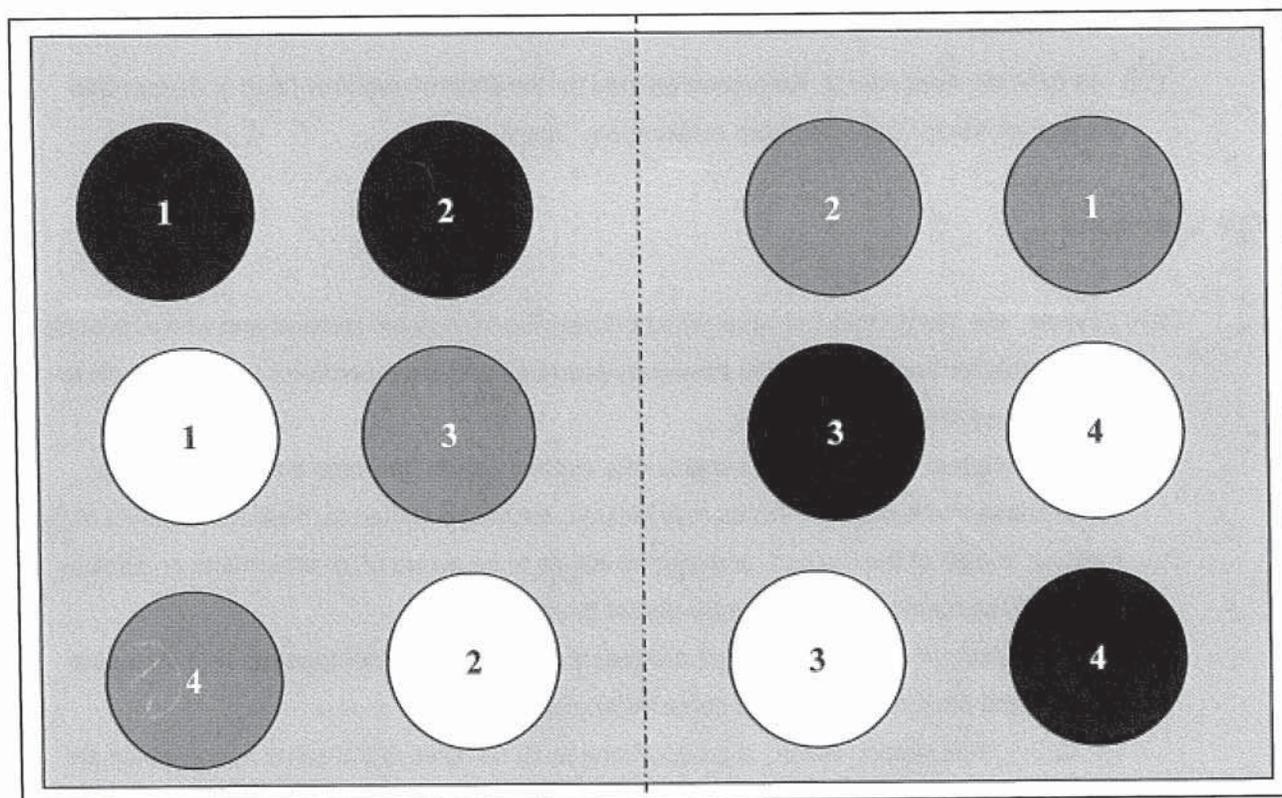
12.5 Matrix/Matrices: the component or substrate that contains the analyte of interest.

12.6 QA/QC: Quality Assurance/Quality Control. A series of samples or metrics designed to show precision, accuracy and bias of the procedure are within acceptable limits.

12.7 Reagent: a single chemical or combination of chemicals or a chemical solution used in the preparation or analysis of samples.

13.0 Analysts' Notes

13.1 N/A



- Solid black line Corresponds to the edge of the entire filter
- Dotted line in the middle Corresponds to the crease where filter has been folded for shipment
- Rectangular grey area Corresponds to the deposit area of the filter.
- Black circles 1-4 Correspond to punches taken from the filter for sample digestion
- Gray circles 1-4 Correspond to punches taken for duplicate or spike sample digestion
- White circles 1-4 Correspond to punches remaining for possible redigestion

Diagram 1. Punching sequence and positions for RMA filters.

APPENDIX A: Differences from Promulgated methods

*SA 2-15-15*

Note: There are various methods which reference subsectioning of 8" x 10" Quartz or Glass Fiber filters. Most of these methods reference 40CFR50 Appendix G for the subsectioning of filters into 1" x 8" strips.

*SA 2-15-15*

Initially, Appendix G used a stainless steel pizza cutter to cut the filter. The 2013 version of the method now uses a ceramic knife. Not all methods that reference Appendix G have been updated to reflect this change, and thus may still refer to the use of a pizza cutter.

It has been the laboratory's experience that not all filters have a homogenous enough deposit to make this style of subsectioning representative of the sample. The laboratory developed this procedure to alleviate the problems associated with the "pizza cutter" method of subsectioning.

The primary difference between this SOP and other promulgated methods is that the laboratory uses a punch of known diameter to take only those sections of filter containing deposit (e.g. the white unsampled-on "margin" of the filter is not digested) and, as a result of the punch's size, is able to take a more homogenous subsample of the filter deposit than is possible using any of the 1" x 8" strip subsampling methods.

Not all clients load or fold the 8" x 10" filters squarely, thus the deposit can rub off on the "margin" of the filter. By taking strips of the filter, this creates a known inaccuracy of incalculable amount in the deposit mass (as a percentage of the total mass). Use of a circular punch and avoidance of the filter "margin" or areas where the deposit has rubbed off on the "margin" allows the analyst to completely avoid using "margin" areas of the filter during digestion.

*SA 2-15-15*

40 CFR 50 Appendix G Reference Method for the Determination of Lead in Total Suspended Particulate Matter (July3, 2013)

Item	Promulgated requirement	SOP	Justification
1	1.0 ... This method is for the analysis of Pb from TSP filters by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)...	This method is applicable to the subsectioning of any 8"x10" filter for analysis by a number of different analytical techniques, including ICP, GFAA, CVAA, IC, OC/EC, and XRF.	This procedure only pertains to the subsectioning of filters for any type of digestion/extraction and analysis, and does not include digestion or analytical procedures.

*SA 3-17-16*

Item	Promulgated requirement	SOP	Justification
2	6.4. ... Plastic tweezer...	Stainless Steel forceps cleaned with ethanol and a Kimwipe	<p>This laboratory has not had any known issues with the use of stainless steel forceps.</p> <p>In addition, the laboratory has encountered issues with deposit transferring irrevocably onto plastic forceps, resulting in a loss of particulate matter from the filter during handling.</p>
3	6.4 ... Ceramic knife ... and non-metal ruler or other suitable cutting tools for making straight cuts for accurately measured strips.	<p>One 46mm diameter stainless steel rubber punch creating a punch with an area of 66.4 cm<sup>2</sup>.</p> <p>16.6 Set 3-17-16</p>	<p>Removing a 3/4" x 8" or a 1" by 8" strip of filter is prone to homogeneity issues. See Appendix B for photographic discussion of commonly encountered problems.</p> <p>The use of a punch enables the analyst to ensure that subsections of filters used in digestion/extraction are as representative of the sample deposit as possible.</p>
4	10.1.2 Use a ceramic knife and non-metal ruler, or other cutting device that will not contaminate the filter with Pb.	<p>Use a 46mm diameter stainless steel rubber punch creating a punch with an area of 66.4 cm<sup>2</sup>.</p> <p>16.6 Set 3-17-16</p>	<p>This laboratory has not had any known issues with the use of stainless steel forceps or punch.</p>

Item	Promulgated requirement	SOP	Justification
5	<p>10.1.2 ... Cut a 3/4 inch X 8 inch strip from the ... filter by cutting a strip from the edge of the filter where it has been folded along the 10 inch side at least 1 inch from the right or left side to avoid the un-sampled area covered by the filter holder.</p>	<p>Perform a single punching action through both layers of the folded filter, approximately 0.5 cm from outer edge of the deposit area, and approximately 0.5 cm from either the top or the bottom of the deposit edge.</p> <p><del>Perform a single punching action a second time through both layers of the folded filter, approximately 0.5 cm from fold line of the filter, and approximately 0.5 cm from either the top or the bottom of the deposit edge, whichever was not used above.</del></p> <p><i>4/23/16</i></p>	<p>Most clients fold their filters on the 8 inch axis, not the 10 inch axis.</p> <p>Depending on the samplers' technique, the deposit may not be centered on the filter, so cutting a strip "1 inch from the right or left side" may still result in a subsection of filter containing "the un-sampled area covered by the filter holder."</p> <p>Removing a strip of filter is prone to homogeneity issues.</p> <p>The use of a punch enables the analyst to ensure that subsections of filters used in digestion/extraction are as representative of the sample deposit as possible.</p> <p>See Appendix B for photographic discussion of commonly encountered problems.</p>
6	<p>10.1.3 Using plastic tweezers, roll the filter strip up in a coil and place the rolled strip in the bottom of a labeled 50 mL extraction tube.</p>	<p>Using stainless steel forceps, place the <del>four</del> punches in a labeled container (digestion vessel, Petri slide, Petri dish).</p> <p><i>appropriate 5/11-16</i></p>	<p>This laboratory has not had any known issues with the use of stainless steel forceps.</p> <p>Depending on analysis, different (or no) extraction/digestion vessels may be used.</p>

Item	Promulgated requirement	SOP	Justification
7	<p>11.1.2 ... Cut a 1-inch X 8-inch strip from the ... filter by cutting a strip from the edge of the filter where it has been folded along the 10 inch side at least 1 inch from the right or left side to avoid the un-sampled area covered by the filter holder.</p>	<p>Perform a single punching action through both layers of the folded filter, approximately 0.5 cm from outer edge of the deposit area, and approximately 0.5 cm from either the top or the bottom of the deposit edge.</p> <p><del>Perform a single punching action a second time through both layers of the folded filter, approximately 0.5 cm from fold line of the filter, and approximately 0.5 cm from either the top or the bottom of the deposit edge, whichever was not used above.</del></p> <p><i>ok 3-17-16</i></p>	<p>Most clients fold their filters on the 8 inch axis, not the 10 inch axis.</p> <p>Depending on the samplers' technique, the deposit may not be centered on the filter, so cutting a strip "1 inch from the right or left side" may still result in a subsection of filter containing "the un-sampled area covered by the filter holder."</p> <p>Removing a 1" x 8" strip of filter is prone to homogeneity issues.</p> <p>The use of a punch enables the analyst to ensure that subsections of filters used in digestion/extraction are as representative of the sample deposit as possible.</p> <p>See Appendix B for photographic discussion of commonly encountered problems.</p>
8	<p>13.1 ... 3/4" X 8" strip = 5.25 in<sup>2</sup> analyzed, ... 1" X 8" strip = 7 in<sup>2</sup> analyzed</p> <p>[note: 7 in<sup>2</sup> = 45.2cm<sup>2</sup>]</p> <p>[note: this area assumes a loss of exactly 1 inch in length, based upon the assumption that each filter edge will have exactly 1/2 inch of un-sampled area covered by the filter holder]</p>	<p>1 punch = 16.6 cm<sup>2</sup>                  2 punches = 33.2 cm<sup>2</sup>                  4 punches = 66.4 cm<sup>2</sup></p>	<p>Differing analytical techniques will require different sized subsections.</p> <p>Use of a punch negates the need to adjust for un-sampled area of filter covered by the filter holder, leading to more accurate results. The punch allows the analyst to avoid digesting any un-sampled area.</p>
9	<p>13.1 ... The calculation assumes the use of a standard 8-inch x 10-inch TSP filter which has a sampled area of 9-inch x 7-inch ... due to the 1/2-inch filter holder border around the outer edge.</p>	<p>This procedure makes no assumptions about the field sampling activities and relies solely on the analysts' observation of the deposit.</p>	<p>See Appendix B for photographic discussion of commonly encountered problems.</p>

APPENDIX B: Photographic Examples and Discussion of Commonly Encountered Problems.

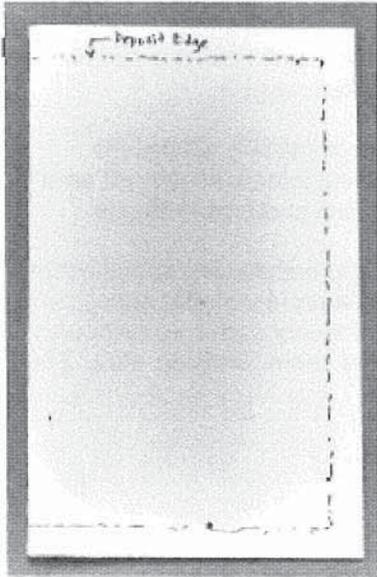


Figure 1a. Correctly sampled folded filter

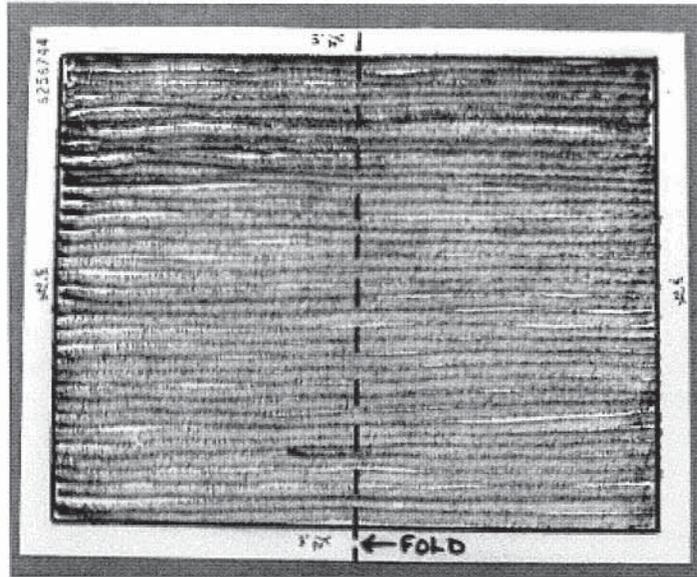


Figure 1b. Correctly sampled open filter

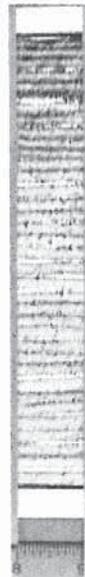


Figure 1c 1" strip

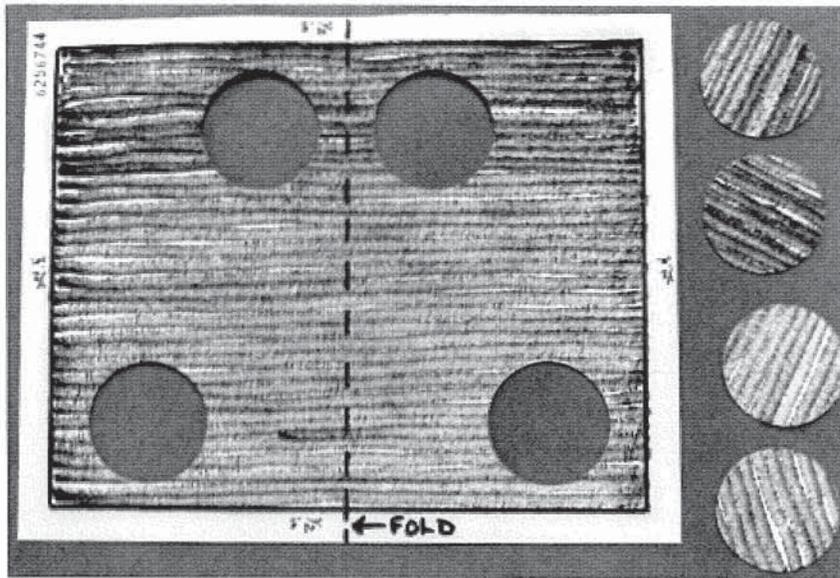


Figure 1d. Correctly sampled filter punched per this SOP.

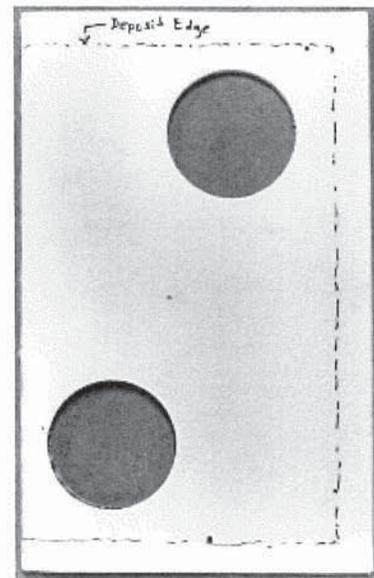


Figure 1e. Correctly sampled filter punched per this SOP and refolded.

1. The primary difference between the promulgated method and this SOP is the inclusion of the unsampled filter ("margins") in the 1" strip versus the exclusion of this extra filter material in the laboratory's method.
2. Inclusion of the margin is problematic if no blank subtraction is being used, as the amount of analyte contributed by the margin will elevate some analyte results. The promulgated method uses 7 square inches as the deposit area on the strip (1x8 inches less a 1 inch margin), which does not take contribution of analytes from the margins into account. This SOP uses none of the margin.
3. While the punches will also include any contaminant analytes present in the blank filter, the amount of analyte contributed by the filter vs. deposit is lessened by not including the filter margins.
4. Refolding the filter after a 1" strip has been taken results in exposed deposit rubbing against the container in which the filter is stored. By taking punches through the filter when folded, no deposit area is exposed to the filter container after subsectioning the filter, thus there is no loss of deposit integrity.
5. Where possible, the laboratory attempts to take two punches at the top and bottom, and two punches near the deposit edge and near the fold to maximize the likelihood of getting a representative subsection of filter deposit. The 1" strip technique assumes that the deposit will be homogenous, evenly distributed and to have no defects (e.g. finger prints, shoe prints, moisture leaks, insects, tears, wrinkles, etc.). The laboratory has found this assumption to be false.

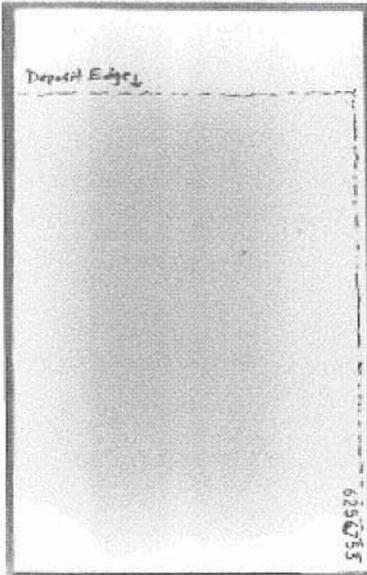


Figure 2a. Filter loaded incorrectly in sampler. Deposit on edge of filter. Filter folded for shipment.

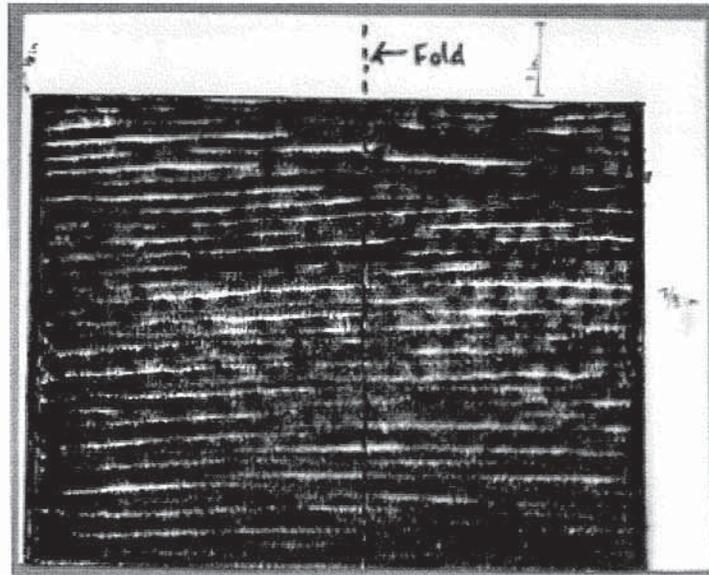


Figure 2b. Open filter with deposit on edge of filter.



Figure 2c. 1" strip deposit on edge

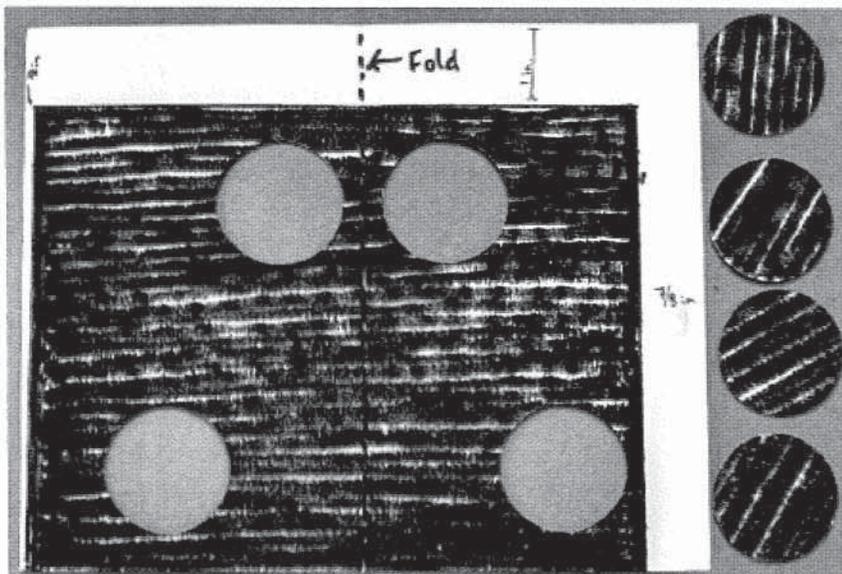


Figure 2d. Deposit on edge of filter. Filter punched per this SOP.

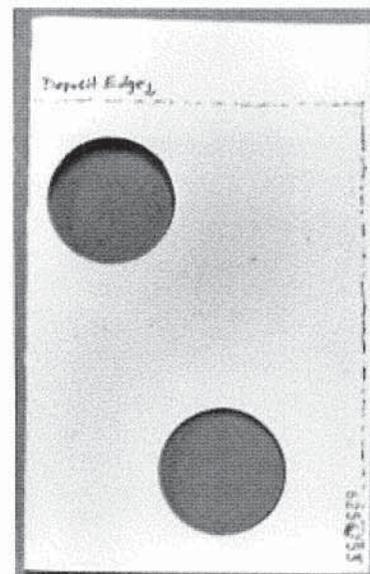


Figure 2e. Deposit on edge of filter, punched per this SOP and refolded.

Notes:

Figure 2b. This type of deposit is the result of loading the filter off center into the sampler filter holder. The top margin in this case is 1" and the right margin is 7/8<sup>th</sup>s inches.

Figure 2c. To obtain a 1" strip of filter without running the risk of taking the right-hand margin, the analyst must take the strip from the left side of the filter.

Figure 2d. This laboratory's SOP by-passes all filter margin issues by only taking punches from within the deposit area.

