Standard Operating Procedures for Preparation, Handling and Extraction of Dry Deposition Plates:

Dry Deposition of Atmospheric Particles

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1.0 Introduction

Dry deposition plates are used to measure the mass flux of particles and metals. This standard operating procedure (SOP) addresses the protocol for preparation, handling and acid extraction of these plates. The SOP also discusses quality assurance and quality control measures, and performance criteria.

A schematic of the dry deposition plate is presented in Figure 1. The plate is made of PVC and is 21.5 cms long, 7.6 cms wide, and 0.65 cms thick with a sharp leading edge (<10 degree angle) to ensure laminar flow. The plate is pointed into the wind by a wind vane. Each plate is covered with 4 Mylar strips (7.6 cm x 2.5 cm) coated with approximately 8 mg of Apezion L grease (thickness $\approx$ 8 μm) to collect impacted particles (123 cm^2 total exposed surface). The film is placed on the plate and held down on the edges with a 5 mil thick Teflon or Mylar template, which is secured at each end by spring clips. The strips are weighed before and after exposure to determine the total mass of particles collected. The mass flux is determined by dividing the collected mass by the exposure time and the exposed surface area.

2.0 Preparation of Dry Deposition Plates

Preparation and collection of accurate and reliable data on mass and metal fluxes with dry deposition plates requires that proper laboratory procedures be used during preparation. Laboratory equipment and reagents are listed in Appendix A. The various activities which have been sequentially described in this section include cleaning of glassware used for preparation of dry deposition plates; and cleaning, greasing, equilibrating, and weighing of the sampling media.

2.1 Cleaning of Glassware

Particle-free nylon gloves are used during all cleaning steps. All glassware (e.g., petri dishes, beakers) used in connection with this research will be scrubbed with soap and rinsed in hot tap water. Next, the glassware is rinsed three times in distilled water. Subsequently, it is soaked in a nitric acid bath (5%) for at least 12 hours. After being removed from the bath, the glassware is rinsed three times in distilled water. The final cleaning step involves rinsing the items three times in deionized water.

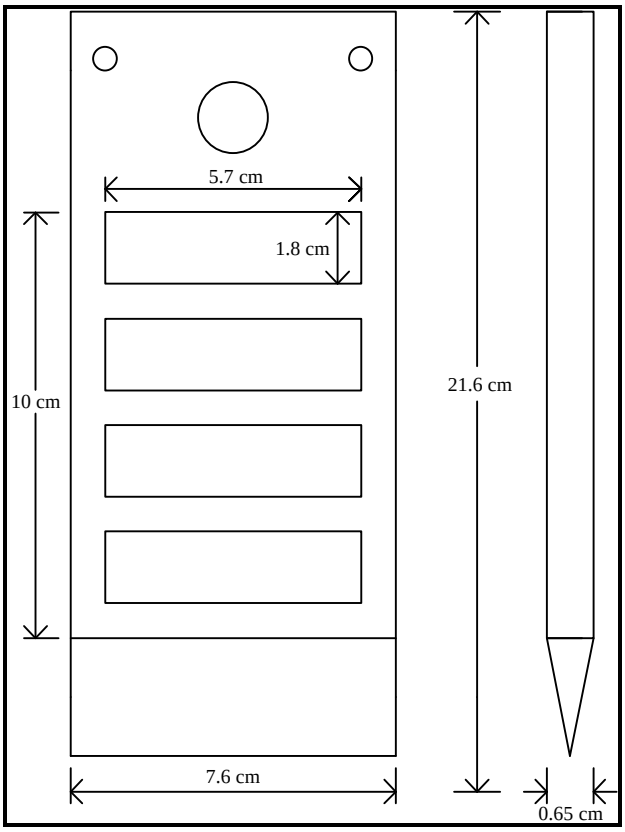

Figure 1. Top View of a Dry Deposition Plate

2.2 Cleaning of Plates

The first step in the cleaning procedure involves wiping the dry deposition plate with a particle free wipe (S/P Brand S/Pec-Wipe) wetted with double distilled methanol. The plates are subsequently placed in a clean plastic wash tray. The second step involves rinsing the plates with deionized water. Finally the plates are dried in a laminar flow clean bench.

