

PIMA COUNTY
DEPARTMENT OF ENVIRONMENTAL QUALITY
BERYLLIUM
MONITORING NETWORK PLAN

2007

AQ-359



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**BERYLLIUM MONITORING NETWORK PLAN
IDENTIFICATION AND APPROVAL**

The attached Beryllium Monitoring Network Plan for Ambient Air Monitoring in the Sunnyside Unified School District located within Pima County is hereby recommended for approval and concurrences and commits the resources and personnel to follow the elements described within.



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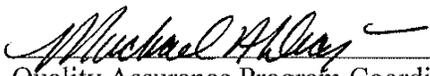
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1.0 INTRODUCTION

The Pima County Department of Environmental Quality's mission is to identify and respond to environmental issues by providing public service including monitoring, enforcement, outreach, small business assistance, solid waste and hazardous waste disposal, and environmental education. The Pima County Department of Environmental Quality (PDEQ) monitors air quality to ensure that the county meets and maintains national air quality health standards. PDEQ also provides public outreach and education regarding air quality issues. Our goal is to improve air quality by identifying air pollution problems, conducting inspections and reviewing permit applications to assure compliance with existing air pollution regulations. The department also partners with educational institutions, industry and other governmental agencies to perform special studies to increase knowledge and awareness of environmental issues.

1.1 Project Purpose/Objective

Our project's goal is to collect air data on beryllium oxide to determine the levels within the Sunnyside Unified School District area. This plan will be designated as the "PDEQ Beryllium Study". The Pima County Department of Environmental Quality will establish an air quality monitoring network to measure beryllium levels in the ambient air throughout the Sunnyside Unified School District. Data collected from the network will allow PDEQ to provide information to all interested parties, including but not limited to health officials, Sunnyside Unified School District personnel, elected officials and the general public.

2.0 SAMPLING DESIGN

The primary purpose of the Monitoring Network is to measure beryllium levels in the ambient air. Monitoring for beryllium will be take place over a five year period.

The sampling design is based on guidance provided in the Code of Federal Regulations which assures the desired level of confidence in the data recovered. A primary issue is the sampler siting and sampling frequency. The siting is designed to assure complete coverage for the neighborhood surrounding the Brush Wellman facility. The monitoring frequency will assure everyday coverage of the monitoring area.

2.1 Network Design

The Beryllium Study Network configuration is based initially on the pre-existing Sunnyside Unified School District monitoring site locations. The existing network consists of four monitoring sites:

- Site No. 1: Transportation Building
- Site No. 2: Los Niños Elementary School
- Site No. 3: Los Amigos Elementary School
- Site No. 4: Ocotillo Elementary School

PDEQ will establish two new monitoring sites in addition to the four existing monitoring sites. PDEQ will also add a co-locate sampler which will be installed at the Ocotillo Elementary School to provide a precision site for the network. The two additional sites will be located at:

- Site No. 5: Sunnyside High School
- Site No. 6: Chaparral Middle School

All samplers will operate on a 1 in 6 day sampling schedule on a rotating basis (one sampler running each day) so that one monitor will be running at all times during the five year period. This will produce a total of 438 samples per year, which includes 12 field blanks.

SUSD will participate in the project by assisting in the collection of samples and the general operation of the monitors. PDEQ will perform quarterly audits and calibrations on all the monitors.

A current PDEQ PM₁₀ monitoring site, Santa Clara, located at 6910 S. Santa Clara Avenue, may be utilized for background monitoring. This site operates on a 1 in 6 day sampling schedule utilizing a 47mm Teflon filter based sampler. If there are any abnormal background readings present in the beryllium network, an additional sample may be taken from PDEQ's Orange Grove particulate sampling site for analysis to determine additional background concentrations over a larger area.

Figure 2-1 displays a map of the monitoring sites.

2.2 Probe/Monitoring Criteria

The probe and monitoring criteria will be in accordance with 40 CFR Part 58, Appendix E.

2.3 Meteorological Data

All meteorological data will be obtained from the National Weather Service located at the Tucson International Airport (670-6526, <http://www.wrh.noaa.gov/twc/>).

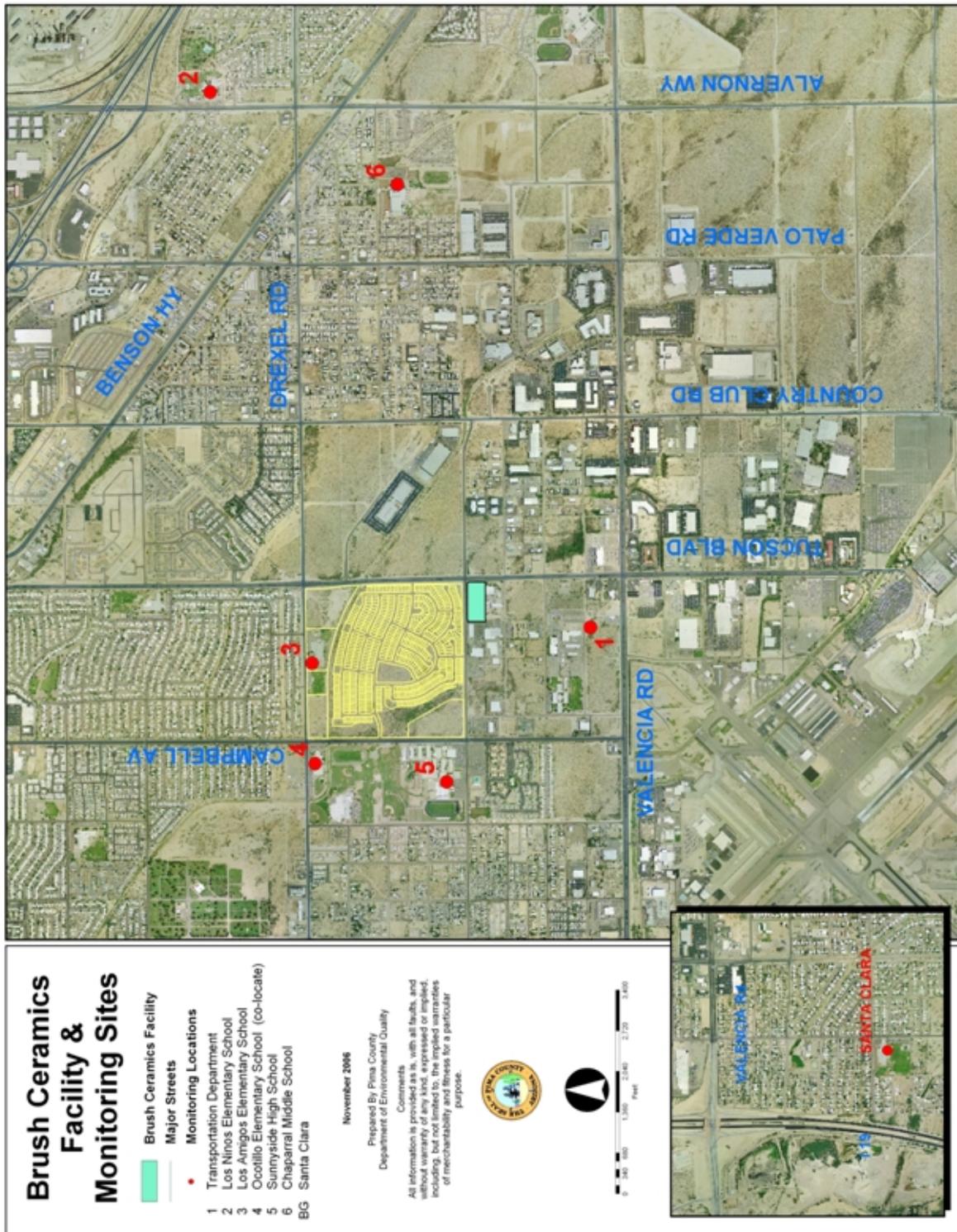


Figure 2-1 Monitoring Site Locations

3.0 SAMPLING METHODOLOGY

This method provides for measurement of the mass concentration of particulate matter having a aerodynamic diameter less than or equal to 10 micrometers (PM₁₀) in the ambient air over a 24-hour period for the purposes of determining particulate matter concentrations in accordance with 40 CFR 50, Appendix B.

3.1 Sampler Type

FRM samplers will be used for collection of PM₁₀ mass concentrations to be analyzed for beryllium. The Pima County Department of Environmental Quality (PDEQ) Beryllium Monitoring Network (BMN) will consist of the Andersen Model SAA 1200 and Tisch Critical Flow High Volume particulate samplers utilizing a Tisch brushless motor, a rheostat for flow control, an electronic or mechanical timer, and a Dickson chart recorder for recording flow and sample run time. Each sampler will be installed in compliance with the requirements set forth in 40 CFR Parts 50, 53 and 58.

3.1.1 Measurement Principle

For PM₁₀, air is drawn through a size-selective inlet, through a quartz fiber filter at a set flow rate of 40 cubic feet per minute. Particulate matter is collected on the filter.

The mass of particles collected on the filter is determined by the difference in filter weights before and after sampling. The concentration of suspended particulate matter in air is determined by dividing the net weight gain of the filter by the volume of air sampled.

3.2 EQUIPMENT AND SUPPLIES

3.2.1 Field Equipment

PM₁₀ volumetric flow:

- High volume vacuum motor shelter
- Rheostat or step-down transformer
- Filter holder assembly
- High volume vacuum motor
- PM₁₀ size-selective inlet
- Seven-day mechanical timer or a digital timer/programmer
- Dickson chart recorder
- Digital manometer
- Quartz filter

3.2.2 Calibration Equipment

- A variable flow/resistance plate calibration orifice, gasket and adapter plate
- Digital manometer for measurement of pressure readings with a range of 0 to 20 inches of water and minimum divisions of 0.1 inch
- Thermometer, minimum scale divisions, 0.1°
- Digital voltmeter in case of power problems

3.2.3 Supplies

- Backup vacuum motor
- 3/16" Tygon tubing
- Spare filter gasket
- Dickson chart and pen (PM₁₀)
- 10 amp, 250 volt fuses
- Notebook and pen
- Clean rags
- Duct tape
- Hand tools

3.3 SAMPLE SET-UP/RECOVERY

For the purposes of this monitoring network, quartz fiber filters are used for the collection of PM₁₀ particulates. All filters should be handled with care to avoid inadvertent damage to the filters, contamination, and weighing errors. All filters should be examined closely for loose fibers, which should be removed before initial weighing.

Clean, dry hands are required to prevent any possible contamination of the filters during weighing or other handling. Precautions also should be taken to prevent accidental contamination from other sources, such as soaps, detergents, and cosmetics.

All filters should be visually inspected for defects prior to use. Examine both the front and back of each filter for tears, holes, lines, spots, loose material, discoloration or other irregularities. Prepare filters for transport to the field as follows:

3.3.1 Sample Set-up

Sample set-up of the FRM sampler in the network takes place the same day that the previous sample is recovered. All samplers will be set up to sample in a 1 in 6 day sampling schedule, on a rotating basis, so one sampler runs each day of the week. The only holding time that affects sample set-up is the 30 day window from the time a filter is pre-weighed to the time

of the sample period. At co-located sites, the second monitor will be set up to run on the same day and at the same sample frequency (1 in 6 day) as the primary sampler. Set-up will take place on the same day. Detailed sample set-up procedures are listed below:

1. Obtain a supply of clean filters that have been tared (pre-weighed), pre-numbered and inspected in the weigh lab per section 8.0 of Appendix B, Weigh Lab Procedures.
2. Open the shelter lid, remove the filter holder face plate, wipe the inside of the filter shelter with a clean cloth to remove dust, dirt and debris.
3. Carefully place the filter, labeled side down, on the screen. Replace the face plate and carefully tighten it to the holder; under-tightening may result in leakage, over-tightening may damage the gasket and cause the filter to stick to the gasket.
4. Turn on the motor and allow the sampler to run for at least 5 minutes or until operating temperature is reached to establish run-temperature conditions. After establishing run-temperature conditions, connect the flow meter with a length of tubing to the pressure tap nipple located at or near the bottom of the motor. Ensure the indicated flow is within limits ($\pm 10\%$ of 40 CFM). If the indicated flow rate is not within limits, adjust the flow rate to the desired setting. Record the manometer reading on the Dickson chart or site log slip and turn off the motor.
5. Reset the elapsed time indicator if it is the re-settable type. Record the site, sample date, total sample time and inches of water on the front of a new Dickson chart or site log slip. Install the new Dickson chart in the recorder or place the site log slip in the holder provided. Refer to section 3.3.2 for details on setting up the Dickson chart recorder.
6. Check the timer to ensure that it is set to start the sampler at midnight (± 30 minutes) and to stop the sampler at midnight (± 30 minutes) the next day. The normal sampling period is 1440 (± 60) minutes. Refer to the manufacturer's manual for resetting the timers. The mechanical timers may need to be manually rotated to the correct day and time.

3.3.2 Setting Up The Dickson Chart Recorder

The Dickson chart recorder verifies that the sampler operated without failure during the 24-hour sampling period and maintained the normal operational flow rate. Large deviations from the average flow rate on the recorder would indicate that there has been a power failure, a vacuum motor failure, or a leak. If the flow rate looks stable, set up the Dickson chart recorder as follows:

1. Install a new chart that has been properly labeled into the Dickson chart recorder. Replace the ink pen if needed.
2. Ensure that the Dickson chart recorder is properly connected to the pressure tap on the lower side of the sampler motor housing.
3. Check that it is properly zeroed (pen rests on innermost circle of the chart).

Gently tap the side of the recorder to make sure the pen is not hung up on the chart. Adjust the zero set screw if necessary.

4. While the sampler is running, determine the actual flow rate from the manometer reading (nominally 1.8 - 3.0 inches H₂O for 40 cfm).
5. Gently tap the side of the recorder to make sure the pen is not hung up on the chart.
6. Lift the pen off the chart, then rotate the chart with the center slot until the time is properly indicated on the chart. Be sure the pen is back down on the chart surface.

3.3.3 Sample Recovery

Sample recovery of any individual filter from the FRM sampler in the network must occur prior to the next scheduled sample day for that sampler. A recovery and sample set-up will be required for every sample taken prior to the next scheduled sample date. At co-located sites the sample from the secondary monitor will be recovered on the same day as the primary monitor. Each site will have to be visited a minimum of once per week. Detailed sample recovery procedures are listed below:

1. Turn on the motor and allow the sampler to run for at least 5 minutes to re-establish run-temperature conditions. Verify the ending flow rate.
2. Remove the Dickson chart or site log slip and record the elapsed time meter indication and the ending flow rate. Record any conditions that may affect the measurement, such as unusual meteorological conditions, construction activity, fires, dust storms, etc. Make notes if there is any indication that the filter is defective or the data would be unrepresentative of actual sampling conditions and insert into the manila folder for that site.
3. Remove the filter holder face plate and carefully remove the filter, touching only the outer edges. Fold the filter in half so the collected particulate matter is inside and place the filter in the manila folder.
4. Store the sampled filters in a clean, secure environment until received by PDEQ, at which time the sample chain-of custody form will be completed and retained by a PDEQ representative.

NOTE: The sampler's bounce plate will be greased with a silicon spray (provided by PDEQ) once per month unless conditions (i.e., excessive amount of collection build-up) warrants service sooner.

Refer to Section 5.4 for post-sampling custody details.