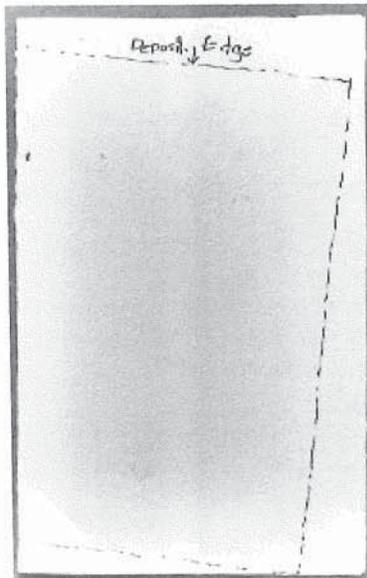


Figure 3a. Filter skewed in sampler. Filter folded for shipment.

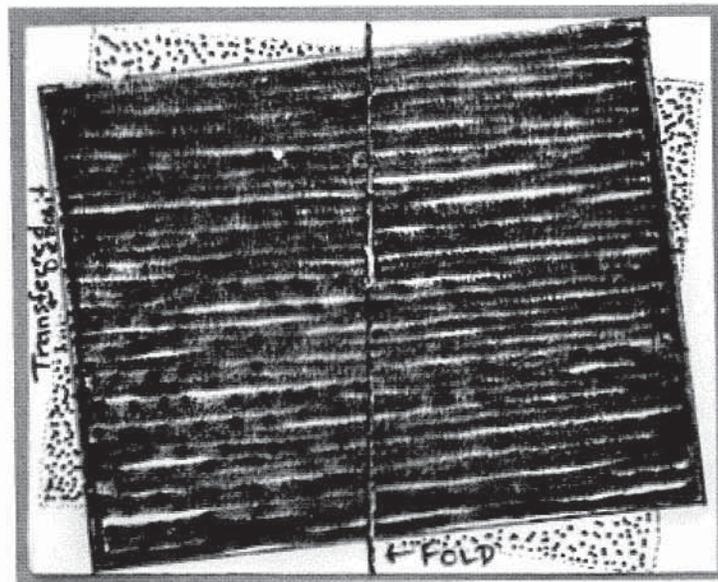


Figure 3b. Open filter showing skewed deposit due to improper mounting in filter holder. Dotted areas represent deposit transference to margins due to rubbing of margin against deposit after removing from sample holder and shipping.



Figure 3c. 1" strip, showing deposit transference.

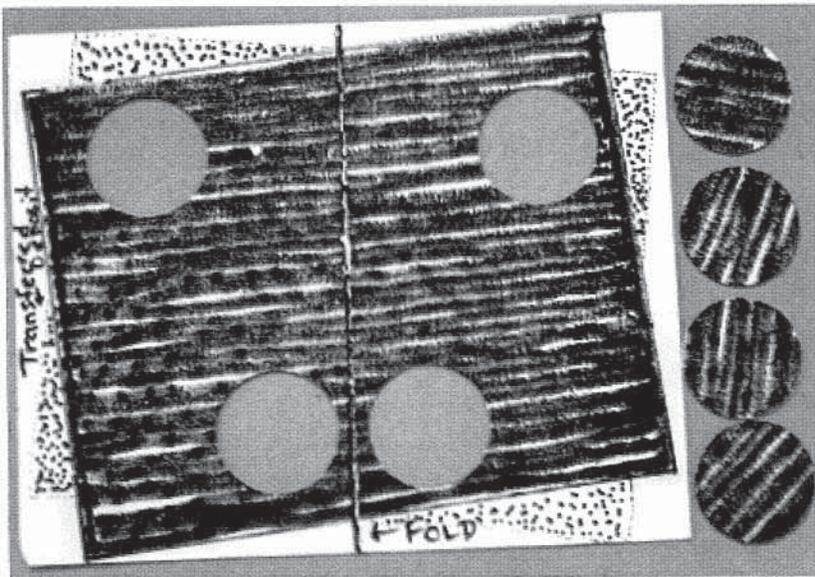


Figure 3d. Skewed deposit. Filter punched per this SOP.

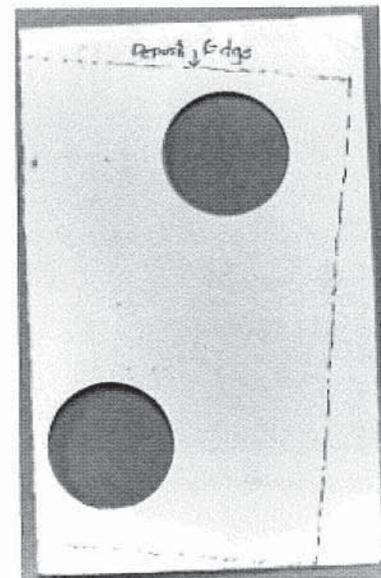


Figure 3e. Filter with skewed deposit. Punched per this SOP and refolded.

Notes:

Figure 3b. This type of deposit is the result of loading the filter off-true to the edges in the filter holder. The dotted areas in the margin show the transference of deposit from the deposit area onto the margins of the filter.

Figure 3c. With this type of deposit, it is not possible to take a 1" strip without also taking some of the transferred deposit in the margins. In addition, part of the left- or right-side filter margin (no deposit) would be included in the 1" strip if the analyst follows the promulgated method as written.

Figure 3d. This laboratory's SOP by-passes all filter margin issues by only taking punches from within the deposit area, and only where the deposit contacts other deposit when folded. No punches are taken where deposit may have either rubbed off or been transferred onto filter margins.

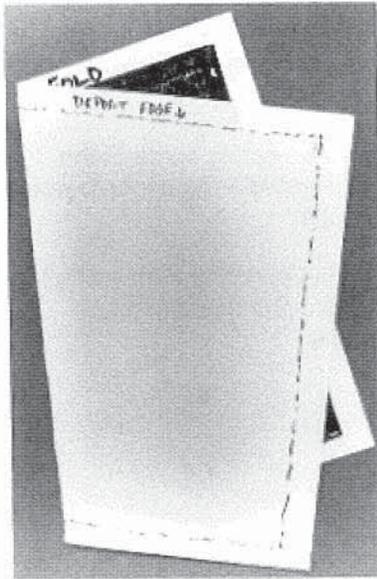


Figure 4a. Filter loaded in sampler properly, skewed when folded.

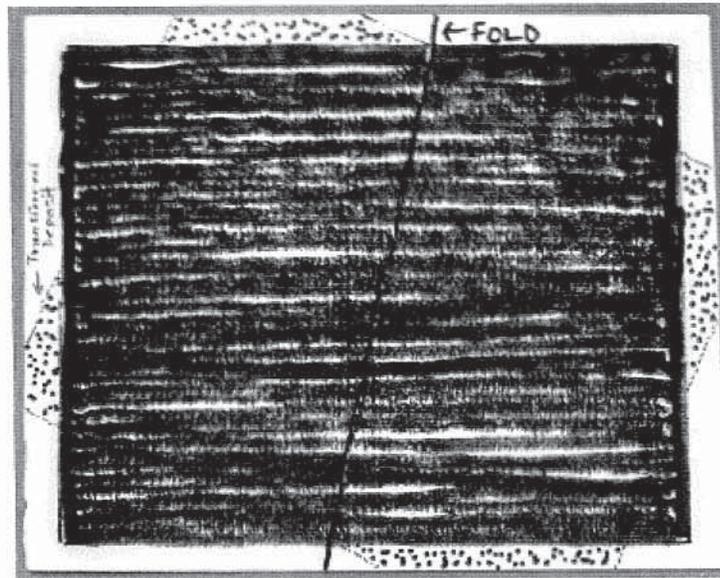


Figure 4b. Open filter showing transferred deposit and deposit "overhang" due to skewed folding of filter.



Figure 4c. 1" strip showing deposit transference.

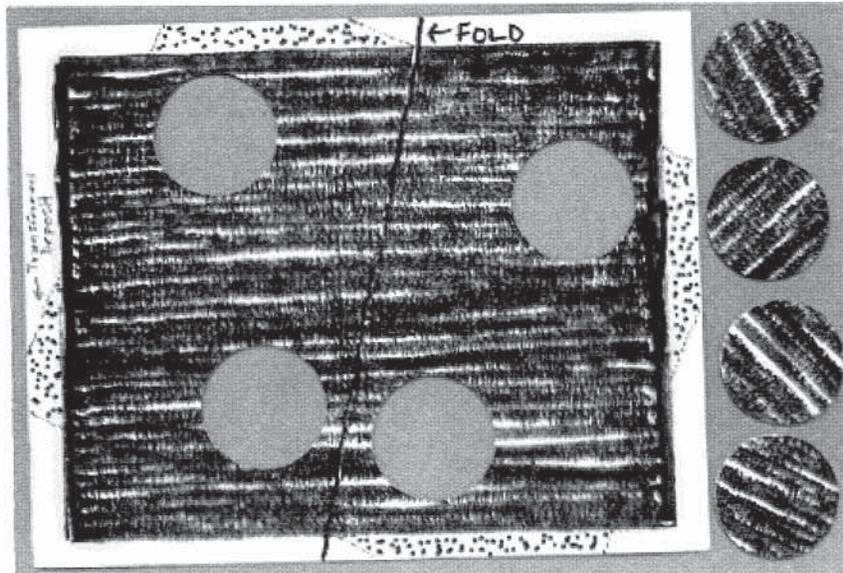


Figure 4d. Skewed fold. Filter punched per this SOP.

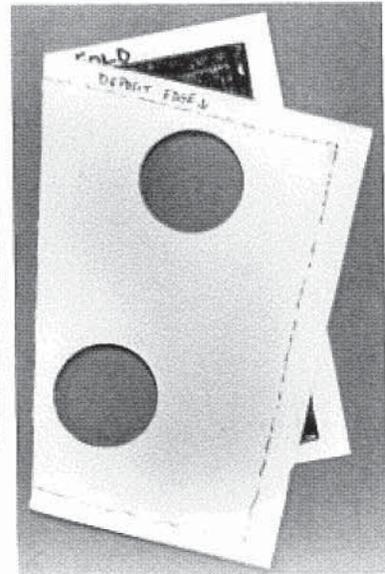


Figure 4e. Filter with skewed fold. Punched per this SOP and refolded.

Notes:

Figure 4a. When the filter is folded skewed as in this picture, two issues arise. The first is that some sample deposit transfers to the margins of the filter. The second is that some of the deposit is not sandwiched between the two halves of the filter and may be lost due to transfer into/onto the filter's shipping container. The 1" strip taken per the promulgated method would be taken just to the right of the

word "fold" on this example filter, causing the strip to contain an area of deposit which may have lost some particles to the shipping container after sampling.

Figure 4a and 4b. When the filter is folded severely skewed as shown, it is not possible to take a 1" strip without also taking some of the transferred deposit in the margins, and possibly taking some area of deposit that has had particulate loss into/onto the filter container. In photograph 4b, above, there is no 1" width where a strip might be taken that has no deposit transference (positive or negative) present.

Figure 4d. This laboratory's SOP by-passes all filter margin issues by only taking punches from within the deposit area, and only where the deposit contacts other deposit when folded. No punches are taken where deposit may have either rubbed off or been transferred onto filter margins.

# CHESTER LabNet

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## Standard Operating Procedure ME-011.01

Analysis of Elements by Inductively-Coupled Plasma Emission  
(Perkin-Elmer OPTIMA 8300)  
Based on SW-846 Method 6010C (SW-846) and  
Inorganics Air Compendium Method IO-3.4

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Approvals:

 _____ Author	<u>5.5.14</u> _____ Date
 _____ Lead Analyst	<u>5.5.14</u> _____ Date
 _____ QA/QC	<u>5.5.14</u> _____ Date

Effective from: 5.5.14  
Effective until: present

### REVIEW HISTORY

Review date:	Changes made:	Changes made by:
5/5/14	Addition of data for detection limit and Precision & Bias study for ICAP 7 analytes.	Sheri Heldstab
4/3/14	No changes. Date of origination.	Sheri Heldstab

### ANNUAL REVIEW

The undersigned attests that this standard operating procedure has undergone annual review for adherence to current practices and the latest QA/QC protocols:

Sheri Heldstab

signature

Conv. Chem. Tech Dir

title

5-7-15

date

Sheri Heldstab

signature

Conv ChemTech Dir

title

4-22-16

date

\_\_\_\_\_

signature

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title

\_\_\_\_\_

date

**Analysis of Elements by Inductively-Coupled Plasma Emission  
(Perkin-Elmer OPTIMA 8300)  
Based on SW-846 Method 6010C (SW-846) and  
Inorganics Air Compendium Method IO-3.4**

### 1.0 Introduction

- 1.1 Test Method Reference ID: This SOP is based on SW-846 Method 6010C (SW-846) and IO-3.4. IO-3.4 is a technologically archaic method. SW-846 Method 6010C is not intended for air methods.
- 1.2 Applicability: This method is applicable to the determination of elements by ICP in digestates falling under the 2009 TNI Quality Matrix of "Air." Refer to method specific SOPs for digestion protocols.
- 1.3 Detection Limit: Detection limit studies are performed annually and will vary from one element to another. Detection limits may vary over time as the instrument ages. The table below lists the instrument detection limits determined when the instrument was first installed in 2014, and represents the most commonly requested analytes. Other analytes may be analyzed using this SOP after a detection limit study and Precision and Bias study have been performed.

Clients may waive the detection limit study and Precision and Bias study. At a minimum, an estimated detection limit must be performed by determining three times the standard deviation of seven analyses of a standard with a concentration at 1-4 times the expected detection limit for that analyte.

Element	Detection Limit (µg/L)	Element	Detection Limit (µg/L)
Antimony	5	Magnesium	0.5 (SHS-7-15)
Aluminum	5 2 <sup>3-22-14</sup>	Manganese	0.2 0.3 <sup>3-22-16</sup>
Arsenic	7	Molybdenum	0.5   SHS-7-15
Barium	0.5	Nickel	1
Beryllium	0.1 0.2 <sup>SH</sup> 3-7-15	Phosphorous	20-15 <sup>SH</sup> 3-22-16
Boron	N/A	Potassium	5
Cadmium	0.5	Selenium	10
Calcium	7 8 <sup>SH</sup> 5-7-15	Silver	2 3 <sup>SH</sup> 3-22-16

Element	Detection Limit (µg/L)	Element	Detection Limit (µg/L)
Chromium	0.5	Sodium	12-6 <sup>3-22-16</sup>
Cobalt	<del>0.4</del> 0.5 <sup>3-22-16</sup>	Thallium	5   10 <sup>3-22-16</sup>
Copper	7.5 <sup>3-22-16</sup>	Titanium	0.4
Iron	<del>0.5</del> 1 <sup>3-22-16</sup>	Vanadium	1
Lead	5	Zinc	1

1.4 Method Performance: In 2014, a Precision and Bias Study was performed in the 2009 TNI standard defined quality matrix of "air". Three analyses of three different concentrations of standards were analyzed on three different days. The concentrations of the standards were as follows:

Low Level Standard: at or near the Quantitation Level for element of interest

Mid Level Standard: at the mid-point of the calibration curve

High Level Standard: At 90% of the highest calibration standard

The results are summarized in the table below, as follows:

Low %Rec: Average % Recovery of 3 runs of the Low level standard

Mid %Rec: Average % Recovery of 3 runs of the Mid level standard

High %Rec: Average % Recovery of 3 runs of the High level standard

Ave. %Rec: Average % Recovery of all three standard concentrations

Low %RSD: Average % RSD of 3 runs of the Low level standard

Mid %RSD: Average % RSD of 3 runs of the Mid level standard

High %RSD: Average % RSD of 3 runs of the High level standard

Ave. %RSD: Average % RSD of 3 runs of all three standard concentrations

Element	Low %Rec.	Mid %Rec.	High %Rec.	Ave. %Rec.	Low %RSD	Mid %RSD	High %RSD	Ave. %RSD
Sb	94.01	96.43	100.58	97.06	3.34	1.71	.526	1.86
Al	92.71	100.53	99.58	97.61	3.46	1.63	1.59	2.23
As	97.85	98.77	100.81	99.15	1.59	1.95	0.73	1.43
Ba	100.07	100.57	99.88	100.17	1.27	1.78	1.41	1.49

<u>Element</u>	<u>Low</u> <u>%Rec.</u>	<u>Mid</u> <u>%Rec.</u>	<u>High</u> <u>%Rec.</u>	<u>Ave.</u> <u>%Rec.</u>	<u>Low</u> <u>%RSD</u>	<u>Mid</u> <u>%RSD</u>	<u>High</u> <u>%RSD</u>	<u>Ave.</u> <u>%RSD</u>
Be	100.27	99.55	99.52	99.78	4.49	0.50	1.70	2.23
Cd	100.05	99.75	99.84	99.88	12.93	2.04	1.88	5.62
Ca	96.59	99.48	99.69	98.58	6.39	2.71	1.78	3.63
Cr	107.47	100.87	99.61	102.65	6.65	1.98	1.76	3.46
Co	102.13	96.09	99.68	99.30	3.72	1.95	1.77	2.48
Cu	107.67	97.16	99.37	101.40	3.26	2.12	1.79	2.39
Fe	100.51	100.97	99.64	100.38	3.59	2.04	1.80	2.48
Pb	97.84	99.97	100.46	99.42	5.24	1.96	0.82	2.67
Mg	92.41	103.67	100.26	98.78	0.48	0.94	1.73	1.05
Mn	102.33	99.45	99.53	100.44	4.74	2.06	1.74	2.84
Mo	99.73	99.63	99.54	99.63	0.79	2.00	1.68	1.49
Ni	97.84	98.21	99.7	98.59	10.09	1.99	1.80	4.63
P	90.32	99.57	101.26	97.05	5.55	1.47	1.18	2.73
K	89.75	92.63	98.43	93.60	8.65	1.09	1.51	3.75
Se	90.12	100.32	100.34	96.93	2.97	1.69	0.81	1.82
Ag	99.92	104.77	95.70	100.13	21.67	20.62	10.87	17.72
Na	87.56	94.69	99.02	93.76	10.64	1.57	1.85	4.69
Tl	97.75	100.15	100.39	99.43	6.12	1.96	0.60	2.90
Ti	103.18	101.08	99.39	101.22	3.28	2.06	1.75	2.36
V	95.57	99.53	99.41	98.17	2.65	1.98	1.74	2.12
Zn	98.13	99.8	99.78	99.24	8.68	1.88	1.81	4.12
<i>Average</i>	<i>98.59</i>	<i>99.52</i>	<i>99.94</i>	<i>--</i>	<i>4.83</i>	<i>1.85</i>	<i>1.47</i>	<i>--</i>

## 2.0 Summary

### 2.1 Scope and Application:

- 2.1.1 The intended use of this method is for the determination of elements by ICP in digestates falling under the 2009 TNI Quality Matrix of "Air." Refer to method specific SOPs for digestion protocols. This method meets its intended use.

2.1.2 This method is only applicable to analyses performed on the Perkin-Elmer Optima 8300 model ICP.

2.2 This procedure may only be performed by analysts with hands-on training and experience. This standard operating procedure is not to be used in lieu of proper training, nor is it designed to include all of the fine details that a trained operator should already know.

2.3 Summary of Method: Inductively coupled argon plasma atomic emission spectroscopy (ICAP-AES or, simply, ICP) combines spectrophotometric detection with the atomization capabilities of an argon plasma. Sample digestate is pumped through a nebulizer. The sample mist is then forced, by backpressure in the spray chamber, into an argon plasma, where the sample is atomized.

Each element is identified by a characteristic emission line and is detected by a charge coupled device (CCD) array detector. The data from the CCD are collected and processed by computer. The ICP is calibrated with NIST traceable standard solutions containing known quantities of the analytes of interest. The ICP software calculates the calibration curve parameters and reports data in  $\mu\text{g/L}$  analyte present in digestate. Hard copy is provided by a printer.

2.4 Interferences:

2.4.1 Spectral interferences may be caused by overlap of spectral lines, limited resolution of band spectra, background emission, or stray light. Background emission and stray light are compensated for by using background correction at a wavelength adjacent to the emission line of interest. Resolution problems can be compensated for by using an alternative wavelength. Spectral overlap, if present, is corrected by measuring any signal present at the analyte emission wavelength for a sample containing only the interferent element. For common interferences, see Appendix B copied from EPA SW-846.

2.4.2 Physical interferences are typically caused by the instrument sample introduction system (pump and/or nebulization systems). Inaccurate results can be caused by changes in viscosity or solids content between standards and samples or between individual samples. If present, physical interferences can be reduced by

sample filtration, centrifugation, dilution, by using the method of standard additions or by ensuring matrix matching between standards and samples.

2.4.3 Chemical interferences include incomplete atomization (formation of ions and/or molecular compounds) and solute vaporization effects. Although not commonly observed when using ICP, they can be compensated for by matrix matching, careful selection of operating parameters including Axial/Radial viewing positions, or by using the method of standard additions.

2.5 Sample collection/preservation/shipment/storage: Collection, field preservation and shipment of samples is performed by the client. Chester LabNet has no control over the actions of the client in the field. Upon receipt, samples are stored as required by the specific method being used.

2.5.1 Sample extracts and digestates are most commonly preserved with HNO<sub>3</sub> and stored at room temperature.

2.5.2 Stock standards and working standards are stored at room temperature in HDPE or PTFE bottles with screw caps. Each working standard is labeled with the element, concentration, solution ID, date prepared, analyst initials, and the expiration date of the commercial, primary standard from which it was prepared. All primary and working standards are discarded at or before the expiration date.

### **3.0 Safety**

3.1 Follow the Chester LabNet Chemical Hygiene plan. Always treat samples of unknown origin and/or constitution as hazardous.

3.2 This method presents no safety risk beyond typical laboratory safety hazards, with the exception of Method 29 Hydrofluoric Acid digests. These digests present an acute risk of injury to tissues and may cause death upon contact with skin.

3.3 No carcinogenic reagents are used in this method.

#### 4.0 Pollution Prevention and Waste Management

4.1 The smallest quantity of chemical feasible is removed from its primary container for use.

4.2 Chemicals are used in amounts needed by the method, and excess reagents are not made.

4.3 Chester LabNet is a conditionally exempt small quantity generator and as such does not require formal chemical waste processing.

4.3.1 Acidic and Basic wastes are neutralized prior to disposing of them in the sanitary sewer system.

4.3.2 Organic liquids are usually primarily used for cleaning purposes. Organic wastes are generated in very small quantities, and evaporate off with no need for more formal disposal.

4.4 Larger quantities of known hazards are returned to the client for disposal.

4.5 Expired Chemicals:

4.5.1 Dry chemicals beyond their <sup>SH 5.7.15</sup> ~~real or arbitrary~~ expiration date are lab packed and disposed of by a qualified chemical disposal company.

4.5.2 Acids and Bases beyond their <sup>SH 5.7.15</sup> ~~real or arbitrary~~ expiration date are neutralized prior to being disposed of via the sanitary sewer system.