2.3 Cleaning of Strips

Mylar (0.002 inches thick) is cut into 1-inch x 3-inch pieces. The area to be greased is marked on each strip with a scratch pen. Prior to being coated with grease the strips are cleaned. The first step in the cleaning procedure involves dipping the strips in glass petri dish containing double distilled methanol and scrubbing both sides with particle free wipe (S/P Brand S/Pec-Wipe). The strips are subsequently dipped in a second petri dish containing deionized water and both sides are again scrubbed with a particle free wipe. The third and fourth steps involve dipping the strips again in deionized water. However, in these steps the strip is not scrubbed. Finally, the strips are put in a storage box for drying.

2.4 Greasing and Equilibrating of Strips

After the strips dry, they are given a thin coat of L-Apiezon grease on the marked area. This is accomplished by melting the grease in a small glass petri dish on a hot plate. A small paint brush is used to coat the strips, which are also warmed on the hot plate. The brush is cleaned prior to use with pure Hexane, followed by Double-Distilled-Methanol. After the strips are coated with the grease, they are put into a dust-free storage box to equilibrate for at least 24 hours before weighing

2.5 Weighing and Mounting of Strips

The initial weight of strips is recorded using a micro balance able to measure at least 0.01 mg. After initial weighing, the strips are mounted on the clean, dry deposition plates. The un-greased edges of the strips are covered with a template made of a thick Mylar film. The Mylar templates are subsequently held down with spring clips. The Mylar templates are cleaned with the same procedures used for the strips. Four strips are mounted on each plate. The dry deposition plates with the mounted strips are put in a dust-free plastic storage box in preparation for field sampling.

3.0 Field Sampling, Labeling, Shipping, and Post-sampling Equilibration and Weighing of Plates

3.1 Field Sampling

The sample box is not opened until all the other preparations are made for field measurements. A list of equipment and supplies for field investigations is provided in Appendix B. The plates and strips are handled with particle free gloves to ensure that there is no physical contact with the greased surface. After sampling, the plates are taken off by unscrewing the hold down nuts, and put in the storage container. The plates are slid sideways into the slots, with the sharp edge into the thin slot. The total sampling time is recorded. Details of field sampling are available in the field sampling SOP.

Each sample set includes field blanks. Field blanks are obtained by mounting four pre-weighed grease-coated Mylar strips on a dry deposition plate. This plate is placed in the storage container along with the sample plates and remain there.

3.2 Labeling/Tracking

All samples will be tagged in indelible ink to indicate the site, the sequence/number of sample, and the status of sample (e.g., field blank). Every sample is assigned a unique identification code which follows the sample through analysis and logging of all data. The label should follow the following format:

3.3 Site-Number/Status

Status would communicate whether the sample is a field blank, a regular sample, or a duplicate sample. Field blanks are designated BK, while duplicates are labeled A and B. For example, the field blank associated with the first sample will be labeled as <site>-01BK. Samples are logged in the sample log sheet. An example of the sample log sheet is presented in Appendix C. One copy of the sample data sheet should be kept in the three-ring binder and the original returned with the sample.
The project evidence will be under the custody of the Principal Investigator and the sample custodian is

the Laboratory Coordinator. The project evidence will contain all sample log sheets and results of laboratory analyses. All pertinent information from the data sheets is transferred to electronic media via computerized spreadsheets. The computer files are backed-up whenever new data is added and two disk or tape copies are kept in separate secure areas at all times. Data generated by the analytical instrument are stored in both electronic and hard copy formats.

If sample integrity is questionable, the PI will decide whether to discard the sample

3.4 Shipping

The samples are transported to the IITAQL immediately after sampling. If it is not possible to ship the samples to IITAQL immediately after sampling, they must be stored at room temperature away from any sources of contamination.

The samples are shipped to the following address:

Dr. Thomas M. Holsen
10 West 33rd Street
Department of Chemical and Environmental Engineering
Illinois Institute of Technology
Chicago, IL 60616-3793

3.5 Equilibration/Weighing

At IITAQL, strips are unloaded from plates, and put back into the storage box for a 24 hour equilibration period before the strips are again weighed.