3.4 Determining Concentrations

Mass concentrations for particulate matter are determined at the Pima County Air Monitoring weigh lab with the use of an Excel spreadsheet. **DAILYCONPM10.xls** (Figure A-2 of Appendix A) is a sample spreadsheet for PM₁₀. The spreadsheets utilize the average flow indicated and the appropriate motor calibration curve to determine Q_a (the actual flow rate in cfm at site conditions) and Q_{std} (the flow rate in cfm under standard atmospheric conditions of 25°C (298°K) and 760 mmHg (millimeters of mercury)). Concentrations for particulate matter are calculated using the following formula:

$$PM_{10} = (W_f - W_i) \times 10^6 / V_{std}$$

Where

PM₁₀ = mass concentration of PM₁₀, μg/std m³

W_f = final filter weight

W_i = initial filter weight

10⁶ = conversion of g to μg

V_{std} = total air sampled in standard volume units, std m³

Refer to Section 9.1 of Appendix B for conversion to standard temperature and pressure.

Concentrations for beryllium are calculated using the following formula:

- 1) Read absorbance of samples, A; average media blanks, A_b; average sulfate reagent blanks, A_r; and working standards, A_s.
- 2) Using the working standard, C_s (μg/mL), analyzed adjacent to the sample of interest, calculate concentration, C (μg/m³), of Be in the air volume sampled, V (L):

$$C = \frac{(A - A_b) * C_s * 10^4}{(A_s - A_r) V}, \mu\text{g}/\text{m}^3$$

Schneider Laboratories, Inc. will perform quality control analysis for beryllium using NIOSH Method 7102 “Beryllium and Compounds of Be” specified HF acid full digestion (see Appendix C). A report will be generated showing the analysis for beryllium, as well as a list of other elements (if applicable).

A control sample may be sent to a secondary laboratory for beryllium analysis and be used for accuracy and bias comparison.

3.5 MAINTENANCE

3.5.1 Routine Maintenance

Routine maintenance procedures are performed at regular intervals to reduce instrument down time. The following tasks are performed at the specified frequency:

| <u>Task</u> | <u>Frequency</u> |
|--|------------------------------|
| 1. Inspect sampler housing (power cords, gaskets, recorder, flexible tubing, mass flow controller) | Every filter change |
| 2. Bounce plate greased | Every 4th sample |
| 3. Clean size-selective inlet (PM ₁₀) | During quarterly calibration |
| 4. Clean sampler housing | During quarterly calibration |

3.6 CALIBRATION

3.6.1 Discussion of Flow Rate Designations

During operation of the sampler, the rheostat will maintain an actual flow rate of 40cfm ($\pm 10\%$). This flow rate is a function of ambient conditions and the pressure differential across the filter. The approved filter media is a Quartz fiber filter. Clean filter media will have a pressure drop ranging from 15 to 20 inches of water. The VFC is designed so that proper operating flow rate is maintained over a broad range of temperature and pressure conditions.

Since the actual flow rate is so critical for particle fractionalization, the operator must have an understanding of the flow rate designations used in PM₁₀ monitoring. Confusion between various flow rates is the most frequent source of error in the particulate monitoring network.

Keep in mind that all calibrations are performed with respect to **ACTUAL** site conditions. Corrections to standard conditions are performed **ONLY** when determining mass concentrations for data reporting.

All samplers used in the Beryllium Monitoring Network (as defined in Section 2.1) will be calibrated on a quarterly basis by PDEQ. Prior to any calibrations, a performance audit will be performed by an independent auditor using independent equipment to determine accuracy. Once the audit is performed, a PDEQ Sr. Instrumentation Technician will perform the calibration.

A detailed description of the calibration leak test, sampler calibration/audit procedures, and weigh lab procedures are found in Appendix A and Appendix B.

4.0 QUALITY CONTROL REQUIREMENTS

To assure the quality of data from air monitoring measurements, two distinct and important interrelated functions must be performed. One function is the control of the measurement process through broad quality assurance activities, such as establishing policies and procedures, developing data quality objectives, assigning roles and responsibilities, conducting oversight and reviews, and implementing corrective actions. The other function is the control of the measurement process through the implementation of specific quality control procedures, such as audits, calibrations, checks, replicates, routine self-assessments, etc. In general, the greater the control of a given monitoring system, the better will be the resulting quality of the monitoring data.

4.1 Quality Control Procedures

QC procedures consist of routine procedures designed to control the quality of collected data and include instrument calibrations, precision checks against standard references, preventive maintenance procedures, etc. Effectiveness of the QC procedures is assured through the QA (Quality Assurance) system, whereby QA audits and QC review are performed independent of routine QC procedures, equipment and personnel. This section provides an overview of QC procedures for the measurement of particulates.

4.1.1 High Volume Andersen PM10

1. Site visit at least once a week to verify instrument operation, sample inlet and general site integrity.
2. Routine preventive maintenance procedures to reduce the occurrences of equipment failure and lost data.
3. Co-location of selected PM10 monitors.
4. Calibration of motors, elapsed time meter/Dickson chart recorders on a quarterly basis.
5. Calibration of orifices by a Dresser Roots Meter (by Arizona Department of Environmental Quality) on an annual basis.
6. Calibration of weighing balances with NIST traceable weights.

4.1.2 Instrument Logs

All field QC procedures, instrument malfunctions, on-site repairs and maintenance, and out of control conditions are recorded and kept in a network logbook. All forms are retrieved from monitoring sites on a monthly basis, duplicated and copies returned to the appropriate monitoring site and reinserted in the network logbook. The original forms are inserted in an annual logbook and kept in a secure cabinet in the main PDEQ office.

4.1.3 Calibration

Calibration is the comparison of a measurement standard or instrument with another standard or instrument to report, or eliminate by adjustment, any variation (deviation) in the accuracy of the instrument being compared. The purpose of the calibration is to minimize the bias.

Calibration activities follow a two step process:

1. Certifying the calibration standard against an authoritative standard yearly
2. Comparing the calibration standard against the routine sampling instrument quarterly.

4.2 Blanks

Blank samples are used to determine contamination arising principally from four sources: the environment from which the sample was collected/analyzed, the reagents used in the analysis, the apparatus used, and the operator/analyst performing the data operation.

Laboratory blanks are conditioned, un-sampled filters used to determine any weight change between pre and post sampling weightings due to contamination in the balance environment.

Field blanks are conditioned, un-sampled filters used to provide an estimate of total measurement system contamination. By comparing information from laboratory blanks against the field blanks, one can assess contamination from field activities. One field blank will be used each month.

4.2.1 Blank Evaluation

The following statistics will be generated for data evaluation purposes:

Difference for a single check (d) - The difference, d , for each check is calculated using Equation 1, where X represents the concentration produced from the original weight and Y represents the concentration reported for the duplicate weight:

$$d = |Y - X| \quad \text{Equation 1}$$

Percent Difference for a single check (d_i) - The percentage difference, d_i , for each check is calculated using Equation 2 where X_i represents the original weight and Y_i represents the concentration reported for the duplicate weight.

$$d_i = \frac{Y_i - X_i}{(Y_i + X_i)/2} \quad \times 100 \quad \text{Equation 2}$$

Corrective action - The acceptance criteria for lot and lab blanks is 15 μ g difference and is determined by equation 1. If the acceptance criteria of the weigh lab blanks is greater than 15 μ g, the weigh lab balance will be checked for proper operation. If the criteria for the blanks is still greater than 15 μ g, the weigh lab technician will alert the laboratory team leader of the problem.

4.3 Precision Checks

Precision is the measurement of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. In order to meet the data quality objectives for precision, the Department must ensure the entire measurement process is within statistical control. Two types of precision measurements will be made in this program:

1. Collocated monitoring
2. Filter duplicates

The Ocotillo site has been designated as the co-locate monitoring site for the network. Sampler OC1 is designated as the primary sampler while sampler OC2 is designated as the duplicate sampler for assessing precision. As recommended in *40 CFR, Part 58, Appendix A, Section 5.3.1*, collocated measurement pairs are selected for use in the precision calculations only when both measurement pairs are above 20 μ g/m³. Duplicate samples that do not meet the 20 μ g/m³ condition will be omitted for the purposes of the precision checks.

4.3.1 Duplicate Weigh Lab Filter Measurements

During weigh lab pre-weighing and post-weighing sessions, a routine filter from the sampling batch will be selected for a second weighing. Equations 1 and 2 will be generated for this information. The difference among the weights of these two filters must be less than 15 μ g. If the criteria are not met, the pair of values will be flagged. Failure may be due to transcription errors, balance malfunction, or that the routine samples have not met equilibrium. Other QC checks (balance standards and lab blanks) will eliminate balance malfunction. If the duplicate does not meet the criteria, a second routine sample will be selected and reweighed as a second duplicate check. If this second check fails the acceptance criteria and the possibility of balance malfunction and transcription errors have been eliminated, all samples in the batch will be equilibrated for another 24 hours and reweighed. Corrective actions will continue until duplicate weights for the batch meet acceptance criteria.

4.4 Accuracy or Bias Checks

Accuracy is defined as the degree of agreement between an observed value and an accepted reference value and includes a combination of random error (precision) and systematic error (bias). Three accuracy checks are implemented in this program:

1. Co-located monitors
2. Flow rate audits
3. Balance checks

4.4.1 Co-located Monitors

Although the co-located monitors are primarily used for evaluating and controlling precision, they can be used to determine accuracy or bias. By using Equation 2 to determine percent difference, one can track trends or bias between the two instruments without knowing which instrument is producing the "true" value.

Corrective Action - The percent difference of the pair values will be used to determine trends. If it appears that there is a statistically significant bias (>10%) between the pairs, corrective action will be initiated. The process will include eliminating uncertainties that may be occurring at filter handling, transport and laboratory stages, in order to determine that the bias is truly at the instrument. Corrective actions at the instrument will include flow rate checks as well as complete maintenance activities.

4.4.2 Flow Rate Audits

Since the department will be implementing manual sampling devices, we will implement a flow rate audit every quarter. The audit is made by measuring the analyzer's normal operating flow rate using a certified flow rate transfer standard. The flow rate transfer standard used for auditing will not be the same flow rate standard used to calibrate the analyzer. However, both the calibration standard and the audit standard may be referenced to the same primary flow rate standard. The procedures used to calculate measurement uncertainty are described below:

Accuracy of a single sampler - Single check (Quarterly) Basis (d_i). The percent difference (d_i) for a single flow rate audit i is calculated using Equation 3, where X_i represents the audit standard flow rate (known) and Y_i represents the indicated flow rate.

$$d_i = \frac{Y_i - X_i}{X_i} \times 100 \quad \text{Equation 3}$$

Corrective Action - If the audit flow rate percentage difference is less than or equal to ± 7 percent, the sampler calibration is acceptable. Differences exceeding ± 7 percent require sampler recalibration. Differences exceeding ± 10 percent will result in invalidation of all data subsequent to the last calibration or valid flow check.

Accuracy of a single sampler - Design flow rate (Quarterly) (d_i). The percent difference (d_i) for a design flow rate audit i is calculated using equation 4, where Q_a represents the indicated flow rate (corrected) and the inlet design flow rate equals 40 cfm.

$$d_i = \frac{Q_a - 40}{40} \times 100 \quad \text{Equation 4}$$

Corrective Action - If the design flow rate percentage difference is greater than or equal to ± 7 percent, the sampler should be investigated for possible causes.

Deviations exceeding ± 10 percent (or the acceptable design flow rate range specified by the inlet manufacturer) will result in invalidation of all data obtained subsequent to the last calibration or valid flow check.

4.4.3 Balance Checks

Balance checks are frequent checks of the balance working standards against the balance to ensure that the balance is within acceptable criteria. The calibration should be verified any time the balance has been moved or subjected to rough handling or during routine operations when a standard weight cannot be weighed within ± 0.5 mg of its weight.

Corrective Action - A set of three to five weights covering the range normally encountered in weighing filters should be weighed. If the weighed values of one or more of the standard weights does not agree within ± 0.5 mg of the stated value, the balance should be re-calibrated or adjusted by the manufacturer or a certified technician. The results of all balance checks should be recorded in the QC notebook.

5.0 DATA REPORTING

All raw data required for the calculation of particulate matter and beryllium concentrations, the submission to the database, and QA/QC data are collected electronically or on data forms that are included in Appendix A. All this information will be stored electronically. All hardcopy information will be filled out in indelible ink. Corrections will be made by inserting one line through the incorrect entry, initialing this correction, and placing the correct entry alongside the incorrect entry, if this can be accomplished legibly, or by providing the information on a new line. All data will be retained by PDEQ for a period of 2 years after the end of the 5 year study is completed.

5.1 Notebooks

PDEQ will issue notebooks for record keeping, operational comments, data logging, and chain of custody for all monitoring sites. These notebooks will be uniquely numbered and identified. The notebooks will include:

Field Notebook - A notebook will be issued to the site operator for all sampling sites. This will be a 3-ring binder that will contain forms for routine operations as well as inspection and maintenance forms and SOP's.

Lab Notebook - A notebook will also be available for the weigh lab. This notebook will be designated for the Beryllium Study Network. This notebook will contain general comments, all pre, post and net weights, and all information necessary for the determination of PM₁₀ and Beryllium concentrations. This notebook will be kept in the weigh lab.

Chain-of-Custody Notebook - A notebook will be designated for the BMN which will contain all Chain-of-Custody documentation. This notebook will also be kept in the weigh lab.

5.2 Electronic Data Collection

All data that will be collected and logged into the weigh lab notebook will also be entered into the weigh lab database. This will be performed to reduce the possibility for lost data and so appropriate system backups can be utilized.

5.3 Data Validation

Data validation is a systematic review of a body of data against a set of criteria to detect possible erroneous values that may have slipped through previous quality control checks. It is a continuous process that takes place at all levels of monitoring and data collection.

The site technician will annotate on the chart recorder the beginning and ending flow rate taken from the digital manometer, the start and stop digital timer reading, and any noticeable

irregularities (i.e., site condition, construction, etc.) that may affect the sample. Once the samples are returned to the PDEQ weigh lab, all necessary information is entered into the lab notebook and the database and all weigh lab procedures are completed and concentrations calculated.

On a monthly basis, PDEQ's data analyst will verify all data entered into the database and any special notations made to determine if data needs to be invalidated. If so, the data are flagged as invalid. After these checks and verifications, the data is put into a spread sheet which will be available to the public on the PDEQ webpage at <http://www.airinfnow.org/>.

5.4 Sample Custody

5.4.1 Pre-Sampling Custody

The Weigh Lab SOP defines how the filters will be enumerated, conditioned, weighed and stored in the weigh lab. For each sampling period, weigh lab personnel will select filters that will be sent to the field. These filters will be bundled by sample run date and delivered every other week to the Sunnyside school district.

A Chain-of-Custody Record form (Figure 5-1) containing the filter ID numbers, site names for each filter, filter sampling dates and signatures will accompany the filter bundles when delivered to Sunnyside School District.

PDEQ personnel will deliver the samples to the site operator along with the Filter Chain-of-Custody record every two weeks. PDEQ personnel will sign his/her name and date in the top "Relinquished by:" box. The person receiving the samples will sign his/her name and date in the top "Received by:" box. The chain-of custody form will be kept by the site operator until the post sampled filters are picked up by PDEQ.

5.4.2 Post-Sampling Custody

PDEQ will retrieve the sampled filters from Sunnyside School District on a weekly basis. At the time of sample retrieval, the transfer custody signatures will be collected on the Chain-of-Custody form. The samples will be received by designated personnel at the receiving end. Upon receipt of the sampled filters, they will be placed in the weigh lab for equilibration and particulate gravimetric analysis.