4.5.3 Organic liquids beyond their <sup>SH 5.7.15</sup> ~~real or arbitrary~~ expiration date <sup>SH 5.7.15</sup> are disposed of by a qualified chemical disposal company if the volume or type of liquid warrants such disposal. Disposal of organic liquids is rare.

## 5.0 Apparati, Equipment and Supplies

### 5.1 Preparation of Calibration Standards.

- 5.1.1 Volumetric flasks
- 5.1.2 Adjustable volumetric pipettes
- 5.1.3 HDPE or PTFE storage bottles

### 5.2 Analysis of Samples.

- 5.2.1 Perkin-Elmer Optima 8300 Inductively Coupled Argon Plasma Atomic Emission Spectrophotometer with MiraMist nebulizer and cyclonic spray chamber.
- 5.2.2 Chiller capable of maintaining 15 °C
- 5.2.3 Air compressor capable of supplying shear gas at 100 PSI.
- 5.2.4 Perkin-Elmer S10 autosampler
- 5.2.5 PC capable of running Perkin-Elmer WinLab32 software and compatible printer.
- 5.2.6 15 mL polystyrene centrifuge tubes

## 6.0 Reagents and Standards

### 6.1 Preparation of Standards.

- 6.1.1 ASTM Type II de-ionized water (>16.7 megohm)
- 6.1.2 Reagent grade or better concentrated nitric acid
- 6.1.3 1,000 ppm, NIST-traceable, single-element standards for instrument calibration
- 6.1.4 1,000 ppm, second source, NIST-traceable, single-element standards for CRI standard.
- 6.1.5 100 ppm, second source, NIST-traceable, multi-element standards for calibration verification and spiking.

6.2 Liquid argon suitable for operation of ICP (argon plasma) at 100 – 110 PSI.

6.3 Compressed air suitable for operation of ICP (shear gas).

6.4 Acidified rinse solution: ① 5% HNO<sub>3</sub>, 5% HCL: to approximately 750 mL DI water, add 50 mL conc. HNO<sub>3</sub> and 50 mL conc. HCl, then dilute to 1 L with DI water.

② HF/HNO<sub>3</sub>: 4% / 6%

③ DI water

④ ~~7.5% HNO<sub>3</sub> 4.22 to~~ 1L HCl / 6% HNO<sub>3</sub>

**7.0 Preparation, Calibration and Standardization**

7.1 Preparation of Instrument Calibration Standards.

7.1.1 Calibration standards:

7.1.1.1 Calibrate the ICP with a reagent blank and a single, multi-element working standard prepared from individual, commercial, NIST-traceable, single-element standards.

7.1.1.2 Because of the incompatibility of some of the element chemical forms, it is necessary to prepare two working calibration solutions.

7.1.1.3 The final element concentrations in mg/L for each solution are as follows:

Calibration Solution #1				Calibration Solution #2	
Analyte	Concentration	Analyte	Concentration	Analyte	Concentration
Sb	5	Mn	5	Ag	5
As	5	Mo	5	Al	5
Be	5	Ni	5	Ba	5
Ca	5	P	5	K	5
Cd	5	Pb	5	Na	5
Cr	5	Se	5		
Co	5	Ti	5		
Cu	5	Tl	5		
Fe	5	V	5		
Mg	5	Zn	5		

7.1.1.4 Note that the two mixed standards contain those elements most-requested by clients and do not contain elements such as gold, hafnium, zirconium, lanthanum and others. Standards for non-routine elements and/or concentrations are prepared on a project-specific basis, usually in

~~50~~ 100 mL amounts.  
SH 4.22.16

7.1.2 The matrix of the working calibration standards must be similar to that of the digested samples. For most digestates, this is roughly 7% HNO<sub>3</sub>. To prepare 1 L of calibration standard, add the following, in order, to a 1000 mL volumetric flask:

500 mL DI water

~~70 mL concentrated nitric acid~~ acid(s) <sup>SH 5.7.15</sup> to match digestion solution

required volume of each individual 1000 ppm commercial stock standard

dilute to 1 L with DI water.

(See reuse solutions)

Commercial, single-element standards may be obtained in a variety of concentrations. For this reason, the required volume of each individual stock standard is left to the analyst.

Generally, one standard in 7% HNO<sub>3</sub> and one standard in 16% HCl/6% HNO<sub>3</sub> are sufficient.  
SH 5.7.15  
SH 4.22.16

7.1.3 After thorough mixing, transfer the standard to a clean HDPE or PTFE bottle.

7.1.4 Label and store the bottles per Section 2.4.2, above. <sup>SH 4.22.16</sup>

7.1.5 Record the preparation of the standard in the metals standards and reagents logbook. Include the following information:

7.1.5.1 Date and Initials of analyst preparing the standard;

7.1.5.2 Laboratory solution ID in the format LLL-PP-XX where:

LLL = logbook number

PP = page in logbook

XX = chronological number of solution on page

7.1.5.3 Matrix of the standard (7% HNO<sub>3</sub>); <sup>SH 5.7.15</sup>

7.1.5.4 Concentration and Analyte of the stock standard;

- 7.1.5.5 Volume of stock standard used;
- 7.1.5.6 Dilution volume of the working standard;
- 7.1.5.7 The manufacturer and lot number of the primary standard; and,
- 7.1.5.8 Expiration date of the <sup>stock</sup> primary standard. <sub>SH 5.7.15</sub>

7.2 Preparation of Calibration Verification Standards.

7.2.1 Initial calibration verification (ICV) and continuing calibration verification (CCV) working standards for the most commonly analyzed elements are prepared from two commercial, NIST-traceable, multi-element standards colloquially known as ICAP-7 and ICAP-19.

7.2.2 The matrix of the working calibration standards must be similar to that of the digested samples. <sup>SH 5.7.15</sup> For most digestates, this is roughly 7% HNO<sub>3</sub>. To prepare 1 L of calibration standard, add the following, in order, to a 1000 mL volumetric flask:

- 500 mL DI water
- 70 mL concentrated nitric acid <sup>SH 5.7.15</sup> acid(s) to match digestion solution (see rinse solutions)
- required volume of each individual 1000 ppm commercial stock standard
- dilute to 1 L with DI water.

Commercial, single-element standards may be obtained in a variety of concentrations. For this reason, the required volume of each individual stock standard is left to the analyst.

<sup>SH 4.22.16</sup> Generally, 7% HNO<sub>3</sub> or 16% HCl/6% HNO<sub>3</sub> ...  
If the matrix is other than 7% HNO<sub>3</sub>, a different standard solution must be <sup>SH 5.7.15</sup> prepared to match the matrix of the standards used and samples analyzed.

7.2.3 After thorough mixing, transfer the standard to a clean HDPE or PTFE bottle <sup>SH 4.22.16</sup> & label as in section 2.5.2

7.2.4 The ICAP-19 working standard is prepared at a concentration of 2.5 <sup>OK</sup> mg/L, and contains Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, P, Se, Sr, Ti, Sn, Ti, V, and Zn.

7.2.5 The ICAP-7 working standard is prepared at a concentration of 2.5 mg/L, and contains Al, Ba, B, K, Ag, and Na.

7.2.6 For other elements, the ICV is prepared using a different lot number standard than that used for the calibration solutions. See Analyst Note 13.6.

7.2.7 These working standards are prepared and documented in the same manner as the procedures describe in Section 7.1.2, 7.1.5 and 7.1.6.