4.0 Extraction Procedure and Analysis

Extraction is conducted in a Class 100 clean room on the Campus of the University of Michigan. The procedure begins with washing the greased mylar strips with 10-20 mL of hexane in a Teflon vessel. The hexane is subsequently evaporated with a stream of ultra-pure nitrogen. Twenty mL of 10% (v/v) ultra-pure nitric acid is then added to the Teflon container and the container placed in a digestion bomb and loaded into the microwave oven. Acid digestion is carried out for 30 minutes at 160°C and approximately 160 psi. Following digestion, the bomb is allowed to cool for a period of 1 hour. The samples will be analyzed on the ICP-MS.

Method detection limits (MDLs) will be calculated by injecting a low concentration sample 7 times into the ICP. MDL is defined as three times the standard deviation of the concentrations obtained in the seven runs.

Field blanks (unexposed mylar strips) will be monitored to determine whether the sample preparation and transport, the Apezion L grease coating on the mylar film, and the hexane wash contribute to contamination. It is anticipated that the field blanks will have trace concentrations of metals due to the grease, the hexane used for extraction, and the acid used for digestion. Sample concentrations will be corrected by subtracting the concentration obtained for the field blank.

Extraction efficiencies will be calculated by measuring metal concentration after spiking a 10% nitric

acid solution with NIST Urban Particulate Matter (UPM). The ICP-MS will be calibrated daily. A standard curve will be deemed acceptable only if the r^2 (coefficient of determination) is greater than 95%. After every 10 samples a standard will be analyzed as a sample. If the variation between sample and standard concentration is more than 5% the instrument will be recalibrated. Instrument accuracy will be checked daily by analyzing a 2% NIST standard, to ensure that the % recovery is between 70 to 120%. Precision will be estimated by analyzing split samples (e.g., two separate strips from the same plate), and replicate sample extract analysis (same sample analyzed at different times).

Working standards are prepared daily by dilution of commercially available stock solution. Standardization is accomplished with a four point calibration curve (one blank and three standards) that bracket the expected concentration of the samples. To validate the accuracy of the calibration the four standards are injected again to ensure that the relative percent deviation is within 15%. If the concentration is out of range, the calibration curve is recalculated till the criteria are met. Refer to the following section for further details on quality assurance/quality control (QA/QC).

5.0 Performance Criteria, Quality Assurance and Quality Control

The issues which need to be addressed in connection with quality control are as follows:

- Precision
- Accuracy
- Completeness
- Blanks

The QA/QC and performance criteria are illustrated in Table 1. In Appendix C, the statistical parameters that are used during QA/QC are defined.

5.1 Precision

A measure of the reproducibility among multiple measurements of the same property, usually under prescribed similar conditions. Quantitative measurements of precision include replicate field samples, replicate laboratory samples, and analysis by different methods for comparison. The applicability of these measurements is parameter dependent. In this protocol, at least 5 percent of the samples will be split and analyzed. If the relative standard deviation falls below 20% the samples will be re-extracted and analyzed.

5.2 Accuracy

Accuracy is a measure of the degree to which a measurement or computed value reflects the true value of analyte present. Accuracy will be assessed as the recovery of a standard reference material or surrogate/matrix spikes for organic analytes.

5.3 Blanks

Field blanks (FB) will be used to assess the extent of background contamination present in the field. Process blanks (PB) are used to monitor the degree of background contamination introduced during the laboratory analysis and must meet the criteria of mass < MDL.

5.4 Completeness

Completeness is the measure of the number of valid samples (meeting all QA requirements) obtained compared to the number required to achieve the objectives of the study. Overall completeness in the number of valid samples compared to the number planned. Laboratory completeness is the number of valid samples obtained compared to the number analyzed. Both types of completeness will be reported. As with the other data quality attributes, completeness can be controlled through adherence to the SOPs in order to minimize contamination and sampling errors.

6.0 References

6.1 EPA. 1994. Quality Assurance Project Plan - Atmospheric Monitoring for Lake Michigan MassBalance and the Lake Michigan and Superior Loading Studies. Revision 1. EMP-A-QAPP.

6.2 University of Michigan Air Quality Laboratory. 1994. Draft Sampling and Analysis of Vapor Phase Mercury in Ambient Samples, Revision 7.