Once the particulate gravimetric analysis is completed, PDEQ personnel will prepare the sampled filters for shipping to Schneider Laboratories, Inc. for NIOSH Method 7102 analysis. A Chain-of-Custody Record form will accompany the filters when delivered and all required signatures will be collected.

Once the NIOSH Method 7102 analysis is completed, the analysis results and Chain-of-Custody form will be sent back to the PDEQ weigh lab for data analysis and archiving.

5.4.3 Filter Archive

Upon completion of post-sampling weighing and analysis activities, each filter will be placed in a manila envelope, along with the Dickson chart. The outside of the envelope will be labeled with the filter ID number, site name, sample date, analysis data. The manila envelopes will be packaged and stored in an identified box. Samples will be archived in the filter storage facility for two years past the date of collection.

Figure 5-1
Example Chain-of-Custody Form PDEQ

CHAIN-OF-CUSTODY RECORD

| | |
|---|---|
|  | Pima County Dept. of Environmental Quality |
| | 150 W. Congress St. 1st Floor |
| | Tucson, AZ. 85701 |
| | (520) 740-3340 |
| | Fax (520) 882-7709 |

| | |
|---|----------------------------|
| Company: Sunnyside School District | |
| Address: 2238 E. Ginter Road | |
| Tucson, AZ. 85704 | |
| Contact: Gene Repola | |
| Phone: (520) 545-2016 | Fax: (520) 545-2121 |
| E-Mail: gener@susd12.org | |

| Sample ID | Site Name | Sample Date | Site Operator Initials | | Remarks |
|--|-----------|-------------|------------------------|------------------------------------|---------|
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| | | | | | |
| | | | | | |
| Relinquished by: (Signature) Date/Time | | | | Received by: (Signature) Date/Time | |
| Relinquished by: (Signature) Date/Time | | | | Received by: (Signature) Date/Time | |
| Relinquished by: (Signature) Date/Time | | | | Received by: (Signature) Date/Time | |
| Relinquished by: (Signature) Date/Time | | | | Received by: (Signature) Date/Time | |

6.0 PERSONNEL and TRAINING

6.1 Organizational Structure and Responsibilities

An organizational chart showing key personnel involved in the ambient air monitoring program is presented in Figure 6-1.

The PDEQ director is the Air Pollution Control Officer responsible for the operations of the ambient air monitoring program. The Control Officer is responsible for appointing a Technical Operations Manager to oversee the ambient air monitoring program. Two QA positions oversee different aspects of the monitoring program, that of the data collection systems and that of the data management systems.

The Technical Operations Manager ensures that sufficient financial support is provided to the monitoring program and is responsible for the following:

1. Support and supervision of the QA data collection and management positions in accomplishing QA activities.
2. Supervision of all personnel responsible for operation of field monitors/samplers and analytical laboratory operations.
3. Ensuring that all personnel collecting data have been adequately trained and are familiar with and are implementing the procedures required by the QA Plan.
4. Arranging for special calibrations by other agencies in support of the QA program.
5. Instituting corrective action, if necessary, based on audit reports.

The Quality Assurance personnel that oversee the data collection and data management QA programs are responsible for the following:

1. Approval of all QA/QC procedures used in the program.
2. Development of the QA plan, keeping the plan up to date, and assuring that revisions to the plan are provided to all holders.
3. Performance of internal audits to assure that data collection personnel possess the QA plan (and any current revisions), are knowledgeable of its requirements, and are successfully implementing those requirements.
4. Coordination of the execution of systems, performance, and data quality audits
5. Provision of an independent review of precision checks, zero/span checks, multipoint calibrations, analytical spikes and replicates.
6. Investigation of any special problems with monitors and methods.
7. Review of current literature to insure that the latest procedures and regulatory requirements are being implemented.
8. Notification of the Technical Operations Manager and/or the Air Pollution Control Officer of any deficiencies in the procedures based on the audits.

It is the responsibility of all air quality technicians to collect and analyze data according to approved SOPs and to perform the specified QC procedures at the required frequency. The QA Program Coordinator and the Technical Operations Manager are authorized to stop work in the event of non-compliance with federal air monitoring requirements.

6.2 Training

PDEQ staff or other persons involved in the study, who are assigned to perform new tasks involving air quality measurements and/or data handling are trained by a principle or senior instrumentation technician experienced in performing the task. Once trained, the trainee performs the task under the direct supervision of the experienced technician until such time that the technician judges the trainee as competent to perform the task. Effectiveness of the training is verified by systems and performance audits. If data acceptance on any instrument falls below 75% in a given month, additional supervision and training may be required for the technician responsible for that instrument.

All personnel involved in any function affecting data quality (sample collection, analysis, data reduction, and quality assurance) should have sufficient training in their appointed jobs to contribute to the reporting of complete and high quality data.

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Pima County
Department of Environmental Quality
Air Monitoring Quality Assurance Plan

Appendix A
Operation and Maintenance
of the
High Volume Particulate Sampler



Pima County Department of Environmental Quality
150 West Congress St., 1st Floor
Tucson, AZ. 85701
(520)740-3340

Standard Operating Procedures

Operation and Maintenance of the High Volume Particulate Sampler

1.0 GENERAL DISCUSSION

1.1 Purpose of This Document

This document provides operation, maintenance and quality assurance procedures for the high volume particulate sampler used to measure particles in the 0 to 10 μ m size range (PM₁₀).

Local agencies involved in Federal air monitoring programs must comply with Federal Quality Assurance requirements described in **Appendix A of 40 CFR 58**. The Pima County Department of Environmental Quality has developed a Quality Assurance (QA) program to provide data of adequate quality to meet national, state and local monitoring objectives. The QA program is documented in a QA Plan, which is updated to reflect procedural or policy changes as necessary.

This appendix reflects the requirements of the July 2003 version of the **Code of Federal Regulations** and the September 1997 version of **Section 2.11** of the **Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Part II, Section 2.11**,

1.2 Measurement Principle

For PM₁₀, air is drawn through a size-selective inlet, through a quartz fiber filter at a flow rate of 40 cfm. Particles with aerodynamic diameters less than the design of the inlet are collected on the filter.

The mass of particles collected on the filter is determined by the difference in filter weights before and after sampling. The concentration of suspended particulate matter in air is determined by dividing the net weight gain of the filter by the volume of air sampled.

1.3 Potential Error Sources

The following can interfere with or cause errors in particulate measurements. Appropriate measures should be taken to reduce or eliminate the occurrence of each item when possible:

- Poor documentation causing errors in determining flow rate or mass concentrations
- Filter weighing errors

- Non-constant flow rate due to leaks or equipment failure
- Out-of-range flow rate (PM₁₀ must be within 40 cfm, ± 4 cfm)
- Loss of volatile particles during handling
- Contamination due to dirt and oil from hands
- Torn filter due to improper handling
- Formation of particulate matter on the filters by oxidation of gases in the air sample
- High humidity resulting in additional weight gain by hygroscopic particulate matter
- Wind blown particulate collection when the sampler is inoperative (passive deposition)
- Material loading in PM₁₀ size-selective inlets with subsequent re-entrainment in sample flow

2.0 EQUIPMENT AND SUPPLIES

2.1 Field Equipment

PM₁₀ High-Volume:

- High volume vacuum motor shelter
- Brushless motor speed voltage controller
- Filter holder assembly
- High volume brushless vacuum motor
- PM₁₀ size-selective inlet
- Seven-day mechanical timer
- Dickson chart recorder
- Digital manometer
- Quartz filter

2.2 Filter Handling Equipment

- A clean laboratory environment for filter conditioning, inspection, and weighing. EPA recommends an environment controlled at 15°C to 30°C, ± 3°C variability and a relative humidity of 20% to 45% with ± 5% variability.
- An analytical balance with a sensitivity of 0.1 mg and an expanded weighing chamber to accommodate the filters
- A filter rack for separation of filters during conditioning
- Manila envelopes for filter storage
- Class "S" weights for calibration of the analytical balance

2.3 Calibration Equipment

- A variable flow calibration orifice, gasket and adapter plate
- Digital manometer for measurement of pressure readings with a range of 0 to 20 inches of water and minimum divisions of 0.1 inch
- Thermometer, minimum scale divisions, 0.1°
- Digital voltmeter in case of power problems

2.4 Supplies

- Backup vacuum motor
- 3/16" Tygon tubing
- Spare filter gasket
- Dickson chart and pen (PM₁₀)
- 10 amp, 250 volt fuses
- Notebook and pen
- Clean rags
- Duct tape
- Hand tools

3.0 OPERATION

3.1 Operating Schedule

Procedures for determining the sampling frequency are defined in **40 CFR 58.13**. PM₁₀ samplers are run for 24 hours (\pm 1hr), from midnight to midnight, with a sampling frequency of once every six days. The six Sunnyside monitoring sites run once every six days on a rotating schedule, with the Ocotillo site designated as a co-locate site for precision purposes.

3.2 Preparing Filters

For the purposes of this Standard Operating Procedure (S.O.P.), quartz fiber filters are used for the collection of PM₁₀ particulates. All filters should be handled with care to avoid inadvertent damage to the filters, contamination, and weighing errors. All filters should be examined closely for loose fibers, which should be removed before initial weighing.

Clean, dry hands are required to prevent any possible contamination of the filters during weighing or other handling. Precautions also should be taken to prevent accidental contamination from other sources, such as soaps, detergents, and cosmetics.

All filters should be visually inspected for defects prior to use. Examine both the front and back of each filter for tears, holes, lines, spots, loose material, discoloration or other irregularities. Prepare filters for transport to the field as follows:

1. Condition the inspected filters for at least 24 hours in the laboratory environment prior to weighing.
2. Ensure all loose fibers are removed from the filters, and then record the appropriate sample run date and sampler identification on the outer ½-inch of the top side of the filters near the serial number. Record the filter serial numbers on the appropriate pages in the particulate log book (Figure A-1).
3. Place the unfolded filters upright on the rack of the analytical balance and record the weight to 0.1 milligram as tare weight.
4. Transport the filters to the sampler site operator prior to the scheduled day for sample collection:
 - a. Filters are transported to the site in manila file folders specifically labeled for each sampler.
 - b. Filters are installed in the sampler, labeled side down.

3.3 Process exposed filters as follows:

1. Exposed filters should be collected as soon as possible after the sampling period to reduce the potential for passive deposition.
2. Condition the exposed filters in the laboratory environment for at least 24 hours.
3. Immediately after conditioning, weigh the filter to the nearest 0.1 milligram and record the weight as gross weight. The filter will require a second fold to fit in the balance, filter information side out (the filter will have already been folded lengthwise when picked up after sampling).
4. Record the average indicated flow rate obtained by adding the starting and ending flow rates and dividing the total by 2.
5. Record the sampler identification, the filter serial number, the date of the sample, the gross weight and tare weight on the front of a 5 x 7½ inch scarf envelope. Insert the filter into the envelope for storage (or mailing). Include the Dickson chart or site log slip in the envelope with the inked side of the chart facing away from the filter.
6. Enter the same information in the particulate log book. The remaining information (net weight, flow rates Q_a and Q_{std} , standard flow (V_{std}), and mass concentration are computed by using an Excel spreadsheet. See **Section 3.6, Determining Mass Concentrations.**

3.4 Installing Filters

1. Obtain a supply of clean filters that have been tared, pre-numbered and inspected in the laboratory per 3.2, item 1 thru 4.
2. Open the shelter lid, remove the filter holder face plate, wipe the inside of the filter shelter with a clean cloth to remove dust, dirt and debris.
3. Carefully place the filter, labeled side down, on the screen. Replace the face plate and carefully tighten it to the holder; under-tightening may result in leakage, over-tightening may damage the gasket and cause the filter to stick to the gasket.
4. Power up the motor and allow the sampler to run for at least 5 minutes or until operating temperature is reached to establish run-temperature conditions. After establishing run-temperature conditions, connect the flow meter with a length of tubing to the pressure tap nipple located at or near the bottom of the motor. Ensure the indicated flow is as exact as possible as determined by the pre-established set point. If the indicated flow rate is not within limits ($\pm 10\%$ of 40 CFM), adjust the flow rate to the desired setting. Record the manometer reading on the Dickson chart or site log slip and turn off the motor.
5. Reset the elapsed time indicator if it is the re-settable type. Record the site, sample date, total sample time and inches of water on the front of a new Dickson chart or site log slip. Install the new Dickson chart in the recorder.
6. Check the timer to ensure that it is set to start the sampler at midnight (± 30 minutes) and to stop the sampler at midnight (± 30 minutes) the next day. The normal sampling period is 1440 (± 60) minutes. The mechanical timers may need to be manually rotated to the correct day and time. Refer to the manufacturer's manual for resetting the timers.

3.5 Picking Up Filters

1. Power up the motor and allow the sampler to run for at least 5 minutes to re-establish run-temperature conditions. Verify the ending flow rate.
2. Remove the Dickson chart or site log slip and record the elapsed time meter indication and the ending flow rate. Record any conditions that may affect the measurement, such as unusual meteorological conditions, construction activity, fires, dust storms, etc. Make notes if there is any indication that the filter is defective or the data would be unrepresentative of actual sampling conditions and insert into the manila folder for that site.
3. Remove the filter holder face plate and carefully remove the filter, touching only the outer edges. Fold the filter in half, lengthwise, so the collected particulate matter is inside and place the filter in the manila folder.

NOTE: The sampler's bounce plate will be greased with a silicon spray (provided by PDEQ) once a month unless conditions (ie. excessive collection build-up) warrant service sooner.

3.6 Determining Mass Concentrations

Mass concentrations are determined with the use of Excel spreadsheets on the weigh lab PC. **DAILYCONPM10.xls** (Figure A-2) is a sample spreadsheet for PM₁₀. The spreadsheets utilize the average flow indicated and the appropriate motor calibration curve to determine Q_a (the actual flow rate in cfm at site conditions), and Q_{std} (the flow rate in cfm under standard atmospheric conditions of 25°C (298°K) and 760 millimeters of mercury). Record Q_a as **ACTUAL** cfm, and Q_{std} as **CORRECTED** cfm, corrected volume (V_{std}) and the mass concentration in micrograms per cubic meter (µg/m³) in the particulate log book. Concentrations for particulate matter are calculated using the following formula:

$$PM_{10} = (W_f - W_i) \times 10^6 / V_{std}$$

Where:

PM₁₀ = mass concentration of PM₁₀, µg/std m³

W_f = final filter weight

W_i = initial filter weight

10⁶ = conversion of g to µg

V_{std} = total air sampled in standard volume units, std m³

You can avoid problems with using the wrong motor calibration numbers (slope and y-intercept) on the spreadsheets by keeping the particulate log book updated each week. When you perform a motor change, make sure the data for that site is current.

4.0 CALIBRATION

4.1 Discussion of Flow Rate Designations

The particle size discrimination characteristics of the PM₁₀ fractional inlet are dependent upon the air velocity through the acceleration jets. A change in the entrance velocity will result in a change in the nominal particle size collected. For this reason, it is imperative that the flow rate through the inlet be maintained at a constant actual flow rate of 40 cfm (± 10%).

During operation of the sampler, the rheostat will maintain an actual flow rate of 40cfm (±10%). This flow rate is a function of ambient conditions and the pressure differential across the filter. The approved filter media is a glass fiber filter. Clean filter media will have a pressure drop ranging from 15 to 20 inches of water.

Since the actual flow rate is so critical for particle fractionalization, the operator must have an understanding of the flow rate designations used in PM₁₀ monitoring. Confusion between various flow rates is the most frequent source of error in the particulate monitoring network.

