SEAS Chemistry

RP – DRAFT -

MEASUREMENT AND ANALYSIS OF THE CHEMICAL COMPOSTION OF THE AMBIENT AEROSOL USING SEAS

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SEAS Chemistry

NOTE: GRAY SENTENCES HAVE BEEN REMOVED OR REPLACED IN THE CURRENT VERSION

MEASUREMENT AND ANALYSIS OF THE CHEMICAL COMPOSTION OF THE AMBIENT AEROSOL USING SEAS

1. PURPOSE AND APPLICABILITY

This research protocol contains the protocol for measurement and analysis of the chemical composition of ambient aerosol particles at the Baltimore PM supersite using SEAS. This is an evaluation version of an anticipated standard operating procedure (SOP), which will result from experiences with this RP. Due to this nature this RP is subject to changes. Every addition to this RP will be added as an Appendix during this study.

2. DEFINITIONS

SEAS	semi-continuous ambient aerosol sampler
RP:	research procedure

3. QUALITY ASSURANCE

We expect to obtain a sample completeness exceeding 80 % of scheduled measurements. Due to the experimental nature of the instrument both precision and accuracy of the obtained data have to be determined from the results of the supersite measurements. Several tests will be performed in the field to quantify the sampling system performance before, during and after measurement campaigns. Performance checks will be scheduled during the sampling campaign. The performance tests include (but are not limited to)

1. Two collocated samplers at the Baltimore PM supersite to quantify sampler precision.
2. Field blanks obtained at least on a weekly basis.
3. Daily check of the minor and major flow-rate of the virtual impactor
4. Daily check of the steam generator performance

Laboratory operations will follow established, written protocols. These procedures will include tests to determine the accuracy and test the precision of the measurements. Procedures to ensure the quality of the data collected from laboratory analysis include:

1. Routine and thorough instrument calibration using traceable standards when available;
2. Rigorous record keeping and auditing;
3. Replicate analysis of single samples to measure precision; and
4. Analysis of laboratory and field blanks to monitor possible contamination problems.

Minimum detection limits for instruments will be determined from analysis of field blanks. A concentration equal to 2 times the average measured field blank level will be considered the minimum detection limit. At least weekly blanks will be collected and analyzed. Instrument precision and analytical precision of laboratory analysis will be calculated as the standard deviation between replicate analysis of authentic standards (for the laboratory precision) or the parallel analysis of co-located sample collection (instrument precision) according to:

$$Standard\ \ Deviation(s) = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

A minimum of replicate analyses will be performed to calculate the standard deviation. For further details see the SOP for the GFAA analysis.

4. HEALTH AND SAFTEY WARNINGS

1. Pressurized air is used to remove the sample from the impinger. Observe safety precautions for pressurized non-flammable gases.
2. The surfaces of the steam generator and the steam inlet may be extremely hot. Don't touch these areas with your hands.
3. Sample vials contain concentrated nitric acid. Handle only with gloves and use safety goggles.

5. CAUTIONS

N/A

1. INTERFERENCES

Any metal contamination of the samples must be avoided. This includes e.g. that no Hi-Volume sampler should be located close to the inlet of the SEAS.

7. RESPONSIBILITIES

NA

8. EQUIPMENT AND MATERIALS

8.1 Equipment

8.1.1 Field

1. SEAS
2. Personal computer
3. National Instruments LabView Program for instrument control with data I/O cards
4. Trays for X-Y sampler
5. Cleaned prepared sample vials
6. Distilled water for steam generator
7. Spare boiling flask for steam generator
8. Spare tubing for metering pump

8.1.2 Laboratory

1. SIMAA with lamps
2. Microbalance
3. Personal computer
4. 20 µl pipette
5. X-Y sampler trays
6. Clean inner transport containers
7. Outer transport containers (not in the clean room)

8.2 Miscellaneous materials

1. Sample vials
2. Caps for sample vials
3. Diskettes for spreadsheet data
4. 0.5 % reagent grade nitric acid
5. 50 % reagent grade nitric acid
6. 70 % ultra-pure nitric acid
7. Argon
8. Milli-Q water
9. Disposable gloves (sizes for all involved personal)
10. Safety goggles

8.3 Paper materials

1. Field forms to record performance parameters of SEAS in the field
2. Laboratory book for SEAS (field)
3. Laboratory book “sample preparation”
4. Laboratory book SIMAA

9. PROCEDURES

a. Sample handling

Due to the large number of samples per day sample handling procedures could be a major source for missing data. Correct sample handling must be strictly enforced.

i. Cleaning of sample vials, vial caps, reagent bottles and autosampler cups

1. Rinse material with Milli-Q water.
2. Soak overnight in 50% reagent grade nitric acid.
3. Rinse 3x with Milli-Q water.
4. Soak overnight in Milli-Q water.
5. Dry overnight in clean hood.

NOTE: Wear disposable gloves for all handling of the materials after step 1)
Cleaning may be done in bulk quantities

9.2.2 Preparation of vials and X-Y trays

Note: The following procedures must be done in a clean room

1. Prepare X-Y tray and vials for one day
2. Label X-Y tray with appropriate ID
3. Load X-Y tray into inner transport container
4. Take inner transport container out of the clean room
5. Load inner container into outer transport container
6. Mark loaded outer container with a green label (=prepared vials)

Note: More than one X-Y tray can be loaded in one session. There must be at least 3 loaded trays available in the laboratory during the whole measurement campaign.
Note 2: These steps have been modified. Each vial will receive a unique ID after sampling. This allows for continuous sample Ids.