### 7.3 Preparation of Calibration and Continuing Calibration Blanks.

7.3.1 The matrix of the blanks must be similar to that of the digested samples. *ICB #4.22.16*  
~~prepare 1 L of the blank solution, add the following, in order, to the 1 L Teflon bottle labeled "7% HNO<sub>3</sub> Blank".~~ *and standards set 5-7-15*

~~~800 mL DI water~~

~~70 mL concentrated nitric acid~~

~~dilute to ~1 L with DI water~~

7.3.2 After thorough mixing, transfer the standard to a clean HDPE or PTFE bottle. Store the blank solution at room temperature, tightly capped to prevent contamination when not in use.

7.3.3 ~~If the matrix is other than 7% HNO<sub>3</sub>, a different blank solution must be prepared to match the matrix of the standards used and samples analyzed.~~ *see RMSE Sol'n's section 2.5.2 set 4-22-16*

### 7.4 Warm-up of ICP:

#### 7.4.1 From Stand-by shut-down.

7.4.1.1 The following should still be on:

7.4.1.1.1 Chiller

7.4.1.1.2 Argon tank (not pressure building valve)

7.4.1.1.3 Optima 8300

7.4.1.1.4 Computer

7.4.1.2 Open the pressure building valve on the Argon tank.

7.4.1.3 Turn on the air compressor

7.4.1.3.1 Flip small red switch to the up or on position to power on the compressor.

7.4.1.3.2 Turn on the air dryer.

7.4.1.4 Inspect the torch and windows, then close the front door to the ICP torch chamber.

7.4.1.5 Remove the cover from the torch chamber chimney.

7.4.1.6 Start up WinLab32 (online).

7.4.1.7 Attach tubing to Sample Introduction pump on ICP:

7.4.1.7.1 Change tubing if needed:

7.4.1.7.1.1 Sample tubing (black-black): replace every 8 hours of tubing use time, or when tubing becomes flattened.

7.4.1.7.1.2 Drain tubing (red-red): replace when the spray chamber waste no longer drains properly.

7.4.1.7.2 Prior to clamping the tubing in place, turn the pump on using the "Pump" button in the Plasma Control window. Allow the pump to turn several rotations prior to seating the clamps. Ensure that the tubing is in the correct location on the rollers.

7.4.1.7.3 Close the clamps while the pump is still rotating. Turn pump back off once tubing is firmly clamped in place.

7.4.1.8 Close the lever on the Autosampler tubing pump.

7.4.1.9 Wait for the purge delay to finalize, then light the plasma.

7.4.1.9.1 In the Plasma Control Window, verify the settings. The settings should default to the following:

7.4.1.9.1.1 Plasma: 15 L/min

7.4.1.9.1.2 Auxiliary: 0.2 L/min

7.4.1.9.1.3 Nebulizer: 0.65 L/min

7.4.1.9.1.4 Power: 1500 kW

7.4.1.9.1.5 Pump: 1.50 mL/min

7.4.1.9.1.6 Heat: off

7.4.1.9.2 Light the plasma on by clicking the Plasma On "switch" in the Plasma Control window.

7.4.1.10 Run the Mn Align.

7.4.1.10.1 Place the autosampler probe in 1 ppm Mn standard

7.4.1.10.2 Wait until sample reaches the spray chamber.

7.4.1.10.3 Click the Align Optics button in the Spectrometer Control window. A new dialog box will appear.

7.4.1.10.4 Click the appropriate radio button (Axial or Radial) and start the alignment process by clicking "ok".

7.4.1.10.5 When the alignment is complete, repeat the process for the other view (Radial or Axial).

7.4.1.10.6 When both views have been aligned, print out the report using the following menu choices: File → Print → ~~New Page:~~

*Active Window  
SH 4-22-16*

7.4.1.10.7 At the bottom of each set of readings, a summary of the X and Y viewing position settings is printed.

7.4.1.10.7.1 In Axial mode, the magnitude of the X setting should not be greater than 0.4 mm and the Y setting should be within 14.5 to 15.5 mm.

7.4.1.10.7.2 In Radial mode, the magnitude of the X setting should not be greater than 0.5 mm.

7.4.1.10.8 Place the printouts of the Mn Axial/Radial Alignments in the Optima 8300 MnBEC binder.

7.4.1.11 Instrument is now ready for analytical work.

**7.4.2 From Multi-day shutdown:**

7.4.2.1 The following should still be on:

7.4.2.1.1 Argon tank (not pressure building valve)

7.4.2.1.2 Optima 8300

7.4.2.2 Turn on the computer if it is not already on.

7.4.2.3 Turn on the chiller.

7.4.2.4 Open the pressure building valve on the Argon tank.

7.4.2.5 Turn on the air compressor

7.4.2.5.1 Flip small red switch to the up or on position to power on the compressor.

7.4.2.5.2 Turn on the air dryer.

7.4.2.6 Inspect the torch and windows, then close the front door to the ICP torch chamber.

7.4.2.7 Remove the cover from the torch chamber chimney.

7.4.2.8 Start up WinLab32 (online). Wait until software indicates that instrument is thermally stable (around 90 minutes).

7.4.2.9 Attach the tubing to the sample introduction pump on the ICP.

7.4.2.9.1 Change tubing if needed:

7.4.2.9.1.1 Sample tubing (black-black): replace every 8 hours of tubing use time or when tubing becomes flattened.

7.4.2.9.1.2 Drain tubing (red-red): replace when the spray chamber waste no longer drains properly.

7.4.2.9.2 Prior to clamping the tubing in place, turn the pump on using the "Pump" button in the Plasma Control window. Allow the pump to turn several rotations prior to seating the clamps. Ensure that the tubing is in the correct location on the rollers.

7.4.2.9.3 Close the clamps while the pump is still rotating. Turn pump back off once tubing is firmly clamped in place.

7.4.2.10 Close the lever on the Autosampler tubing pump.

7.4.2.11 Wait for the purge delay to finalize, then light the plasma.

7.4.2.11.1 In the Plasma Control Window, verify the settings. The settings should default to the following:

- 7.4.2.11.1.1 Plasma: 15 L/min
- 7.4.2.11.1.2 Auxiliary: 0.2 L/min
- 7.4.2.11.1.3 Nebulizer: 0.65 L/min
- 7.4.2.11.1.4 Power: 1500 kW
- 7.4.2.11.1.5 Pump: 1.50 mL/min
- 7.4.2.11.1.6 Heat: off

7.4.2.11.2 Light the plasma on by clicking the Plasma On "switch" in the Plasma Control window.

7.4.2.12 Run the Mn Align.

7.4.2.12.1 Place the autosampler probe in 1 ppm Mn standard

7.4.2.12.2 Wait until sample reaches the spray chamber.

7.4.2.12.3 Click the Align Optics button in the Spectrometer Control window. A new dialog box will appear.

7.4.2.12.4 Click the appropriate radio button (Axial or Radial) and start the alignment process by clicking "ok".

7.4.2.12.5 When the alignment is complete, repeat the process for the other view (Radial or Axial).

7.4.2.12.6 When both views have been aligned, print out the report using the following menu choices: File → Print → ~~New Page:~~

*Active Window  
Set 4-22-16*

7.4.2.12.7 At the bottom of each set of readings, a summary of the X and Y viewing position settings is printed.

7.4.2.12.7.1 In Axial mode, the magnitude of the X setting should not be greater than 0.4 mm and the Y setting should be within 14.5 to 15.5 mm.

7.4.2.12.7.2 In Radial mode, the magnitude of the X setting should not be greater than 0.5 mm.

7.4.2.12.8 Place the printouts of the Mn Alignments in the Optima 8300 MnBEC binder.

7.4.2.13 Instrument is now ready for analytical work.

7.4.3 **From complete shutdown:** Note that complete shutdown of the system should only occur during instrument servicing, power outages or if the instrument is being physically moved.

7.4.3.1 Turn on the Argon Tank, and open the pressure building valve.

7.4.3.2 Turn on the Optima 8300

7.4.3.3 Turn on the computer if it is not already on.

7.4.3.4 Turn on the chiller.

7.4.3.5 Turn on the air compressor

7.4.3.5.1 Flip small red switch to the up or on position to power on the compressor.

7.4.3.5.2 Turn on the air dryer.

7.4.3.6 Inspect the torch and windows, then close the front door to the ICP torch chamber

7.4.3.7 Remove the cover from the torch chamber chimney.

7.4.3.8 Start up WinLab32 (online). Wait until software indicates that instrument is thermally stable (around 90 minutes).

7.4.3.9 Connect the sample tubing to the sample pump.

7.4.3.9.1 Change tubing if needed:

7.4.3.9.1.1 Sample tubing (black-black): replace every 8 hours of tubing use time or when tubing becomes flattened.

7.4.3.9.1.2 Drain tubing (red-red): replace when the spray chamber waste no longer drains properly.

7.4.3.9.2 Prior to clamping the tubing in place, turn the pump on using the "Pump" button in the Plasma Control window. Allow the pump to turn several rotations prior to seating the clamps. Ensure that the tubing is in the correct location on the rollers.

7.4.3.9.3 Close the clamps while the pump is still rotating. Turn pump back off once tubing is firmly clamped in place.

7.4.3.10 Close the lever on the Autosampler tubing pump.

7.4.3.11 Wait for the purge delay to finalize, then light the plasma.

7.4.3.11.1 Wait for the purge delay to finalize, then light the plasma. In the Plasma Control Window, verify the settings. The settings should default to the following:

7.4.3.11.1.1 Plasma: 15 L/min

7.4.3.11.1.2 Auxiliary: 0.2 L/min

7.4.3.11.1.3 Nebulizer: 0.65 L/min

7.4.3.11.1.4 Power: 1500 kW

7.4.3.11.1.5 Pump: 1.50 mL/min

7.4.3.11.1.6 Heat: off

7.4.3.11.2 Light the plasma by clicking the Plasma On "switch" in the Plasma Control window.

7.4.3.12 Run the Mn Align.

7.4.3.12.1 Place the autosampler probe in 1 ppm Mn standard

7.4.3.12.2 Wait until sample reaches the spray chamber.

7.4.3.12.3 Click the Align Optics button in the Spectrometer Control window. A new dialog box will appear.

7.4.3.12.4 Click the appropriate radio button (Axial or Radial) and start the alignment process by clicking "ok".

7.4.3.12.5 When the alignment is complete, repeat the process for the other view (Radial or Axial).

7.4.3.12.6 When both views have been aligned, print out the report using the following menu choices: File → Print → ~~New Page~~

*Active Window  
Set 4.22.16*

7.4.3.12.7 At the bottom of each set of readings, a summary of the X and Y viewing position settings is printed.

7.4.3.12.7.1 In Axial mode, the magnitude of the X setting should not be greater than 0.4 mm and the Y setting should be within 14.5 to 15.5 mm.

7.4.3.12.7.2 In Radial mode, the magnitude of the X setting should not be greater than 0.5 mm.

7.4.3.12.8 Place the printouts of the Mn Alignments in the Optima 8300 MnBEC binder.

7.4.3.13 Instrument is now ready for analytical work.

## 7.4.4 Run Hg realign:

7.4.4.1 On the first run of each week, perform a Hg Realign.

7.4.4.2 Click the "Hg Realign" button in the Spectrometer Control window.

7.4.4.3 Record the intensity value obtained in the Run Log.

7.4.4.4 If the intensity value is significantly different than previous Hg Realign intensities, perform the Hg Realign again. If the second value is still significantly different than the historical intensities, troubleshoot the instrument.

## 7.5 Set Up the Sample Information File (SIF).

## 7.5.1 Open SIF.

7.5.1.1 Click the Smpinfo button on the toolbar to open the Sample Information Editor.

7.5.1.2 For most methods, positions 1, 2, 3, 4, and 5 are reserved for the calibration blank, working calibration standard, ICV/CCV standard, ICB/CCB solution, and CRI standard respectively.

| Position # | Solution             |
|------------|----------------------|
| 1          | Calibration Blank    |
| 2          | Calibration Standard |
| 3          | ICV/CCV standard     |
| 4          | ICB/CCB solution     |
| 5          | CRI standard         |

Note that these position assignments can be changed, if necessary. These are the current settings. Also note that positions 6 through 8 may be left empty due to the size of container needed to fit in that position in the sampler. More complex methods may use more than one calibration

and ICV/CCV solution, which may shift these position numbers around a bit. The listing here is for general guidance only.

**7.5.2 Run Sequence:**

7.5.2.1 The run sequence and QC program are patterned after that used in the U.S. EPA Contract Laboratory Program (CLP).

7.5.2.2 An example run sequence, along with the identities and common abbreviations of the various QC checks, is provided in Table 2.

7.5.2.3 Note that the SIF does not have to specify the frequency for the analysis of ICV/ICB/CRI standards or CCV/CCB pairs as this is specified in the method file.

**7.5.3 Create and Save SIF.**

7.5.3.1 In the sample information editor, enter the appropriate client sample IDs in their corresponding autosampler location lines.

7.5.3.2 Save the sample information file as YYMMDDX...X, where YYMMDD is the year/month/date of sample preparation/digestion and X..X is the client name.

**8.0 Procedure**

**8.1 Load the sample information file (SIF):**

8.1.1 In the Automated Analysis window, click on the Set Up tab.

8.1.2 Click on the "open" button next to the SIF box, highlight the appropriate Sample Information file, then click "OK".

8.2 Set up the data file:

- 8.2.1 In the Automated Analysis window, click on Results → Open.
- 8.2.2 In the Results Data Set box, type in the data file name (same as the SIF filename, see Section 7.5.3), or choose an existing Result Data File name by clicking on the “open” button next to the results box, then double clicking on the appropriate filename.
- 8.2.3 Click OK.

8.3 Set up the run sequence:

- 8.3.1 In the Set Up tab of the Automated Analysis window, under the heading “Sample Info File”, pull down the menu that defaults to “All Defined” and choose “Sample Locations” instead.
- 8.3.2 In the Use Autosampler Locations column, type in the locations of all client samples, including the duplicate and spike. Do NOT type in the locations of the calibration standards, ICV, ICB, CRI, CCV, CCB, etc. For example, the “Use Autosampler Locations” box may read “9-27”.
- 8.3.3 Uncheck the “Print Log During Analyses” box.
- 8.3.4 Verify that all elements are to be saved by verifying the Enable/Disable Elements box in the Analysis window. All elements must be selected, even if they are not to be reported to the client.

8.4 Load the autosampler:

- 8.4.1 Click on the “Analyze” tab at the bottom of the Automated Analysis window, then click on the “Rebuild List” button.
- 8.4.2 Using the displayed analytical list as a guide, load the autosampler as follows:

8.4.2.1 Prepare dilutions or pour the appropriate standards and samples into appropriate autosampler vials.

8.4.2.2 Place the standards and samples into their corresponding autosampler locations.

8.5 Start run:

8.5.1 In the "Analyze" tab of the "Automated Analysis" window, click "Analyze All".

8.5.2 "Analyze All" will run, in order, the calibration blank/standards, ICV/ICB, CRI, standards and all continuing QC standards.

8.6 Monitor the run to ensure instrument performance.

8.6.1 Watch the instrument analyze the standard, calibration blank, ICV, ICB and CRI to ensure proper operation of the system.

8.6.2 After this, the instrument may be left unattended, although the analyst should check intermittently to ensure that all systems are operating properly. ~~See~~ ~~Analyst Notes 13.3 and 13.4.~~ *9/4 4-22-16*

8.6.3 As the data is generated, note the response factor. A response of "saturation" or any other error code indicates detector saturation. For such cases, there are several different means by which to lower the count.

8.6.3.1 Dilute the sample and reanalyze.

8.6.3.1.1 This is the favored method as it retains the previous detection limit and does not require separate settings or element files to achieve usable data.

8.6.3.1.2 Samples must be diluted using the same matrix as the other samples/standards to ensure proper matrix matching. This is most easily performed by utilizing the blank solution as the diluent.

8.6.3.2 Use a different emission line or switch to a different viewing axis:

8.6.3.2.1 Each element has more than one emission line and two different views by which it can be read. By utilizing a secondary or tertiary emission line or by switching to a different view (Axial to Radial), then recalibrating the instrument, the analyst can lower the emission counts at the higher concentration level.

8.6.3.2.2 See the index of emission lines in the method development window of the WinLab32 software for more specific information.

8.6.3.2.3 Note that using a different emission line or viewing axis will change the detection limit for that analyte, and will require the analyst to develop a new method to include the completion of a detection limit study and Precision and Bias study.

8.7 Examine Spectra:

8.7.1 After analysis, use the Examine Spectra function of the software to check the data. *This may be performed in the Winlab Offline program. Set 4.22.16*

8.7.1.1 Click the Examine button on the toolbar at the top of the screen.

8.7.1.2 In the "Data" pull down menu, click on "Select Data Set", then choose the data file associated with the samples of interest.

8.7.1.3 A new window will appear containing a list of samples to choose from. Scroll down and highlight the samples of interest, then click "Next".

- 8.7.1.4 Another window will appear containing a list of elements to choose from. Click "select all", then click "Finish".
- 8.7.1.5 The spectra of the first element in the file will be shown for all selected samples.
- 8.7.1.6 Examine the spectra for peak centroid location and background marker locations. Only the elements requested by the client need to be examined, although examination of other elements may be of value in data interpretation or instrument troubleshooting.
- 8.7.1.7 If peak centroids or background correction markers are incorrect, reprocess the data as follows:
  - 8.7.1.7.1 Within the Examine Spectra window, use the mouse to drag the yellow wavelength marker line to the highest point of the peak shown. To save this change, either press "p" on the keyboard, or choose "set peak wavelength" from the "Method" pull down menu.
  - 8.7.1.7.2 Use the mouse to drag the green crosshair background adjustment markers to either side of the analyte peak such that the marker is not on the shoulder of the analyte or any other interferent peak and is as low as possible.
  - 8.7.1.7.3 Next SAVE THE CHANGES TO THE METHOD by choosing the "Update Method Parameters" option under the "Method" pull down menu at the top of the "Examine" Window. A new dialog box will appear, click "Update and Save Method".
  - 8.7.1.7.4 Click the double arrow button at the bottom of the window to progress to the next element. Perform the steps outlined above to each element in the series until all wavelengths for all elements requested by the client have been verified or corrected.

8.7.1.7.5 Next, reprocess the data using the reprocess function of the software. To avoid confusion, save the reprocessed data to a file named "YYMMDDX..X RE."

8.7.1.7.6 Print the run, including all calibration and QC samples, selecting only those analytes requested by the client.

8.8 Instrument shut down.

8.8.1 **Standby shut-down:** Shut the instrument down in the following manner if the instrument will be used again within the next 48 hours.

8.8.1.1 Leave the following ON:

- 8.8.1.1.1 Chiller
- 8.8.1.1.2 Instrument
- 8.8.1.1.3 Argon tank
- 8.8.1.1.4 Computer

8.8.1.2 Turn off the plasma using the "switch" in the Plasma Control window of the software.

8.8.1.3 Close the WinLab<sup>32</sup> software.

8.8.1.4 Remove spray chamber from torch assembly.

8.8.1.5 Remove tubing from the sample introduction peristaltic pump.

8.8.1.6 Open the pressure lever on the Autosampler peristaltic pump.

8.8.1.7 Turn off the argon pressure building valve (leave the tank on and the regulator open).

8.8.1.8 Turn off air compressor and dryer.

8.8.1.9 If desired, turn off the computer.

8.8.1.10 Cover chimney with stainless steel pan to avoid contamination from exhaust venting.

8.8.1.11 Open torch chamber door to cool inside of chamber.

8.8.2 **Long term shut-down:** If the instrument is not going to be used for more than 48 hours, shut down in the following manner :

8.8.2.1 Leave the following ON:

8.8.2.1.1 Instrument

8.8.2.1.2 Argon tank

8.8.2.1.3 Computer, if desired

8.8.2.2 Turn off the plasma using the "switch" in the Plasma Control window of the software.

8.8.2.3 Close the WinLab32 software.

8.8.2.4 Turn off the chiller.

8.8.2.5 Remove spray chamber from torch assembly.

8.8.2.6 Remove tubing from the sample introduction peristaltic pump.

8.8.2.7 Open the pressure lever on the Autosampler peristaltic pump.

8.8.2.8 Turn off the argon pressure building valve (leave the tank on and the regulator open).

8.8.2.9 Turn off air compressor and dryer, and drain the water from the compressor tank.

8.8.2.10 If desired, turn off the computer.

8.8.2.11 Cover chimney with stainless steel pan to avoid contamination from exhaust venting.

8.8.2.12 Open torch chamber door to cool inside of chamber.

8.8.3 **Complete shut-down:** This is only performed for instrument servicing, power outages or if the instrument is being physically moved:

8.8.3.1 Turn off the plasma using the "switch" in the Plasma Control window of the software.

8.8.3.2 Close the WinLab32 software.

8.8.3.3 Turn off the instrument once the software has fully shut down.

8.8.3.4 Turn off the computer.

8.8.3.5 Shut off the Argon tank pressure building valve, gas valve and gas regulator valve.

8.8.3.6 Turn off the chiller.

8.8.3.7 Remove spray chamber from torch assembly.

8.8.3.8 Remove tubing from the sample introduction peristaltic pump.

8.8.3.9 Open the pressure lever on the Autosampler peristaltic pump.

8.8.3.10 Turn off air compressor and dryer, and drain the water from the compressor tank.

8.8.3.11 Cover chimney with stainless steel pan to avoid contamination from exhaust venting.

## 9.0 QA/QC

## 9.1 Triplicate readings.

- 9.1.1 Frequency: all standards and samples
- 9.1.2 QC statistic: percent relative standard deviation (%RSD)
- 9.1.3 Control limits:  $\pm 20\%$
- 9.1.4 Corrective action: check sample introduction system and torch condition; re-analyze sample; if control limits exceeded second time, flag result(s). See analyst's note 13.3.
- 9.1.5 Report the average of the readings.
- 9.1.6 Note: control limits do not apply if one or more of the triplicate readings are less than the quantitation limit.

## 9.2 Calibration Correlation Coefficient (for routine ICP analyses, the correlation coefficient is always 1.000 as calibration consists of a blank and a single standard)

- 9.2.1 Frequency: once, immediately after analysis of the calibration standard(s)
- 9.2.2 QC statistic: correlation coefficient,  $r$
- 9.2.3 Control limits:  $> 0.995$
- 9.2.4 Corrective action: terminate analysis, recalibrate using same standards. If control limits exceeded a second time, review instrument operating parameters, recalibrate using freshly prepared standards.

*Control limit where result is near or below DL: 2 of the three readings must be above or below the DL and*

*must be the same as the average (e.g.,  $\bar{x} < DL$ , 2 readings must be  $< DL$ )*

*Corrective action: reanalyze if possible. Sit 4.22-16*

## 9.3 Initial Calibration Verification Standard (ICV).

- 9.3.1 Frequency: once, immediately after generating an acceptable calibration curve
- 9.3.2 QC statistic: percent recovery
- 9.3.3 Control limits: 90-110 %
- 9.3.4 Corrective action: terminate analysis, recalibrate using same standards. If control limits exceeded a second time, review instrument operating parameters, recalibrate using freshly prepared standards.
- 9.3.5 Note: this QC check and the recalibrate corrective action are done automatically by the WinLab32 <sup>Sit 4.22-16</sup> software and can be modified in the method file for each element. See Analyst Notes 13.1 and 13.2.

## 9.4 Initial Calibration Blank (ICB).

- 9.4.1 Frequency: once, immediately after the analysis of the ICB
- 9.4.2 QC statistic: analysis result
- 9.4.3 Control limits: no analyte result above detection limit. For CLP QC, the absolute value of the result cannot be greater than the IDL (check for large negative interferences)
- 9.4.4 Corrective action: terminate analysis, recalibrate using the same standards, reanalyze the ICB and ICB. If analyte is above detection limit, review instrument operating parameters, recalibrate using freshly prepared standards. See Analyst Notes 13.1 and 13.2.
- 9.4.5 Note: this QC check and the recalibrate corrective action are done automatically by the WinLab32 software and can be modified in the method file for each element. The acceptable parameters set in each method file are -DL to +DL for each element.

## 9.5 Low Level Calibration Recovery ICP Standard (CRI or LLCCV)

- 9.5.1 Frequency: once, immediately after ICB
- 9.5.2 QC statistic: percent recovery
- 9.5.3 Control limits: 70-130 %
- 9.5.4 Corrective action: terminate analysis, recalibrate using same standards. If control limits exceeded a second time, review instrument operating parameters, recalibrate using freshly prepared standards.
- 9.5.5 Note: ~~The instrument will automatically abort the run if this QC element is out of control.~~ 3-22-16 *TKW*

## 9.6 Preparation Blank.

- 9.6.1 Frequency: once, immediately after the analysis of the ICB *CRF 3-22-16 ymr*
- 9.6.2 QC statistic: analysis result
- 9.6.3 Control limits: analyte result less than the method blank result, within  $\pm$  the detection limit from the method blank result, or *less than set 4-22-16* ~~within  $\pm 20\%$  RPD~~ of the method blank result. For CLP QC, the absolute value of the result cannot be greater than the DL.
- 9.6.4 Corrective action: reanalyze if possible. If re-analysis concentration(s) above DL, terminate analysis and redigest sample batch. If redigestion is not possible, note the results in the Case Narrative. See Analyst Notes 13.1 and 13.2.

## 9.7 Method Blank.

- 9.7.1 Frequency: once, immediately after the analysis of the reagent blank
- 9.7.2 QC statistic: analysis result
- 9.7.3 Control limits: none, but analyte(s) should be  $<$  the lowest sample result, within either  $\pm 20\%$  RSD of the lowest sample result, or  $\pm$  detection limit of the lowest sample result.
- 9.7.4 Corrective action: report concentration and note in the Case Narrative. Sampling media *commonly set 4-22-16* ~~often~~ contribute to analyte results.

## 9.8 Laboratory Control Sample (LCS).

- 9.8.1 Frequency: one per digestion batch of twenty client samples
- 9.8.2 QC statistic: percent recovery (with blank subtraction as needed)
- 9.8.3 Control limits: 80-120%
- 9.8.4 Corrective action: reanalyze if possible. If re-analysis concentration(s) remain out of control, terminate analysis and redigest sample batch. If redigestion is not possible, note the results in the Case Narrative. See Analyst Notes 13.1 and 13.2.
- 9.8.5 Note: control limits do not apply for silver and antimony

9.9 Continuing Calibration Verification Standard (CCV).

- 9.9.1 Frequency: after every ten analyses past the CRI and at the end of the analytical run.
- 9.9.2 QC statistic: percent recovery
- 9.9.3 Control limits: 90-110 %
- 9.9.4 Corrective action: terminate analytical run, recalibrate; reanalyze ICV, ICB, all affected samples. See Analyst Note 13.1 and 13.2.

9.10 Continuing Calibration Blank (CCB).

- 9.10.1 Frequency: immediately after the analysis of every CCV
- 9.10.2 QC statistic: analysis result
- 9.10.3 Control limits: no analyte above instrument detection limit (DL). For CLP QC, the absolute value of the result cannot be greater than the IDL (check for large negative interferences)
- 9.10.4 Corrective action: terminate analytical run, recalibrate, reanalyze ICV, ICB, method blank, all affected samples, CCV. See Analyst Note 13.1 and 13.2.

9.11 Duplicate Sample.

- 9.11.1 Frequency: once per digestion batch of  $\leq 20$  samples
- 9.11.2 QC statistic: relative percent difference (RPD)
- 9.11.3 Control limits:  $\pm 20\%$
- 9.11.4 Corrective action: re-analyze sample and duplicate; if still outside control limits, report to client and note in case narrative.
- 9.11.5 Note: control limits do not apply if one or both of the analysis results is below the quantitation limit.

## 9.12 Laboratory Replicate.

- 9.12.1 Frequency: once per digestion batch of  $\leq 20$  samples. This is a duplicate aliquot of the final sample digestate and is performed in lieu of a duplicate when there is not enough original sample to take more than one aliquot for digestion.
- 9.12.2 QC Statistic: relative percent difference (RPD)
- 9.12.3 Control limits:  $\pm 20\%$  RPD
- 9.12.4 Corrective action: re-analyze sample and replicate; if still outside control limits, report to client and note in case narrative.
- 9.12.5 Note: control limits do not apply if one or both of the analysis results is below the quantitation limit

## 9.13 Matrix (Pre-Digestion) Spike.

- 9.13.1 Frequency: once per digestion batch of  $\leq 20$  samples
- 9.13.2 QC statistic: percent recovery
- 9.13.3 Control limits: 75-125%
- 9.13.4 Corrective action: re-analyze sample and spike. If control limits still exceeded, report to client and note in case narrative.
- 9.13.5 Note: control limits do not apply for the elements silver or antimony or if the sample concentration exceeds the spike concentration by a factor of four or more (spike amount  $\leq \frac{1}{4}$  sample result).

## 9.14 Analytical (Post-Digestion) Spike.

- 9.14.1 Frequency: once per digestion batch of  $\leq 20$  samples. This is a spike of a duplicate aliquot of the final sample digestate and is performed in lieu of a pre-digestion spike when there is not enough original sample to take more than one aliquot for digestion.
- 9.14.2 QC statistic: percent recovery
- 9.14.3 Control limits: 75-125%
- 9.14.4 Corrective action: re-analyze sample and spike; if still outside control limits, report to client and note in case narrative.
- 9.14.5 Note: control limits do not apply for the elements silver or antimony or if the sample concentration exceeds the spike concentration by a factor of four or more (spike amount  $\leq \frac{1}{4}$  sample result).

9.15 CLP QC (Client request only). Interference Check Sample ICS-A.

- 9.15.1 Frequency: immediately after the analysis of the ICB and at the end of the run before the final CCV/CCB pair
- 9.15.2 QC statistic: analysis result
- 9.15.3 Control limits: except for the interferents, no analyte result above the instrument detection limit (IDL)
- 9.15.4 Corrective action: terminate analysis, correct problem, recalibrate instrument, re-analyze client samples

9.16 CLP QC (Client request only). Interference Check Sample ICS-AB.

- 9.16.1 Frequency: immediately after the analysis of interference check sample ICS-A.
- 9.16.2 QC statistic: percent recovery
- 9.16.3 Control limits: 80-120%
- 9.16.4 Corrective action: terminate analysis, correct problem, recalibrate instrument, reanalyze client samples. See Analyst Note 13.4.

9.17 CLP QC (Client request only). Serial Dilution (5-fold dilution of sample or digestate).

- 9.17.1 Frequency: once per digestion batch of twenty client samples
- 9.17.2 QC statistic: percent difference from the undiluted sample
- 9.17.3 Control limits:  $\pm 10\%$
- 9.17.4 Corrective action: re-analyze sample and serial dilution; if control limits still exceeded, flag all client sample analysis results with the letter " E "
- 9.17.5 Note: control limits do not apply if the concentration in the undiluted sample is less than fifty times the instrument detection limit

## 10.0 Calculations

10.1 Calibration curve: The calibration curve utilized is that of the "line of best fit" or "regression line" (see 10.2) The calibration curve is algebraic, in the form of:

$$y = mx + b$$

where:

y = dependent variable (instrument response in milli-absorbance units)

m = slope of the line of best fit as determined by the instrument software

x = independent variable (concentration)

b = y intercept of the line of best fit as determined by the instrument software

10.2 Linear regression: It is unclear from the software or the manual exactly how WinLab32 software performs linear regression. In general, the statistical computation of the regression line is as follows:

$$\hat{y} = \beta_0 + \beta_1 x$$

Where:

$$\beta_0 = \bar{y} - \beta_1 \bar{x}$$

$$\beta_1 = r * (\sigma_y / \sigma_x)$$

Where:

$\bar{y}$  = average of all y data points

$\bar{x}$  = average of all x data points

r = correlation coefficient (see 10.3)

$\sigma_y$  = standard deviation of y values

$\sigma_x$  = standard deviation of x values

$\beta_0$  = constant in the regression equation

10.3 Correlation coefficient: The correlation coefficient or "Pearson product moment coefficient of correlation" is the proportion of the variance in the dependent variable that is predictable from the independent variable. In English, it is a measurement of how close the data set fits a "true line". The closer to 1 the correlation coefficient is, the closer all points are to lying on the line of best fit.