Keep in mind that all calibrations are performed with respect to **ACTUAL** site conditions. Corrections to standard conditions are performed **ONLY** when determining mass concentrations for data reporting.

All samplers used in the PDEQ Beryllium study network will be calibrated on a quarterly basis by PDEQ. Prior to any calibrations, a performance audit will be performed by an independent auditor using independent equipment to determine accuracy. Once the audit is performed, a PDEQ Sr. Instrumentation Technician will perform the calibration.

4.2 Pre-Calibration Leak Test

This test should be conducted after sampler assembly, after motor maintenance and at routine intervals throughout the year.

1. PM₁₀ samplers are calibrated without a filter or filter cartridge installed. When installing the orifice on the sampler filter support screen, tighten the face-plate nuts on alternate corners to prohibit leaks and to ensure even tightening. The fittings should be hand tightened; too much compression can damage the sealing gasket. Make sure the orifice gasket is in place and the orifice is not cross threaded on the face-plate.
2. Disconnect the motor from the flow controller and plug it directly into the line voltage using the AC/DC motor patch cord.
3. Connected a flow meter to the pressure tap on the lower side of the sampler motor housing and assure that there are no crimps or cracks along the tubing.
4. Cover or tape the inlet of the orifice with duct tape or a suitable material (palm of hand). Check the manometer and verify the manometer zero.
5. Turn on the sampler. Gently wiggle the orifice and listen for a whistling sound that would indicate a leak in the system. A leak-free system will also indicate no change in response on the flow meter. Leaks are usually caused by either a missing or damaged gasket at the junction of the orifice and face plate, cross-threading the orifice on the face plate or cross threading the motor on the filter holder.
6. Turn off the sampler and remove the tape from the orifice.

4.3 PM₁₀ Sampler Calibration

The PM₁₀ sampler calibration procedure relates known flow rates (as determined by a calibrated transfer standard orifice) to the pressure differential across the orifice at the exit of the blower housing. This pressure differential is referred to as the plenum pressure. The plenum is the region within the motor housing (downstream of the motor unit) where the pressure level exceeds atmospheric pressure. The calibration orifice has been calibrated in terms of **ACTUAL** laboratory conditions. The PM₁₀ sampler must also be calibrated in terms of **ACTUAL** site conditions.

Regardless of which type of orifice calibrator used (multi-hole load plate unit or the Vari-flo), the calibration procedure remains the same. The sampler inlet should be opened completely to prevent flow interference with the calibration transfer orifice. The calibration orifice is installed in place of the filter cassette in the PM₁₀ sampler. Flexible tubing is used to connect the orifice pressure tap to a water manometer. The pressure tap on the motor housing is connected to a separate water manometer or flow meter. Pressure drops and flow meter readings are recorded and entered onto a **MOTORCAL07.Wb2** spreadsheet (Figure A-3) and a seasonally adjusted set point (SSP) is calculated.

Following are the procedures used for PM₁₀ sampler calibration:

1. Assemble the following calibration equipment:
 - Calibrated orifice, face plate and restrictor plates
 - Digital manometer(s)
 - Centigrade thermometer; all temperatures must be expressed in degrees Kelvin for the calculations in this section ($^{\circ}\text{K} = ^{\circ}\text{C} + 273$)
 - Barometric pressure readings are obtained from the National Weather Service at **670-6526** or can be found on their website at <http://www.wrh.noaa.gov/twc/>. Be sure to ask for "station pressure" (uncorrected to sea level) expressed in mm Hg. Pressures may however need to be corrected for changes in elevation between the airport and monitoring site, if the difference in elevation exceeds 1000 ft.
 - Miscellaneous hand tools and notebook
2. Remove the filter and filter housing (calibration is performed *without* a filter).
3. Position the orifice face plate on the sampler filter support screen and tighten the four corner nuts. **Do not** use a filter or filter cartridge during calibration.
4. Make sure there is a gasket on the bottom of the orifice. Install the orifice on the face-plate and tighten.
5. Check that the flow meter is properly connected to the pressure tap on the lower side of the sampler motor housing.

6. Connect the motor directly to line voltage and allow it to warm up (5 minutes) to operating temperature.
7. Read and record the following parameters in your notebook:
 - Ambient temperature (T_a), ° K
 - Station barometric pressure (P_a), mm Hg (from weather service)
 - Sampler s/n, model, and motor number
 - Orifice s/n, slope and y-intercept (on computer)
 - Date, time and sampler designation
8. Read and record the manometer deflection and its corresponding flow meter response (in inches of water, H_2O).
9. Remove the calibration orifice and place restrictor plate #18 between the face plate and the calibration orifice and tighten. Repeat step 8 above.
10. Repeat steps 8 and 9 above for the remaining restrictor plate numbers 13, 10, 7 and 5.
11. Turn off the sampler and remove the calibration orifice and the manometer.
12. Re-connect the motor to the rheostat.
13. Install a clean filter (within a filter cartridge) in the sampler. Retighten the four wing nuts to ensure an even seal; do not over tighten or the gasket may warp.
14. Install a clean Dickson chart in the flow recorder and verify that the recorder is zeroed (the pen rests on the innermost circle of the chart). Gently tap on the side of the sampler to seat the ink pen. Rotate the chart until it indicates correct time.
15. You will need to determine the sampler's seasonally adjusted set point (SSP) as calculated on the **MOTORCAL07.Wb2** (Figure A-3) spreadsheet (Section 4.5).
16. The set point is set by adjusting the rheostat until the flow meter response indicates the correct flow.

4.4 Setting Up The Dickson Chart Recorder

The Dickson chart recorder verifies that the sampler operated without failure during the 24-hour sampling period and maintained the normal operational flow rate. Large deviations from the average flow rate on the recorder would indicate that there has been a power failure, a vacuum motor failure, or a leak. If the flow rate looks stable, set up the Dickson chart recorder as follows:

1. Install a new chart that has been properly labeled into the Dickson chart recorder. Replace the ink pen if needed.
2. Ensure that the Dickson chart recorder is properly connected to the pressure tap on the lower side of the sampler motor housing.

3. Check that it is properly zeroed (pen rests on innermost circle of the chart). Gently tap the side of the recorder to make sure the pen is not hung up on the chart. Adjust the zero set screw if necessary.
4. While the sampler is running, determine the actual flow rate from the manometer reading (nominally 2.8 - 3.0 inches H₂O for 40 cfm).
5. Gently tap the side of the recorder to make sure the pen is not hung up on the chart.
6. Lift the pen off the chart, and then rotate the chart with the center slot until the time is properly indicated on the chart. Be sure the pen is back down on the chart surface.

4.5 Lab Calculations

1. Load and run the **MOTORCAL07.Wb2** Quattro Pro spreadsheet on the laptop computer (Figure A-3).
2. Actual flow rate Q_a (cfm) is calculated for each calibration point as:

$$Q_a = \{[(dH_2O) (T_a/P_a)]^{1/2} - b\} \{1/m\} \{35.31\}$$

Where:

Q_a = orifice flow rate, actual cfm
 dH_2O = pressure drop across the orifice, inches of water
 T_a = ambient temperature, °K
 P_a = station barometric pressure, mm Hg
 b = intercept of the orifice calibration relationship
 m = slope of the orifice calibration relationship

3. The corrected motor tap flow response for each calibration point is calculated as:

$$dP = I (T_a/P_a)^{1/2}$$

Where:

dP = corrected motor tap flow response
 I = sampler flow rate indication

4. The actual orifice flow rates (Q_a , x-axis) are plotted versus the corresponding corrected motor tap flow response (dP , y-axis) to obtain a visual calibration curve and indication of the calibration linearity. A five-point calibration should yield a regression equation with correlation coefficient $r > 0.990$. Since the determination of actual flow rates requires the addition of ambient temperature and pressure corrections, the graphic plot of the calibration relationship is **NOT**

used for determining mass concentrations. Each sampler, therefore, must be provided with a mathematical expression that indicates the slope, y-intercept, and the correlation of the calibration relationship. Using the Quattro Pro **MOTORCAL07.Wb2** spreadsheet, the best-fit straight line is determined by linear regression. The equation of this line is:

$$dP = m (Q_a) + b$$

5. The slope - m, and intercept - b, are then calculated to determine the sampler's actual flow rate (Q_a) from:

$$Q_a = 1/m [I (T_a/P_a)^{1/2} - b]$$

6. The set point flow rate (SFR) is calculated as:

$$SFR = 40(P_s/P_a) (T_a/T_s)$$

Where:

$$SFR = \text{sampler's seasonally adjusted set point flow rate, cfm.}$$

7. The sampler set point (SSP) is the Dickson chart response that corresponds to the SFR calculated in Step (6) and is calculated as:

$$SSP = \{[m (SFR) + b]^2 (P_a/T_a)\}$$

8. Each sampler will have its own set point. Record the set point and date on the corresponding manila folder for that sampler so that you have it with you on the dirt runs. Check the set point at the site on the next dirt run.

5.0 MAINTENANCE

5.1 Routine Maintenance

Routine maintenance procedures are performed at regular intervals to reduce instrument down time. The following tasks are performed at the specified frequency:

- | <u>Task</u> | <u>Frequency</u> |
|--|---------------------|
| 1. Inspect sampler housing (power cords, gaskets, recorder, flexible tubing, mass flow controller) | Every filter change |

- | | | |
|----|--|---------------------|
| 2. | Bounce plate greased | Every 4th sample |
| 3. | Clean size-selective inlet (PM ₁₀) | During motor change |

6.0 AUDIT PROCEDURES

A specific detail for auditing PM₁₀ samplers follows in this section.

6.1 Flow Rate Transfer Standard Certification

Both flow rate transfer standards used for routine sampler calibrations and the one used for audits are certified each year at the Environmental Engineering Lab in Phoenix (Office of Air Quality Management, Arizona Department of Environmental Quality). Arrangements to use their facilities must be made in advance by calling their representative. A stopwatch, a calculator, a supply of Orifice Transfer Standard Certification Worksheets (Figure A-4), manometer, and the orifices to be certified are the only equipment items that need to be taken to the laboratory in Phoenix. The laboratory has a certified Roots meter, mercurial manometer, thermometer, and mercurial barometer.

The certification procedure is as follows:

1. Obtain the following information and enter it on the transfer standard certification worksheets:
 - Orifice ID
 - Roots meter ID
 - Ambient temperature during calibration T_a (°K)
 - Station barometric pressure during calibration
 - Line voltage
 - P_a (mm Hg)
 - Operator
2. Connect the orifice transfer standard to the inlet of the Roots meter. Connect the mercurial manometer to the pressure tap on the inlet of the Roots meter and slack tube manometer to the pressure tap on the transfer standard.
3. Check for pressure leaks by temporarily clamping the lines to the manometers (to prevent fluid loss) and blocking the orifice inlet with a large diameter rubber stopper, wide piece of duct tape, or other suitable means. Start the air pump and note any change in the Roots meter reading, which should remain constant. If there is any change in the reading, try to locate any leaks by listening for a whistling sound. Re-tighten all connections and ensure that all gaskets are properly installed.

4. When the leak check is completed, unclamp both manometer lines, unblock the orifice inlet, and zero the manometers.
5. Record the orifice differential pressure (dH₂O) and corresponding pressure differential at the inlet of the Roots meter (dHg), run time (t), and volume passed through the system for each test condition (dVol).
6. Calculate the actual volume for each test condition (V_a).
7. Calculate the actual flow rate (Q_a) for each test condition as follows:

Note: P_a and dHg must be in consistent units.

$$Q_a = [(P_a - dHg)/P_a] (V_a/t)$$

8. The orifice calibration relationship is in the form:

$$Q_a = (y - b)/m$$

Where:

Q_a = orifice flow rate, actual cfm
y = [(dH₂O) (T_a/P_a)]^{1/2}
b = y - intercept of the orifice calibration
m = slope of the orifice calibration relationship

9. Calculate y for each test condition:

$$y = [(dH_2O) (T_a/P_a)]^{1/2}$$

10. Determine the best-fit straight line by linear regression. The equation of the line is:

$$y = m (Q_a) + b$$

Perform the linear regression on the data set and record the intercept (b), slope (m), and the correlation coefficient (r) of the curve fit.

11. The correlation coefficient (r) must be 0.990 in order for the calibration to be valid. If r < 0.990, recheck calculations. If necessary, repeat the calibration procedure.
12. To determine the actual flow rate in cfm from the orifice calibration relation, use:

$$Q_a = [((dH_2O) (T_a/P_a))^{1/2} - b]/m$$

6.2 Flow Rate Performance Audit Procedures for PM₁₀

The site operator is responsible for providing the manometer that is normally used for measuring the sampler's flow rate, the sampler calibration relationship that is currently in effect for determining the flow rate for sample periods and any other information or equipment that is normally used to determine the sampler's indicated flow rate.

The auditor should adhere to the following procedures during an audit of PM₁₀ samplers:

1. Transport the following equipment to the monitoring site:
 - Audit orifice transfer standard with calibration relationship in actual cfm and traceable to NIST. This orifice transfer standard should not be the same one that is used for routine calibrations and flow checks.
 - Slack-tube manometer/digital flow meter
 - Thermometer
 - Clean filter and clean Dickson chart.
 - A high volume particulates audit worksheet (Figure A-5)
2. Record the site location, sampler s/n, and date in a log book.
3. Install a clean filter in the PM₁₀ sampler. Do not use a filter cassette; place the filter directly on the sampler filter screen. An audit filter should never be used for subsequent sampling because particles larger than 10 µm can be collected on the filter while the inlet is raised. The sampler mass will be biased as a result of using a filter for both an audit and subsequent sampling.
4. Install the audit orifice transfer standard's faceplate on the sampler. Check that gaskets are in good condition and have not deteriorated. Tighten the faceplate nuts evenly on alternate corners to properly align and uniformly seat the gaskets. The nuts should be hand tightened only; too much compression can damage the sealing gaskets.
5. Install the audit orifice transfer standard with no restrictor plate, making sure the orifice gasket is present and the audit orifice is not cross-threaded on the faceplate. Seal the audit orifice's pressure port with a rubber cap or similar device.
6. Leak test the audit system (refer to **Subsection 4.2.**). Identify and correct any leaks before continuing.
7. Inspect the manometer flexible tubing for crimps or cracks. Open the manometer valves fully and blow gently through the tubing, watching for the free flow of the fluid. Adjust the manometer sliding scale so that the zero line is at the bottom of the meniscus. Connect the manometer to the pressure port on the orifice. Make sure the unconnected side of the manometer is open to the atmosphere. Make sure that the tubing fits snugly on the pressure port and on the manometer.
8. Remove the audit orifice and place restrictor plate #18 between the face plate and the audit orifice and tighten.