7.1.3. Field procedures for sample vials

1. Remove inner transport container in the “dirty” area of the trailer
2. Take inner container into clean area
3. Record position of tray in the file and store sample Ids both on diskette and LabPC. Print out ID list for the sample if possible.
4. Wait until 30 minute sample is finished and transferred to vial

5. Remove X-Y tray from sampler and install new tray. Check tray ID again.
6. Record start time for new tray both on paper and on file
7. Store file both on PC and on diskette
8. Screw caps on every sample vial of the old tray
9. Put tray into inner transport container
10. Mark container with red label
11. Freeze samples for transport
12. Transport samples to the lab using outer container

i. Handling procedures for sample analysis

1. Open spreadsheet for the tray to be analyzed
2. Label each vial with the appropriate sample ID as obtained from the SEAS sampling log.
3. Add 20 µl of ultra-pure 70 % nitric acid
4. Add approximately 5 mL of high-purity water to laboratory and field blanks.
5. If immediate analysis of the sample is not possible remount cap and store in vial tray
6. Prepare multi-element standards as needed for GFAAS analyses. Generally, two standards are needed: one about 10x the lower limit, and the other about 2x the upper limit of expected concentrations.
7. Prepare Standard Reference Materials. SRM 1643d should be diluted 5-fold. SRM 1648 should be prepared as slurry of about 1.5 mg in 100 mL of 0.5% nitric acid.
8. Dilute samples 10-fold with 0.5% nitric acid prior to analysis for Al, Fe, and Zn.

Refer to SIMAA 6000 manuals for detailed information on instrument operation

<u>GFAAS Startup</u>

1. Turn on argon supply and set to 50 psi.
2. Turn on HEPA filter and exhaust fan.
3. Turn on SIMAA 6000.
4. Wait 1 minute, then start AA Analyst on control computer.
5. Select default window layout.
6. Choose method to use for analysis. Refer to *AA WinLab for SIMAA 6000: Software Guide* for more information.
7. Install lamps as needed and activate. Allow at least 1 hour for warmup.
8. Change graphite furnace if needed (refer to *SIMAA 6000: Installation, Maintenance, System Description*), and clean furnace area with a cotton swab.
9. Align lamps for maximum intensity.
10. Load autosampler tray and setup Sample Information File.
11. To reduce concentration changes due to evaporation, add distilled water to cover the bottom of the autosampler tray.
12. Enter Sample Information File location and Results location in the Automated

Analysis Control window. Make sure results will be saved and printed.

13. Check level of rinse solution (0.5% reagent grade nitric acid).

GFAAS Analysis

1. Analyze several Milli-Q blanks until signal reaches a minimum.
2. Enter autosampler locations for sample to be analyzed in the Automated Analysis Control window.
3. Press "Analyze All" to start the analysis. The system will measure calibration blank, calibration standards, reagent blank, and samples.

GFAAS Shutdown

1. Turn off lamps.
2. Exit AA Analyst on control computer.
3. Turn off SIMAA 6000.
4. Turn off HEPA filter and exhaust fan.
5. Turn off argon supply.

10 Instrument maintenance

i. Every other day maintenance

1. Check and record position of X-Y tray, compare with position indicated by the SEAS software
2. Stop sampling.
3. Check all minor and major flow of the virtual impactor using an independent reference meter (gas meter, bubble flow meter)
4. Switch of the sampling pumps and reset baseline of the flow controllers in SEAS software
5. Check for visible contamination of glassware and tubing
6. Check the amount of water in the reservoir for the steam generator. Refill if necessary. Record refill in the maintenance book
7. Replace X-Y tray
8. Restart SEAS

1. Weekly maintenance of SEAS

1. Samle system blank
2. Replace inlet impactor

10.3 Biweekly maintenance of the SEAS

1. replace inlet impactor with cleaned impactor, clean old impactor in the laboratory
2. to be determined

a. Monthly maintenance of the SEAS

1. to be determined

11. Quality assurance

11.1 QA after changes of the OP

If any modification of this OP is necessary this modification will be added to this OP as an appendix. Changes will be applied to SEAS Cytokine first. At least three samples of the first tray after modification of the OP will be analyzed according to the protocol of SEAS chemistry to ensure reproducibility of the measurements. These vials have to be analyzed as soon as possible to avoid data losses due to modifications of the OP. The results for these parallel samples will be included in the appendix to this OP.

11.2. Check for critical operation parameters

The following operation parameters are checked on daily basis:

1. Major and minor flow as indicated by the SEAS program. Check Standard Deviation
2. Indicated temperature and relative humidity
3. Steam generator flask for visible cracks and water level
4. Water supply for steam generator
5. Metering pump tubes for visible wear
6. Any irregularities in the SEAS program

If one or more of the operating parameters are deviating from the nominal, the instrument should be checked and adjusted to the nominal parameters as soon as possible. Data collected with that instrument during the period of malfunction should be corrected, if possible, for the observed deviations.

12.3. Data storage

All original data and the cleaned sets of data will be stored in duplicate on appropriate media for further re-evaluations. One copy of the data should be stored at the main campus, the other copy will remain at the supersite during the study period.

13. REFERENCES

Kidwell, C.B. (2000). Sub-hourly airborne metal analysis by graphite furnace atomic absorption spectrometry after dynamic aerosol concentration. Doctoral thesis UMCP