$$\frac{n\sum xy - (\sum x)(\sum y)}{\{\sqrt{[n(\sum x^2) - (\sum x)^2]}\} \{\sqrt{[n(\sum y^2) - (\sum y)^2]}\}}$$

Where:

n = number of (x,y) data points in the curve

y = dependent variable (instrument response in milli-absorbance units)

x = independent variable (concentration)

Note that for a calibration curve consisting of only two point (blank and one standard), the correlation coefficient will always be 1.0000, as the minimum number of data points required to define a line is two.

10.4 Final Concentrations of Samples. The WinLab32 software calculates the concentrations of analytes in the final digestates based upon the standard curve determined by the line of best fit. Dilution factors, including final digestate volumes, aliquot sizes, weights of soils digested, etc., can be entered into the sample information file. The computer will then automatically calculate the correct concentrations. Alternately, the analyst can perform the calculations by hand.

10.5 Analysis of Filters in  $\mu\text{g}/\text{filter}$ :

$$(\mu\text{g}/\text{L from instrument})(\text{L extraction solution used})(\text{total filter area}/\text{filter area digested})$$

Note: when the entire filter is digested, as with Teflon filters, *(total filter area/filter area digested)* will be 1. For large filters, such as 8" x 10" high vol filters, a portion of the deposit area is digested, at which point, *(total filter area/filter area digested)* becomes critical in the calculation.

10.6 Analysis of Filters in  $\mu\text{g/L}$  (air volume):

$$\frac{(\mu\text{g}/\text{filter})}{L \text{ air volume sampled}}$$

10.7 Analysis of Filters in  $\mu\text{g}/\text{m}^3$  (air volume)

$$\frac{(\mu\text{g}/\text{filter})}{\text{m}^3 \text{ air volume sampled}}$$

10.8 Analysis of source samples in  $\mu\text{g}/\text{sample}$ :

$$(\mu\text{g}/L \text{ from instrument})(L \text{ total impinger solution volume})$$

10.9 Analysis of source samples in  $\mu\text{g}/\text{L}$  (air volume):

$$\frac{(\mu\text{g}/\text{sample})}{L \text{ air volume sampled}}$$

10.10 Analysis of source samples in  $\mu\text{g}/\text{m}^3$  (air volume)

$$\frac{(\mu\text{g}/\text{sample})}{\text{m}^3 \text{ air volume sampled}}$$

10.11 Analysis of samples in  $\mu\text{g}/\text{dscm}$  or  $\mu\text{g}/\text{dscf}$  or any other "dry standard" gas volume: the laboratory does not do any calculations to convert data into "dry standard" volumes. This is the responsibility of the client.

- 10.12 Air volume in Standard Temperature and Pressure: if requested by the client, and if the client provides the meteorological data, flow rate, and length of time sampled, the laboratory will convert the air results into standard temperature and pressure using the following equations (obtained from the QA handbook, section 2.12, PM2.5 reference for particulate emissions as promulgated by the EPA in the CFR):

$$V_{std} = F_{std}(T_2 - T_1)$$

Where:

$V_{std}$  = total volume pulled (L or m3) at standard temperature and pressure

$F_{std}$  = flow rate at standard temperature and pressure (see above)

$T_2$  = time of end of sampling

$T_1$  = time of beginning of sampling

$$F_{std} = F(\bar{P}/P_{std})(T_{std}/\bar{T})$$

Where:

$F_{std}$  = flow rate in standard temperature and pressure

$\bar{F}$  = average flow rate during sampling

$\bar{P}$  = average pressure during sampling

$P_{std}$  = standard pressure

$\bar{T}$  = average temperature during sampling

$T_{std}$  = standard temperature

- 10.13 Analysis of samples in  $\mu\text{g/L}$ :

$$(\mu\text{g/L from instrument})(\text{dilution or concentration factor of digestion})$$

- 10.14 Analysis of samples in  $\mu\text{g/g}$ :

$$(\mu\text{g/L from instrument})(L \text{ digestate volume/g sample aliquot digested})$$

- 10.15 For calculation of QC sample statistics, refer to the Chester LabNet Quality Assurance Management Plan.

## 11.0 References

- 11.1 Perkin-Elmer Optima 8300 Emission Spectrophotometer Operators Manual.
- 11.2 U.S. EPA. 1990. U.S. EPA Contract Laboratory Program Statement of Work. ILM01.0, 3/90. U.S. Environmental Protection Agency, Washington, DC.
- 11.3 U.S. EPA. 1999. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, Method IO-3.4. EPA-625/R-96/101a. Office of Research and Development, Washington, DC.
- 11.4 U.S. EPA. Feb. 2007. Test Methods for Evaluating Solid Waste. SW-846, Method 6010C. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC.

## 12.0 Definitions

- 12.1 Analyst: the designated individual who performs the “hands-on” method and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.
- 12.2 Analysts' Notes: Non-essential aspects of a method, which may help the analyst during some phase of the method. Notes may include, but not be limited to, historical aspects of the method, “tricks” of the method, unexpected issues to be aware of, or other facts or opinions related to the method, but not directly part of the procedure.
- 12.3 Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.
  - 12.3.1 Analytical Batch: a group of prepared samples (extracts/digests etc) that are analyzed together as a group, although they may have been prepared separately.
  - 12.3.2 Preparation Batch: a group of one to 20 samples of the same matrix which are prepared together as a group, and which share common QC samples.
- 12.4 Blank: a clean aliquot of the same matrix as the digested samples. A blank is subjected to the usual analytical and measurement processes.
  - 12.4.1 Calibration Blank: An unspiked clean matrix of similar constitution as the sample extracts or digests (e.g. DI Water, 5% HNO<sub>3</sub> etc) used to establish the zero intercept of the calibration curve.

- 12.4.2 Method Blank: An unspiked clean sampling media aliquot, taken through the entire preparation and analytical processes associated with a method. This blank determines if the sampling media may be contributing any analyte of interest in the samples.
- 12.4.3 Preparation Blank: All reagents involved in the preparation, without sampling media (if any), taken through the entire preparation and analytical processes associated with a method. This blank demonstrates cleanliness of reagents and of the preparation process itself.
- 12.4.4 Reagent Blank: All reagents, mixed in correct proportion, used in the preparation of samples, however, not taken through the preparation process. This blank is rarely used, and usually only used when some question arises as to the source of contamination (reagents vs. process).
- 12.4.5 Field Blank: A blank prepared by the client in the field. This blank is treated as a sample by the laboratory.
- 12.5 Calculations (Data Reduction): the mathematical process of transforming raw data into a more useable form.
- 12.6 Calibrate: to determine, by measurement or comparison with a standard, the correct value of each reading of the instrument.
- 12.7 Calibration Curve: the graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements where possible.
- 12.8 Calibration Standard: a substance or reference material used to calibrate and instrument.
- 12.9 Continuing Calibration Blank (CCB): A blank "standard" analyzed at the end of an analytical batch and at least every 10 samples during an analytical batch to verify that the lower end of the calibration curve remains valid during the course of the analytical run.
- 12.10 Continuing Calibration Verification Standard (CCV): A calibration standard analyzed at the end of an analytical batch and at least every 10 samples during an analytical batch to verify that the calibration curve remains valid during the course of the analytical run. The concentration of the CCVs should vary over the course of the analytical run.
- 12.11 Control Limit: A mathematical representation of acceptable limits for a given Quality Control Metric such as percent recovery or percent difference. Limits may be in the form of an absolute number or represented as a percentage.
- 12.12 Corrective Action: the action taken to address and/or eliminate where possible the causes of a nonconformity, such as exceeding a control limit. Actions may include reanalyzing a sample, or noting the non-conformance in the data report.

- 12.13 Correlation Coefficient: the statistical representation of how closely a set of x,y coordinates comes to a true line. A correlation coefficient of 1.000 is considered a perfectly straight line. Correlation coefficients above 0.995 are usually attainable by most instruments.
- 12.14 CRI: low level standard analyzed at the beginning of each run to verify low end accuracy of calibration curve. Typically this standard concentration is three- or five-times the detection limit, depending on the regulatory agency.
- 12.15 Detection Limit: the lowest concentration of an analyte of interest that can be identified, measured and reported with confidence that the analyte concentration is not a false positive value.
- 12.15.1 Instrument Detection Limit (IDL or LOD): The detection limit determined at the instrument using a clean matrix and no preparation. (Note that "LOD" may refer to either an instrument detection limit or a method detection limit, depending on the method being utilized).
- 12.15.2 Method Detection Limit (MDL or LOD): The detection limit determined by processing clean matrix through the entire method, including all preparatory steps. (Note that "LOD" may refer to either an instrument detection limit or a method detection limit, depending on the method being utilized).
- 12.15.3 Quantitation Limit (PQL or LOQ): The limit at which, not only is the laboratory confident that the concentration is not a false positive, but that the concentration reported is within acceptable limits from the true value.
- 12.16 Duplicate: A second aliquot of a sample, taken through all steps of the method, including digestion/preparatory stages.
- 12.17 Frequency: The number of occurrences of a specified event within a given interval. The number of samples or analytical runs with which a given QC sample or metric must be analyzed or verified.
- 12.18 Holding Time: the maximum times that samples may be held prior to analysis while still being considered valid or non-compromised.
- 12.19 Initial Calibration Blank (ICB): A blank "standard" analyzed at the beginning of an analytical batch immediately after calibration.
- 12.20 Initial Calibration Verification Standard (ICV): A standard analyzed at the beginning of an analytical batch immediately after calibration that verifies the calibration curve. This standard must be of a different source than the standards used to calibrate the instrument.
- 12.21 Laboratory Control Standard (LCS): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. Generally used to establish analyst specific precision and bias or to assess the performance of the method.

- 12.22 Laboratory Control Standard Duplicate (LCS-D): a duplicate sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. Generally used to establish analyst specific precision and bias or to assess the performance of the method.
- 12.23 Laboratory Information Management System (LIMS): a comprehensive computerized database system that a laboratory uses for sample tracking and data management, from sample receipt to reporting and archiving.
- 12.24 Matrix/Matrices: the component or substrate that contains the analyte of interest.
- 12.25 QA/QC: Quality Assurance/Quality Control. A series of samples or metrics designed to show precision, accuracy and bias of the procedure are within acceptable limits.
- 12.26 QC Statistic: any of a number of statistical permutations performed on raw data to generate a metric capable of being subjected to control limits and corrective actions.
- 12.27 Reagent: a single chemical or combination of chemicals or a chemical solution used in the preparation or analysis of samples.
- 12.28 Replicate: A second aliquot of a single preparation (digest, extract etc) analyzed in tandem with the primary aliquot. Usually a replicate is analyzed only when a true duplicate is not possible, which normally occurs with very small sample quantities.
- 12.29 Spike: to add verified known amounts of analytes or a material containing known and verified amounts of analytes to a sample or matrix prior to analysis.
- 12.29.1 Analytical (Post-Digestion) Spike: an aliquot of prepared sample to which verified known amounts of analytes or a material containing known and verified amounts of analytes are added to a sample prior to analysis.
  - 12.29.2 Matrix Spike: a sample prepared by adding verified known amounts of analytes or a material containing known and verified amounts of analytes to a sample or matrix prior to preparation for analysis.
- 12.30 Standard: a solution or matrix of a known amount of analyte(s).
- 12.30.1 Primary standard: a standard received from a vendor with NIST or equivalent traceability.
  - 12.30.2 Secondary standard: a standard received from a vendor with NIST or equivalent traceability of a different manufacturer or lot number than the primary standard.
  - 12.30.3 Working standard: any standard created when mixing, diluting or otherwise manipulating aliquots of primary standards. May be called "working standards" or "intermediate standards".

### 13.0 Analysts' Notes

- 13.1 If standard and sample matrices are not similar, one or more of the following QC checks may fail: preparation blank, method blank, LCS, and spiked sample.
- 13.2 Wide variability may be observed between the triplicate readings. This can result in blanks and ICVs or CCVs being out of control limits. Problems that can cause this are (in order of increasing difficulty in corrective actions):
- 13.2.1 Worn peristaltic pump tubing (replace tubing or adjust pump clamp pressure).
  - 13.2.2 Partially clogged sample introduction system: replace nebulizer tubing, clean sample probe tip with cleaning wire, back flush nebulizer with syringe and Acetone followed by DI water. (Note that touching the tip of the nebulizer may ruin the nebulizer entirely as the tip is composed entirely of Teflon, which is very soft).
  - 13.2.3 Drain line is not functioning well (replace drain line peristaltic tubing or adjust pump clamp pressure)
  - 13.2.4 Worn torch assembly o-rings (remove torch assembly and replace all o-rings and seals)
  - 13.2.5 RF power unstable (must be addressed by Perkin Elmer technician)
  - 13.2.6 Air leak into plasma or torch chamber (must be addressed by Perkin Elmer technician)
- 13.3 Failure of the ICS-AB QC check is often caused by picking inadequate background correction wavelengths for the element file. To correct, aspirate the ICS-AB solution and re-set the upper and lower background correction lines per Section 8.7, above.
- 13.4 Silver and Tin standards may need to be prepared as single element standards. Silver standards are best stored in a Teflon bottle. Both Silver and Tin have shown rapidly decreasing levels over time even when stored in HNO<sub>3</sub> or HCl solutions. Both elements are known to have problems staying in solution when prepared with other elements in the same

solution.

- 13.5 For some clients, a second source of standard is not used for ICV/CCV or spike solutions. This can be the case when the client requests an uncommon analyte (Hafnium, Lanthanum, Polonium etc) and the client is either providing or being billed for the standard itself. Frequently the client does not wish to incur the additional charge for a second source standard. In such cases, although a different lot is not used, a second standard will be prepared. The lack of a second source is noted in the case narrative.

| <u>ELEMENT</u> | <u>WAVELENGTH</u><br>(nm)         | <u>AXIAL OR RADIAL</u> | <u>STANDARDS</u><br>(ppm) |
|----------------|-----------------------------------|------------------------|---------------------------|
| Aluminum       | 308.215 <i>376.153</i>            | Axial                  | 5                         |
| Antimony       | 206.836                           | Axial                  | 5                         |
| Arsenic        | 193.696                           | Axial                  | 5                         |
| Barium         | 233.527                           | Axial                  | 5                         |
| Beryllium      | 313.107                           | Axial                  | 5                         |
| Boron          | 249.677 <i>3-22-16 76</i>         | Axial                  | 5                         |
| Cadmium        | <del>214.440</del> <i>226.502</i> | Axial                  | 5                         |
| Calcium        | 317.933                           | Axial                  | 5                         |
| Chromium       | 267.716                           | Axial                  | 5                         |
| Cobalt         | 228.616                           | Axial                  | 5                         |
| Copper         | 324.752                           | Axial                  | 5                         |
| Iron           | 238.204                           | Axial                  | 5                         |
| Lead           | 220.353                           | Axial                  | 5                         |
| Magnesium      | 279.553                           | Axial                  | 5                         |
| Manganese      | 257.610                           | Axial                  | 5                         |
| Molybdenum     | 202.031                           | Axial                  | 5                         |
| Nickel         | 231.604                           | Axial                  | 5                         |
| Phosphorous    | 214.914                           | Axial                  | 5                         |
| Potassium      | 766.490                           | Axial                  | 5                         |
| Selenium       | 196.026                           | Axial                  | 5                         |
| Silver         | 328.068                           | Axial                  | 5                         |
| Sodium         | 589.592                           | Axial                  | 5                         |
| Titanium       | 334.940                           | Axial                  | 5                         |
| Thallium       | 190.801 <i>3-22-16 76</i>         | Axial                  | 5                         |
| Vanadium       | <del>309.310</del> <i>292.402</i> | Axial                  | 5                         |
| Zinc           | 213.857                           | Axial                  | 5                         |

Note: The standard concentrations and wavelengths may change, depending upon the samples being run or at client request. The values listed are only to be used as guidelines; they are not mandatory and should not be considered static.

**Table 1. Element-Specific Operating Information**

Table 2: Run sequences for ICP.

| Routine Run Sequence                                           | CLP Run Sequence         |
|----------------------------------------------------------------|--------------------------|
| Calibration Standard                                           | Calibration Standard     |
| Calibration Blank                                              | Calibration Blank        |
| ICV                                                            | ICV                      |
| ICB                                                            | ICB                      |
| <i>CPI →</i><br><i>3-22-16</i><br><i>Pub</i> Preparation Blank | ICS-A                    |
| Method/Matrix Blank                                            | ICS-AB                   |
| LCS                                                            | CRI-I                    |
| Sample 1                                                       | Preparation Blank        |
| Sample 1 Duplicate                                             | Method/Matrix Blank      |
| Sample 2                                                       | LCS                      |
| Sample 2 Spike                                                 | Sample 1                 |
| Sample 3 - 5                                                   | Sample 1 Duplicate       |
| CCV 1                                                          | Sample 2                 |
| CCB 1                                                          | Sample 2 Spike           |
| Sample 6 - 15                                                  | CCV 1                    |
| CCV 2                                                          | CCB 1                    |
| CCB 2                                                          | Sample 3                 |
| Sample 16 - 20                                                 | Sample 3 Serial Dilution |
| CCV 3                                                          | Sample 4 - 12            |
| CCB 3                                                          | CCV 2                    |
|                                                                | CCB 2                    |
|                                                                | Sample 13 - 20           |
|                                                                | CCV 3                    |
|                                                                | CCB 3                    |
|                                                                | CRI-F                    |
|                                                                | ICS-A                    |
|                                                                | ICS-AB                   |
|                                                                | CCV 4                    |
|                                                                | CCB 4                    |

Notes:

- ICV = Initial Calibration Verification Check Standard
- ICB = Initial Calibration Blank Check
- LCS = Laboratory Control Sample
- CCV = Continuing Calibration Verification Check Standard
- CCB = Continuing Calibration Blank Check
- ICS-A = Interference Check Blank
- ICS-AB = Interference Check Standard
- CRI-I = Initial Contract Required Detection Limit Standard
- CRI-F = Final Contract Required Detection Limit Standard

Note: Some clients/regulators/projects require an LCS-D (LCS duplicate). Some may request an MSD instead of a sample duplicate, however there is typically not enough sample to enable the laboratory to perform an MSD.

Table 3: Interferent list from EPA SW-846.

POTENTIAL INTERFERENCES AND ANALYTE CONCENTRATION EQUIVALENTS  
(mg/L) ARISING FROM INTERFERENCE AT THE 100 mg/L LEVEL

| Analyte | $\lambda$ (nm) | Interferant <sup>a,b</sup> |      |      |      |       |       |      |      |      |      |
|---------|----------------|----------------------------|------|------|------|-------|-------|------|------|------|------|
|         |                | Al                         | Ca   | Cr   | Cu   | Fe    | Mg    | Mn   | Ni   | Tl   | V    |
| Al      | 308.215        | --                         | --   | --   | --   | --    | --    | 0.21 | --   | --   | 1.4  |
| Sb      | 206.833        | 0.47                       | --   | 2.9  | --   | 0.08  | --    | --   | --   | 0.25 | 0.45 |
| As      | 193.696        | 1.3                        | --   | 0.44 | --   | --    | --    | --   | --   | --   | 1.1  |
| Ba      | 455.403        | --                         | --   | --   | --   | --    | --    | --   | --   | --   | --   |
| Be      | 313.042        | --                         | --   | --   | --   | --    | --    | --   | --   | 0.04 | 0.05 |
| Cd      | 226.502        | --                         | --   | --   | --   | 0.03  | --    | --   | 0.02 | --   | --   |
| Ca      | 317.933        | --                         | --   | 0.08 | --   | 0.01  | 0.01  | 0.04 | --   | 0.03 | 0.03 |
| Cr      | 267.716        | --                         | --   | --   | --   | 0.003 | --    | 0.04 | --   | --   | 0.04 |
| Co      | 228.616        | --                         | --   | 0.03 | --   | 0.005 | --    | --   | 0.03 | 0.15 | --   |
| Cu      | 324.754        | --                         | --   | --   | --   | 0.003 | --    | --   | --   | 0.05 | 0.02 |
| Fe      | 259.940        | --                         | --   | --   | --   | --    | --    | 0.12 | --   | --   | --   |
| Pb      | 220.353        | 0.17                       | --   | --   | --   | --    | --    | --   | --   | --   | --   |
| Mg      | 279.079        | --                         | 0.02 | 0.11 | --   | 0.13  | --    | 0.25 | --   | 0.07 | 0.12 |
| Mn      | 257.610        | 0.005                      | --   | 0.01 | --   | 0.002 | 0.002 | --   | --   | --   | --   |
| Mo      | 202.030        | 0.05                       | --   | --   | --   | 0.03  | --    | --   | --   | --   | --   |
| Ni      | 231.604        | --                         | --   | --   | --   | --    | --    | --   | --   | --   | --   |
| Se      | 196.026        | 0.23                       | --   | --   | --   | 0.09  | --    | --   | --   | --   | --   |
| Na      | 588.995        | --                         | --   | --   | --   | --    | --    | --   | --   | 0.08 | --   |
| Tl      | 190.864        | 0.30                       | --   | --   | --   | --    | --    | --   | --   | --   | --   |
| V       | 292.402        | --                         | --   | 0.05 | --   | 0.005 | --    | --   | --   | 0.02 | --   |
| Zn      | 213.856        | --                         | --   | --   | 0.14 | --    | --    | --   | 0.29 | --   | --   |

<sup>a</sup> Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

|                |                |
|----------------|----------------|
| Al - 1000 mg/L | Mg - 1000 mg/L |
| Ca - 1000 mg/L | Mn - 200 mg/L  |
| Cr - 200 mg/L  | Tl - 200 mg/L  |
| Cu - 200 mg/L  | V - 200 mg/L   |
| Fe - 1000 mg/L |                |

<sup>b</sup> The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

<sup>c</sup> Interferences will be affected by background choices and other interferences may be present.

APPENDIX A: Differences from Promulgated methods

(Note: This SOP is based on SW-846 Method 6010C and Inorganics Air Compendium (IO) Method 3.4)

A.1: SW-846 Method 6010C  
 Inductively Coupled Plasma – Atomic Emission Spectrometry  
 (Revision 3. February, 2007)

(Note: SW-846 Method 6010C is, as promulgated, applicable to "trace elements in solution", with the caveat that "With the exception of groundwater samples, all aqueous and solid matrices need acid digestion prior to analysis." No mention of the 2009 TNI Quality Matrix of "Air" is made within the method.)

| Item | Promulgated requirement                     | SOP                           | Justification                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
|------|---------------------------------------------|-------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1    | 4.2.3 – 4.2.9<br>[Interelement Corrections] | No IEC's routinely performed. | <p>IEC studies are performed (per 6010C) by analyzing interferent analytes at a concentration <math>\geq</math> 100 mg/L.</p> <p>Using Chester LabNet's digestion SOP, 100 mg/L equates to 24.46 mg/Filter for an 8" x 10" filter.</p> <p>A heavily loaded filter has a total sample mass (net weight of deposit) of around 100 mg/filter.</p> <p>Thus, nearly 25% of the filter deposit would need to be comprised entirely of interferent for a heavily loaded filter to encounter interferents in sufficient quantities to impact the results.</p> <p>In 2014, 100 filters out of 983 total 8"x10" filters had a mass greater than 100 mg, or roughly 10%.</p> <p>It is highly unlikely that a filter deposit would contain enough interferent to make interelement corrections necessary.</p> <p>For Source Sampling Methods, all spectra are visually inspected for baseline markers and interfering peaks. In addition, emission lines are chosen that are generally considered to be largely interference-free.</p> |

| Item | Promulgated requirement                                                                                                                                                              | SOP                                                                                                                                                                                                                                                                                                 | Justification                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
|------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 2    | <p>4.2.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.</p> <p>4.2.10.2 ... analyze an interference check solution...</p> | <p>ICS-A and ICS-AB solutions are only analyzed at client request.</p>                                                                                                                                                                                                                              | <p>IEC studies are performed (per 6010C) by analyzing interferent analytes at a concentration of 100 mg/L.</p> <p>Using Chester LabNet's digestion SOP, 100 mg/L equates to 24.46 mg/Filter for an 8" x 10" filter.</p> <p>A heavily loaded filter has a total sample mass (net weight of deposit) of around 100 mg/filter.</p> <p>Thus, nearly 25% of the filter deposit would need to be comprised entirely of interferent for a heavily loaded filter to encounter interferences in sufficient quantities to impact the results.</p> <p>In 2014, 100 filters out of 983 total 8"x10" filters had a mass greater than 100 mg, or roughly 10%.</p> <p>It is highly unlikely that a filter deposit would contain enough interferent to make interelement corrections necessary.</p> <p>For Source Sampling Methods, all spectra are visually inspected for baseline markers and interfering peaks. In addition, emission lines are chosen that are generally considered to be largely interference-free.</p> |
| 3    | <p>7.3 Standard stock solutions may be purchased or prepared...</p>                                                                                                                  | <p>NIST-traceable stock standard solutions are purchased from known suppliers.</p>                                                                                                                                                                                                                  | <p>Clarification of option in promulgated method.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| 4    | <p>7.5 Two types of blanks are required ... calibration blank...method blank.</p>                                                                                                    | <p>Three types of blanks are required:</p> <p>Calibration Blank (usually 7% HNO<sub>3</sub>)<br/> <i>"Matrix matched" 3-22-14</i></p> <p>Preparation blank (all reagents taken through preparation)</p> <p>Method/matrix blank (all reagents plus any sampling media taken through preparation)</p> | <p>The preparation blank indicates problems in the digestion.</p> <p>The Method Blank indicates amounts of analytes contributed by the sampling media.</p> <p>Refer to Section 9 for further detail.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |

*QHS*

| Item | Promulgated requirement                                                                                                                                                                                                                         | SOP                                                                                                                                                            | Justification                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 5    | 7.7 The ... CCV standard should be prepared ... using the same standards used for calibration...                                                                                                                                                | The CCV standard is the same solution as the ICV standard, and is prepared using a second source stock standard.                                               | More stringent than promulgated method.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |
| 6    | 7.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors.                                                                           | ICS-A standard is only prepared at client request.                                                                                                             | See item 2.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