9. Turn on the sampler and allow it to warm up to operating temperature (5 minutes).
10. Observe and record the following parameters on the audit data sheet:
 - Sampler location, date, time
 - Sampler model, s/n and calibration relationship
 - Ambient temperature (T_a), °K (°K = °C + 273)
 - Ambient barometric pressure (P_a), mm Hg
 - Unusual weather conditions
 - Audit orifice s/n, slope, y-intercept
11. Observe the pressure drop across the orifice by reading the total manometer deflection, and record as Orifice dH₂O on the audit data sheet.
12. Read the flow meter connected to the motor tap and record as Sampler pdex on the audit data sheet.
13. Repeat steps 11 and 12 above for the remaining restrictor plate numbers 13, 10, 7 and 5.
14. Turn off the sampler and remove the audit orifice transfer standard, but do not remove the filter. Turn the sampler on again and repeat step 12 for the normal operating flow rate.
15. Gather together all audit data, including the audit orifice's calibration data, and the sampler's calibration data.
16. Verify that the correct readings have been inscribed on the data sheet.
17. Determine the flow rate through the audit orifice, as follows:

$$Q_a \text{ (audit)} = \{ [dH_2O (T_a/P_a)]^{1/2} - b \} \{ 1/m \}$$

Where:

| | |
|-----------------------|---|
| $Q_a \text{ (audit)}$ | = actual flow rate as indicated by the audit orifice transfer standard, cfm |
| dH_2O | = pressure drop across the orifice, inches H ₂ O |
| T_a | = ambient temperature, °K (°K = °C + 273) |
| P_a | = ambient barometric pressure, mm Hg |
| b | = y - intercept of the audit orifice transfer standard's calibration relationship |
| m | = slope of the audit orifice transfer standard's calibration relationship |

18. Calculate the sampler's indicated flow rate, Q_a (sampler) with and without the orifice installed, using the sampler's calibration relationship and record both Q_a (sampler) values on the data sheet.

19. Calculate the percentage difference between the sampler's indicated flow rate, $Q_a(\text{sampler})$ with the orifice installed, and the corresponding audit flow rate, $Q_a(\text{audit})$, determined from the audit orifice transfer standard as:

$$\text{Audit flow rate \% difference} = [Q_a(\text{sampler}) - Q_a(\text{audit})]/Q_a(\text{audit}) \{100\}$$

20. Record the audit flow rate percentage difference on the data sheet. If the audit flow rate percentage difference is less than or equal to ± 10 percent, the sampler calibration is acceptable. Differences exceeding ± 10 percent require sampler recalibration. Differences exceeding ± 15 percent will result in invalidation of all data subsequent to the last calibration or valid flow check. Before invalidating any data, double-check the sampler's calibration, the audit orifice transfer standard's certification, and all calculations.
21. Calculate the corrected sampler flow rate, $Q_a(\text{corrected sampler})$, using:

$$Q_a(\text{corrected sampler}) = Q_a(\text{sampler}) \{[100 - \text{audit \% difference}]/100\}$$

Where:

$Q_a(\text{sampler})$ is for the measurement without the audit orifice transfer standard installed. Be sure to carry over the sign of the audit % difference from Step 19.

7.0 Precision, Accuracy and Validity of Particulate Data

Specific details regarding the particulate network are in accordance with **40 CFR 50, Appendix J**, and **40 CFR 58, Appendix A**, July 2003.

7.1 Precision

Precision of the particulate sampling network is determined by co-locating samplers for duplicate sampling. The Ocotillo site has been designated as the co-located site for PM_{10} . Sampler OC1 is designated as the primary sampler. Sampler OC2 is designated as the duplicate sampler for assessing precision. Collocated measurement pairs are selected for use in the precision calculations only when both measurement pairs are above $20\mu\text{g}/\text{m}^3$.

7.2 Accuracy

Accuracy is determined by conducting performance audits of the samplers (**Section 6.2**). Audits are conducted by an independent auditor, with an audit device not used in routine

operations. All samplers in the PDEQ BMN will be audited every quarter. Sampler flow rates must be within 10 percent of the audit flow rates.

7.3 Validity

PM₁₀ samples are considered valid if the actual flow rate during the sampling period is found to be within $\pm 10\%$ of the set point flow rate for the specified sampler. Damaged or severely smudged filters are discarded as invalid. The normal sampling period is twenty-four hours; filters that do not run for the full cycle, or do not start or end at midnight (± 30 minutes) are also discarded as invalid. Any sampler malfunction during a sampling period invalidates the sample. Wet filters are discarded. Unusual site conditions such as heavy construction or circus activity are noted but data is not invalidated.

If during a performance audit the flow rate percentage difference is within $\pm 10\%$ of the audit flow rate, the sampler calibration is acceptable. Differences exceeding $\pm 10\%$ are investigated. Differences exceeding $\pm 15\%$ result in invalidating data back to the last acceptable flow check.

Figure A-2
Example DAILYCONPM10.xls

| Date | Filter Number | Tare Wt | Gross Wt | Net Wt | 10% Reweigh | Diff | Flow Ind | Qa cfm | Qstd cfm | Vstd m3 | Std Conc | Local Conc | Motor Cal Date | m | b | Ts |
|-----------|---------------|---------|----------|--------|-------------|---------|----------|--------|----------|---------|----------|------------|----------------|-------|-------|-------|
| 1/1/2004 | Q3002659 | 4.5824 | 4.6041 | 0.0217 | 4.6037 | 0.0004 | 3.43 | 41.3 | 39.2 | 1600.3 | 13.6 | 12.9 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 1/2/2004 | | | | | | | | | | | | | | | | |
| 1/3/2004 | | | | | | | | | | | | | | | | |
| 1/4/2004 | Q3002644 | 4.4773 | 4.5087 | 0.0314 | | | 3.23 | 40.0 | 38.0 | 1549.7 | 20.3 | 19.3 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 1/5/2004 | | | | | | | | | | | | | | | | |
| 1/6/2004 | | | | | | | | | | | | | | | | |
| 1/7/2004 | Q3002641 | 4.4686 | 4.5486 | 0.08 | | | 3.36 | 40.8 | 38.8 | 1582.8 | 50.5 | 48.1 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 1/8/2004 | | | | | | | | | | | | | | | | |
| 1/9/2004 | | | | | | | | | | | | | | | | |
| 1/10/2004 | Q3002625 | 4.5109 | 4.5620 | 0.0511 | | | 3.31 | 40.5 | 38.5 | 1570.1 | 32.5 | 30.9 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 1/11/2004 | | | | | | | | | | | | | | | | |
| 1/12/2004 | | | | | | | | | | | | | | | | |
| 1/13/2004 | Q3002622 | 4.5114 | 4.5735 | 0.0621 | | | 3.24 | 40.0 | 38.1 | 1552.3 | 40.0 | 38.0 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 1/14/2004 | | | | | | | | | | | | | | | | |
| 1/15/2004 | | | | | | | | | | | | | | | | |
| 1/16/2004 | Q3002606 | 4.4755 | 4.5164 | 0.0409 | | | 3.29 | 40.4 | 38.4 | 1565.1 | 26.1 | 24.8 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 1/17/2004 | | | | | | | | | | | | | | | | |
| 1/18/2004 | | | | | | | | | | | | | | | | |
| 1/19/2004 | Q3002603 | 4.4958 | 4.5327 | 0.0369 | | | 3.28 | 40.3 | 38.3 | 1562.5 | 23.6 | 22.5 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 1/20/2004 | | | | | | | | | | | | | | | | |
| 1/21/2004 | | | | | | | | | | | | | | | | |
| 1/22/2004 | Q3002587 | 4.48 | 4.4892 | 0.0092 | | | 3.26 | 40.2 | 38.2 | 1557.4 | 5.9 | 5.6 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 1/23/2004 | | | | | | | | | | | | | | | | |
| 1/24/2004 | | | | | | | | | | | | | | | | |
| 1/25/2004 | Q3002584 | 4.4823 | 4.4944 | 0.0121 | | | 3.31 | 40.5 | 38.5 | 1570.1 | 7.7 | 7.3 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 1/26/2004 | | | | | | | | | | | | | | | | |
| 1/27/2004 | | | | | | | | | | | | | | | | |
| 1/28/2004 | Q3002568 | 4.4837 | 4.5293 | 0.0456 | | | 3.3 | 40.4 | 38.4 | 1567.6 | 29.1 | 27.7 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 1/29/2004 | | | | | | | | | | | | | | | | |
| 1/30/2004 | | | | | | | | | | | | | | | | |
| 1/31/2004 | Q3002565 | 4.5002 | 4.5420 | 0.0418 | 4.5420 | 0.00000 | 3.4 | 41.1 | 39.1 | 1592.8 | 26.2 | 25.0 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 2/1/2004 | | | | | | | | | | | | | | | | |
| 2/2/2004 | | | | | | | | | | | | | | | | |
| 2/3/2004 | Q3002548 | 4.4741 | 4.5205 | 0.0464 | | | 3.27 | 40.2 | 38.3 | 1560.0 | 29.7 | 28.3 | 12/12/03 | 0.027 | 0.075 | 286.5 |
| 2/8/2004 | | | | | | | | | | | | | | | | |
| 2/9/2004 | Q3002531 | 4.5001 | 4.5458 | 0.0457 | | | 3.27 | 40.2 | 38.3 | 1560.0 | 29.3 | 27.9 | 12/12/03 | 0.027 | 0.075 | 286.5 |

Figure A-3
Example MOTORCAL07.Wb2 Spreadsheet

MOTOR CALIBRATION SPREADSHEET FOR PARTICULATES

| | | | | |
|-------|-------|-------|--|--------------|
| | | | Sampler: | Ts = 300.6 |
| | | | Cal Date: 05/14/07 | Ps = 692.9 |
| Month | Ts | Ps | Motor: 1417 | |
| ----- | ----- | ----- | Temp: 31.9 | Ta = 304.9 |
| Jan | 288.8 | 693.9 | Press: 27.402 | Pa = 696.0 |
| Feb | 292.4 | 693.2 | Altim: 30.080 | |
| Mar | 296.0 | 692.8 | Orifice Calibration Relationship: | |
| Apr | 298.9 | 692.9 | m = 1.26803 | b = -0.04827 |
| May | 300.6 | 692.9 | | |
| Jun | 300.3 | 693.4 | Point | Orifice |
| Jul | 297.6 | 694.0 | No. | dH2O |
| Aug | 293.8 | 694.5 | 1 | 14.2 |
| Sep | 290.1 | 694.9 | 2 | 10.7 |
| Oct | 287.2 | 695.3 | 3 | 8.1 |
| Nov | 285.8 | 695.2 | 4 | 4.7 |
| Dec | 286.5 | 694.7 | 5 | 2.8 |
| | | | Qa | Sampler |
| | | | Orifice | dPex |
| | | | 70.7 | 5.9 |
| | | | 61.6 | 4.6 |
| | | | 53.9 | 3.7 |
| | | | 41.4 | 1.6 |
| | | | 31.9 | 0.6 |
| | | | | dPext |
| | | | | 1.60 |
| | | | | 1.42 |
| | | | | 1.27 |
| | | | | 0.83 |
| | | | | 0.49 |

Run Regression after all data is entered.

Regression Output:

| | |
|---------------------|----------|
| Constant | -0.38533 |
| Std Err of Y Est | 0.071267 |
| R Squared | 0.981595 |
| No. of Observations | 5 |
| Degrees of Freedom | 3 |

Sampler Calibration Relationship:

| | |
|-----|--------|
| m = | 0.029 |
| b = | -0.385 |
| r = | 0.991 |

| | | | | |
|------------------|---------|--------------------|-------------|------------|
| X Coefficient(s) | 0.02909 | Set Point (CFM) | 40.4 (pm10) | 50.5 (tsp) |
| Std Err of Coef. | 0.0023 | Set Point (in H2O) | 1.4 (pm10) | 2.7 (tsp) |

Figure A-4

Example Orifice Transfer Standard Certification Worksheet

Orifice Transfer Standard Certification

Date: 9/28/2005
Calibrating Company: ADEQ
Operator: John Doe

ROOTS Meter S/N: 7660983
Orifice S/N: B

Temperature °C: 24
Temperature °K: 297.15
Pa inHg: 28.86
Pa mmHg: 733

Certification for: Pima County

ROOTS Meter Calibrations

| Restrictor Plates | Initial Volume Counter | Final Volume Counter | Delta Volume Ltrs | Delta Time | | Delta Hg (mm) x 25.4 | | Delta H2O in. W.C. |
|-------------------|------------------------|----------------------|-------------------|------------|------------|----------------------|--------|--------------------|
| | | | | Minutes | Seconds/60 | | | |
| Open | 19871 | 19874 | 3 | 1.15.28 | 1.254 | 1.35 | 34.29 | 20 |
| 18 | 19878 | 19881 | 3 | 1.26.91 | 1.448 | 2.1 | 53.34 | 14.05 |
| 13 | 19884 | 19887 | 3 | 1.35.61 | 1.593 | 2.5 | 63.5 | 11.25 |
| 10 | 19890 | 19893 | 3 | 1.45.91 | 1.765 | 2.8 | 71.12 | 8.8 |
| 7 | 19895 | 19898 | 3 | 2.10.64 | 2.177 | 3.45 | 87.63 | 5.45 |
| 5 | 19900 | 19903 | 3 | 2.43.35 | 2.722 | 3.95 | 100.33 | 3.35 |

Calculations
 $V_a = \text{delta Vol} [(Pa - \text{Delta Hg})/Pa]$
 $Q_a = V_a / \text{Delta Time}$
 $Y = mx + b$
 $Q_a = \{[\text{Delta H2O} (Ta/Pa)]^{1/2} - b\} \{1/m\}$

Data Tabulation

| Va | (x axis) Qa | (Y axis) [deltaH2O(Ta/Pa)] ² |
|-------|----------------|--|
| 2.860 | 2.280 | 2.8474 |
| 2.782 | 1.921 | 2.3866 |
| 2.740 | 1.720 | 2.1356 |
| 2.709 | 1.535 | 1.8888 |
| 2.641 | 1.213 | 1.4864 |
| 2.589 | 0.951 | 1.1654 |
| m= | | 1.26803 |
| b= | | -0.04827 |
| r= | | 0.99990 |

SUMMARY OUTPUT

| <u>Regression Statistics</u> | |
|------------------------------|-------------|
| Multiple R | 0.999952213 |
| R Square | 0.999904428 |
| Adjusted R | 0.999880534 |
| Standard E | 0.006661715 |
| Observator | 6 |

ANOVA

| | <i>df</i> | <i>SS</i> | <i>MS</i> | <i>F</i> | <i>Significance F</i> |
|------------|-----------|-------------|-------------|-------------|-----------------------|
| Regression | 1 | 1.857196899 | 1.857196899 | 41849.07143 | 3.42539E-09 |
| Residual | 4 | 0.000177514 | 4.43784E-05 | | |
| Total | 5 | 1.857374413 | | | |

| | Coefficients | Standard Error | t Stat | P-value | Lower 95% | Upper 95% | Lower 95.0% | Upper 95.0% |
|------------|--------------|----------------|--------------|-------------|--------------|--------------|--------------|--------------|
| Intercept | -0.04826740 | 0.010304617 | -4.684056543 | 0.009419254 | -0.076877609 | -0.019657204 | -0.076877609 | -0.019657204 |
| X Variable | 1.268030288 | 0.006198502 | 204.5704559 | 3.42539E-09 | 1.250820488 | 1.285240087 | 1.250820488 | 1.285240087 |

Figure A-5
 Example High Volume Particulates Audit Worksheet

AUDIT SPREADSHEET FOR PARTICULATES

| Month | Ts | Ps | Sampler: | Ts = | 300.6 | | |
|-------|-------|-------|-----------|--------------|-----------------------------------|--------------|---------------|
| Jan | 288.8 | 693.9 | Cal Date: | 05/14/07 | Ps = 692.9 | | |
| Feb | 292.4 | 693.2 | Motor: | 1417 | Temp c = 26.11 | | |
| Mar | 296.0 | 692.8 | Temp f: | 79 | Ta = 299.1 | | |
| Apr | 298.6 | 692.9 | Press: | 27.400 | Pa = 696.0 | | |
| May | 300.6 | 692.9 | Altim: | 30.000 | Orifice Calibration Relationship: | | |
| Jun | 300.3 | 693.4 | | | m= 1.30636 b= -0.04132 | | |
| Jul | 297.6 | 694.0 | Point No. | Orifice dH2O | Qa Orifice | Sampler dPex | Sampler dPext |
| Aug | 293.8 | 694.5 | 1 | 2.55 | 29.4 | 1.13 | 0.70 |
| Sep | 290.1 | 694.9 | 2 | 2.20 | 27.4 | 0.94 | 0.64 |
| Oct | 287.2 | 695.3 | 3 | 1.85 | 25.2 | 0.76 | 0.57 |
| Nov | 285.8 | 695.2 | 4 | 1.30 | 21.3 | 0.52 | 0.47 |
| Dec | 286.5 | 694.7 | 5 | 0.84 | 17.4 | 0.31 | 0.37 |

| Sampler Calibration Relationship: | | |
|-----------------------------------|-------------|------------|
| m = | 0.027 | |
| b = | -0.110 | |
| r = | 0.999 | |
| | pm10 | tsp |
| Set Point (cfm) | 39.6 | 49.5 |
| Set Point (H2O) | 2.2 | 3.6 |

Orifice dH2O 1.748
 Sample dPex 0.7
 Orifice Qa(m3/m) 0.695116
 Sample Qa dPex 24.6019

Audit flow rate % diff. 4.34%

| Orifice | | |
|-------------------|---------|----------|
| dH2O | Qa(CFM) | Qa(M3/m) |
| <u>1.748</u> | 24.54 | 0.70 |
| Sampler w/Orifice | | |
| dPex | Qa(CFM) | Qa(M3/m) |
| 0.73 | 25.61 | 0.73 |

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Pima County
Department of Environmental Quality
Air Monitoring Quality Assurance Plan

Appendix B
Weigh Lab Procedures



Pima County Department of Environmental Quality
150 West Congress St., 1st Floor
Tucson, AZ. 85701
(520)740-3340

PDEQ STANDARD OPERATING PROCEDURES

Weigh Lab Procedures

1.0 GENERAL DISCUSSION

The quality of data from the PM10 sampling program depends on several factors. A primary consideration is the analytical laboratory staff's attention to detail and their balance operation techniques. This section offers guidelines to enhance the data quality of the laboratory operation and hence, the PM10 mass concentration and any additional chemical qualitative and quantitative determinations.