Table 1. Data Quality Objectives for Dry Deposition Plate - Metals

QA Criteria	Sample Type	Frequency	Criteria	Control Action	Units
precision	method: split samples (collocated field samples)	5%	RSD < 20%	re-extract and analyze*	%
	instrument: replicate sample extract analysis (different times)	10%	RSD < 15%	repeat measurement until criteria met	%
accuracy	NIST certified reference samples	5%	70% <R <120%	re-extract and analyze until criteria met &/or recalibrate	%
blanks	field	1/set	See footnote	re-extract and analyze	
	procedural	1/set	< MDL	re-extract and analyze	
completeness	field samples		85%		%
calibration	std curve blank + at least 3 stds	daily	$r^2 \geq 95\%$	reoptimize instrument, repeat calibration	

Field blanks: Anthropogenic metals: Not exceed the MDL by more than 0.3 ppb.
Crustal metals: Not exceed MDL by more than 3 ppb.

Appendix A. Laboratory Facilities, Equipments and Reagents

A.1 Preparation of Strips

1. Particle-free nylon gloves.
2. Balance.
3. Double-distilled methanol.
4. Plastic wash tray.
5. Laminar hood.
6. Plates.
7. Mylar strips.
8. Apezion L grease.
9. Deionized water.
10. Scratch pen.
11. Particle free wiper.
12. Storage box.
13. Glass petri dish.

A.2 Extraction of Strips

1. Teflon beaker.
2. Nitric acid (trace metal grade)
3. Ultrasonic bath.
4. Deionized water
5. Hot plate.
6. Volumetric flask (25 mL)
7. Polyethylene bottle.

Appendix B. Equipment and Supplies for Field Investigations

1. SOP
2. Plate holder (PVC).
3. Dry deposition plates.
4. Pre-weighed grease coated Mylar strips.
5. Mylar strip covers.
6. Teflon coated clips.
7. Particle free gloves.
8. Labelling tape.
9. Sample and field blank tracking forms.
10. Teflon tape.
11. Rubbermaid plate container.
12. Teflon coated tweezers.

Appendix C. Sample Log Sheet

EAGLE SAMPLE LOG SHEET		DATE	
SAMPLE NUMBER			
SAMPLE LOCATION			
WEATHER CONDITIONS (CIRCLE ONE)	SUNNY	RAINY	CLOUDY
COVER STATUS (CIRCLE ONE)	OPEN	CLOSED	
OPEN TIME, MIN			
TOTAL TIME,MIN			
RESET TIMER?*	YES	NO	
WET TEST RESULTS (CIRCLE ONE)	COVER THEN UNCOVER	NO RESPONSE	OTHER (EXPLAIN BELOW)
* - RESET TIMER ONLY WHEN STARTING A NEW SAMPLE			
COMMENTS			

Appendix D
QA Definitions

D.1 Precision

The precision will be evaluated by performing multiple analyses. Precision will be assessed by the following three methods:

1.0 Difference

Difference = $X_1 - X_2$

Where: X_1 = *larger of the two observed values*
X_2 = *smaller of the two observed values*

This formula is used for parameters with concentrations below some established value.

2.0 Relative Percent Difference (RPD)

$RPD = (X_1-X_2)*100/(X_1+X_2)/2$

This formula is used for duplicate measurements.

3.0 Relative Standard Deviation (RSD)

$RSD = (s/y) \times 100$

Where: s = *standard deviation*
y = *mean of replicate analyses*

This formula is used for three or more replicate values and may be used when reporting precision on aggregated data.

Standard deviation is defined as follows:

$$S = \sqrt{\sum_{n=1}^{n} \frac{(Y_i - \bar{Y})^2}{(n-1)}}$$

Where: y_i = *measured value of the I th replicate*
y = *mean of replicate analyses*
n = *number of replicates*

Appendix D.
QA Definitions (Cont'd)

D.2 Accuracy

Percent recovery, R, is used to assess accuracy for surrogate spikes, matrix surrogate spikes, and standard reference materials. Recovery is calculated as:

*R = (Measured mass/Actual mass) * 100*

D.3 Completeness

Completeness is defined:

*Completeness = (v/n) * 100*

Where: V = number of samples judged valid
n = total number of measurements necessary to achieve project objectives

The completeness will be reported on an annual basis.