| 7    | 9.3 ... They [IDLs] are not to be confused with the lower limit of quantitation, nor should they be used in establishing this limit.                                                                                                            | The quantitation limit is set at five times the detection limit as determined during annual detection limit studies.                                           | Follows CLP guidelines.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |
| 8    | 9.3 ... IDLs in µg/L can be estimated ... from the analysis of a reagent blank...                                                                                                                                                               | IDLs are calculated based on the analysis of low level standard at 1-4 times the likely detection limit.                                                       | Follows SW846 Chapter 3 detection limit procedure.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| 9    | 9.3 ... IDLs should be determined at least every three months...                                                                                                                                                                                | IDLs are determined annually.                                                                                                                                  | Per CLP guidelines and 2009 TNI Standard requirements.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| 10   | 9.6 ... if the [preparation] blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration...blank is considered acceptable. | Preparation blank control limits are < detection limit.<br><i>or</i><br><i>&lt;method blank;</i><br><i>depending on digestion method.</i><br><i>St 4.22-1b</i> | <p>1a. &lt;10% of the lower limit of quantitation check sample (CRI) would be ½ the detection limit. The instrument cannot accurately measure analytes below the detection limit.</p> <p>1b. Note that the promulgated control limit implies that the quantitation limit is ≥ 10x the detection limit, contradicting Section 9.3 (see item 7)</p> <p>2. The laboratory is usually not informed of the regulatory limit.</p> <p>3. Filter samples with very light deposits may have results similar to blanks. Many of these samples allow the analyst only one opportunity for analysis (e.g. insufficient sample for redigestion).</p> <p>In all cases, detected quantities of analytes of interest are noted in the Case Narrative.</p> |

| Item | Promulgated requirement                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | SOP                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | Justification                                                                                                                                                                                                                                                                                                                                                                                     |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 11   | 9.6 ... If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples ... should be reprepared and reanalyzed ...                                                                                                                                                                                                                                                                                                                     | Report method blank results to client and note any detectable levels of analytes of interest in the case narrative.                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | Many samples allow the analyst only one opportunity for analysis (e.g. insufficient sample for redigestion)                                                                                                                                                                                                                                                                                       |
| 12   | 9.8 ... Documenting the effect of the matrix ... should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair.                                                                                                                                                                                                                                                                                                                     | Where possible, one duplicate and one spike are performed.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | <p>Many samples have insufficient sample for a true duplicate and true spike.</p> <p>These samples have a replicate and post-digestion spike performed on the digestate in lieu of a true duplicate and spike.</p>                                                                                                                                                                                |
| 13   | 10.1.1 Before using this procedure to analyze samples, data should be available documenting the initial demonstration of performance. The required data should document the location of the background points being used for correction; the determination of the linear dynamic ranges; a demonstration of the desired method sensitivity and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. | <p>1. Background correction markers may change from one sample type to another, and are determined on a run-by-run basis when the analyst examines the spectra.</p> <p>2. The determination of linear ranges is only performed once, when the instrument is brought online. The calibration standard is set at a concentration below the linear range, and no results above the calibration standard are reported.</p> <p>3. CRI's are analyzed with every analytical run. Detection limits are performed annually.</p> <p>4. Mathematical interelement corrections are not performed.</p> | <p>1. The variety of "air" matrices requires each analysis to have the background correction markers verified by the analyst.</p> <p>2. Since no data is ever reported above the calibration standard concentration, there is no need for linearity studies.</p> <p>3. Detection limits performed annually per CLP and 2009 TNI Standard guidelines/requirements.</p> <p>4. See item 1 above.</p> |

| Item | Promulgated requirement                                                                                                                                                                                                              | SOP                                                                                                                                                        | Justification                                                                                                                            |
|------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|
| 14   | 10.1.3 The lower limits of quantitation should be ....<br>Established from the lower limit of quantitation check sample and then confirmed using either the lowest calibration point or from a low-level calibration check standard. | Quantitation Limits are set at five times the detection limits.<br><br>Quantitation limits are checked using a CRI standard set at the quantitation limit. | Per CLP guidelines and 2009 TNI Standard requirements.                                                                                   |
| 15   | 10.1.4 ... Because of differences among various makes and models of spectrometers, specific instrument operating conditions are not provided.                                                                                        | Plasma: 15 L/min<br>Auxiliary: 0.2 L/min<br>Nebulizer: 0.65 L/min<br>Power: 1500 kW<br>Pump: 1.50 mL/min<br>Heat: off                                      | Clarification of option in promulgated method.                                                                                           |
| 16   | 10.3.1 ... It is recommended that the ICV solution be obtained commercially as a certified traceable reference material such that an expiration date can be assigned.                                                                | NIST traceable Stock Standard used for ICV/CCV preparation is obtained from a commercial source.                                                           | Clarification of option in promulgated method.                                                                                           |
| 17   | 10.3.1 ... Note: ... For purposes of verifying the initial calibration, only the mid-level ICV needs to be prepared from a source other than the calibration standards.                                                              | Second source stock standards are used in the preparation of the ICV, CCV and CRI (low level ICV).                                                         | More stringent than promulgated method.                                                                                                  |
| 18   | 10.3.1.2 The response of the calibration blank should be less than the response of the typical laboratory lower limit of quantitation...                                                                                             | No specific requirement.                                                                                                                                   | The CRI will fail if the calibration blank response is higher than the CRI response. CRI concentration is set at the quantitation limit. |
| 19   | 10.3.2 ... The calibration curve should be prepared daily with a minimum of a calibration blank and a single standard...                                                                                                             | The instrument is calibrated prior to each and every analytical run with a blank and a single calibration standard.                                        | More stringent than promulgated method.                                                                                                  |
| 20   | 10.3.2 ... Alternatively, the calibration curve can be prepared daily with a minimum of a calibration blank and three non-zero standards...                                                                                          | The instrument is calibrated prior to each and every analytical run with a blank and a single calibration standard.                                        | Clarification of option in promulgated method.                                                                                           |

| Item | Promulgated requirement                                                                                                                              | SOP                                                                                | Justification                                                                                                                                                                                                                               |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 21   | 10.3.2 ... Note: ... the upper limit of the quantitation range may exceed the highest concentration calibration point...                             | The laboratory does not report any data higher than the highest calibration point. | More stringent than promulgated method.                                                                                                                                                                                                     |
| 22   | 10.3.4 ... The CCV should be made from the same material as the initial calibration standards...                                                     | CCV is the same solution as the ICV and made from a second source stock standard.  | More stringent than promulgated method.                                                                                                                                                                                                     |
| 23   | 10.3.4 ... The low-level continuing calibration verification (LLCCV) standard should also be analyzed at the end of each analysis batch [aka CRI-F]. | The laboratory analyzes a CRI-F only on client request.                            | 2009 TNI standard requires a CRI-I standard to be run at the beginning of each run, but does not require a CRI-F.<br><br>No air quality methods require a CRI of any sort.                                                                  |
| 24   | 11.3 ... It is recommended that a CCV, LLCCV, and CCB ... be analyzed after every ten samples and at the end of the analysis batch.                  | A CCV and CCB are analyzed after every ten samples and at the end of the run.      | LLCCV (CRI) is not required every ten samples and at the end of the run by the 2009 TNI standard nor by any air quality method performed by this laboratory.<br><br>CRI-F is required by CLP guidelines and is performed on client request. |

A.1: Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air Method IO-3.4  
Determination of Metals in Ambient Particulate Matter using Inductively Coupled Plasma (ICP) Spectroscopy  
(June 1999)

(Note: IO-3.4 was written for older technology including the use of a "teletype". It was written for a JarrellAsh Model 975 Plasma AtomComp ICP. Many changes listed below have been generalized or grouped together to avoid repeating "more modern technology" in the Justification column. IO-3.4 also includes sections which pertain to sampling, digestion and data reporting. This table only discusses changes from those sections pertinent to analysis by ICP or associated QC elements)

| Item | Promulgated requirement                                                                                                                              | SOP | Justification                                                                                                                                                                          |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1    | 5.3 Simultaneous ICPs have an array of photo multiplier tubes positioned...<br><br>[and all other references to photomultiplier tubes within IO-3.4] | N/A | Newer technology employs a Charge-Coupled device (CCD) array as a detector. No photomultiplier tubes are present in the instrument used in this method.<br><br>More modern technology. |

6x

| Item | Promulgated requirement                                                                                                                                                                                                                                                                                           | SOP                                                                                                                                                                                       | Justification                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 2    | <p>5.9 ... If lines free of interference can't be found, approximate concentrations of the element of interest can be calculated by calibrating that element and the interferent (inter element correction).</p>                                                                                                  | <p>No IEC's routinely performed.</p>                                                                                                                                                      | <p>IEC studies are performed (per 6010C) by analyzing interferent analytes at a concentration of 100 mg/L.</p> <p>Using Chester LabNet's digestion SOP, 100 mg/L equates to 24.46 mg/Filter for an 8" x 10" filter.</p> <p>A heavily loaded filter has a total sample mass (net weight of deposit) of around 100 mg/filter.</p> <p>Thus, nearly 25% of the filter deposit would need to be comprised entirely of interferent for a heavily loaded filter to encounter interferences in sufficient quantities to impact the results.</p> <p>In 2014, 100 filters out of 983 total 8"x10" filters had a mass greater than 100 mg, or roughly 10%.</p> <p>It is highly unlikely that a filter deposit would contain enough interferent to make interelement corrections necessary.</p> <p>For Source Sampling Methods, all spectra are visually inspected for baseline markers and interfering peaks. In addition, emission lines are chosen that are generally considered to be largely interference-free.</p> |
| 3    | <p>10.4 Stock Calibration Standards. ... Multi-element and single-element plasma-grade stocks are used for the analysis. The stocks are purchased from ... The calibration standard stocks used for instrument calibration and initial calibration verification (ICV) are purchased from different suppliers.</p> | <p>Commercially available NIST-traceable stock standards are purchased for use.</p> <p>ICV/CCV/CRI and spike stock solutions are from a second source than that used for calibration.</p> | <p>Clarification of unclear text in promulgated method.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |

| Item | Promulgated requirement                                                                                                                                              | SOP                                                                                                                                       | Justification                                                                                                                                                                                                   |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 4    | 10.4 Stock Calibration Standards. ... Stock solutions should be stored in Teflon bottles.                                                                            | Stock standards are stored in the bottles supplied by the manufacturer.<br><br>Diluted standards are stored in HDPE or Teflon containers. | The laboratory has found no difference between HDPE and Teflon storage containers for any element since January of 1990 (24 years as of this writing).<br><i>with the exception of Ag</i> <sup>Sk 4-22-16</sup> |
| 5    | 11.1.3 ... The final concentration of the ICV should be in the range of 25 µg/mL for Al, Ca, Fe, Mg, K and Na. All other analytes should be in the range of 2 µg/mL. | ICV concentration is 2.5 µg/mL for all elements listed in this SOP (mid-point of the calibration curve).                                  | More modern technology has lower detection limits. 25 µg/mL (ppm) would saturate the detector.                                                                                                                  |
| 6    | 11.1.4 Prepare Interference Check Standard (ICS)...                                                                                                                  | ICS-A and ICS-AB solutions are only analyzed at client request.                                                                           | See item 2.                                                                                                                                                                                                     |
| 7    | 11.1.5 ... The LCS is prepared for all analytes at the 2 µg/mL level ...                                                                                             | LCS is prepared at the mid-point of the calibration curve (2.5 µg/mL for all elements listed in this SOP)                                 | 2009 TNI Standard and CLP guidelines require the LCS to fall at the mid-point of the calibration curve.                                                                                                         |
| 8    | 11.1.6 The spike is added before the digestion...                                                                                                                    | Not all samples have sufficient material to split into two aliquots (one for sample, one for spike)                                       | Pre-digestion spikes are performed where possible.                                                                                                                                                              |
| 9    | 11.1.6 ... The MS should be at the 25µg...level.                                                                                                                     | Spike concentrations (whether pre- or post-digestion) are at a concentration at the mid-point of the calibration curve.                   | 2009 TNI Standard requires the spike amount to fall at the mid-point of the calibration curve.                                                                                                                  |
| 10   | 11.1.7 ... The running frequency of analysis of a reagent blank [aka Preparation Blank] is about 1 for every 40 real samples.                                        | Preparation Blanks are analyzed once per preparation batch of ≤ 20 samples.                                                               | 2009 TNI Standard and CLP guidelines require once per preparation batch of ≤ 20 samples.                                                                                                                        |
| 11   | 11.2 ... A daily log of the operating parameters should be maintained for reference.                                                                                 | N/A                                                                                                                                       | More modern technology has made this unnecessary.                                                                                                                                                               |

| Item | Promulgated requirement                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | SOP                                                                                                                                                                                                                                                                                                                      | Justification                                                                                                                                                                                                                                                                                                                                                                        |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 12   | 11.3.1 ... investigation for linearity for elements expected to exceed concentrations of about 25 µg/mL may be necessary.                                                                                                                                                                                                                                                                                                                                                                                              | The determination of linear ranges is only performed once, when the instrument is brought online. The calibration standard is set at a concentration below the linear range, and no results above the calibration standard are reported.                                                                                 | Since no data is ever reported above the calibration standard concentration, there is no need for linearity studies.                                                                                                                                                                                                                                                                 |
| 13   | 11.5 ICP Operation...<br>11.5.1 – 11.5.23 – [older technology including DOS-based software and the use of a teletype to print results.]                                                                                                                                                                                                                                                                                                                                                                                | N/A                                                                                                                                                                                                                                                                                                                      | More modern technology, including Windows-based software and the use of LaserJet or inkjet printers.                                                                                                                                                                                                                                                                                 |
| 14   | 12.1 A discrimination limit must be defined so that possible contributions from an individual filter are not falsely reported as being from the particulate material. Calculate the filter batch mean ... and the standard deviation of the [filter batch mean] for each filter. If [the mean] is greater than the instrumental detection limit, then the [mean] must be subtracted from the total elemental content for each particulate bearing filter when the net metal in the particulate material is calculated. | A method blank containing the same amount of the same sampling media from the same lot (where possible) are analyzed with each digestion batch of ≤ 20 samples.<br><br>The result of the Method Blank(s) analysis is reported to the client.<br><br>Any blank subtraction performed is the responsibility of the client. | The laboratory is not provided with any information as to the use of the data, any applicable regulatory limits, the scope of the project(s) or any other information with which the laboratory could make a reasonable decision as to a "discrimination limit".<br><br>In addition, often clients send their own filters, and may or may not send a blank filter from the same lot. |
| 15   | 13.3.2.1 At least two calibration standards and a calibration blank are analyzed at the beginning of an analysis run.                                                                                                                                                                                                                                                                                                                                                                                                  | The instrument is calibrated using a blank and one calibration standard.                                                                                                                                                                                                                                                 | Manufacturer's recommendations, CLP guidelines and 2009 TNI Standard all allow for the use of a blank and single standard during calibration.                                                                                                                                                                                                                                        |

| Item | Promulgated requirement                                                                                                                                                                                                                                                    | SOP                                                                                                                                                                                                    | Justification                                                                                                                                              |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 16   | 13.3.2.4 High Standard Verification (HSV). Immediately after the analysis of the ICB, and prior to the analysis of samples, the HSV's are reanalyzed. ...                                                                                                                  | No HSV is analyzed.                                                                                                                                                                                    | Not required by CLP guidelines or 2009 TNI Standard.<br><br>This QC element is run only at client request.                                                 |
| 17   | 13.3.2.5 ... The ICS's are analyzed at the beginning and end of the run and for every 8 hours of continuous operation. ...                                                                                                                                                 | ICS-A and ICS-AB solutions are only analyzed at client request.                                                                                                                                        | See item 2.                                                                                                                                                |
| 18   | 13.3.2.6 ... CCV standards are prepared from the calibration standard stocks ...                                                                                                                                                                                           | The CCV standard is prepared from second source stock standards and is the same solution as that used for the ICV                                                                                      | More stringent than promulgated method.                                                                                                                    |
| 19   | 13.3.2.12 ... The ICP serial dilution analysis must be performed on one sample per batch. After a fivefold serial dilution, the analyte concentration must be within 90% and 110% of the undiluted sample results.                                                         | Serial dilutions are only analyzed at client request.<br><br>Control limits are $\pm 20\%$ RPD between the two samples, when both the sample and serial dilution result are $\geq$ quantitation limit. | Serial dilutions are not required by the 2009 TNI Standard.<br><br>Newer technology has decreased the need to prove linearity by use of a serial dilution. |
| 20   | 13.3.2.13 ... Dilute and reanalyze samples that are more concentrated than the linear calibration limit.                                                                                                                                                                   | All samples with results above the calibration standard are diluted with a matrix-matched diluent and reanalyzed.                                                                                      | Matrix matching is critical to the precision and accuracy of results from ICP analysis.                                                                    |
| 21   | Table 4. ICP... Elements with Wavelengths.<br><br>[Note: wavelengths used are the same as those given in Table 4 unless listed below]<br><br>As 193.76<br>Be 313.04<br>Ca 396.85<br>Cd 226.50<br>Cr 357.87<br>Fe 259.94<br>Se 196.09<br>Ti 351.92<br>V 292.40<br>Zn 206.19 | As 193.696<br>Be 313.107<br>Ca 317.933<br>Cd 214.400<br>Cr 267.716<br>Fe 238.204<br>Se 196.026<br>Ti 190.801<br>V 309.310<br>Zn 213.857                                                                | More modern technology. Charged-coupled device array detector functions entirely differently than photomultiplier tubes.                                   |

Appendix B: Instrumental "ICAP 19" and "ICAP 7" Methods

# CHESTER LabNet

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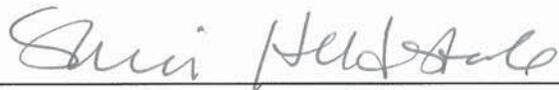
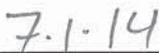
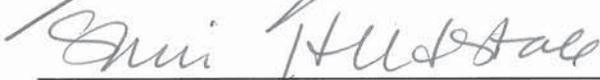