The first five sections of this standard operating procedure deal primarily with the 46.2mm polytetrafluoroethylene (PTFE) Teflon filter used in the PM₁₀ reference methods and/or Class 1 equivalent methods used to monitor ambient air for particles with an aerodynamic diameter equal to or less than 10µg, known as PM₁₀. The last three sections will deal with the High Purity Quartz Microfibre filter used in the PM₁₀ Hi-Volume method and the Mettler Type H15 Macro Balance.

2.0 MICROBALANCE ENVIRONMENT

Gravimetric analysis of the filters is performed with a microbalance with a readability of 0.001 µg and a repeatability of 1 µg. Because of the greater sensitivity needed for measuring microgram range weights or weight differences, microbalances are vulnerable to relatively small changes in physical environmental conditions, such as vibration, electrostatic charge buildup, temperature, and relative humidity (RH).

A balance number should identify each microbalance used the weighing procedures. Make sure that the microbalance has been calibrated (at least annually) and maintained according to the manufacturer's recommendations. If it is out of calibration, the microbalance should be calibrated by a microbalance service technician according to the manufacturer's directions. The analyst should not try to repair the microbalance. On an annual basis, PDEQ has its microbalance certified by microbalance technician and receives a Certificate of Calibration.

Dust contamination can be minimized by taking clean room measures such as cleaning the weighing area weekly, installing sticky floor covering on the entrance to the weighing area and wearing clean laboratory clothing over anything exposed to uncontrolled environments.

3.0 MASS REFERENCE STANDARDS

Two separate sets of mass reference standards are recommended. *Working calibration standards* should be used for routine filter weighing and kept next to the microbalance in a protective container. *Laboratory primary standards* (mass standards) should be handled very

carefully and should be kept in a locked compartment. The working standards' masses should be verified against the laboratory primary standards every 3 to 6 months or after any incident of rough handling to check for mass shifts associated with handling or contamination. The verified values of the working standards as measured relative to the laboratory primary standards should be recorded in a laboratory QC notebook and used to check the calibration of the microbalance.

Mass reference standards should be in the range of 100 to 200 μg , given that the mass range of a typical 46.2 mm diameter filter is from 110 to 160 μg . They should be certified as being laboratory measures holding a NIST certificate of traceability or at a calibration laboratory accredited by the National Voluntary Laboratory Accreditation Program (NVLAP). The recalibration frequency should be determined from records of previous recalibrations of these standards.

Always use smooth, nonmetallic forceps when handling mass reference standards. The standards are handled only with these forceps, which are not to be used for any other purpose. Mark these forceps to distinguish them from forceps used to handle filters. Forceps should be cleaned with alcohol and lint-free wipes before handling standards and then should be allowed to air-dry. Handle the standards carefully to avoid damage that may alter their masses.

4.0 FILTERS (46.2mm Teflon)

4.1 Filter Handling

Careful handling of the filter during sampling, conditioning and weighing is necessary to avoid measurement errors due to damaged filters or a gain or loss of collected particles on the filters. Whenever filters are handled, the analyst should wear antistatic, powder-free gloves (if available). These gloves act as an effective contamination barrier. It is a good practice to discharge them by touching a good electrical ground after putting them on. The filters should be handled carefully by the support ring, rather than by the filter material, with smooth, non-serrated forceps that are used only for that purpose. Mark these forceps to distinguish them from forceps used to handle mass reference standards. Make sure that the forceps are clean prior to using them. These precautions reduce the potential effect from body moisture or oils contacting the filters and subsequently affecting the measured weights.

In the laboratory, each filter should be transferred from its sealed manufacturer's packaging to a clean filter-handling container, such as a glass or plastic Petri dish, to reduce the risk of contamination. The filter should remain in this container, except for weighing, until it is loaded into a filter cassette prior to sampling. Each filter should have a unique identification number.

4.2 Filter Integrity Check

All filters should be inspected for defects *before* the initial weighing. If any defects are found, discard the filter. Return any lot of filters containing a high number of defects to the supplier. Specific filter defects to look for are as follows:

- Pinhole: A small hole appearing; (A) as a distinct and obvious bright point of light when examined over a light table or screen or (B) as a dark spot when viewed over a dark surface.
- Separating of the ring: Any separation or lack of seal between the filter and the filter border reinforcing the ring.
- Chaff or flashing: Any extra material on the reinforcing, polyolefin ring or on the heat seal area that would prevent an airtight seal during sampling.
- Loose material: Any extra loose material or dirt particles on the filter.
- Discoloration: Any obvious discoloration that might be evidence of contamination.
- Filter non-uniformity: Any obvious visible non-uniformity in the appearance of the filter when viewed over a light table or black surface that might indicate graduations in porosity or density across the face of the filter.
- Other: A filter with any imperfection not described above, such as irregular surfaces or other results of poor workmanship.

4.3 Filter Conditioning

New filters should be placed in the conditioning environment immediately upon arrival and stored there until the pre-sampling weighing. Filters must be conditioned before both the pre and post-sampling weighings. Filters must be conditioned for at least 24 hours (PDEQ filter conditioning time is **48 hours**) to allow their weights to stabilize before being weighed.

Filters must be conditioned at the same conditions (humidity within $\pm 5\%$ RH) before the pre and post sampling weightings. **Mean RH** must be held between 30-40%, with a variability of not more than $\pm 5\%$ over 24 hours. However, where it can be shown that the mean ambient RH during sampling is less than 30%, conditioning is permissible at a mean RH within $\pm 5\%$ RH of the mean ambient RH, but in *no* case less than 20% RH. **Mean Temperature** should be between 20-23°C (68-73.4°F) with a variability of not more than $\pm 2^\circ\text{C}$ over 24 hours. RH and temperature is measured and recorded on a continuous basis during filter conditioning using a Dickson TM121 RH/Temperature recorder. All data from the Dickson TM121 is downloaded every week onto PDEQ's database for evaluation by the analyst.

If spikes of temperature or, especially, RH occur during the conditioning period, the appropriate decision maker should evaluate all relevant data and decide if the spikes are significant enough to compromise the conditioning period. The evaluation should also include the significance of the timing of the spikes in relation to the timing of weighing, the closer to the weighing, the more significant the effect on the weight.

The data evaluator may use a rolling (accumulative) average or standard deviation of the averages for the 24-hour period. These methods of comparing variability to the control limits ($\nabla 2^{\circ}\text{C}$ or $\nabla 5\%$ RH) will appropriately minimize the effect of a spike at the end of the 24-hour period (such as entering the weighing room prior to weighing). Using a standard deviation of averages during the period will be more statistically representative of the conditions and will probably minimize spikes more than the rolling average method. Another consideration is whether a 95 or 99% confidence interval is more acceptable.

Within the conditioning chamber, the filters should be placed on a covered rack or an open sided cabinet that will allow air circulation over the filters while reducing the chance that airborne material inside the chamber will settle onto the filters.

Care should be taken to avoid contaminating the 46.2 mm polytetrafluoroethylene (PTFE) Teflon filters inside the conditioning chamber with particulates released by other filter media (e.g. quartz and glass) that are also being conditioned in the chamber. **Laboratory blanks** will be used to check for potential cross-contamination from airborne particulates inside the conditioning chamber. If there is evidence of cross-contamination, corrective action should be taken. One possible solution could be to maintain separate conditioning chambers for 46.2 mm Teflon filters and other filter media.

Filters should be conditioned in their filter-handling containers. Label each container and partially cover the container with the lid to allow air into the container so the filters can "breathe". All 46.2mm filters should be laid out in Petri dishes and placed in conditioning chambers for proper conditioning. To improve filter inventory control, place the filters in the chamber in numerical order so that the analyst can more easily weigh the filters in numerical order.

Typically, filters come packed together in large groups or in a container with separators. This package is usually contained inside another clear, re-closeable plastic container. The more time that each filter is exposed to the conditioning environment, the more likely that its weight will be stable by the end of a conditioning period.

4.4 Lot Blanks, Laboratory Blanks, Field Blanks and Trip Blanks

There are four types of blanks that should be used. **Lot blanks** are un-sampled filters used to determine filter weight stability over long periods of time due to the volatilization of

material from the filter or to the absorption of gaseous material into the filter from the atmosphere. **Laboratory blanks** are conditioned, un-sampled filters used to determine any weight change between pre and post sampling weightings due to contamination in the microbalance environment. **Field blanks** are conditioned, un-sampled filters used to determine whether similar contamination occurs during sampling. **Trip blanks** are conditioned, un-sampled filters used to determine whether contamination occurs during transport only.

The weight stability of filters can be determined by assigning three un-sampled filters from each new filter exposure lot as exposure lot blanks. A filter lot is defined as a single shipment of filters from a manufacturer. A filter exposure lot is defined as a sub-sample of filters from the filter lot to be conditioned within a specific period of time.

After an initial 24-hour conditioning, these three exposure lot blanks are re-weighed periodically (e.g. monthly/weekly/daily) and stored in the conditioning chamber (with the other filters) between weightings. These measurements should be recorded in the QC notebook or equivalent database. These weightings should continue until the 24-hour weight change is less than 15 μ g (micrograms). This filter weight experiment determines the period that the entire filter lot should be conditioned before it can be used for routine sampling. This experiment need not be continued during routine sampling but should be repeated when a new lot of filters are received. PDEQ's filter conditioning time is 48 hours.

4.4.1 Laboratory blanks should be kept inside the conditioning chamber except during weighing sessions. Weigh enough laboratory blanks during the pre-sampling weighing session to provide at least one single-use laboratory blank during each subsequent post-sampling weighing session. The pre and post-sampling weights should be recorded in the QC notebook and the laboratory database. If the weight change *exceeds 15 μ g*, contamination in the conditioning chamber may be occurring. Take appropriate and corrective action.

4.4.2 Field blanks should be transported to the sampling site, loaded into the sampler, kept there during the sampling interval, and retrieved with the exposed filters. This approach presumes that the unused slots are available and that the sampler can be programmed to not sample the field blanks.

Field blanks should be implemented at approximately 10% of a monitor's sampling frequency (i.e. there should be a field blank for every 10th sampled filter). Therefore, a monitor operating on a 1 in 6 day schedule would be expected to have approximately 6 blanks in a year while a monitor operating every day would be expected to have approximately 36 blanks. The pre and post-sampling weights should be recorded in the QC notebook and the laboratory database. If the weight change *exceeds 30 μ g*, contamination during transportation or at the sampling site may be occurring. Since field blanks reflect the effect of field factors occurring at *all* steps of the data collection

process, evaluation of the effects of field factors requires removing the lab blank variability from the field variability values and then looking at the remainder to see the variability due to factors having an effect in the cassette assembly, transport to the field, sampling, transport back to the laboratory, and recovery of the filters from the cassette. This consideration does not mean that the field blank acceptance criteria might be changed from 30 μ g or the laboratory blank criteria from 15 μ g by the field blank.

4.4.3 Trip blanks should be transported to the sampling site (but not loaded or left in the sampler cabinet) and then returned to the laboratory. The filter should *not* be exposed to the outside elements. The purpose of the trip blank is to evaluate possible contamination during transport only. Trip blanks should be implemented at approximately 10% of a monitor's sampling frequency (i.e. one for every field blank). The pre and post-sampling weights should be recorded in the QC notebook and the laboratory database. If the weight change *exceeds 20 μ g*, contamination during transportation may be occurring.

4.5 Electrostatic Charge Neutralization

Electrostatic charge buildup will prevent a microbalance from operating properly. Static charge is the accumulation of electrical charges on the surface of a nonconductive material. Common symptoms of this problem include noisy readout, drift and sudden readout shifts. To reduce static charge within the balance, it is necessary to place a **radioactive antistatic strip** containing a very small amount (I.E. 500 Pico curies) of 210Po in the weighing chamber. It is also necessary to pass each filter near, but not touching, an antistatic strip *before* it is weighed.

210Po antistatic strips are used to reduce electrostatic buildup in the microbalance's weighing chamber and on individual filters by charge neutralization. They neutralize electrostatic charge on items brought within an inch of them. These antistatic strips are safe. **210Po has a half-life of 138 days.** Change the antistatic strips *every 6 months* and dispose of the old strips according to the manufacturer's recommendations. Charge neutralization times may need to be longer than 60 seconds for sampling situations in which (1) a high amount of charge has developed on collected particles due to their origin or (2) the particle loading on a filter is large. Electrostatic charge buildup becomes greater as the air becomes drier. A 60-second charge neutralization may be sufficient in ambient indoor air, conditioned to 37% RH and 23°C but not in 20% RH and 23°C in arid environments. This latter environment may require that the filter sit for more time on the antistatic strip.

4.6 Pre-Sampling Filter Weighing (Tare weight)

The Reference Method (EPA 1997) requires that the pre-sample filter weighing be conducted *within 30 days* of the sampling period. Following are the procedures used for pre-sampling filter weighing:

1. Prepare the laboratory database software programs according to **Section 5.0, Software Preparation.**
2. Record the RH and temperature of the conditioning chamber in the laboratory QC notebook or database.
3. Clean the microbalance's weighing chamber with a fine brush, if necessary. Avoid using pressurized gas, which may blow damaging debris and oils into the microbalance's mechanism. Clean the surfaces near the microbalance with pre-moistened (in de-ionized water) clean-wipes and dry with a Kimwipe. Clean the standard forceps with a lint free cloth and the filter forceps with the moistened wipes. Allow the forceps to air dry. Make sure the forceps are thoroughly dry before use. A small amount of moisture can cause a significant measurement bias.
4. To ensure maximum stability, the microbalance should be left on at all times (in "Standby" mode when not being used). This enables the microbalance to be operational at all times and eliminates the need for a warm up period before analyses are performed.
5. Zero (i.e. tare) and calibrate (if necessary) the microbalance. Pressing the long "re-zero" bar down will re-zero the microbalance. The microbalance will perform an "auto-cal" after being idle for 2-3 minutes.
6. Using smooth, non-serrated, non-metallic forceps, weigh two working mass reference standards as a QC check (PDEQ uses 100 mg and 200mg weights). Handle the working standards carefully to avoid damage that may alter their masses. Wait until the microbalance's display indicates that a stable reading has been obtained. Record the certified and measured values of these standards on the laboratory QC notebook and in the database. Use the following procedure to properly weigh the working mass standards:
 - a. Place the 100mg working standard onto the center of the microbalance using the proper forceps. Press either one of the "Select" buttons to close the microbalance door.
 - b. Allow the microbalance's display to indicate that a stable reading has been obtained. The LED screen will blink an "I/O" icon until the balance is satisfied with the accuracy of the weight. The small square in the upper left corner of the screen will fade.
 - c. Ensure that the desired cell on the database spreadsheet is active (highlighted).
 - d. Press the "Print" button on the microbalance to print the weight onto the spreadsheet. The microbalance will sound a soft "ding" and the door will open.
 - e. Enter the weight into the QC notebook.
 - f. Remove the 100mg working standard from the microbalance and place back into its protective case.

- g. Repeat steps 1-6 again using the 200mg working standard.

If the verified and measured values of a working standard disagree by more than 3 micrograms (μg), reweigh the working standard. If the two values still disagree, troubleshoot and take appropriate action, which may include (1) re-certifying the working standards against the laboratory primary standards and/or (2) having a service technician repair the microbalance. The analyst *should not* attempt to repair the microbalance.

Weigh enough laboratory blanks during pre-sampling weighing sessions to provide at least 10% or one single-use laboratory blank during each subsequent post-sampling weighing session. Record the pre-sampling weights in the database and in the QC notebook using steps a thru e above. Check each filter's integrity as discussed in section 4.2. After weighing each one of the laboratory blanks, place each filter into a "Analyslides" container and properly mark the outside with a label containing the filter designator (LB for laboratory blank), followed by the filter number (LB4200473), then underneath the number must be the date of use (6/5/05). Place into the proper holding container for future weighing.

7. Weigh the filters. Operate the microbalance according to the manufacturer's directions. Take the filter from its filter-handling container by gently slipping the filter handling forceps under the outer polyolefin support ring. Hold the filter only by the ring, not by the filter material. Check the filter's integrity as discussed in section 4.2. Pass the filter, support ring-side up, through the antistatic strip for between 10 and 60 seconds immediately prior to weighing. Immediately transfer the filter to the microbalance's pan and close the chamber door by pressing one of the "Select" buttons. After the microbalance's display indicates that a stable reading has been obtained, record the filter number, the filter tare weight, the expected run date of the filter and the date of the filter weighing session in the database. Also record the filter number, tare weight and run date in the QC notebook.
8. After approximately every 10th filter weighing, the analyst should reweigh both working standards. Record the measurement in the database. If the measurement disagrees from the verified value by more than 3 micrograms, reweigh the standard. If the two measurements still disagree, take appropriate action, which may include (1) reweighing some or all of the previously weighed filters, (2) re-certifying the working standards against the laboratory primary standards, and/or (3) having a service technician repair the microbalance. At the end of the weighing session, reweigh both working standards and record them in the database.
9. Any unused filter whose weight is outside the normal range (i.e. 110 to 160mg) should be investigated. If there is a consistent negative replication (>15 micrograms) for laboratory blank filters, it is usually a sign that the filters have not equilibrated long enough.

10. Check the filter cassettes and backing screens for fractures, cracks, evidence of wear, or contamination. Clean or replace as necessary. The cassettes can be washed in a dishwasher and/or wiped with de-ionized wipes.
11. Install each filter into a filter cassette and then put the filter/cassette assembly into a filter cassette magazine for transport to the sampler. Make sure that the filters are stacked in the filter magazine in the correct order that they are to run, including the field blanks. Attach a label with the filter number(s) and the run date(s) to the outside of the magazine. Double-check the entries in the database.
12. One routine filter should be re-weighed at the end of the weighing session. Record the duplicate measurement on the laboratory data form. If the replicate measurement disagrees from the original measurement by more than 15 micrograms, reweigh the filter. If the measurement still disagrees, troubleshoot and take appropriate action.

4.7 Post-Sampling Documentation and Inspection

Upon receipt of the sample from the field, the analyst should follow these steps:

1. Examine the field data sheet. Determine whether all data needed to verify sample validity and to calculate mass concentration (e.g., average flow rate, average ambient temperature, average barometric pressure and elapsed time) is provided. If data is missing or unobtainable from a field operator or if a sampler malfunction is evident, save the filter for inspection and record on the data form and database that the sample has been voided using the proper code. Notify the proper personnel.
2. Remove the filter from the filter magazine and the filter cassette. Be careful when removing the filter from the cassette. Do not touch or in any way disturb the filter and its contents. Use the filter handling forceps and carefully slip them between the outer polyolefin support ring and the screen, grasping only the support ring. Transfer the filter to the glass holding container "dirt side" up. Keep the particles from contacting the walls or other filters.
3. Transfer the filter and its filter-handling container to the conditioning chamber. Fill out a post-sampling label to include start day of conditioning and the sampler number and site designation. Place this label under the container.
4. Allow the filters to condition (equilibrate) for a minimum of 24 hours (48 hours for PDEQ).

4.8 Post-Sampling Filter Weighing (Gross Weight)

Both the pre and post-sampling filter weighing should be performed on the same balance. Different analyst can perform the pre and post-sampling filter weighing as long as the appropriate standard operating procedures have been followed and the working standard and

replicate measurements are within specifications. Use an effective technique to neutralize static charges on the filter. The post-sampling conditioning and weighing shall be completed **240 hours (10 days)** after the end of the sampling period.

Following are the steps used during post-sampling filter weighing:

1. Group filters in numerical order according to the microbalance used for per-weighing and by their filter numbers.
2. Prepare the database software programs according to **Section 5.0, Software Preparation**. Be sure that the proper cell is active (highlighted) according to the filter number that you are about to weigh. Inspect each filter for filter integrity as described in **Section 4.2**. Be careful not to disturb the filter and its contents.
3. Using the filter handling forceps, run the filter through the antistatic strips and then place the filter into the chamber and onto the microbalance's pan.
4. Press the "Select 1" button on the left side of the balance control panel. This will close the chamber door and start the measurement.
5. The LED screen will blink an "I/O" icon until the balance is satisfied with the accuracy of the weight. The small square in the upper left corner of the screen will fade.
6. Press the "Print" key and the value will be transferred to the active cell in the spreadsheet and move down on cell.
7. Using the filter handling forceps, remove the filter from the microbalance's chamber and place into an Analyslide protective container. Mark the Analyslide with an address label containing the complete filter number and the run date. Place in the proper storage box.
8. Continue until all the filters are weighed. Also ensure that the working standards and laboratory blanks are re-weighed following the sequence used during pre-sample weighing.
9. The flow value **V_a**, which can be obtained from the field data sheets, needs to be entered next. Enter the value for each of the filters that are being weighed in the **H** column. As the values are entered, the cursor will move down one row and the concentration values will automatically be calculated.
10. At least one laboratory blank and any field and trip blanks should be weighed. If the pre and post-sampling weights for the laboratory blanks disagree by more than 15 micrograms, repeat the measurement. If the pre and post-sampling weights for the field blanks disagree by more than 30 micrograms, repeat the measurement. If the pre and post-sampling weights for the trip blanks disagree by more than 15 micrograms, repeat the measurement. If the two measurements still disagree, troubleshoot and take corrective action as specified in the reporting organization's QAPP. Measurements for sampled filters should not be corrected to account for blank measurements. High blank values should not cause the automatic invalidation of sampled filters that were measured during the same weighing

session. Instead, high blank values should trigger troubleshooting and corrective action to reduce blank values to acceptable values.

11. One routine filter should be re-weighed at the end of the weighing session. Record the duplicate measurement on the laboratory data form and the database. If the duplicate measurement disagrees from the original measurement by more than 15 micrograms, re-weigh the filter. If the measurement still disagrees, troubleshoot and take appropriate corrective action.
12. If the filter will receive further analysis, return it to the filter-handling container and note on the container and the laboratory data form that additional analyses are required.

4.9 Calculations

4.9.1 Sample Volume Calculation

Both reference and equivalent method samplers are required to provide measurements of the total volume of air sampled (V_a), in m^3 at actual ambient temperatures and pressures during sampling (40 CFR Part 50, Appendix L, paragraph 7.4.5.2). In the event that the total sample volume measurement from the sampler is not available, the total sample volume may be calculated by multiplying the average flow rate, in actual m^3/min , by the elapsed sample collection time in minutes. Use the following formula only if V_a is not available directly from the sampler:

$$V_a = Q_{avg} H t H 10^3 \quad \text{Equation 1}$$

Where

V_a = total sample volume, actual m^3

Q_{avg} = average sample flow rate over the sample collection period, L/min

t = total elapsed sample collection time, min

10^3 = units conversion (m^3/L)

4.9.2 Net PM Mass Calculation

The mass of particulate matter collected on the filter during the sampling period is determined by subtracting the initial (tare) mass of each filter from the final mass of each filter, as follows:

$$M_{10/2.5} = (M_f - M_i) \times 10^3 \quad \text{Equation 2}$$

Where

$M_{10/2.5}$ = total mass of PM₁₀ or PM_{2.5} collected during the sample period, μg

M_f = final mass of the equilibrated filter after sample collection, μg

M_i = initial (tare) mass of the equilibrated filter before sample collection, μg

10^3 = units conversion ($\mu g/mg$)

4.9.3 PM Concentration Calculation

Each PM mass concentration measurement is calculated by dividing the total mass of PM (Equation 2) collected during the sample period (M) by the total volume of air sampled (V_a), taken directly from the sampler readout display or calculated using equation 1. Use the following formula to calculate PM concentration:

$$PM_{10/2.5} = M_{10/2.5} \div V_a \quad \text{Equation 3}$$

5.0 Software Preparation

The laboratory database will need to be activated before each pre and post sample weighing session. Following are the procedures used to activate both the microbalance scale and the database.

1. Turn of the microbalance by pressing the "RE-ZERO"/ON-OFF space bar located at the bottom of the microbalance control pad.
2. Ensure that the 9-pin cable from the Mettler microbalance is connected to the serial port on the back of the computer.
3. Turn on the computer and allow the boot-up sequence to complete.
4. Once the boot-up sequence is complete, start the Mettler Balance software by double-clicking the icon located on the desktop. Minimize the program.
5. Start the Excel program by going to My Computer\G:\Air\Technical Operations\Monitoring\Weighlab, then chose the proper folder until the desired location is reached.
6. Once in the proper Excel spreadsheet, go to the bottom of the screen and click on the TEMP/RH tab. Enter in your initials, date, start time, start TEMP and start RH.
7. Once the pre-sampling specifications are entered, click on the desired "site" tab at the bottom of the screen. Perform either pre or post-sample weighing sessions or both.
8. Once the weighing session is complete, click on the TEMP/RH tab at the bottom of the screen. Enter the end time, end TEMP and end RH.

NOTE: If the filter conditioning requirements specified in Section 4.3 are not within specifications, a warning will appear on the computer screen. Read the warning and then choose either Yes or No. If you are unsure, contact your laboratory or data analyst for guidance.

9. Save all data entered on the spreadsheet by clicking on the "floppy disk" icon at the top left of the screen.

10. Close all programs and shut down the computer.
11. To set the microbalance in "Standby" mode, lift the "RE-ZERO"/ON-OFF space bar up.

6.0 Macro Balance (Mettler Type H15)

The Mettler Type H15 macro balance is used by PDEQ to perform pre and post weighing sessions on the High Purity Quartz Microfibre filter with a size of 8 x 10 inches (20.3 x 25.4 cm). The calibration should be verified (1) when the macro balance is first purchased, (2) any time it has been moved or subjected to rough handling (3) during routine operations when a standard weight cannot be weighed within ± 0.5 mg of its weight. A set of three to five weights covering the range normally encountered in weighing filters should be weighed. If the weighed values of one or more of the standard weights does not agree within ± 0.5 mg of the stated value, the balance should be re-calibrated or adjusted by the manufacturer or a certified technician. The results of all balance checks should be recorded in the QC notebook. On an annual basis, PDEQ has its macro balance calibrated by a certified technician and receives a Certificate of Calibration.

6.1 Load and unload balance only when arrested

When arrested, the beam and the suspension each rest on three arrestment pins. Thus the knife edges are not under load and not liable to damage by sudden load changes such as are caused by laying on or removing the object to be weighed. The arrestment lever (2) should be moved slowly until the scale illumination has been switched on (see Figure 1).

6.2 Only turn weight setting knobs with balance partially released

Partial release protects the knife edges from damage during weight setting. Abrupt load changes resulting from applying and removing the weights are, to a large extent, absorbed by the arrestment pins as the beam movement is limited, when partially released.

7.0 FILTERS (8" x 10") Quartz Microfibre

7.1 Filter Handling

Careful handling of the filter during sampling, conditioning and weighing is necessary to avoid measurement errors due to damaged filters or a gain or loss of collected particles on the filters. The filters should be handled carefully by the outer most edge (1/2 inch), with clean, dry hands. These precautions reduce the potential effect from body moisture or oils contacting the filters and subsequently affecting the measured weights.

7.2 Equilibration

Each filter should be equilibrated in the conditioning environment for 48 hours prior to performing any pre or post weighing sessions to minimize errors in weight. The conditioning environment temperature should be between 15-30°C and should not vary by more than $\nabla 3^{\circ}\text{C}$. The relative humidity (RH) should be $< 50\%$ and not vary by more than $\pm 5\%$. PDEQ will use the filter conditioning standards specified in **Section 4.3; Filter Conditioning (46.2mm Teflon)** as the standards for equilibration of the 8" x 10" quartz microfibre filters. The quartz microfibre filters should be left in the lot box with the lid cracked at an angle in order to allow air to circulate to the filters. When the box of filters is almost used up, a new box should be placed in the laboratory and equilibration started.

8.0 Pre-Sampling Filter Weighing (Tare weight)

Following are the procedures used for pre-sampling filter weighing. Refer to Figure 1 for knob locations and knob positions.