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## Standard Operating Procedure ME-012.01

Digestion of Filters for Metals Analysis  
40 CFR 50 Appendix G (Hot Sonication Option)

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### Approvals:

|                                                                                                              |                                                                                                        |
|--------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|
| <br>_____<br>Author       | <br>_____<br>Date |
| <br>_____<br>Lead Analyst | <br>_____<br>Date |
| <br>_____<br>QA/QC        | <br>_____<br>Date |

Effective from: 7-1-14  
Effective until: present



## Digestion of Filters for Metals Analysis 40 CFR 50 Appendix G (Hot Sonication Option)

### 1.0 Introduction

- 1.1 Test Method Reference ID: 40 CFR 50 Appendix G, "Reference Method for the Determination of Lead in Total Suspended Particulate Matter"
- 1.2 Applicability: This method is applicable to the digestion of air particulates captured on Quartz, Glass Fiber or Teflon filters.
- 1.3 Detection Limit: N/A
- 1.4 Method Performance: In 2014, a comparability study was performed against modified EPA Method 3050.

The following elements were analyzed: As, Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, Sb, Se, Ti, Tl, V, Zn. "Real world" samples were digested using both the modified 3050 method and Appendix G, Hot Sonication Option. Of the analytes tested in the samples, the following analytes were above the quantitation limit, below the calibration standard, and had historical LCS data for comparison: Ca, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Ti, V and Zn. The data in the method performance tables below were generated using this comparison study.

Preparation Blanks: Two preparation blanks were analyzed for Ca, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Ti, V and Zn. Of these elements, only Zn had an average result greater than the detection limit (average Zn = 2.0165 µg/L; DL = 1 µg/L, QL = 5 µg/L)

LCS Recoveries: Seven LCS's were analyzed at a spiking level of 2500µg/L (mid-point of the calibration curve. All recoveries for all analytes were within 10% of the true value, well within the 80% - 120% control limits for LCS recoveries. All %RSD values for the set of 7 LCS's were <3% RSD, well within the ±20% RPD control limits for duplicate analysis. The average recoveries and %RSD's were as follows:

| Analyte | 47mm Teflon<br>Average<br>%Recovery | 47mm Teflon<br>Average %RSD<br>(n=7) | 66.4cm <sup>2</sup> of 8x10"<br>Quartz Average<br>%Recovery | 66.4cm <sup>2</sup> of 8x10"<br>Quartz Average<br>%RSD (n=7) |
|---------|-------------------------------------|--------------------------------------|-------------------------------------------------------------|--------------------------------------------------------------|
| Ca      | 94.4                                | 2.1                                  | 102.8                                                       | 1.9                                                          |
| Cr      | 94.7                                | 1.9                                  | 94.6                                                        | 0.6                                                          |
| Cu      | 99.2                                | 1.5                                  | 98.8                                                        | 0.7                                                          |
| Fe      | 93.7                                | 1.6                                  | 94.8                                                        | 0.7                                                          |
| Mg      | 100.9                               | 2.3                                  | 105.0                                                       | 1.6                                                          |
| Mn      | 94.6                                | 1.6                                  | 94.1                                                        | 0.8                                                          |
| Mo      | 96.1                                | 1.8                                  | 95.8                                                        | 0.7                                                          |
| Ni      | 93.5                                | 2.0                                  | 93.4                                                        | 0.6                                                          |
| Pb      | 93.6                                | 2.2                                  | 94.0                                                        | 0.5                                                          |
| Ti      | 97.5                                | 1.6                                  | 97.1                                                        | 0.6                                                          |
| V       | 96.9                                | 1.8                                  | 96.6                                                        | 0.6                                                          |
| Zn      | 95.6                                | 1.7                                  | 96.3                                                        | 0.6                                                          |

## 2.0 Summary

- 2.1 Scope and Application: This intended use of this method is for the digestion of metals in air particulates captured on filters (Quartz, Glass Fiber, Teflon). This method is not intended to be used in lieu of proper training and does not contain all of the details which a trained analyst should know. *This method meets its intended use. Sat 7-21-15*
- 2.2 Summary of Method: If necessary, the filter is sub-sectioned per SOP ME-008. Filters or filter punches are placed in 50mL plastic centrifuge tubes. An extraction solution containing HNO<sub>3</sub> and HCl is added to the 30 mL mark, completely submerging the filter material. The centrifuge tubes are then placed in a heated Ultrasonicator, pre-heated to 80°C ± 5°C, and sonicated for 60 min ± 5 min by timer. Once sonication time is complete, the samples are removed and allowed to cool, then diluted to 40 mL with extraction solution. After dilution, samples are inverted several times, then centrifuged for 10 minutes at 2,000 RPM. Samples are then ready for analysis.

2.3 Interferences: This method is not a total digestion technique. It is a strong acid digestion that will dissolve almost all elements that could become "environmentally available." Elements bound in silicate structures or other strongly formed mineralogical structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If total digestion is required, the use of a hydrofluoric bomb digestion, such as that given in 40 CFR 50 Method 29, is preferable, although it should be noted that the complete dissolution of the filter matrix will lead to more background noise and greater contribution of elements of interest from the filter material.

2.4 Sample collection/preservation/shipment/storage: Collection, field preservation and shipment of samples is performed by the client. Chester LabNet has no control over the actions of the client in the field. Upon receipt, samples should be stored per the collection method specifications. If the collection method does not specify a storage requirement, filters are stored at ambient temperature and humidity.

### **3.0 Safety**

3.1 Follow the Chester LabNet Chemical Hygiene plan. Always treat samples of unknown origin and/or constitution as hazardous.

3.2 This method presents no safety risk beyond typical laboratory safety hazards.

3.3 No carcinogenic reagents are used in this method.

### **4.0 Pollution Prevention and Waste Management**

4.1 The smallest quantity of chemical feasible is removed from its primary container for use.

4.2 Chemicals are used in amounts needed by the method, and excess reagents are not made.

4.3 Chester LabNet is a conditionally exempt small quantity generator and as such does not require formal chemical waste processing.

4.3.1 Acidic and Basic wastes are neutralized prior to disposing of them in the sanitary sewer system.

4.3.2 Organic liquids are usually primarily used for cleaning purposes. Organic wastes are generated in very small quantities, and evaporate off with no need for more formal disposal.

4.4 Larger quantities of known hazards are returned to the client for disposal.

4.5 Expired Chemicals:

4.5.1 Dry chemicals beyond their <sup>SH 7-21-15</sup> ~~real or arbitrary~~ expiration date are lab packed and disposed of by a qualified chemical disposal company.

4.5.2 Acids and Bases beyond their <sup>SH 7-21-15</sup> ~~real or arbitrary~~ expiration date are neutralized prior to being disposed of via the sanitary sewer system.

4.5.3 Organic liquids beyond their <sup>SH 7-21-15</sup> ~~real or arbitrary~~ expiration date are disposed of by a qualified chemical disposal company if the volume or type of liquid warrants such disposal. Disposal of organic liquids is rare.

## 5.0 Apparati, Equipment and Supplies

5.1 LabCon metals clean 50mL centrifuge tubes

5.2 Heated Ultrasonicator bath capable of holding  $80^{\circ}\text{C} \pm 5^{\circ}\text{C}$  and operating at a minimum of 37 kHz.

5.3 1 L volumetric flask, metals cleaned.

5.4 500 mL Teflon wash bottle

5.5 Centrifuge capable of maintaining 2,000 RPM for 10 minutes

5.6 Ethanol cleaned stainless steel forceps

## 6.0 Reagents and Standards

6.1 Extraction Solution: in a 1 L volumetric flask, add ~500 mL DI water, 64.4 mL conc.  $\text{HNO}_3$  and 182 mL conc. HCl. Dilute to volume.

6.2 Spike solution: 100 ppm ICAP <sup>23</sup> ~~10~~ standard <sup>SH 7-21-15</sup>

6.3 Spike solution: 100 ppm ICAP 7 standard

## 7.0 Preparation, Calibration and Standardization

### 7.1 Sonicator:

7.1.1 Fill sonicator to level where the water is above the 30 mL mark of the centrifuge tubes.

7.1.2 Plug in sonicator and turn on heat to pre-heat to 80°C

7.2 If necessary, subsection filters following SOP ME-008.

7.3 Using clean stainless steel forceps, bend filters and insert into pre-labeled centrifuge tubes such that the deposit is not in contact with the walls of the tube and the entire filter is below the 30 mL mark.

## 8.0 Procedure

8.1 Spike appropriate filters with 1 mL of 100 ppm spiking solution (section 6.2 and 6.3, above)

8.2 Using the Teflon wash bottle, add extraction solution to the 30 mL mark on the centrifuge tubes.

8.3 Cap each tube tightly.

8.4 After Ultrasonicator has reached 80 °C, place tubes in Ultrasonicator in such a manner that the tubes do not contact the floor or walls of the bath. Note that this will drop the temperature in the bath. Place the cover over the top of the sonicator to prevent water loss from the bath.

8.5 Set the Ultrasonicator to 37kHz.

8.6 Set the timer on the Ultrasonicator to 60 minutes.

8.7 Set the Ultrasonicator to automatically start when the temperature reaches 80°C.

- 8.8 After 60 minutes, the sonicator will shut itself off, however, the heating element will continue to keep the water at 80°C
- 8.9 Turn off the sonicator power and unplug it, if there are no further digestions to be performed.
- 8.10 Remove the centrifuge tubes one at a time, drying each of them with a paper towel and paying close attention to the area near the threads/cap.
- 8.11 Allow tubes to cool to near room temperature.
- 8.12 Add extraction solution to the 40mL mark on the tube using the Teflon wash bottle.
- 8.13 Invert several times and place in the centrifuge. Centrifuge the samples for 10 minutes at 2,000 RPM.
- 8.14 Samples are now ready for analysis by ICP <sup>5/11/15</sup> or ~~GFAA~~.

**9.0 QA/QC**

- 9.1 Preparation Blank: This blank consists of all reagents used during the digestion, and is carried through the entire process in the same manner as a sample.
  - 9.1.1 Frequency: once per digestion batch
  - 9.1.2 QC statistic: result
  - 9.1.3 Control limits: <QL
  - 9.1.4 Corrective action: redigest and re-analyze if possible. If not possible, report results to client and note in the case narrative of the report.
- 9.2 Method Blank: This blank consists of all reagents used during the digestion, plus a filter or filter fraction of the same size and type as the samples (e.g. 66.4cm<sup>2</sup> of Quartz fiber filter or one 47mm Teflon filter). <sup>7-1-14</sup>
  - 9.2.1 Frequency: once per digestion batch
  - 9.2.2 QC statistic: result
  - 9.2.3 Control limits: none, but results will ideally be <QL

9.2.4 Corrective action: Report results to client and note in the case narrative of the report.

9.3 LCS: This QC element consists of a filter or filter fraction of the same size and type as the samples, spiked with the element(s) of interest at the mid-point of the calibration curve.

9.3.1 Frequency: once per digestion batch

9.3.2 QC statistic: %Recovery (blank subtracted if necessary)

9.3.3 Control limits: 80 – 120% Recovery

9.3.4 Corrective action: redigest and re-analyze if possible. If not possible, report results to client and note in the case narrative of the report.

9.4 Duplicate: A duplicate aliquot of the filter sample. Note that for filters smaller than 8x10", there is not enough filter material to perform a duplicate digestion.

9.4.1 Frequency: once per digestion batch

9.4.2 QC statistic: %RPD

9.4.3 Control limits:  $\pm 20\%$

9.4.4 Corrective action: redigest and re-analyze if possible. If not possible, report results to client and note in the case narrative of the report.

9.4.5 Note: filters with visibly non-homogenous sample deposits do not have to be re-digested, but the non-homogenous deposit does need to be noted in the case narrative.

9.5 Spike: A spiked duplicate aliquot of the filter sample. Note that for filters smaller than 8x10", there is not enough filter material to perform a spike.

9.5.1 Frequency: once per digestion batch

9.5.2 QC statistic: %Recovery (blank subtracted if necessary)

9.5.3 Control limits: 75 – 125% Recovery

9.5.4 Corrective action: redigest and re-analyze if possible. If not possible, report results to client and note in the case narrative of the report.

9.5.5 Note: filters with visibly non-homogenous sample deposits do not have to be re-digested, but the non-homogenous deposit does need to be noted in the case narrative.

547.21.15

## 10.0 Calculations

10.1 N/A

## 11.0 References

11.1 40 CFR 50, Appendix G. "Reference Method for the Determination of Lead in Total Suspended Particulate Matter" (Hot Sonication Option). e-CFR, February 27, 2014.

## 12.0 Definitions

12.1 Analyst: the designated individual who performs the "hands-on" method and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.

12.2 Analysts' Notes: Non-essential aspects of a method, which may help the analyst during some phase of the method. Notes may include, but not be limited to, historical aspects of the method, "tricks" of the method, unexpected issues to be aware of, or other facts or opinions related to the method, but not directly part of the procedure.

12.3 Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

12.3.1 Preparation Batch: a group of one to 20 samples of the same matrix which are prepared together as a group, and which share common QC samples.

12.4 Blank: a clean aliquot of the same matrix as the digested samples. A blank is subjected to the usual analytical and measurement processes.

12.4.1 Method Blank: An unspiked clean sampling media aliquot, taken through the entire preparation and analytical processes associated with a method. This blank determines if the sampling media may be contributing any analyte of interest in the samples.

12.4.2 Preparation Blank: All reagents involved in the preparation, without sampling media (if any), taken through the entire preparation and analytical processes associated with a method. This blank demonstrates cleanliness of reagents and of the preparation process itself.

12.4.3 Reagent Blank: All reagents, mixed in correct proportion, used in the preparation of samples, however, not taken through the preparation process. This blank is rarely used, and usually only used when some question arises as to the source of contamination (reagents vs. process).

- 12.4.4 Field Blank: A blank prepared by the client in the field. This blank is treated as a sample by the laboratory.
- 12.5 Calculations (Data Reduction): the mathematical process of transforming raw data into a more useable form.
- 12.6 Control Limit: A mathematical representation of acceptable limits for a given Quality Control Metric such as percent recovery or percent difference. Limits may be in the form of an absolute number or represented as a percentage.
- 12.7 Corrective Action: the action taken to address and/or eliminate where possible the causes of a nonconformity, such as exceeding a control limit. Actions may include reanalyzing a sample, or noting the non-conformance in the data report.
- 12.8 Detection Limit: the lowest concentration of an analyte of interest that can be identified, measured and reported with confidence that the analyte concentration is not a false positive value.
- 12.8.1 Detection Limit (DL): The detection limit determined at the instrument using a clean matrix and no preparation.
- 12.8.2 Method Detection Limit (MDL): The detection limit determined by processing clean matrix through the entire method, including all preparatory steps.
- 12.8.3 Quantitation Limit (QL): The limit at which, not only is the laboratory confident that the concentration is not a false positive, but that the concentration reported is within acceptable limits from the true value.
- 12.9 Duplicate: A second aliquot of a sample, taken through all steps of the method, including digestion/preparatory stages.
- 12.10 Frequency: The number of occurrences of a specified event within a given interval. The number of samples or analytical runs with which a given QC sample or metric must be analyzed or verified.
- 12.11 Holding Time: the maximum times that samples may be held prior to analysis while still being considered valid or non-compromised.
- 12.12 Laboratory Control Standard (LCS): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. Generally used to establish analyst specific precision and bias or to assess the performance of the method.
- 12.13 Matrix/Matrices: the component or substrate that contains the analyte of interest.
- 12.14 QA/QC: Quality Assurance/Quality Control. A series of samples or metrics designed to show precision, accuracy and bias of the procedure are within acceptable limits.
- 12.15 QC Statistic: any of a number of statistical permutations performed on raw data to generate a metric capable of being subjected to control limits and corrective actions.

- 12.16 Reagent: a single chemical or combination of chemicals or a chemical solution used in the preparation or analysis of samples.
- 12.17 Spike: to add verified known amounts of analytes or a material containing known and verified amounts of analytes to a sample or matrix prior to analysis.
  - 12.17.1 Matrix Spike: a sample prepared by adding verified known amounts of analytes or a material containing known and verified amounts of analytes to a sample or matrix prior to preparation for analysis.
- 12.18 Standard: a solution or matrix of a known amount of analyte(s).
  - 12.18.1 Primary standard: a standard received from a vendor with NIST or equivalent traceability.
  - 12.18.2 Secondary standard: a standard received from a vendor with NIST or equivalent traceability, of a different lot number or manufacturer than the primary standard.
  - 12.18.3 Working standard: any standard created when mixing, diluting or otherwise manipulating aliquots of ~~primary~~<sup>stock</sup> standards. May be called "working standards" or "intermediate standards".

**13.0 Analysts' Notes**

13.1N/A

Ⓜ  
9/7-21-15

APPENDIX A: Differences from Promulgated methods

40 CFR 50 Appendix G "Reference Method for the Determination of Lead in Total Suspended Particulate Matter" (Hot Sonication Option)

Note 1: The promulgated method includes both digestion and analytical protocols. This SOP only applies to the digestion of the samples. Sections of the promulgated method pertaining to the analytical techniques which vary from the laboratory's protocols are not addressed in the table below. *SA 2.26.16* Refer to SOP ME-011 for analysis by ICP<sub>o</sub> and ME-002 for analysis by GFAA. *SA 7.21.15*

Note 2: The promulgated method includes sub-sampling of large filters (8x10"). This SOP only applies to the digestion of samples. Sections of the promulgated method pertaining to sub-sectioning of filters which vary from the laboratory's protocols are not addressed in the table below. Refer to SOP ME-008 for subsectioning of filters.

| Item | Promulgated requirement                                                                               | SOP                               | Justification                                                                                                                                                                                                 |
|------|-------------------------------------------------------------------------------------------------------|-----------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1    | 1.1 ICP-MS                                                                                            | ICP-OES <i>SA 7.21.15</i> or GFAA | Metals digestion protocol will work for any of the analytical instrumentation designed to quantitated metals. <i>SA 7.21.15</i>                                                                               |
| 2    | 6.2.3 Vortex Mixer                                                                                    | Invert samples                    | Thorough mixing of the digestate is required. Inversion of the digestate is equally as valid a technique as mixing by vortex mixer.                                                                           |
| 3    | 7.5.6 Standard Reference Materials, NIST SRM 2583, 2586, 2587 or 1648...                              | No SRMs used.                     | LCS and spike recovery demonstrate ability to achieve recovery of analyte of interest. <i>SRMs not available. SA 7.21.15</i>                                                                                  |
| 4    | 8.3 ...One reagent blank spike (RBS)... must be prepared and carried throughout the entire process.   | LCS                               | This is similar to an LCS, however does not include any filter matrix, thus it does not prove ability to recover analyte of interest from the physical matrix.<br><br>More stringent than promulgated method. |
| 5    | 10.1.3 Using plastic tweezers... place the [filter] in the bottom of a labeled 50 mL extraction tube. | Stainless steel forceps           | The laboratory has not found stainless steel forceps to cause any contamination issues.                                                                                                                       |

| Item | Promulgated requirement                                                                                                       | SOP                                                                                                                          | Justification                                                                                                                                                                                                  |
|------|-------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 6    | 10.1.3 .... Add 15.00 ...mL of the extraction solutions using a calibrated mechanical pipette.                                | Add 30 mL extraction solution using a Teflon wash bottle and the volumetric markings on the side of the centrifuge tube.     | 15 mL is insufficient to cover the entire filter.                                                                                                                                                              |
| 7    | 10.1.4 Loosely cap the 50 mL extraction tube...                                                                               | Cap the tubes tightly                                                                                                        | Loosely capping the tubes increases the likelihood that sonicator water will get into the digestate.                                                                                                           |
| 8    | 10.1.4 ... place the racks in an uncovered heated ultrasonic water bath...                                                    | Cover the ultrasonic bath                                                                                                    | Leaving the bath uncovered allows for significant evaporation of the water in the bath, eventually causing the water level to drop below the 30 mL mark on the tubes.                                          |
| 9    | 10.1.6 Add 25.00 ... mL of DI water with a calibrated mechanical pipette to bring the sample to a final volume of 40.0... mL. | Add extraction solution using the Teflon wash bottle to the 40 mL mark on the centrifuge tube.                               | Keeps the digestate matrix the same between 8x10" filters and smaller filters (see promulgated sections 10.2 below), allowing matrix matching for standards to be the same between larger and smaller filters. |
| 10   | 10.1.6 ... Tightly cap the tubes, and vortex mix or shake vigorously.                                                         | Invert samples several times.                                                                                                | Clarification of option in promulgated method.                                                                                                                                                                 |
| 11   | 10.1.6 ... centrifuge for 20 minutes at 2500 revolutions per minute...                                                        | Centrifuge for 10 minutes at 2,000 RPM.                                                                                      | 10 minutes at 2,000 RPM has proven sufficient for clarifying the digestate.                                                                                                                                    |
| 12   | 10.1.8 Decant the extract to a clean tube, cap tightly and store the sample extract at ambient laboratory temperature.        | After analysis, remaining digestate is left in the original centrifuge tube with the filter, and stored at room temperature. | Transference to a different tube increases the likelihood of contamination.                                                                                                                                    |

| Item | Promulgated requirement                                                                                                                     | SOP                                                                                                                      | Justification                                                                                                                                                                                                                                                                           |
|------|---------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 13   | 10.2.2 [Teflon filter] ...add 25.00 mL of the extraction solution...using a calibrated mechanical pipette.                                  | Add 30 mL extraction solution using a Teflon wash bottle and the volumetric markings on the side of the centrifuge tube. | 25 mL is insufficient to cover the entire filter.                                                                                                                                                                                                                                       |
| 14   | 10.2.5 [Teflon filter] Add 25.00 mL of DI water ... to bring the sample to a final volume of 50 mL.                                         | Add extraction solution using the Teflon wash bottle to the 40 mL mark on the centrifuge tube.                           | Keeps the digestate matrix the same between 8x10" filters and smaller filters (see promulgated sections 10.2 below), allowing matrix matching for standards to be the same between larger and smaller filters.<br><br>Less final volume lowers detection limit on a "per filter" basis. |
| 15   | 10.0 All plasticware and glassware used in the extraction procedures is soaked in 1 percent HNO <sub>3</sub> (v/v) for at least 24 hours... | Plasticware not soaked, metals cleaned plasticware purchased.                                                            | Soaking is unnecessary if clean glassware/plasticware purchased.                                                                                                                                                                                                                        |

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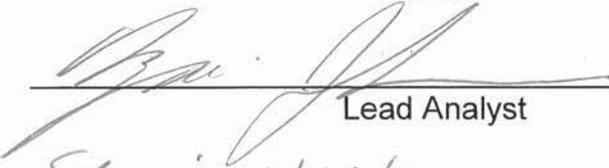
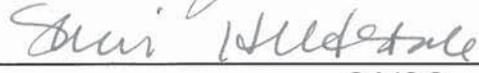
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## Standard Operating Procedure QA-007.04

### CALIBRATION OF LABORATORY PIPETTES CHESTER LABNET PROPRIETARY METHOD

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Approvals:

|                                                                                              |                          |
|----------------------------------------------------------------------------------------------|--------------------------|
| <br>_____ | <u>12-14-13</u><br>_____ |
| Author                                                                                       | Date                     |
| <br>_____ | <u>12-16-13</u><br>_____ |
| Lead Analyst                                                                                 | Date                     |
| <br>_____ | <u>12-14-13</u><br>_____ |
| QA/QC                                                                                        | Date                     |

Effective from: 12-16-13  
Effective until: present

### REVIEW HISTORY

| Review date: | Changes made:                                                                                                                                                                  | Changes made by: |
|--------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|
| 12/11/13     | Updated to reflect new balance, updated to 2009 TNI standard requirements including the addition of Appendix A.                                                                | Sheri Heldstab   |
| 10/2/08      | Expanded section on calibrating balance, minor changes to text for clarification                                                                                               | Sheri Heldstab   |
| 11/12/07     | Updated text to reflect current practices of removing water from the balance rather than adding it to, and the calibration checks of low volume (<20 µL) pipettes.             | Sheri Heldstab   |
| 9/6/05       | Updated to NELAP formatting. Changes section to reflect current verification of measurements by pipets <20 µL.                                                                 | Sheri Heldstab   |
| 10/1/02      | Added section 8.1, incremented previous sections by 1, and modified formatting to reflect standard formatting for QC section of SOPs. Removed "Figure 1. Sample Logbook Page." | S. Heldstab      |
| 10/16/01     | Removed references to glass pipettes and pipettes with volumes less than 20 µL.                                                                                                | S. Heldstab      |
| 3/14/00      | Updated format. Removed section on glass pipette cleaning.                                                                                                                     | C.R. Lytle       |
| 3/4/97       | Text modifications to Sections 2.0 & 8.0                                                                                                                                       | C.R. Lytle       |