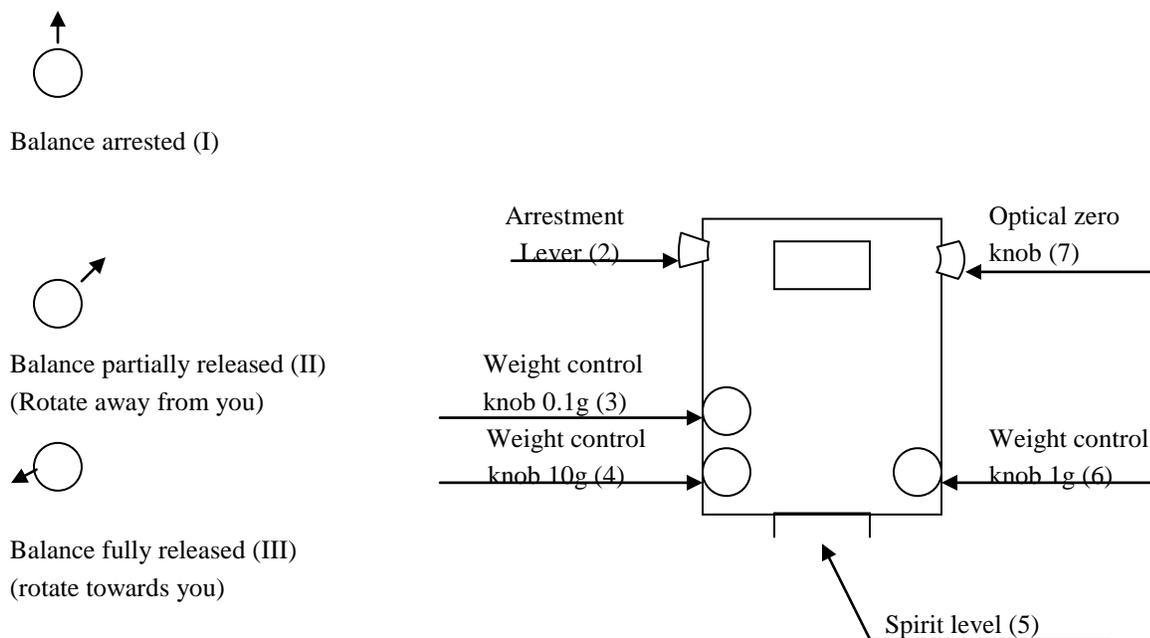


Figure 1

1. Prepare the laboratory database software programs according to **Section 5.0, Software Preparation**, leaving out the activation of the microbalance.
2. Clean the macro balance's weighing chamber with a fine brush, if necessary. Avoid using pressurized gas, which may blow damaging debris and oils into the

macro balance's mechanism. Clean the surfaces near the macro balance with pre-moistened (in de-ionized water) clean-wipes and dry with a Kimwipe. A small amount of moisture can cause a significant measurement bias.

3. Ensure that the balance is level. If the spirit level bubble (5) is not centered within the indicator, turn the foot screws until corrected.
4. Ensure that the balance is arrested. The arrestment knob (2) should be pointing straight up.
5. All weight control knobs (knobs 3, 4 and 6) should be set to zero. The front doors must be closed.
6. Release the balance (arrestment lever (2) moved to position (III)). Turn the optical zero knob (7) clockwise as far as it will go. Using knob (7) adjust optical scale zero line so that it agrees exactly with the zero line of the vernier.
7. Arrest the balance by turning the arrestment lever (2) to position (I).

NOTE: All weighing should be made from the same body position to ensure that no readability error occurs due to sitting up straighter or from slouching.

8. **Lightly** mark, with a bold (dull) pencil, the site abbreviation and run date on the top right edge of the filter opposite the filter ID number.
9. Place the filter to be weighed, long edge down, on the filter tray that is connected to the pan. Be sure to touch only the very edge of the filter as to not contaminate the sampling area. Close the chamber doors.
10. Partially release the balance by moving the arrestment lever (2) to position (II).
11. Turn weight control knob (4) clockwise. When scale moves up, turn knob (4) back one step.
12. Repeat step 10b for knobs (6 and 3).
13. Arrest balance by moving arrestment lever (2) to position (I).
14. After a short pause, release the balance (arrestment lever (2) to position (III) and allow the scale to come to a rest.
15. If the reading of the optical scale is between 100 and 200mg, add one unit to the last decimal place shown on the counter.

NOTE: If any adjustments are to be made using the weight setting knobs, the balance **must** be in the partially released position (II).

16. Read the result and arrest the balance (arrestment lever (2) moved to position (I).

NOTE: The first decimal place, tenths of a gram, is controlled by the weight control knob (3). The second two decimal places are read from the optically projected scale graduation immediately below the zero line of the vernier. The last decimal place is read from the vernier graduation which aligns most perfectly with the projected scale graduation.

17. Record the results in the database, QC notebook and on the manilla envelope created for that filter. See note below for further instructions on the manilla envelope.

NOTE: For each filter weighed, there must be a small manilla envelope designated for that particular filter. These envelopes will be used for storage of the filter and Dixon chart after post weighing is performed. Annotate on the top left of the envelope the site abbreviation, on the top right the filter run date and directly below the run date in the filter ID number. In the lower middle portion of the envelope write the pre and post sample filter weight. In the middle portion of the envelope write the laboratory temperature and humidity taken from the Dixon T/RH sensor. See Figure 2.

| | |
|-------------------|---------------------|
| Site | 06/23/05 3001929 |
| T=74.2 RH=35.6 | |
| | 4.4932 4.5129 |

Figure 2

18. Remove the filter from the pan chamber and place in a site designated folder assembly for transport to the field. Also include a Dixon chart insert with the site abbreviation, run date and motor flow set-point annotated on it. Place the recorder insert, writing side facing away from the filter, into the folder assembly.
19. Repeat steps 8-18 for each additional filter to be weighed. After every 10th filter weighing, re-zero the scale following steps 3-7 above.
20. When all weighing is completed, re-check zero by following steps 3-7 above.

8.1 Post-Sampling Documentation and Inspection

Upon receipt of the sample from the field, the analyst should follow these steps:

1. Remove the filter and Dixon chart from the site folder assembly and place in the filter equilibration tray, open end up.
2. Allow the filters to condition (equilibrate) for a minimum of 24 hours (48 hours for PDEQ).

8.2 Post-Sampling Filter Weighing (Gross Weight)

Both the pre and post-sampling filter weighing should be performed on the same balance. Different analyst can perform the pre and post-sampling filter weighing as long as the appropriate standard operating procedures have been followed. The post-sampling conditioning and weighing shall be completed **240 hours (10 days)** after the end of the sampling period.

Following are the steps used during post-sampling filter weighing:

1. Prepare the database software program according to **Section 5.0, Software Preparation**, leaving out the activation on the microbalance
2. Inspect each filter for filter integrity.
3. Inspect the Dixon chart for verification of a valid sample run of 24 hours. Enter in the database and QC notebook the average of the flow pre set-point and post set-point numbers. Also verify that the filter number matches the number entered in the database, QC notebook and manilla envelope for that site and run date.
4. Repeat steps 9-17 above to weigh each filter.
5. After every 10th filter weighing, re-zero the scale following steps 3-7 of **Section 8.0**.
6. Immediately after weighing each filter, fold the filter and place both the filter and Dixon chart into the respective envelope. The Dixon chart's printed side should **not** touch the filter. Fold the envelope flap inside.
7. When all weighing is completed, re-check zero by following steps 3-7 of **Section 8.0**.
8. If the filter will receive further analysis, return it to the filter re-weigh tray.

9.0 NIOSH Method 7102, “Beryllium and Compounds, as Be”

This method provides for preparation and analysis of filters used in the Pima County DEQ Beryllium Monitoring Network. All beryllium analysis will be performed by Schneider Laboratories, Inc. A report will be generated showing the analysis for beryllium, as well as a list of other elements (if applicable). See Appendix C for a more detailed description of the NIOSH Method 7102.

In order to determine accuracy and bias of the chemical analysis performed by Schneider Laboratories, Inc, an additional strip of the same sample may be analyzed for beryllium by an independent laboratory.

9.1 Preparation of Samples

Pre-sampled filters are conditioned in a controlled laboratory of constant temperature (20-23°C) and relative humidity (30-40%) for a minimum period of 24 hours and then tare weighed. After air samples have been collected, the filters are returned to the laboratory and

conditioned as before and weighed again. The final filter weight minus the tare weight is calculated and a net weight is determined. Once calculated, the net weight gain can be used with the total volume to calculate the particulate concentrations. The procedure for the weighing of filters is based on 40 CFR 50, Appendix B, "*Reference Method for the Determination of Suspended Matter in the Atmosphere (High-Volume Method)*". Below is the formula used to calculate PM concentrations:

$$PM_{10} = (W_f - W_i) \times 10^6 / V_{std}$$

Where

PM_{10} = mass concentration of PM_{10} , $\mu\text{g}/\text{std m}^3$

W_f = final filter weight

W_i = initial filter weight

10^6 = conversion of g to μg

V_{std} = total air sampled in standard volume units, std m^3

Calculate the air volume sampled, corrected to EPA-standard conditions:

$$V_{std} = V_s (T_{std}/T_m)(P_{bar}/P_{std})$$

Where

V_{std} = volume of ambient air sampled at EPA-standard conditions, m^3

V_s = volume of ambient air pulled through the sampler, m^3 .

T_{std} = absolute EPA-standard temperature, 298EK.

T_m = average ambient temperature, EK.

P_{bar} = barometric pressure during sampling measurement condition, mmHg

P_{std} = EPA-standard barometric pressure, 760 mmHg.

After the post-sampled filter final weights have been obtained, the filter is sub-sampled by cutting a filter strip consisting of half of the overall filter and digested using NIOSH Method 7102 specified HF acid full digestion. These extracts are then analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

Concentrations of beryllium are calculated using the following formula:

- 1) Read absorbance of samples, A ; average media blanks, A_b ; average sulfate reagent blanks, A_r ; and working standards, A_s .
- 2) Using the working standard, C_s ($\mu\text{g}/\text{mL}$), analyzed adjacent to the sample of interest, calculate concentration, C ($\mu\text{g}/\text{m}^3$), of Be in the air volume sampled, V (L):

$$C = \frac{(A - A_b) * C_s * 10^4}{(A_s - A_r)V}, \mu\text{g}/\text{m}^3$$

Sectioning the filter for extraction is based on 40 CFR 50, Appendix G, "*Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air*".

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Pima County
Department of Environmental Quality
Air Monitoring Quality Assurance Plan

Appendix C

NIOSH Method 7102
Beryllium and Compounds, as Be



Pima County Department of Environmental Quality
150 West Congress St., 1st Floor
Tucson, AZ. 85701
(520)740-3340

BERYLLIUM and compounds, as Be

7102

Be MW: 9.01 CAS: 7440-41-7 RTECS: DS1750000

METHOD: 7102, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984
Issue 2: 15 August 1994

OSHA : 2 µg/m³; C 5 µg/m³; P 25 µg/m³/30 min
NIOSH: not to exceed 0.5 µg/m³ (suspect carcinogen)
ACGIH: 2 µg/m³ (suspect carcinogen)

PROPERTIES: hard, light metal; valence +2;
MP 1284 to 1300 °C

SYNONYMS: Vary as to compound.

APPLICABILITY: The working range is 0.5 to 10 µg/m³ for a 90-L air sample. The method is applicable to ceiling measurements using a 25-L air sample.

INTERFERENCES: Calcium interference is masked by 3% (v/v) sulfuric acid. Sodium, potassium, and aluminum enhance beryllium absorbance; this effect is overcome by addition of 2% (w/v) sodium sulfate to both standards and samples. Perc hloric, phosphoric, and hydrofluoric acids produce interfering non-atomic peaks. These must be removed by digesting to dryness.

OTHER METHODS: This revises Method P&CAM 288 [2], which replaced Method S339 [3]. Flame atomic absorption and plasma emission (ICP-AES) are not sensitive enough for beryllium at these concentrations.

REAGENTS:

1. Nitric acid, conc., reagent grade or better.
2. Sulfuric acid, conc., reagent grade or better.
3. Sodium sulfate, reagent grade.
4. Sodium sulfate, 2% (w/v)/3% sulfuric acid (v/v). Add 10 g sodium sulfate and 15 mL H₂SO₄ to deionized water. Dilute to 500 mL.
5. Calibration stock solution, 1000 µg Be/mL,* commercially available, or dissolve 1.000 g Be metal in a minimum volume of 1:1 HCl, dilute to 1 L with 1% (v/v) HCl
6. Argon, prepurified.
7. Water, distilled or deionized.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: mixed cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter in two-piece cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with graphite furnace and background corrector.
4. Beryllium hollow cathode lamp.
5. Pressure regulator, two-stage, for Argon.
6. Beakers, Phillips, 125-mL.*
7. Watchglasses.*
8. Volumetric flasks, 10-mL.*
9. Pipets, 10-mL volumetric, with pipet bulb.*
10. Automatic pipettor with tips, 10-µL and assorted sizes for standards.
11. Hotplate, 150 to 400 °C.
12. Waterbath, 60 to 70 °C.
13. Bottles, polyethylene, 25-mL.

* Clean all glassware with conc. nitric acid and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Beryllium is very toxic and a suspected human carcinogen [4]. Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 25 to 1000 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open cassettes and transfer filters to clean Phillips beakers.
4. Add 10 mL conc. HNO₃ and 1 mL conc. H₂SO₄. Cover with watchglass.
5. Heat in fume hood on hotplate (150 °C) until brown fumes of HNO₃ disappear, then at 400 °C until dense fumes of H₂SO₄ appear.
NOTE: Verify that the compounds in the samples are soluble with this ashing procedure, e.g., ore or mining samples will require HF in the digestion. If additional ashing acids are used (e.g., HF, HClO₄, or H₃PO₄), evaporate to complete dryness at this point.
6. Cool and rinse watchglass and sides of beaker with distilled water and evaporate just to dryness. Remove beaker immediately and air-cool.
7. Pipet 10.0 mL 2% Na₂SO₄/3% H₂SO₄ solution into beaker and cover.
NOTE: Start sulfate reagent blanks at this step.
8. Heat in 60 to 70 °C waterbath for 10 min. Allow to stand overnight before analysis to ensure complete dissolution of BeSO₄.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.005 to 1 µg Be per sample.
 - a. Use serial dilutions of known amounts of calibration stock solution in 2% Na₂SO₄/ 3% H₂SO₄ to prepare working standards. Store in polyethylene bottles. Stable at least four weeks.
 - b. Analyze together with samples and blanks (steps 11 and 12).
- NOTE: Analyze working standards alternately with the samples to compensate for the increasing Be signal as the graphite tube ages.
10. Analyze three quality control blind spikes and three analyst spikes.

MEASUREMENT:

11. Set spectrophotometer and graphite furnace according to manufacturer's recommendations and to conditions on page 7102-1.
12. Inject 10-µL aliquots of samples into graphite tube. Record absorbance (peak height mode).

CALCULATIONS:

13. Read absorbance of samples, A_s; average media blanks, A_b; average sulfate reagent blanks, A_r; and working standards, A_s.
14. Using the working standard, C_s (µg/mL), analyzed adjacent to the sample of interest, calculate concentration, C (µg/m³), of Be in the air volume sampled, V (L):

$$C = \frac{(A - A_b) \cdot C_s \cdot 10^4}{(A_s - A_r)V}, \mu\text{g}/\text{m}^3.$$

EVALUATION OF METHOD:

This method was evaluated using NIOSH Standard Reference Material No. 2675 for Be over the range of 0.1 to 0.4 µg Be/filter (equivalent to one-half to two times the OSHA PEL). Beryllium recovery was 98.2% with a measurement precision, \bar{S}_r , of 0.008 [2]. This method is an improvement of S339 [3], which was validated over the range of 2.68 to 11.84 µg/m³ using a 40-L sample. Mean recovery was 106.9% with overall precision of 0.064 [1].

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S339, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 77-185 (1977).
- [2] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 288, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 79-141 (1979).
- [3] Ibid., V. 3, S339, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [4] Criteria for a Recommended Standard...Occupational Exposure to Beryllium, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 72-10268 (1972); and as revised in August, 1977 in NIOSH testimony at OSHA hearing.

METHOD REVISED BY:

Mary Ellen Cassinelli, NIOSH/DPSE; S339 validated under NIOSH Contract CDC-99-74-45.