| 1/19/96      | Number changed from QA-8 to QA-7                                                                                                                                               | C.R. Lytle       |
| 1/3/96       | No changes. Date of origination.                                                                                                                                               | C.R. Lytle       |

### ANNUAL REVIEW

The undersigned attests that this standard operating procedure has undergone annual review for adherence to current practices and the latest QA/QC protocols:

|                                    |                                                        |                         |
|------------------------------------|--------------------------------------------------------|-------------------------|
| <u>Sheri Heldstab</u><br>Signature | <u>QA Officer/<br/>Conv. Chem. Tech. Dir.</u><br>title | <u>12-15-14</u><br>date |
| <u>Sheri Heldstab</u><br>Signature | <u>Conv. Chem. Tech. Dir.</u><br>title                 | <u>11-6-15</u><br>date  |
| _____<br>Signature                 | _____<br>title                                         | _____<br>date           |

## CALIBRATION OF LABORATORY PIPETTES CHESTER LABNET PROPRIETARY METHOD

### 1.0 Introduction

- 1.1 Test Method Reference ID: Chester LabNet proprietary method.
- 1.2 Applicability: N/A
- 1.3 Detection Limit: The balance measures down to ~~0.1~~ <sup>0.01 mg</sup> mg. There is no true detection limit for this method. *SA 12-15-14*
- 1.4 Method Performance: N/A

### 2.0 Summary

- 2.1 Scope and Application: The intended use of this method is for the calibration of variable pipettes used to measure and/or dispense liquids in the laboratory and to the documentation of the calibrations. *This method meets its intended use. SA 11-6-15*
- 2.2 Summary of Method: The manufacturer calibrates autopipettes prior to shipment; however this calibration may change over time and usage. After the desired volume is set, the pipette calibration is checked by pipeting room temperature de-ionized water <sup>into SA 11-6-15</sup> out of a weighing vessel. If the resultant volume is not within  $\pm 1\%$  of the set volume, the autopipette mechanism is adjusted and the setting rechecked. Autopipette calibrations are checked once per month. All data are entered ~~in ink~~ <sup>SA 11-6-15</sup> in the pipette calibration logbook located in the laboratory.
- 2.3 Interferences: air currents may affect both the balance stage stability and the rate of evaporation of water being measured.
- 2.4 Sample collection/preservation/shipment/storage: N/A

### 3.0 Safety

- 3.1 Follow the Chester LabNet Chemical Hygiene plan.
- 3.2 This method presents no safety risk beyond typical laboratory safety hazards.
- 3.3 No carcinogenic reagents are used in this method.

### 4.0 Pollution Prevention and Waste Management

- 4.1 Only De-ionized water is utilized in this method. No pollution or chemical waste is generated by this method.

### 5.0 Apparati, Equipment and Supplies

- 5.1 Variable volume autopipettes.
- 5.2 Bound pipette calibration logbook
- 5.3 Analytical balance sensitive to  $\pm 0.1$  mg *SA 12.15.14*  
*0.01 mg*

### 6.0 Reagents and Standards

- 6.1 De-ionized water  $\geq 16.7$  megohm-cm

### 7.0 Preparation, Calibration and Standardization

- 7.1 Calibrate the balance: *per SOP QA-010 SA 12.15.14*
  - 7.1.1 On the front panel of the balance, push the CAL button. The balance will automatically calibrate using an internal weight, then tare itself. Wait until the balance display reads "0.0000g" before proceeding. *200g CAL*  
*"0.0000g" 12.9.14 CSK*
  - 7.1.2 Check the calibration of the balance by weighing and recording the masses of three non-NIST traceable weights (5mg, 50mg, 500mg) and <sup>two</sup> one NIST traceable weight (200mg). *0.5g / 500mg 50g*  
*3g and 5g. CSK 12.9.14*

The non-NIST traceable weights are used as a precision check only and are not certified weights. They are used to verify the internal calibration weight, which is certified annually.

*St 12-15-14*

7.2 Record all calibration data in the Balance Logbook kept in the drawer underneath the balance.

### 8.0 Procedure

8.1 If it has not already been done, assign autopipette a unique number consisting of the nominal pipette size, followed by a sequential letter assigned at the time of purchase. For example, two pipettes of nominal size 0.1 mL purchased on different dates would be labeled:

0.1A (purchased first)

0.1B (purchased second)

8.2 Set autopipette to the volume desired. Pipet room temperature de-ionized water into a tared weighed vessel and weigh the mass to the nearest 0.1 mg. The weight in grams is the pipette volume in mL. Repeat three times to verify pipet accuracy. Record the final weight.

*St 11-6-15*  
*record*  
*0.01mg St 12-15-14*  
*St 11-6-15 For pipets with maximum volumes of 100µl or greater, record mass to 0.1mg. For pipets with max volumes <100µl, record mass to 0.01mg.*

8.3 If the pipette is used at other volumes than the nominal volume, change the setting and check the calibration at the other commonly used volumes. For example, a 1.000 mL variable pipette may be checked at 1.000 mL, 0.500 mL and 0.250 mL settings.

8.4 Record the date, analyst's initials, pipette identification number and setting, and recorded weight into the pipette calibration logbook.

8.5 10 µL pipet:

8.5.1 Tare weigh a small piece of non-static absorbent material (piece of paper towel, small piece of filter, etc). Pipette 5 or 10 µL of DI water onto the material and record the mass. Note that this variation must be performed for any small volume pipette as the large surface:volume ratio causes rapid evaporation and causes an accurate reading to be nearly impossible to obtain without an absorbent material

*x0.01mg. St 11-6-15*

to hold the water on the balance.

8.5.2 The primary use of this pipette is in spiking samples for analysis by IC and adding concentrated anion eluent to each sample. If the spike recoveries trend high or low on a regular basis, or the water dip becomes more pronounced or becomes a peak, check this pipette immediately.

8.6 Occasionally, an analyst will do a rapid check on a pipet of that volume, however, none of the control limits may apply to these checks, as the checks are used simply as a rough approximation (e.g. to check for gross errors in the pipet) of the true volume.

9.0 QA/QC

9.1 Balance Calibration Check (non-NIST traceable weights)-

*refer to SOP QA-010  
2A 12-15-14*

- 9.1.1 Frequency: once, immediately after balance calibration
- 9.1.2 QC statistic: mass (g) of 5mg, <sup>50g</sup>50mg and 500mg weights
- 9.1.3 Control limits:  $\pm 0.0001$  g from previous measurement.
- 9.1.4 Corrective action: Recalibrate balance and verify weights again. If still out of control, contact balance servicing company.
- 9.1.5 Note: This check is a precision check only, to verify that no significant change has occurred with the calibration weight which is located internal to the balance. The internal calibration weight is certified annually during the servicing of the balance.

9.2 Balance Calibration Check (<sup>3g + 5g</sup>200mg NIST traceable weight):

- 9.2.1 Frequency: once, immediately after balance calibration
- 9.2.2 QC statistic: mass (g) of <sup>3g + 5g</sup>200mg weights
- 9.2.3 Control limits: within the uncertainty as shown on the annual NIST certification of the weight.
- 9.2.4 Corrective action: Recalibrate balance and verify weights again. If still out of control, contact balance servicing company.

9.3 Pipet Calibration Check:

- 9.3.1 Frequency: monthly at a minimum of one volume setting (more if more settings are commonly used)
- 9.3.2 QC statistic: mass (g)
- 9.3.3 Control limits:  $\pm 1\%$  of set value <sup>544.10.6-15</sup> or  $\pm 0.1$  mg, whichever is greater.
- 9.3.4 Corrective action: Adjust pipet such that the reading is within control. Follow manufacturer's instructions for how to adjust each pipet. After adjustment, recheck pipet.

**10.0 Calculations**

10.1 1.000 mL of DI water at room temperature = 1.000 g delivered.

**11.0 References**

11.1 Refer to the User's Manual for each individual pipet for instructions on adjusting pipets.

**12.0 Definitions**

- 12.1 Analyst: the designated individual who performs the "hands-on" method and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.
- 12.2 Analysts' Notes: Non-essential aspects of a method, which may help the analyst during some phase of the method. Notes may include, but not be limited to, historical aspects of the method, "tricks" of the method, unexpected issues to be aware of, or other facts or opinions related to the method, but not directly part of the procedure.
- 12.3 Calculations (Data Reduction): the mathematical process of transforming raw data into a more useable form.
- 12.4 Calibrate: to determine, by measurement or comparison with a standard, the correct value of each reading of the instrument.
- 12.5 Control Limit: A mathematical representation of acceptable limits for a given Quality Control Metric such as percent recovery or percent difference. Limits may be in the form of an absolute number or represented as a percentage.

12.6 Corrective Action: the action taken to address and/or eliminate where possible the causes of a nonconformity, such as exceeding a control limit. Actions may include reanalyzing a sample, or noting the non-conformance in the data report.

12.7 Frequency: The number of occurrences of a specified event within a given interval. The number of samples or analytical runs with which a given QC sample or metric must be analyzed or verified.

12.8 QA/QC: Quality Assurance/Quality Control. A series of samples or metrics designed to show precision, accuracy and bias of the procedure are within acceptable limits.

12.9 QC Statistic: any of a number of statistical permutations performed on raw data to generate a metric capable of being subjected to control limits and corrective actions.

12.10 Reagent: a single chemical or combination of chemicals or a chemical solution used in the preparation or analysis of samples.

### **13.0 Analysts' Notes**

13.1 N/A

**Appendix A: Differences from Promulgated methods**

There is no promulgated method for pipet calibration checks. This method is a *CHESTER LabNet* proprietary method for internal use.

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## Standard Operating Procedure QA-010.02

### Laboratory Balance Calibration and Verification Chester LabNet Proprietary Method

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#### Approvals:

|                                                                                                              |                                                                                                      |
|--------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|
| <br>_____<br>Author       | <br>_____<br>Date |
| <br>_____<br>Lead Analyst | <br>_____<br>Date |
| <br>_____<br>QA/QC        | <br>_____<br>Date |

Effective from: 5.17.16  
Effective until: present



## Laboratory Balance Calibration and Verification Chester LabNet Proprietary Method

### 1.0 Introduction

1.1 Test Method Reference ID: Proprietary Method

1.2 Applicability: This method is applicable to the calibration and verification of laboratory balances for general laboratory use.

*For balances used in the Gravimetry laboratory, refer to pertinent Gravimetry SOPs (GR-001 and GR-019).*

1.3 Detection Limit:

1.3.1 *Sartorius CPA224S* - Conventional Chemistry Laboratory reads to 0.0001g (0.1mg).

1.3.2 *Sartorius MSA225S* - Source Particulate Matter Laboratory balance (Method 5, 202, etc.) reads to 0.00001g (0.01mg).

1.4 Method Performance: N/A

### 2.0 Summary

2.1 Scope and Application: The intended use of this method is for the calibration and verification of laboratory balances, other than those used in the Gravimetry laboratory. Selectivity is based on the presence of mass. This method meets its intended use.

2.2 Summary of Method: Balances are NIST certified on an annual basis. Balances are calibrated once per day of use per manufacturers' instructions, and calibration is verified using NIST-traceable weights spanning the expected range of use.

2.3 Interferences: static electricity is known to alter the displayed masses of objects and materials. Antimatter would be a negative interferent.

2.4 Sample collection/preservation/shipment/storage: N/A

### **3.0 Safety**

3.1 Follow the Chester LabNet Chemical Hygiene plan.

3.2 This method presents no safety risk beyond typical laboratory safety hazards.

3.3 No carcinogenic reagents are used in this method.

### **4.0 Pollution Prevention and Waste Management**

4.1 The smallest quantity of chemical feasible is removed from its primary container for use.

4.2 Chemicals are used in amounts needed by the method, and excess reagents are not made.

### **5.0 Apparati, Equipment and Supplies**

5.1 Conventional Chemistry Laboratory Balance: *Sartorius CPA224S* with internal calibration.

5.2 Source Particulate Matter (SPM) Laboratory Balance: *Sartorius MSA225S* Analytical Balance with internal calibration.

5.3 NIST-traceable weights (location in parentheses):

- 5.3.1 5.0 mg (Conventional Chemistry Lab)
- 5.3.2 0.5000 g (Conventional Chemistry Lab)
- 5.3.3 50.0000 g (Conventional Chemistry Lab)
- 5.3.4 0.2000g (SPM Lab)
- 5.3.5 3.0000g (Weighroom)
- 5.3.6 5.0000g (Weighroom)
- 5.3.7 100.0000g (SPM Lab)

5.4 Kimwipes (for cleaning balance)

5.5 Camel hair brush (for non-static cleaning of balance)

## 6.0 Reagents and Standards

6.1 Ethanol (for cleaning)

6.2 DI water (for cleaning)

## 7.0 Preparation, Calibration and Standardization

7.1 Annual balance NIST certification:

7.1.1 Once per year, request Quality Control Services or a similar A2LA accredited certified body certify the balances.

7.1.2 Document annual certification by retaining certificates of traceability in the appropriate binder.

7.2 Check cleanliness of balance:

7.2.1 Visually inspect balance stage, chamber and walls of chamber for dirt, dust, spilled material, etc.

7.2.2 If necessary, use the camel hair brush to brush debris off of the stage or out of the weighing chamber.

7.2.3 If necessary, wipe down the stage, chamber floor or chamber walls with ethanol and a Kimwipe to remove debris.

7.2.4 If necessary, disassemble the balance chamber, including stage and stage surround, and rinse thoroughly with DI water. Dry all parts thoroughly, using ethanol if necessary, then reassemble and allow to fully dry before continuing.

7.3 Verify balance is level:

7.3.1 Using the built in level bubble, verify that the balance is level.

- 7.3.2 If not level, adjust the feet until level (CPA224S) or use the autoleveling function of the balance (MSA225S) on the touchscreen.

## 8.0 Procedure

### 8.1 Calibrate balance:

#### 8.1.1 *Sartorius MSA225S:*

8.1.1.1 Press the "Cal" icon on the control panel touch screen. Choose "Internal Calibration".

8.1.1.2 When finished calibrating, press the "back" icon on the control panel touch screen.

8.1.1.3 The balance calibration is now ready to be verified as in Section 8.2.

8.1.1.4 Record the calibration date and analyst's initials in the Sartorius MSA225S Balance logbook.

#### 8.1.2 *Sartorius CPA224S:*

8.1.2.1 Press the "Cal" button. The display will read "C" and the balance will start clicking as it calibrates.

8.1.2.2 When finished calibrating, the display will read "CC", then return to "0.0000 g".

8.1.2.3 The balance calibration is now ready to be verified as in Section 8.2.

8.1.2.4 Record the calibration date and analyst's initials in the Sartorius CPA224S Balance logbook.

8.2 Verify calibration:

8.2.1 *Sartorius CPA224S*:

8.2.1.1 Weigh the following NIST traceable weights:

- 8.2.1.1.1 5.0 mg
- 8.2.1.1.2 0.5000 g
- 8.2.1.1.3 50.0000 g

8.2.1.2 Record the stable displayed masses of each weight in the Balance Calibration Logbook. All weights must have a mass within  $\pm 0.0001\text{g}$  (0.1 mg) of the certified NIST mass for that weight.

8.2.2 *Sartorius MSA225S*:

8.2.2.1 Weigh the following NIST traceable weights:

- 8.2.2.1.1 0.2000g (SPM Lab)
- 8.2.2.1.2 3.0000g (Weighroom)
- 8.2.2.1.3 5.0000g (Weighroom)
- 8.2.2.1.4 100.0000g (SPM Lab)

8.2.2.2 Record the stable displayed masses of each weight in the Balance Calibration Logbook. All weights must have a mass within  $\pm 0.00010\text{g}$  (0.10 mg) of the certified NIST mass for that weight.

**9.0 QA/QC**

9.1 Mass of NIST-traceable calibration verification weights for balances reading to 0.1mg:

- 9.1.1 Frequency: after each daily calibration
- 9.1.2 QC statistic: mass
- 9.1.3 Control limits:  $\pm 0.0001\text{g}$  (0.1 mg) from the NIST certified mass of the weight.
- 9.1.4 Corrective action: recalibrate balance and reweigh verification weights.

9.2 Annual balance certification:

- 9.2.1 Frequency: once annually
- 9.2.2 QC statistic: N/A
- 9.2.3 Control limits: as given by certifying body (QC Services or other A2LA certified company)
- 9.2.4 Corrective action: request certification company to repair balance as needed.

**10.0 Calculations**

10.1 N/A

**11.0 References**

11.1 Proprietary Method.

**12.0 Definitions**

- 12.1 Analyst: the designated individual who performs the "hands-on" method and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.
- 12.2 A2LA: American Association for Laboratory Accreditation, a nonprofit, non-governmental, public service, membership society. A2LA offers programs for the accreditation of inspection bodies, proficiency testing providers, reference material producers and product certification bodies.
- 12.3 Calculations (Data Reduction): the mathematical process of transforming raw data into a more useable form.
- 12.4 Calibrate: to determine, by measurement or comparison with a standard, the correct value of each reading of the instrument.
- 12.5 Control Limit: A mathematical representation of acceptable limits for a given Quality Control Metric such as percent recovery or percent difference. Limits may be in the form of an absolute number or represented as a percentage.
- 12.6 Corrective Action: the action taken to address and/or eliminate where possible the causes of a nonconformity, such as exceeding a control limit. Actions may include reanalyzing a sample, or noting the non-conformance in the data report.

- 12.7 Detection Limit: the lowest concentration of an analyte of interest that can be identified, measured and reported with confidence that the analyte concentration is not a false positive value. For balances, the detection limit is the smallest amount of mass the balance can read (e.g. furthest decimal place the balance displays)
- 12.8 Frequency: The number of occurrences of a specified event within a given interval. The number of samples or analytical runs with which a given QC sample or metric must be analyzed or verified.
- 12.9 NIST: National Institute of Standards and Technology: The US Governmental Agency which defines all tolerances of standard weights and measures, amongst other activities.
- 12.10 QA/QC: Quality Assurance/Quality Control. A series of samples or metrics designed to show precision, accuracy and bias of the procedure are within acceptable limits.
- 12.11 QC Statistic: any of a number of statistical permutations performed on raw data to generate a metric capable of being subjected to control limits and corrective actions.
- 12.12 Reagent: a single chemical or combination of chemicals or a chemical solution used in the preparation or analysis of samples.
- 12.13 Standard: a weight of known and documented mass.

**13.0 Analysts' Notes**

13.1 N/A

## APPENDIX A: Differences from Promulgated methods

There is no promulgated method for the calibration of balances. This method was developed in-house.

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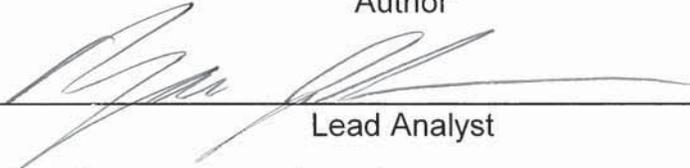
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## Standard Operating Procedure QA-011.01

Control and Handling of Standards and Reference Materials  
Chester LabNet Proprietary Method

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### Approvals:

|                                                                                                              |                                                                                                        |
|--------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|
| <br>_____<br>Author       | <br>_____<br>Date |
| <br>_____<br>Lead Analyst | <br>_____<br>Date |
| <br>_____<br>QA/QC        | <br>_____<br>Date |

Effective from: 5-20-14  
Effective until: present



## Control and Handling of Standards and Reference Materials Chester LabNet Proprietary Method

### 1.0 Introduction

1.1 Test Method Reference ID: N/A

1.2 Applicability: This method is applicable to the use and handling of all standards and reference materials..

1.3 Detection Limit: N/A

1.4 Method Performance: N/A

### 2.0 Summary

2.1 Scope and Application: This intended use of this method is for the appropriate storage, use and handling of all standards and reference materials, including standard weights, thin film standards for XRF and conventional liquid standards for use in conventional chemical analysis. This method meets its intended use.

2.2 Summary of Method: Three major types of standards are used by Chester LabNet.

2.2.1 Standard weights: These are ASTM Class 1 weights used to calibrate or verify the calibration of balances.

2.2.2 Thin Film Standards: These standards were originally obtained from NBS (National Bureau of Standards) prior to NBS becoming NIST. These standards are no longer available from NIST and are comprised of polycarbonate film with thin-layer vapor deposition of a known quantity of metals for use in calibration and calibration verification of XRF's configured for thin-layer deposit analysis (primarily air particulates captured on filters).

2.2.3 Liquid standards: These standards are used in the calibration and calibration verification for a variety of conventional chemical analysis, including, but not limited to, IC, ICP, GFAA and CVAA.

2.3 Interferences: N/A

2.4 Sample collection/preservation/shipment/storage: Standards are obtained from manufacturers, where available, and stored per manufacturers' recommendations. In general, standard weights are stored at room temperature, XRF thin film standards are stored at room temperature. Conventional analyses liquid standards may be stored either refrigerated or at room temperature depending upon the manufacturers' instructions and the type of standard.

### **3.0 Safety**

3.1 Follow the Chester LabNet Chemical Hygiene plan. Always treat samples of unknown origin and/or constitution as hazardous.

3.2 Read the MSDS or accompanying documentation for safety hazards for each standard. Generally, this method presents no safety hazards beyond the normal laboratory safety hazards, however, some metals standards may contain HF, which presents a greater than typical laboratory hazard.

3.3 No carcinogenic reagents are used in this method.

### **4.0 Pollution Prevention and Waste Management**

4.1 The smallest quantity of chemical feasible is removed from its primary container for use.

4.2 Chemicals are used in amounts needed by the method, and excess reagents are not made.

4.3 Chester LabNet is a conditionally exempt small quantity generator and as such does not require formal chemical waste processing.

4.3.1 Acidic and Basic wastes are neutralized prior to disposing of them in the sanitary sewer system.

4.3.2 Organic liquids are usually primarily used for cleaning purposes. Organic wastes are generated in very small quantities, and evaporate off with no need for more formal disposal.

4.4 Larger quantities of known hazards are returned to the client for disposal.

4.5 Expired Chemicals:

4.5.1 Dry chemicals beyond their expiration date are lab packed and disposed of by a qualified chemical disposal company.

4.5.2 Acids and Bases beyond their expiration date are neutralized prior to being disposed of via the sanitary sewer system.

4.5.3 Organic liquids beyond their expiration date are disposed of by a qualified chemical disposal company if the volume or type of liquid warrants such disposal. Disposal of organic liquids is rare.

## **5.0 Apparati, Equipment and Supplies**

5.1 Cotton or polyester glove liners

5.2 Plastic or Teflon coated forceps

5.3 Secondary containers (XRF, Carbon Split and weights only)

## **6.0 Reagents and Standards**

6.1 Commercially available aqueous standards:

6.1.1 IC standards to include F, Cl, Br, NO<sub>3</sub>, PO<sub>4</sub>, SO<sub>4</sub>, Na, NH<sub>4</sub> and K

6.1.2 ICP/GFAA standards to include all metal species being analyzed

6.1.3 CVAA Hg standards

6.1.4 IC-PCR CrVI standards

- 6.2 Commercially available standard weights, NIST-traceable
- 6.3 NIST thin film XRF standards (originally commercially available, no longer manufactured)
- 6.4 Carbon Split "standard" (statistically characterized sample)
- 6.5 Commercially available 5% Methane/95% Helium, certified standard compressed gas.

## **7.0 Preparation, Calibration and Standardization**

- 7.1 All standard weights must be recertified by an A2LA accredited certification laboratory annually.
- 7.2 OC/EC Carbon Split "standard": analyze 20 punches from an 8"x10" quartz filter, spacing the punches in 5 columns and 4 rows, evenly across the sample deposit. Determine the average percent organic carbon and three times the standard deviation of the 20 data points. The Technical Director and QA Officer will determine, based on the precision of the data points, whether or not a given filter is suitable to be used as a "standard."
- 7.3 OC/EC Sucrose standard: prepare standard as described in SOP OC-001.

## **8.0 Procedure**

- 8.1 Standard weights:
  - 8.1.1 Store standard weights in dust proof containers at room temperature.
  - 8.1.2 Store standard weight containers in such a manner as to prevent or severely diminish the likelihood of weights being dropped, knocked to the ground or otherwise physically abused.
  - 8.1.3 Handle smaller standard weights only with plastic or Teflon coated forceps.
  - 8.1.4 Wear cotton or polyester gloves when handling larger (e.g. 100g) standard weights.
  - 8.1.5 When transferring standard weights from one physical location to another, handle in such a manner that the weight is protected from environmental and physical damage (e.g. in a closed container, or protected from the likelihood of being dropped).

SOP: QA - 011.01

8.1.6

for Microbalance

#### Determination of Standard Verification Weight from Certified Value Procedure

The following procedure must be performed each time the working and primary mass reference standards are recertified by Quality Control Services, or similarly accredited entity. This procedure may also be used to re-verify a standard that exceeds the precision acceptance criteria ( $\pm 3 \mu\text{g}$ ).

1. Immediately after standard is received from the certification laboratory, weigh the standard three times daily for five days.
2. Record the weights and calculate the mean for each day.
3. Average the mean from all five days to obtain the verified value.

If the verified value determined for the mass reference standard differs from the certified value by more than  $20 \mu\text{g}$ , verify with secondary standard. Based on the results from secondary standard check, either contact the certification laboratory to calibrate the microbalance, or return the standard for recertification.

JS 6.24.16



## 8.2 Thin film XRF standards

- 8.2.1 Store thin film standards in XRF sample holders.
- 8.2.2 Store the sample holders containing the standards in a dust free secondary container (e.g. plastic box with lid, sample holder trays, instrument sample carousel) in such a manner as to prevent or severely diminish the likelihood of being dropped, knocked to the ground or otherwise physically abused.
- 8.2.3 Handle the standards by hand touching only the edges of the sample holder. DO NOT TOUCH THE THIN FILM STANDARD.

## 8.3 OC/EC Carbon Split "standard"

- 8.3.1 Store the split "standard" frozen (<0 °C).
- 8.3.2 Store the standard inside a glassine envelope inside a manila folder inside a manila envelope.
- 8.3.3 Leave the filter inside its container(s) if at all possible. If handling is necessary, handle the filter only by the edge where there is no deposit.

## 8.4 Methane gas standard

- 8.4.1 Store tank at room temperature, chained to the wall.
- 8.4.2 When replacing the tank, keep the tank fully closed until the regulator is seated properly and regulator threads are completely tightened.
- 8.4.3 When moving the tank, ensure that the tank valve is fully closed and the valve cap is screwed down tightly.

## 8.5 Aqueous standards (including those made in-house):

- 8.5.1 Store stock standards (primary or secondary) per manufacturers' guidelines with the following exceptions:
  - 8.5.1.1 Sucrose standard (in-house) is stored refrigerated (0 – 6 °C)
  - 8.5.1.2 IC anion and cation standards are stored refrigerated (0 – 6 °C)

- 8.5.2 Store commercially available stock standards tightly capped in their original containers. Do not store aliquots of commercially prepared standards in other containers.
- 8.5.3 Store stock standards in locations where environmental contamination is minimized and/or incompatible activities occur (e.g. do not store a NO<sub>3</sub> standard in areas of the lab that use large amounts of conc. HNO<sub>3</sub>)
- 8.5.4 Always use clean pipet tips and sterile technique when removing aliquots of stock standards from their original containers.

## 9.0 QA/QC

### 9.1 Annual standard weight certification

- 9.1.1 Frequency: annually
- 9.1.2 QC statistic: mass
- 9.1.3 Control limits: tolerance and uncertainty given by certifying laboratory
- 9.1.4 Note: if a specific weight is certified to a mass reading significantly different than its previous weights from prior years, verify against a different weight or contact the certifying laboratory for verification.

### 9.2 Expiration dates:

- 9.2.1 Frequency: as needed
- 9.2.2 QC statistic: date
- 9.2.3 Control limits: prior to expiration date
- 9.2.4 Corrective Action: do not use standard after its expiration date. Obtain a non-expired standard for future use.
- 9.2.5 Note: Thin film XRF standards and OC/EC split "standard" have no expiration dates.

## 10.0 Calculations

### 10.1 N/A

## 11.0 References

11.1 N/A

## 12.0 Definitions

12.1 Calculations (Data Reduction): the mathematical process of transforming raw data into a more useable form.

12.2 Calibrate: to determine, by measurement or comparison with a standard, the correct value of each reading of the instrument.

12.3 Control Limit: A mathematical representation of acceptable limits for a given Quality Control Metric such as percent recovery or percent difference. Limits may be in the form of an absolute number or represented as a percentage.

12.4 Corrective Action: the action taken to address and/or eliminate where possible the causes of a nonconformity, such as exceeding a control limit. Actions may include reanalyzing a sample, or noting the non-conformance in the data report.

12.5 Frequency: The number of occurrences of a specified event within a given interval. The number of samples or analytical runs with which a given QC sample or metric must be analyzed or verified.

12.6 QA/QC: Quality Assurance/Quality Control. A series of samples or metrics designed to show precision, accuracy and bias of the procedure are within acceptable limits.

12.7 QC Statistic: any of a number of statistical permutations performed on raw data to generate a metric capable of being subjected to control limits and corrective actions.

12.8 Reagent: a single chemical or combination of chemicals or a chemical solution used in the preparation or analysis of samples.

12.9 Standard: a solution or matrix of a known amount of analyte(s).

12.9.1 Primary standard: a standard received from a vendor with NIST or equivalent traceability.

12.9.2 Secondary standard: a standard received from a vendor with NIST or equivalent traceability, of a different lot number or manufacturer than the primary standard.

12.9.3 Working standard: any standard created when mixing, diluting or otherwise manipulating aliquots of primary standards. May be called "working standards" or "intermediate standards".

**13.0 Analysts' Notes**

13.1 N/A

## APPENDIX A: Differences from Promulgated methods

There is no promulgated method for the storage and handling of standards. This method was developed in-house.